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JOHN JOLY, M.A. D.Sc. F.R.S. F.G.S.

AND

WILLIAM FRANCIS, F.L.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." Just. Lips. *Polit.* lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

ALERE FLAMMAM.

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THE
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[SIXTH SERIES.]

JULY 1910.

I. *On the Amount of Radium Emanation in the Lower Regions of the Atmosphere and its Variation with the Weather.* By JOHN SATTERLY, *A.R.C.Sc., B.Sc., B.A., St. John's College, Cambridge* *.

[Plates I. & II.]

IN the Philosophical Magazine of October 1908 I gave an account of the methods I had employed for measuring the amount of radium emanation in the air. Two methods were used: (1) absorption of the emanation by coconut charcoal, and (2) condensation of the emanation by liquid air. The first method is the more easily performed and gives the more accurate results. In the same paper I described my attempts at finding how the amount of radium emanation in the air was affected by weather conditions. The experiments, however, were not sufficiently sensitive to give any definite results, and the purpose of the following paper is to describe some more accurate experiments made in 1909.

Full experimental details of the charcoal method are given in my former paper, but it may be worth while to recapitulate them here as briefly as possible.

To get the emanation out of the air, the air was drawn by a water-pump through coarsely-powdered coconut charcoal packed in a porcelain or silica tube. In all the experiments the air-stream was kept at a constant value (half a litre per minute), measured by means of a gauge, and regulated

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* Communicated by Sir J. J. Thomson.

by screw-clips on the indiarubber connecting tube. The air-stream was continued for a certain time, and from a knowledge of the time of exposure and the strength of the air-stream the volume of air drawn through could be calculated. At the end of the exposure the tube was taken, placed on a gas-furnace, and connected up to an aspirator formed of two bottles connected by rubber tubing, one of which was filled with water. The tube was heated to redness and the aspirator then started. The emanation absorbed by the charcoal during the "exposure" to the air-stream was driven off by the heat of the furnace, and drawn by the current of air into the aspirator. Two aspirators were used to make sure that all the emanation was withdrawn from the charcoal. In practice, it was found that the air in the first aspirator so collected contained nearly all the emanation absorbed; the air in the second one usually contained just a little or none at all.

The amount of emanation in the air in the aspirators was measured by the increased electrical conductivity it imparted to the air. To do this it was necessary to pass the air into a testing vessel.

The testing vessel consisted of a brass cylinder 40 cms. long and 10 cms. wide. Down through the centre of the vessel there passed an insulated brass wire whose upper extremity was connected to the insulated quadrants of a Dolezalek electrometer. The needle of the electrometer was kept at +80 volts, and the sensitiveness was such that 1 volt of the insulated quadrants gave a deflexion of about 950 millims. on a scale 2 metres distant. The testing vessel was kept at −320 volts. This ensured saturation for all the leaks I had occasion to measure. The normal air-leak was from ·9 to 1·2 cms. per minute, it being practically constant on any one day but varying from day to day. There were two openings into the testing vessel: the upper one led to a mercury manometer, and the lower one served as a means for exhausting the vessel and refilling it with the air whose conductivity was to be measured.

The normal air-leak having been taken, the vessel was exhausted, and the air collected in the second aspirator was passed into the vessel *. The leak was again taken. The difference between this leak and the normal air-leak is a measure of the emanation in the air collected in the second aspirator. The testing vessel was again exhausted and the

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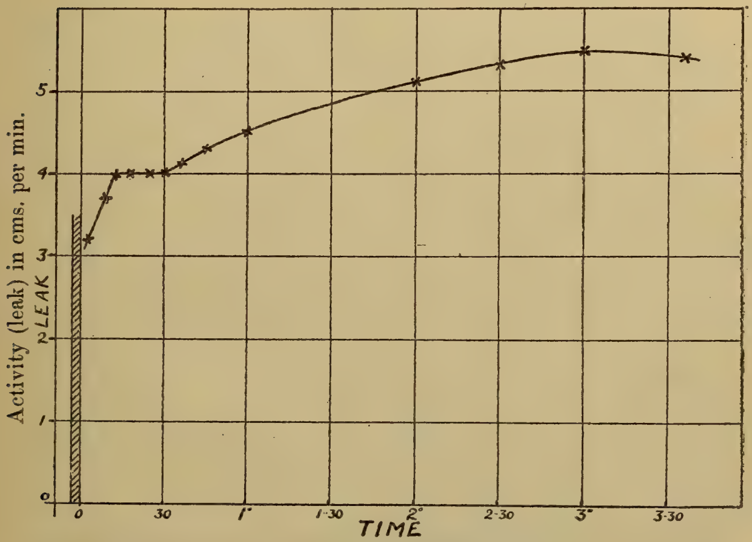
* The volume of air collected in the aspirator was just a little less than the volume of the testing vessel. Thus all the air in the aspirator could be passed into the testing vessel.

emanation-charged air contained in the first aspirator was passed into the vessel. The leak was again taken.

Now when radium emanation is passed into a testing vessel the leak in the vessel does not remain constant. The active deposits Radium A, B, C, &c., are deposited on the walls of the vessel, and the total activity of the contents of the vessel increases for about three hours, after which it gradually decreases, very slowly at first, and then at the rate of the decay of the emanation (half value in 3·86 days). Fig. 1 shows the curve of activity obtained in one particular case (Nov. 6, 1908) from the emanation driven off from the charcoal after an exposure to the air. It takes about 3 minutes to pass a bottle full of gas into the vessel. This is indicated by the shaded area. Some observers make a point of taking the leak at the time of maximum activity which occurs after the emanation has been in the vessel 3 hours. There is, however, as Soddy and Mackenzie * first pointed out, a temporary maximum which occurs after the emanation has been in the vessel about 10 minutes. The leak is practically steady for about 15 minutes after this, and much time is saved if the reading of the leak is taken during this interval. This is especially true if it is required to

Fig. 1.



Curve showing how the leak in the testing vessel after it has been filled with air containing radium emanation varies with the time.

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* Phil. Mag. Aug. 1907.

measure another batch of emanation quickly afterwards, owing to the smaller quantity of excited activity deposited on the interior of the can, and consequently lesser time taken by this to decay into insignificance.

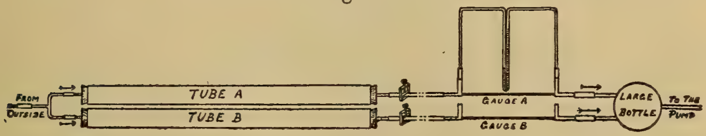
In all cases, therefore, my readings of the leak were made at this first maximum. The leak due to the air from the second aspirator added to the leak due to the air from the first aspirator full, gives the total leak due to the emanation collected from the charcoal. This is not, however, all collected from the air, as the charcoal itself contains radium, and if left to itself gradually accumulates radium-emanation. From the total leak mentioned above must be subtracted the leak due to the emanation produced from the charcoal itself, and the remainder is a measure of the emanation absorbed from the air by the charcoal during the exposure.

The experiments in 1908, the results of which are given in my former paper, were carried out with coconut-charcoal contained in porcelain tubes. These tubes were 2 feet long, and the central foot of the tube was filled with coarsely powdered charcoal kept in place by asbestos wads. The cross section of the tubes was 1·8 sq. cm., and a foot-length of tube contained 39 grms. of charcoal. The amounts of emanation absorbed were small, and to increase the accuracy of the work it was decided to work with tubes of larger bore. In the 1909 experiments opaque silica tubes were used of cross section 8·0 sq. cm.; a foot length of these tubes contained 155 grms. of charcoal. The charcoal was kept in place by spirals of wire gauze. The air-stream being kept the same in the two series of experiments, a greater proportion of the emanation in the air would be absorbed with the silica tubes than with the porcelain tubes.

In the 1908 experiments drying agents (calcium chloride and strong sulphuric acid) were used to absorb the water vapour contained in the atmospheric air drawn through the tubes. The absorptive power of charcoal decreases as the charcoal gets wet. Another reason for drying the air was that if the air was not dried the charcoal absorbed the water from the air; and when the porcelain tube was heated the water was given off and condensed on the cold portions of the tube beyond the furnace, often causing the tube to crack. There is, however, an objection to drying-agents in that they themselves may give off or absorb radium emanation. In the present series of experiments no drying-agents were used. Silica tubes will not crack under the conditions mentioned above. Also, with such a large quantity of charcoal the water caught will be lodged in the first portions of the charcoal column which the air meets, and there will be plenty of dry charcoal behind to absorb the emanation. Experiments, however, were made to test whether the amount of emanation absorbed depended upon the dryness or wetness of the air, and it was found to be practically independent of the amount of moisture present.

In the present series of experiments to measure the amount of emanation in the air, two silica tubes each containing the same amount of charcoal were used, and they were laid side by side upon the bench. The left-hand end of each tube was joined to the side-arms of a T-piece (see fig. 2), the leg of the T communicating by a long glass tube to the outer air, its extremity being about 6 feet above the ground. The right-hand ends of the tubes were joined to gauges which measured the air-stream, and these communicated with a large bottle from which a pipe led to the water-pump. During the experiments, air-streams of the same magnitude (half a litre per minute) were drawn through the two tubes; so that if the charcoal in the tubes is in the same condition as regards size of particles and packing, the tubes ought to absorb and consequently to yield when heated the same amount of emanation. Usually, as will be seen from the tables (pp. 10–17), the amounts were very nearly equal; but in a few cases there were unaccountable discrepancies between them. At any rate one tube served as a check on the other.

Fig. 2.



The tubes having been first cleared of emanation by heating to a red heat and drawing air through them between 2 and 4 P.M. were connected up as described above, and the air-stream started at about 5 P.M. After an hour's reading of gauges and regulating of clips the air-streams were obtained steady at half a litre per minute, and the tubes were left for the night. At about 8 A.M. next morning the gauges were read; and if there had been any wandering away from the mark the air-streams were again adjusted to half a litre per minute. Just about 2 P.M. the gauges were again read and the air-stream stopped. The exposure had thus lasted for about 21 hours, and about 630 litres of air had passed through each tube.

The tubes were then heated in turn, and the emanation was tested as described above. The heating and testing took from 2–6 P.M., but the tubes were cold by 5 P.M., and they were then reconnected up and the air-stream set running for the next day's reading.

The Correction for the Growth of Radium Emanation in the Charcoal.

As explained above, deductions must be made from the observed leaks given by the gas passed into the testing vessel for the leak due to the emanation generated by the charcoal itself since the last heating.

If at a heating the charcoal is completely deprived of its emanation and then the tube is closed up and left to itself, the emanation will gradually accumulate, the equation of the production being

$$I_t = I_0(1 - e^{-\lambda t}),$$

where I_t = the amount in existence at time t,

I_0 = the amount in existence after an infinite time,

e = the base of the natural logarithms = 2·71828 . . . .,

and λ = the radioactive constant of radium emanation.

Taking the time for radium emanation to decay to half value as 3·858 days[*], we have, using the nomenclature of Rutherford,

$$T = 3{\cdot}858 \times 86400 \text{ secs.};$$

and since $$\lambda T = \log_e 2 = {\cdot}693,$$

$$\lambda = 2{\cdot}083 \times 10^{-6} \text{ sec.}^{-1}.$$

Therefore the equation for the production of emanation in the charcoal is

$$I_t = I_0(1 - e^{-2{\cdot}083 \times 10^{-6} \times t}),$$

where t is in seconds or

$$I_t = I_0(1 - e^{-{\cdot}180 t}),$$

where t is in days.

From this equation, and taking the value of I_0 as 100, the following table has been calculated[†].

TABLE I.

t (days).	1.	3.	4.	5.	6.	7.	10.	25.	27.	∞.
I_t	16·5	41·7	51·3	59·3	66·0	71·6	82·7	98·9	99·2	100

The reason why these particular values of t were chosen will be seen later (Table II., p. 8).

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[*] Kolowrat, *Le Radium*, July 1909, and Curie, *ibid.* Feb. 1910.

[†] Tables suitable for these calculations will be found in Kolowrat's paper mentioned above.

From this table we see that, if after a period of rest of six days the amount of emanation accumulated is M, the amount that would be accumulated in one day is

$$\frac{16{\cdot}5}{66{\cdot}0}M.$$

Throughout the experiments it was the accumulation per day that was required. This amount, however, would be hard to measure accurately, and to get the daily accumulation the tubes were allowed to rest for longer periods. At the end of such a period of rest, the emanation accumulated was driven off by heating and the amount tested in the usual way. The usual period of rest was from Friday afternoon to Monday afternoon—3 days,—so that Monday's heating expelled a three days' accumulation. Table II. (p. 8) gives the results obtained for this accumulation. The fifth column was obtained from the third and fourth columns by using the figures in Table I. as described above.

The figures obtained for the daily accumulation of A or B are not quite constant. This is inevitable from the smallness of the quantity under measurement; the agreement, however, indicates that it is radium emanation that is being generated. The average value of the leak due to the daily accumulation works out at ·46 for tube A and ·48 for tube B, or approximately ·5 for each tube.

It was just possible that some of this accumulation might be driven out by the air-stream during an "exposure," so that from the reading of the total emanation collected from the heated tubes after a day's run less than ·5 should be deducted. It is rather difficult to test this point accurately; but experiments made by giving the tubes just an hour's "exposure" showed that none of the accumulation had been driven out in that time, so that perhaps all the accumulation remains proof against a twenty-one hour air-stream.

As a sample reading I will quote that of Thursday–Friday, Aug. 10th–11th.

Air-stream started through tubes at 5.14 P.M., gauges checked at 8.4 A.M. next morning, again read at 2.14 P.M., and current then stopped. The stream had remained practically at ·5 litre per minute all the time, A had gone up slightly, B down. The time of exposure was 1260 minutes, and the gauge readings showed that 635 litres of air had passed through A and 625 litres through B.

TABLE II.

Date of Testing. 1909.	Charcoal Tube.	Period of Rest in days.	Amount accumulated in this period expressed as cms. per min. leak.	Amount accumulated per day expressed as cms. per min. leak.
Mon. Feb. 1 ...	A	3	·8	·32
,, ,, 8 ...	A	6	2·3	·57
Wed. Feb. 10 ...	B	6	2·9	·72
Mon. Feb. 15 ...	B	3	1·1	·44
,, ,, ...	A	6	1·1	·28
Tues. Feb. 23 ...	A	4	1·3	·42
,, ,, ...	B	4	·8	·26
Mon. Mar. 1 ...	B	3	1·4	·56
,, ,, ...	A	3	1·2	·48
Mon. Mar. 15 ...	A	5	1·4	·39
,, ,, ...	B	5	2·1	·59
Mon. Mar. 22 ...	B	3	1·3	·52
Mon. Mar. 29 ...	B	3	1·1	·44
,, ,, ...	A	3	1·2	·48
Mon. Apr. 26 ...	B	25	1·8	·30
,, ,, ...	A	25	1·7	·28
Mon. May 3 ...	B	3	1·0	·40
,, ,, ...	A	3	1·1	·44
Mon. May 17 ...	B	3	3·1	1·2*
,, ,, ...	A	3	5·3	2·1*
Mon. May 24 ...	B	3	1·4	·56
,, ,, ...	A	3	1·4	·56
Mon. May 31 ...	B	3	1·2	·48
,, ,, ...	A	3	1·3	·52
Mon. June 7 ...	B	3	1·1	·44
,, ,, ...	A	3	1·3	·52
Mon. June 21 ...	B	3	1·0	·40
,, ,, ...	A	3	1·5	·60
Mon. July 19 ...	B	27	2·6	·43
Mon. Aug. 2 ...	B	10	1·9	·37
,, ,, ...	A	10	2·4	·47
Tues. Aug. 10 ...	B	4	1·5	·48
,, ,, ...	A	4	1·9	·61
Mon. Aug. 23 ...	A	3	1·8	·71
,, ,, ...	B	3	1·2	·48
Thur. Oct. 14 ...	A	48	2·8	·47
,, ,, ...	B	48	2·7	·45

* Very high. Rejected when finding the mean value. The tubes had been opened up and the supply of charcoal replenished on May 15.

Procedure of Testing.

(1) Exhausted the testing vessel with an oil-pump, refilled with dry air, took the air-leak : leak = 1·0 cm. per min.

(2) Meanwhile heated tube A on the furnace, and collected in succession two aspirators full ; call them *a* and *b*.

(3) Exhausted the testing vessel, passed in the contents of *b*, took the leak : leak = 1·1 cm. per min.

(4) Exhausted the testing vessel, passed in the contents of *a*, took the leak : leak = 4·8 cm. per min.

Hence we get for Tube A :

$$\begin{tikzcd}[column sep=small]
 & a \arrow[ddrr] & & 1\cdot1-1\cdot0=\cdot1 & \\
A \arrow[ur, dash] \arrow[dr, dash] & & & & 3\cdot9 \\
 & b \arrow[uurr] & & 4\cdot8-1\cdot0=3\cdot8 &
\end{tikzcd}$$

The tube had been heated the day before, so taking away ·5 for the day's accumulation we get left 3·4 due to the emanation absorbed by A from 635 litres of atmospheric air.

(5) Exhausted testing vessel twice in succession, refilling with dry air each time. This was to clear out all the emanation due to A (*a*). The leak was now high due to the active deposit from the emanation of A(*a*). The activity of this deposit gradually decayed, and after about an an hour the leak was fairly steady at 1·1 cm. per min.

(6) Meanwhile heated tube B on the furnace, and collected (*a*) and (*b*) as before.

(7) Exhausted the testing vessel, passed in *b* : leak = 1·3 cm. per min.

(8) Exhausted the testing vessel, passed in *a*: leak = 5·3 cm. per min.

Hence we get for Tube B :

$$\begin{tikzcd}[column sep=small]
 & a \arrow[ddrr] & & 1\cdot3-1\cdot1=\ \cdot2 & \\
B \arrow[ur, dash] \arrow[dr, dash] & & & & 4\cdot1 \\
 & b \arrow[uurr] & & 5\cdot0-1\cdot1=3\cdot9 &
\end{tikzcd}$$

Take away ·5 for the accumulation since yesterday and we get left 3·6 due to the emanation absorbed by B from 625 litres of atmospheric air.

(9) Exhausted testing vessel twice and refilled with dry air each time to clear out all the emanation due to B (*b*).

(10) Meanwhile set A and B running for the next day's results *.

Results.

The following tables give my results. Owing to the closing of the laboratory at the week-end it was not possible to take more than four daily readings in succession.

Careful notes were made of the weather phenomena, such as the height of the barometer, the direction and force of the wind, &c., while the experiments were in progress. Most of

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* As this particular set of readings was taken on a Friday, A and B were not set running but were left to stand till the following Monday.

TABLE III.

Date 1909.	Barometer.		Thermometer.		Humidity.		Wind Direction and Force.		Rainfall.	Hours of Sunshine.	Weather Remarks.
	9 A.M.	9 P.M.	Max.	Min.	9 A.M.	9 P.M.	9 A.M.	9 P.M.			
	mm.	mm.	°F.	°F.					in.		
Feb. 28 𝔖	758	757	36	29	83	100	SE 1	NE2–3	...	5·5	Sunny 9 a–3 p.
Mar. 1 M	756	752	35	30	100	87	NE 2	N 1	·02	0·3	Snow. Sleet from 5 p.
2 Tu	747	743	38	21	100	84	SW 1	SE 2	·29	0·2	Fog 9 a. Overcast.
3 W	740	742	34	28	100	83	SE 2-3	E 2	·02	...	Snow² night. Snow showers
4 Th	745	749	35	18	97	100	NW 2	Calm 0	...	5·5	Haze 9 a. Fine and sunny.
5 F	750	750	40	12	100	88	SW 1	„ 0	·01	6·4	„ „ „
6 S	745	737	37	25	100	97	SE 4	SSE5-6	·62	...	Snow² 7 a–3 p.
Mar. 7 𝔖	737	745	44	33	100	100	SW 2	SSE 2	·10	3·0	Snow 6 a -9 a. Fine and sunny.
8 M	751	754	48	31	92	96	SE 2	SE 2	...	9·6	Fine and sunny.
9 Tu	753	753	38	33	95	97	NW 1	Calm 0	·15	...	Snow. Rain 8 a–3 p.
10 W	754	754	42	33	94	92	NE 1	E 5-6	...	...	Overcast, with haze.
11 Th	755	758	36	34	92	93	NE 4	N 4	·01	...	Overcast, with rain.
12 F	760	759	40	34	90	91	NNW4	NW 2	...	1·3	Overcast till 3 p.
13 S	757	752	40	32	82	100	NW3-4	Calm 0	·17	3·0	Sunny a. Snow² 3 p.
Mar. 14 𝔖	744	742	38	31	80	98	W4–5	NW 5	·10	0·1	Overcast, with snow. Cold.
15 M	741	745	36	28	89	100	NW 2	NW 2	·08	...	„ „ „
16 Tu	748	749	41	25	95	95	W 2	Calm 0	...	6·3	Fine and sunny. Snow °.
17 W	750	750	45	22	91	90	SW 1	SE 2	...	7·1	Fine and sunny.
18 Th	746	742	47	33	92	94	SE 3	SE 2	·02	0·4	Overcast, wet.
19 F	741	744	56	42	97	96	SE 2	SE 2	·03	3·3	Sunny intervals.
20 S	747	748	56	42	95	99	S 2	S 1	·06	1·5	Sunny intervals till 2 p. Rain 4 p.
Mar. 21 𝔖	750	749	53	41	81	100	SW3-4	SE 1	·06	6·2	Rime m. Fine and sunny.
22 M	752	751	49	42	98	98	SE 1	SE 2	...	...	Fog² from 6 a. Overcast.
23 Tu	754	758	48	42	99	100	NE 2	Calm 0	...	...	Fog² from 6 a. Overcast.
24 W	755	743	51	38	94	94	S 2–3	SW4–5	·39	...	Overcast. Rain² 2 p–11 p.
25 Th	739	741	54	42	80	82	SW 6	NW 6	·03	2·4	Rain² showers.
26 F	747	753	48	37	78	88	NW 6	Calm 0	...	4·9	Sunny intervals.
27 S	756	755	52	31	79	81	W 2	Calm 0	·01	5·5	Fine and sunny.
Mar. 28 𝔖	749	744	52	37	92	92	SE 3	S 3	·16	...	Rain most of day.
29 M	742	740	60	47	79	98	S 3	S 2	·02	4·1	Fine.
30 Tu	740	746	52	46	92	87	S 2	SW 2	·44	...	Rain a & Rain² 1 p–5 p.
31 W	750	747	55	45	69	94	SW 2	SW 4	·02	4·8	Fine and sunny a.
Apl. 1 Th	758	769	50	39	84	72	N 3	N 1	...	5·2	Sunny intervals.
2 F	773	774	47	29	66	86	N 2	Calm 0	...	3·3	Cloudy. Cold wind.
3 S	774	773	48	28	68	76	SE 3	SE 3	...	9·4	Cold wind.
Apl. 4 𝔖	773	772	51	32	66	77	SE 2	SE 1	...	12·0	Fine and sunny.
			} Lovely weather. No rain, and average 11 hrs. sunshine each day.								
11 𝔖	757	753	𝔖, M, Tu, Fine. W, windy. Th, NW, fine. F & S, SW, showery.								
18 𝔖	757	757	Fine and sunny. Rest of week the same with a little rain.								

TABLE III.

ay	Emanation in 630 litres air.		Weekly Weather Notes (abbreviated from the Weekly Weather Report of the Meteorological Office).
	Tube A	Tube B	
M Tu W Th F S	2·8 2·8 6·7*	2·6 2·6 4·4	*Weather*, wintry. *Barometer and Wind*: The general distribution of pressure favoured winds from some point between N & E. In addition to a large cyclone of irregular form that extended over this country early in the week a well defined system moved southward over Britain and the North Sea during Tu and W, and finally disappeared in the Netherlands. On Friday a band of relatively low pressure extended from the Atlantic over the N part of these islands and winds became W. But on Saturday the advance of a deep cyclone to our S.W. coasts drew wind into NE & SE.
M Tu W Th F S			*Weather*, unsettled. *Barometer and Wind*: At the beginning of the week a depression had arrived and lay over England causing complete cyclone circulation. This system moved SE across the Channel. The barometer meanwhile stood highest in Iceland and N. Europe, but later in the week the pressure gave way over Norway and became high out West. Wind changed from NE to N and increased in force.
M Tu W Th F S	1·9 4·1 2·2 2·4	1·6 4·0 2·0 2·0	*Weather*, unsettled. *Temperature*, low at first but rose later. *Barometer & Wind*: At the commencement of the week a depression covered the North Sea and the general winds were N. This continued till Tuesday when a shallow low-pressure system appeared between Scotland and Ireland, and wind backed to W & SW. This was followed by another cyclone from the Atlantic, deep at first but which got shallow as it travelled over U.K. The wind after blowing strongly SE on our S.W. coasts veered to S and became light.
M Tu W Th F S	2·0 2·4 1·2 2·2	2·2 2·2 1·2 1·6	*Weather*, unsettled. *Barometer and Wind*: During nearly the whole of the week depressions either extended slowly or passed directly over U. K. while the barometer was high in Iceland and Spain. The centre of the chief system passed over Yorkshire Wednesday night. As it increased considerably in depth during its passage the wind blew a strong breeze or high wind between SW & S on the south coast and E & NE in the north, while in the rear on Friday a NW breeze was general. On Saturday another cyclone was approaching.
M Tu W Th F S	2·8 2·2 1·6 3·1	2·2 1·8 1·6 2·5	*Weather*, unsettled, finer after Wednesday. *Barometer and Wind*: During the greater part of the week depressions passed across U. K. while the barometer was high in Iceland and Spain. After a rapid passage of one on Wednesday an anticyclone set in from the north, and the barometer rose rapidly. This increased in size and intensity as it passed across the North Sea on Saturday. With the cyclonic distribution the wind was W & SW in the south and strongly E in the north.
ean	2·7	2·3	

* Decay curve taken and its identity with that of radium emanation verified.

TABLE IV A.

Date 1909.		Barometer.		Thermometer.		Humidity.		Wind Direction and Force.		Rainfall.	Hours of Sunshine.	Weather Remarks.
		9 A.M.	9 P.M.	Max.	Min.	9 A.M.	9 P.M.	9 A.M.	9 P.M.			
		mm.	mm.	° F.	° F					in.		
Apl. 25	𝔖	753	756	60	43	68	78	SW 6	S 2	·01	11·1	Sunny. Thunderstorm at [noon.
26	M	754	753	66	44	60	69	SW 2	SW 1	·03	13·0	Continuous sunshine.
27	Tu	752	755	59	46	74	82	SW 3-4	W 2	·06	6·7	Fine. Rain and hail at 7 p.
28	W	760	760	60	38	81	86	WSW 4	SW 5	·02	8·0	Sunny till 3½ p.
29	Th	757	751	57	39	64	97	W 4	Calm 0	·75	8·8	Sunny 5 a–2 p. Rain^2 after [4 p.
30	F	759	761	52	38	72	88	NW 4	W 5	·02	10·0	Snow$^\circ$ and rain$^\circ$ a. Sunny [day.
May 1	S	761	766	51	34	62	93	NW 4	SE 2	·06	11·0	Fine and sunny. Snow,$^\circ$ [rain$^\circ$ 6 p.
May 2	𝔖	769	771	52	34	68	80	NW 4	SE 2	...	11·1	Haze a. Sunny. Sleet at [noon.
3	M	772	772	57	34	68	81	SE 2	SE 2–3	...	12·3	Fine and sunny.
4	Tu	772	770	62	40	59	65	SSE 2	E 3	...	14·0	Continuous sunshine.
5	W	769	767	64	39	49	78	SE 3–4	NE 4–5	...	14·0	,, ,,
6	Th	767	768	65	39	58	75	E 5	N 4	...	14·0	,, ,,
7	F	768	767	63	42	49	64	E 4	NE 4	...	14·0	,, ,,
8	S	766	764	63	40	44	62	E 3	N 2	...	14·0	,, ,,
May 9	𝔖	762	762	52	29	70	85	N 5	N 4-5	...	4·5	Haze a. Sunny 5–9, then [cloudy.
10	M	762	764	50	40	72	89	N 2–3	Calm 0	...	·9	Overcast, brighter evening.
11	Tu	766	765	71	30	69	70	SW 2–3	SW 2	...	12·8	Fine and sunny.
12	W	765	766	67	40	59	86	W 2	N 4	·02	4·8	Overcast from 1 p. Rain 6 p.
13	Th	768	767	52	35	66	73	N 4	N 2	...	9·0	Sunny intervals, damp.
14	F	765	762	54	35	63	88	Calm 0	Calm 0	...	5·2	,, ,, chilly, damp.
15	S	763	764	49	36	73	84	N 2–3	N 1	·02	3·8	Rain$^\circ$. Sleet 10 a. damp.
May 16	𝔖	762	758	56	30	58	73	SE 4	N 4–5	·01	9·5	Fine and sunny, chilly.
17	M	754	761	51	41	87	98	W 3–4	Calm 0	·02	...	Overcast. Rain$^\circ$ 3 p–5 p.
18	Tu	763	766	62	33	69	64	SW 5–6	W 2	...	10·5	Sunny intervals.
19	W	768	768	69	33	56	76	SW 1	Calm 0	...	11·6	Fine and sunny, hot.
20	Th	768	766	72	37	50	74	S 2–3	SE 2	...	12·5	,, ,,
21	F	764	760	80	45	57	72	ESE 2	Calm 0	...	11·0	,, ,,
22	S	764	762	81	47	56	79	W 1	Calm 0	...	13·8	,, ,,

TABLE IV A.

Day.	Emanation in 630 litres of air.		Weekly Weather Notes (abbreviated from the Weekly Weather Report of the Meteorological Office).
	Tube A	Tube B	
𝔖 M Tu W Th F S	2·8 2·0 1·9	1·9 1·9 1·4	*Weather*, unsettled. *Barometer and Wind*: Throughout the week the barometer was relatively high in Iceland and Spain while cyclonic disturbances either extended or travelled across U. K. These systems were not as a rule deep, and the wind which was mainly between S and W had little force. In the rear of a moderate depression which passed across the North of England on Thursday, the barometer rose briskly and the wind veered to NW or N over the whole of U. K. and increased in force.
𝔖 M Tu W Th F S	1·6 2·5 1·8 1·5	1·4 1·8 1·8 1·6	*Weather*, dry, cloudless. *Barometer and Wind*: Distribution mainly anticyclonic. At first the pressure maximum was over France, and it travelled from there to Germany, and to Scandinavia. During the latter part of the week a large cyclonic system appeared over the Bay of Biscay. This was accompanied by an E wind over England and a SE wind over Scotland At the end of the week a well-marked but not deep depression travelled southward over Scandinavia and highest pressure existed in Iceland.
𝔖 M Tu W Th F S	6·6 5·1 1·7 2·1	5·8 3·8 1·6 2·4	*Weather*, fine. *Barometer and Wind*: At the beginning of the week the barometer was highest in Iceland and lowest to S.W. of U. K., and in Germany. A moderate NE breeze was blowing. On Monday the anticyclone extended over these islands. Later it moved NW to the Atlantic and a depression born in the Shetlands travelled to Finland by Thursday. After this small disturbances travelled southward over U. K. and the North Sea. The general direction of the wind was between N and NW sometimes W and sometimes E.
𝔖 M Tu W Th F S	3·6 8·4 3·0 2·4	3·6 7·8 3·6 2·6	*Weather*, fine and dry. *Barometer and Wind*: The distribution of pressure underwent several changes though the barometrical movements were not brisk. Pressure which was highest over Iceland gradually gave way while it was sometimes highest to the S., E., and N.E. of U. K. No important depressions passed over U. K., but towards the end of the week a large system was spreading in slowly from the Atlantic. Wind, light and variable except in latter half of week when it was S & SW.
Mean	3·1	2·9	

TABLE IV B.

Date 1909.		Barometer.		Thermometer.		Humidity.		Wind Direction and Force.		Rainfall.	Hours of Sunshine.	Weather Remarks.
		9 A.M.	9 P.M.	Max.	Min.	9 A.M.	9 P.M.	9 A.M.	9 P.M.			
		mm.	mm.	° F	° F					in.		
May 23	𝔖	764	766	78	50	59	76	W 1	NNW 3-4	...	10·8	Sunny intervals.
24	M	770	765	73	42	55	62	N 2	SE 4	·34	13·0	Fine and sunny.
25	Tu	754	750	59	51	98	99	SE 2–3	S 2	·40	...	Rain^2 7 a–noon. Overcast.
26	W	749	748	57	45	69	85	SE 5-6	SW 6	·45	4·7	Rain^2 11 a.–1 p. Thunderstorm 2 p–3p.
27	Tu	751	754	62	49	74	93	SW 5	Calm 0	·05	3·8	Showers. Sunny intervals.
28	F	758	758	67	47	65	74	WSW 2	SW 4	·01	9·5	Sunny intervals.
29	S	759	763	65	50	65	81	W 4–5	Calm 0	...	11·7	Fine and sunny.
May 30	𝔖	766	766	70	46	71	91	SW 2–3	Calm 0	...	10·3	Fine and sunny.
31	M	763	758	74	53	78	86	S 2	Calm 0	...	9·3	Sunny intervals. Glorious.
June 1	Tu	757	758	61	51	81	100	NNW 4	N 4	·69	0·2	Overcast. Rain^2.
2	W	760	764	53	49	93	85	N 4	N 4	·07	...	Rain till noon. Overcast.
3	Th	764	761	57	46	71	79	NE 5	NNE 5	·07	4·3	Sunny a., then overcast. Cold.
4	F	756	755	50	46	92	93	NE 4	N 3	·53	...	Rain all day. Cold.
5	S	755	757	55	45	94	83	NW 2	N 2	·03	...	Fog a. Overcast. Cold.
June 6	𝔖	758	761	53	44	78	97	NE 1	Calm 0	·04	...	Wet. Overcast. Cold.
7	M	762	762	61	43	70	93	N 2	NE 1	...	10·5	Haze. Fine and sunny.
8	Tu	762	763	64	41	72	87	W 2	W 1	...	12·2	„ „ „
9	W	763	762	64	48	79	77	W 3	N 4	...	1·7	Overcast till 4 p. Then improve.
10	Th	762	761	57	47	80	85	NE 4	NW 1	·02	1·7	„ „ 5 p. Cold.
11	F	759	760	54	40	65	77	N 4–5	N 4	·12	6·2	Sunny till noon. Rain. Sleet 1½ p.
12	S	760	763	54	43	97	80	NW 4	NW 5-6	·01	1·0	Rain^2 7 a–8 a. Cloudy.
June 13	𝔖	765	766	65	45	74	78	NW 4	N 4	...	7·3	Fine and sunny.
14	M	767	768	63	42	70	80	NW 1	NE 1	...	10·5	„ „
15	Tu	768	766	60	44	72	94	W 2	NE 2	...	2·2	Overcast till 3½ p.
16	W	766	767	62	49	89	86	NW 3	N 4	...	2·9	Cloudy. Cold. Dull.
17	Th	768	769	70	48	75	84	N 1	NE 2	...	6·5	Haze. Sunny 9 a–3 p.
18	F	770	769	68	51	87	88	NW 3	Calm 0	...	5·5	Sunny 10 a–4 p.
19	S	767	764	68	49	78	86	SW 1	SW 2	...	0·3	Overcast till 3 p.
June 20	𝔖	761	758	70	56	79	82	SW 5	SW 4	...	5·4	Sunny a. Thunder 5 p.
21	M	754	748	69	55	77	86	SSE 4–5	SSE 1	·02	3·5	Cloudy. Dull. Rain 2 p.
22	Tu	744	747	63	52	84	74	S 5	S 4	·17	6·0	Rain 10a–noon. Sunny 2p–7p
23	W	748	748	64	47	64	80	SW 6	SSE 2	·22	9·1	Sunny till 1.30 p.

Table IV b.

ay.	Emanation in 630 litres of air.		Weekly Weather Notes (abbreviated from the Weekly Weather Report of the Meteorological Office).
	Tube A	Tube B	
S M Tu W Th F S	1·3 1·3 ·9 2·3	1·9 1·6 ·9 2·8	*Weather*, much less bright. *Barometer and Wind*: Depressions from the Atlantic of variable size and no great depth, travelled over these islands and the pressure changes were consequently frequent and rather considerable. The wind was generally light and moderate between SW and W except in Scotland where it was SSE and E. A strong breeze or high wind prevailed for a time on our southern coast on Wednesday.
S M Tu W Th F S	3·8 ·8 ·8 ·9	4·0 ·8 1·0 ·6	*Weather*, fine and bright, then extremely unsettled. *Barometer and Wind*: In the early part of the week a large V-shaped depression travelled eastwards across U. K., and light to moderate breezes were experienced from S & SW to NW & N. After Wednesday a well defined cyclone spread northwards from Spain and NE breezes set in over all U. K. an increase in the strength of the wind occurring on Thursday. Towards the end of the week the southern depression gradually dispersed and the wind backed to N and became light.
S M Tu W Th F S	2·4 1·4 1·3 2·1	2·5 1·7 1·5 2·1	*Weather*, cloudy, dry. *Barometer and Wind*: Soon after the week commenced a large anticylone extended gradually over these islands from the Atlantic, and by Tuesday almost the whole kingdom was under its influence. During the latter half of the week, however, it retreated very slowly westwards while shallow ill-defined disturbances appeared over theNorth Sea and to the S.E. of England. The general direction of the wind was N and NW but it varied somewhat in places.
S M Tu W Th F S	2·8 1·9 ·9 3·0	2·8 1·9 1·3 3·1	*Weather*, dry, cloudy. *Barometer and Wind*: During the greater part of the week the barometer was high over the Atlantic and low in Denmark and the general current of air was from the North During the end of the period the Atlantic system moved to the Bay of Biscay and France, and depressions began to affect the north and north-west of U. K., so that the wind backed to NW and eventually to W and SW.
S M Tu W	1·9	1·9	*Weather*, dull. *Barometer and Wind*: The depression at the N.W. of U. K. gradually extended over U. K. The winds were SE and strong.
ean	1·7	1·8	

TABLE V.

Date 1909.	Barometer.		Thermometer.		Humidity.		Wind Direction and Force.		Rainfall.	Hours of Sunshine.	Weather Remarks.
	9 A.M.	9 P.M.	Max.	Min.	9 A.M.	9 P.M.	9 A.M.	9 P.M.			
	mm.	mm.	° F.	° F.					in.		
Aug. 1 𝔖	762	759	63	56	74	99	SE 3	S 3	·59	1·0	Rain^2 noon–4.30 p.
2 M	759	765	60	51	94	88	NW 6	NW 2	·03	1·0	Rain 8 a–noon.
3 Tu	766	766	64	49	63	94	NW 4	Calm 0	...	7·1	Fine. Sunny intervals.
4 W	766	766	73	48	72	88	SW 2	Calm 0	...	9·3	Fine and sunny.
5 Th	767	768	78	48	63	88	SW 1	Calm 0	...	13·1	Dew. „ „
6 F	767	765	78	51	47	88	E 2	Calm 0	...	13·8	Dew. „ „
7 S	765	763	79	47	67	95	S 1	SE 1	...	12·4	Dew. „ „
Aug. 8 𝔖	764	763	79	50	54	72	NE 3	NE 2	...	13·0	Dew. Fine and sunny.
9 M	762	763	78	49	96	86	N 3	Calm 0	...	8·0	Fog^2 till 11 a. Dew. Fine.
10 Tu	765	767	74	50	66	89	NE 3	Calm 0	...	12·0	Fog^2 till 7 a. Dew. Fine.
11 W	768	766	81	55	94	92	SW 2	Calm 0	...	9·3	Dew^2. Sunny after 10 a.
12 Th	767	764	85	50	55	88	SW 2	Calm 0	...	13·0	Fine and sunny.
13 F	764	765	75	54	68	81	NW 4	NW 3	...	6·5	Sunny intervals. Gusty.
14 S	765	765	78	53	73	82	SW 5	Calm 0	...	5·9	„ „
Aug. 15 𝔖	763	760	84	55	74	83	S 1	Calm 0	·11	11·3	Hot and close.
16 M	753	753	74	59	93	82	SW 3	WSW 4	·06	·3	Thunderstorm at 9 a. Rain^2
17 Tu	755	752	70	49	67	90	W 1	SE 4	·14	8·0	Sunny till 2 p. Rain 6–9 p.
18 W	747	755	69	55	74	85	S 3	SW 4	·22	6·0	Thunderstorm 9 a–11 a. Rain
19 Th	759	762	71	55	73	76	SW 6	SW 4	·04	10·0	Sunny. Rain$^{\circ}$.
20 F	760	755	66	55	87	90	S 5	SW 5	·12	·1	Overcast. Rain$^{\circ}$.
21 S	753	752	66	49	70	97	W 1	Calm 0	·14	8·6	Fine morning. Rain^2 4 p–5 p.
Aug. 22 𝔖	752	755	63	45	70	85	W 5	Calm 0	·01	8·8	Fine morning Rain $1\frac{1}{2}$ p.
23 M	756	755	67	48	76	94	S 4	SW 4	·08	·9	Overcast. Rain at intervals.
24 Tu	755	754	67	58	80	94	SW 5	Calm 0	·02	...	„ Few showers.
25 W	753	756	68	56	82	95	W 4	NW 3	·27	6·0	Sunny intervals. Thunderst at 11 a–noon. Rain^2 $1\frac{1}{2}$ p.
26 Th	760	762	62	53	89	95	NW 4	Calm 0	...	·8	Overcast.
27 F	762	765	67	46	73	84	SW 2	W 3	...	4·6	Sunny a. Overcast p.

Table V.

Day.	Emanation from 630 litres of air.		Weekly Weather Notes (abbreviated from the Weekly Weather Report of the Meteorological Office).
	Tube A	Tube B	
𝔖			*Weather*, after first day or two great improvement. *Barometer and Wind*: Soon after the commencement of the week an anticyclone of considerable size began to extend over these islands from the Atlantic and it lay over U. K. and district nearly all the week. On Wednesday a large cyclonic system invaded the N.W. of U. K. but it retreated later. The wind varied considerably in direction early in the week: while the highest pressure was on the Ocean it was mainly N, and on Wednesday S & SW. On subsequent days it was W in the north and from the E in the south.
M	1·2	1·7	
Tu	3·1	3·7	
W	4·0	4·3	
Th	3·0	3·6	
F			
S			
𝔖			*Weather*, very fine and bright. *Barometer and Wind*: During the whole of the period the centre of a big anticyclone lay over or near U. K. Winds light and variable. In the extreme north strong westerly breezes occasionally blew, due to an eastward travelling Icelandic depression.
M			
Tu	2·3	2·3	
W	5·5	5·6	
Th	3·4	3·6	
F			
S			
𝔖			*Weather*, unsettled, lot of rain. *Barometer and Wind*: At the commencement an anticyclone extended over England from the Continent. This soon went E, and Atlantic disturbances travelled eastward over the Icelandic regions, while their secondaries travelled E-wards & NE-wards directly over U. K. General current of wind was between W & S and fresh at times, a strong breeze being experienced over our W. & S. coasts. At the end of the week a pressure minimum developed over N. Sea, giving U. K. a NW wind and low temperature.
M	2·1	2·4	
Tu	1·4	1·5	
W	1·4	1·5	
Th	1·2	1·3	
F			
S			
𝔖			*Weather*, unsettled, frequent rain. *Barometer and Wind*: During the earlier part of the week the centre of a depression moved eastwards over Scotland, causing E winds in the far north and SW to NW over U. K. generally. By Thursday the eastern edge of an anticyclone began to extend over us from the Atlantic, and this system continued the chief factor over England and S. of Ireland to the end of the week.
M	1·5	1·6	
Tu	2·8	3·4	
W	1·2	1·3	
Th			
F			
Mean	2·4	2·7	

the weather data in the tables are, however, taken from the records given in the Meteorological Office's publication entitled 'Observations at Stations of the second order and at Anemograph Stations.' The Cambridge station is at the University Botanic Garden, situate about half a mile from the laboratory and at the same level. Readings are taken there twice a day—9 A.M. and 9 P.M. The maximum temperature occurs during the afternoon, so the maximum thermometer is read at 9 P.M. and entered to the day. The minimum temperature usually occurs in the early morning. It is read at 9 A.M. and entered to the day. The humidity is obtained from the ordinary wet and dry bulb thermometers. The rain-gauge is read at 9 A.M. each day, and since most of the 24 hours since the last reading occurs in the previous day, it is entered to that day. The sunshine is measured by a Campbell-Stokes recorder. The wind force is given on the Beaufort scale. It is estimated by the observer using the indications given in the 'Meteorological Observer's Handbook.' The numbers 0, 1, 2, 3, 4, 5, 6, 7, 8 on the Beaufort scale correspond approximately to wind velocities of 0, 2, 5, 10, 15, 21, 27, 35, and 42 miles per hour. A number affixed to a weather phenomenon under the column Weather Remarks indicates the intensity of that phenomenon, thus, $\text{Snow}^{\circ}=$ light fall of snow, $\text{Rain}^{2}=$heavy fall of rain. Also a = A.M., p = P.M. The amount of emanation is given as the leak produced in my testing vessel measured in cms. per minute on my electrometer-scale.

From the figures in these tables the curves (Plate I.) were plotted. Owing to the stoppage of work at the week-end it was unfortunately impossible to obtain a continuous emanation-curve; but in some cases the curves are linked up according to the knowledge gained from the determined portions.

Analysis of the Curves.

(1) Let us now consider the emanation-curve in conjunction with the *barometer-curve.* Table VI. opposite gives the results. The letter D after a date means a decided change in the amount of emanation; and the letter R or S means that rain or snow accompanied the barometric change.

From this table we see that, on the whole, a rise in the barometer is accompanied by an increase of the amount of emanation, a fall of the barometer is accompanied by a decrease in the amount of emanation, while with the barometer fairly steady the issue is doubtful.

TABLE VI.—Effect of Barometer Changes.

Of a Barometric rise.			Of a fairly steady Barometer, or a maximum or minimum.			Of a Barometric drop.		
No Effect.	Decrease of Emanation.	Increase of Emanation.	No Effect.	Decrease.	Increase.	No Effect.	Decrease.	Increase.
		Mar. 3–5 (D)	Mar. 2–4				Before Mar. 15 (S)	
		,, 15–17 (D)				Mar. 17–19 (D)	Mar. 16–18	
Mar. 22–24		,, 24–26					,, 23–25 (R)	
	Mar. 29–31 (S)			May 5–7	May 3–5		Apr. 28–29 (R)	
		Mar. 31–Ap. 2 (D)						
	Before May 3	Before May 10		May 10–13 (D)				May 12–14
		May 17–19 (D)		,, 18–20 (D)			May 19–21 (D)	
		May 26–28 (D)		May 31–June 2 (DR)			,, 24–26 (R)	
		Before June 14						
		June 1–3		June 7–10	June 9–11		June 2–4 (R)	
		,, 16–18 (D)		,, 14–17 (D)				
				Aug. 4–6	Aug. 2–5 (D)			
Aug. 18–20 (R)				,, 11–13 (D)	,, 10–12 (D)		Aug. 16–18 (R)	
	Aug. 24–26 (DR)				,, 23–25 (D)			

(2) It is to be noticed that in England *rain* nearly always accompanies a decrease in the amount of emanation, so that it is advisable next to draw up a table showing the effect of rain (D again means a decided change in the amount of emanation).

TABLE VII.—Effect of Rain (or No Rain).

No Effect.	Decrease.	Increase.	Decrease when no rain.	Increase when no rain.
	Before Mar. 15			
Mar. 2–4 (Snow)	Mar. 23–25 (D)		Mar. 15–17 (D)	Mar. 3–5 (D)
	„ 29–Apl. 1 (D)			„ 31–Ap. 2 (D)
	April 27–30		May 4–7	May 3–5
			„ 10–13 (D)	„ 12–14
	May 24–27		„ 18–21 (D)	„ 17–19 (D)
	„ 31–June 2 (D)			„ 27–28 (D)
	Before Aug. 2		June 7–10	June 16–18 (D)
			„ 14–17 (D)	
	Aug. 16–20 (D)		Aug. 4–6	Aug. 2–5 (D)
	„ 24–26 (D)	Aug. 23–25 (little rain)	„ 11–13 (D)	„ 10–12 (D)

From this table we see that rain (very light falls are not considered) is accompanied by a decrease in the amount of emanation. There are, however, about an equal number of decreases as well as increases which are not accompanied by rain.

(3) Coordinated with barometric changes and rainfall is *wind intensity*. The next table shows the effect of wind force (wind force is not plotted in the curves on Plate I., but is given in the tables of results, Tables III., IV., V., pp. 10–17). Wind changes of less than two steps on the Beaufort scale are not considered. The letter R again means rain (or snow).

TABLE VIII.—Effect of Wind Force.

Of an Increase of Wind Force.			Of a Decrease in Wind Force.		
None.	Decrease.	Increase.	None.	Decrease.	Increase.
					Mar. 3–5
	Mar. 16–18				„ 15–17
	„ 23–25 (R)				
	„ 29–Ap. 1 (R)				„ 31–Ap. 2
	April 26–29 (R)				
	May 4–6				
	„ 11–13				May 13–14
	„ 19–20				„ 18–19
	„ 25–27 (R)				„ 26–28
	May 31–June 1 (R)				
	Aug. 17–19 (R)				Aug. 2–5

The results here are even more definite. An increase of wind is accompanied by a decrease in the amount of emanation and a decrease of wind is accompanied by an increase of the amount of emanation.

(4) Considerations of barometric pressure and wind lead up to a consideration of cyclones and anticyclones.

Search was now made in the 'Weekly Weather Reports' of the Meteorological Office for cyclones, anticyclones, and V-shaped depressions, with the following results:—

CYCLONES.

Mar. 1–5.	Large irregular shallow cyclone shifting about the North Sea.
15–17*a*.	„ „ „ „ ; centre in Denmark.
17–19.	Deep cyclone approaching from the west.
24–26.	„ „ crossed England; centre crossed Yorkshire on the night of the 24th.
29–31.	Cyclone crossed England; centre passed Lincoln at noon on the 30th.
May 25–28.	Deep cyclone advancing; centre reached the Irish Sea, and then retreated northwards.
June 21–22.	Cyclone approaching.
Aug. 17–18.	„ „ ; its centre at Bristol on the morning of the 18th. Then it broke up.
„ 19–12.	Big cyclone; centre between Iceland and Norway. W winds in England.
„ 23–26.	Cyclone crossed Great Britain, centre crossed Scotland on the 24th.

ANTICYCLONES.

April 1–2.	Anticyclone travelled down from the north and settled with its north–south ridge over Great Britain.
May 3–7.	Large irregular anticyclone, centre over Scandinavia.
„ 10–12.	„ „ „ protruding over England.
June 7–11.	„ anticyclone advanced, then retreated.
„ 14–18.	„ „ „ ; centre off Spain. (This with a huge cyclone in Russia gave us cold N winds.)
Aug. 2–13.	Large irregular anticyclone moved eastwards over Central Europe; centre in Denmark on 5th. Centre retreated to the Atlantic on the 8th, and advanced again; centre in France on the 12th.

V-SHAPED DEPRESSIONS.

June 1–3.	Large V-shaped depression travelled Eastwards across the United Kingdom.

In all the above cases the cyclones gave rain, strong winds, and low emanation values. The anticyclones gave us fine weather, and in some cases high emanation values (May 10–12, Aug. 3–6, 10–13), and in other cases low emanation values (May 3–7, June 7–11, 14–18). Anticyclones are by no means as definite in their structure as cyclones. The only V-shaped depression experienced gave plenty of rain, strong winds, and a decided decrease in emanation content.

(5) The effect of *fine weather* was analysed in a similar way to the above. In 1 case there was no effect on the amount of emanation, in 5 cases a decrease of emanation, and in 15 cases an increase. There were also 3 cases of increase on dull days (trace of rain only), and 12 cases of decrease on days which were not fine (these were chiefly rainy days).

(6) *The path of the wind.* One would expect that if the air that was carried over Cambridge had travelled for a long time over land, it would have a large emanation content; while if it had travelled over the sea or very rapidly over the land, it would have a small emanation content. It is not an easy matter to work out the actual path of the surface wind. Shaw and Lempfert [*] have worked it out for certain selected cyclones, anticyclones, and V-shaped depressions, and have traced the life-history of the currents in great detail in their interesting paper. The path of the air has, however, to be traced very warily for the conditions are often very indefinite. Dr. Shaw was kind enough to let me go up to the Meteorological Office and work out the paths of the winds from the Working Charts kept there. These working charts are synchronous maps giving the distribution of the meteorological elements at specified instants. They are got out three times a day, 7 A.M., 1 P.M., and 6 P.M., and are used for the weather forecasts [†]. On these charts the isobars are drawn for every $\frac{1}{10}$ in. of pressure and the wind indicated by arrows, the barbs and feathers showing the strength on the Beaufort scale, or by a simple calculation in miles per hour.

The method adopted by me in drawing the surface trajectories is that given by Shaw and Lempfert in their paper. They say: "If we take the synoptic chart for any epoch we know to a moderate degree of approximation the speed and direction of the wind. The wind observations give us the information for certain points, and the known relation between wind and barometric gradient helps us to interpolate for points on the chart for which no actual wind observations exist. The continuous records of anemographs show in detail what the nature of the changes were for particular localities.

"A knowledge of the direction of the wind at any point

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[*] See Shaw and Lempfert, 'The Life History of Surface Air-Currents. A Study of the Surface Trajectories of Moving Air.' Published by the authority of the Meteorological Committee, 1906.

[†] An interesting elementary account of the Construction and Reading of Weather Maps is given by E. Gold in the 'School World' of July August, and September, 1909.

enables us to draw a step in the surface trajectory which passes through the point if we can assume the average movement of the air to have remained constant during a sufficient interval. Thus, for example, if an observation gives the wind direction at a station as S.W. and its speed the equivalent of 20 miles per hour, we may suppose that within the half-hour preceding the observation the air travelled 10 miles from the South-West, and in the succeeding half-hour it travelled 10 miles further towards the North-East. For longer periods a proportionately longer step must be drawn. .... So long as the motion of the air is of considerable magnitude and remains persistent for a considerable time, there is little difficulty in drawing the steps with considerable confidence; but when we have to deal with a region of light airs, and in the outlying region of an approaching depression, or when the changes are rapid, as in the region of the centre of a depression, the drawing of the trajectory is an uncertain process."

Shaw and Lempfert's air trajectories over the United Kingdom were obtained from charts got out every hour or two hours. The charts at my disposal had successive intervals of 6, 5, 13 hours, so that the trajectories given in Plate II. are not very trustworthy. Still in the absence of anything better they serve a useful purpose.

Again my "exposures" lasted 21 hours, so that the trajectory of the air arriving at the beginning of the exposure might be very different from the trajectory of the air arriving at the end of the exposure. To get over this difficulty I have drawn in some cases trajectories at successive intervals of about a day. The course of the trajectories of the air arriving at Cambridge between the instants taken may thus be roughly approximated to by a consideration of the known trajectories.

Trajectories of the surface air-currents arriving at Cambridge when a low value of the emanation content was obtained (Maps 1, 2).

Curves (1), (2), (3) of Map 1 give the three trajectories for the surface air arriving at Cambridge on March 24, 6 P.M., March 25, 7 A.M., March 25, 6 P.M., during the passage of a deep cyclone, the path of whose centre is represented by the dotted line. The velocity of the centre was 20 miles per hour. The wind velocity was from 5 to 7 on the Beaufort scale, *i. e.* from 15 to 35 miles per hour, so that the cyclone would be said to be a fast traveller. The air represented by curve (2) covered its 320 miles of land travel in 20 hours.

so that it had not much time for picking up emanation from the land over which it passed.

Curve (4) of Map 1 gives the trajectory for the air arriving at Cambridge on June 16 at 6 P.M. It was traced back to June 13, when it was found to come from a northern region of gentle airs between an Icelandic high pressure region and a Norwegian low pressure region. The air leisurely pursued its southerly course to Cambridge, being over the sea all the time except for the last 50 miles. Its emanation-content would naturally be low.

Curves (1) and (2) of Map 2 give the trajectories for the air arriving at Cambridge on June 2, 6 P.M., and June 3, 6 P.M. The air had travelled at a great pace across the Northern Atlantic between a cyclone in the Icelandic region and an anticylone to the south of its course. It hung about for a short time in a quiescent region around the Shetlands, and finally travelled southwards at a great pace behind a very long V-shaped depression which was travelling eastwards to Denmark, and which gave us heavy rains on the evening of June 1 and the morning of June 2.

Curve (3) of Map 2 gives the trajectory of the air arriving at Cambridge on May 25, 6 P.M. The air was traced back to the quiet interior of an anticyclone which had hung about over the continent since May 17. No doubt the interior of this anticyclone was occupied by air which had just descended from the upper regions so that the surface trajectory could not be traced beyond the 24th. The air reaching Cambridge had thus made little contact with land, thus explaining its low emanation content.

All the paths of the trajectories mentioned above agree very well with the small amount of emanation the air in them carried.

The trajectories for the air giving high results do not give such good agreement. This is no doubt partly due to the fact that high results occur in fine weather and the winds in fine weather are light and variable.

Trajectories of the surface air-currents arriving at Cambridge when a high value of the emanation content was obtained (Maps 3, 4, 5).

Curve (1) of Map 3 gives the trajectory of the air arriving at Cambridge on March 5, 7 A.M. There had been a number of sporadic cyclones in N.W. Europe for the past 4 days, and the winds had been light. The air was traced back through the English Midlands and Yorkshire to Norway, where it probably descended in the anticyclone situated there on Feb. 27.

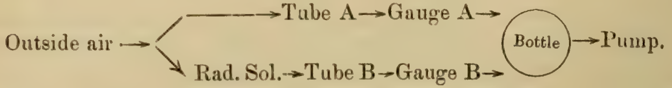
Curves (2) and (3) of Map 3 give the possible trajectories of the air arriving at Cambridge on Aug. 5, 7 A.M. The wind at Cambridge was just S. of W. If on drawing the trajectory a WSW. wind is taken, the path leads back by curve (2) to a point on an anticyclonic ridge to the south of Cornwall on Aug. 3, and it cannot be traced further. If the wind is taken due W. the path leads back by curve (3) to S. Wales, and then by strong northerly winds to Scotland. It is quite doubtful from the working charts which path should be taken, but the emanation content would incline one to the path from Scotland, although the existence of uranium-radium-mines in Cornwall must not be forgotten.

Curves (1), (2), and (3) of Map 4 give the trajectories of the air arriving at Cambridge on May 10, 6 P.M., May 11, 6 P.M., May 12, 6 P.M. All the air had come from the northern region, and from the paths of the trajectories one would expect at first sight (1) to give a low emanation-content, (2) a larger content, and (3) larger still; the actual results were just the reverse (see Table IV. A). The weather phenomena over England were, however, anticyclonic on May 10th and cyclonic with freshening winds on May 11th and 12th.

Map 5 gives three possible trajectories for the air arriving at Cambridge on May 19, 7 A.M. The observers for the Meteorological Office estimate the wind force on the Beaufort scale, and their estimate is of its nature only very approximate. A wind estimated as No. 3 on this scale may be anything between 8 and 13 miles per hour with a mean value of 10 miles per hour. A wind estimated as No. 4 on the scale may be anything between 13 and 18 miles per hour with a mean of 15 miles per hour. It will be observed that the minimum wind velocity according to one number on the scale is the maximum wind velocity allowable for the next lower scale-number. Thus there is a fair latitude allowed for different observers; and probably some will always over-estimate and some always underestimate. On Map 5 I have plotted three trajectories corresponding to the maximum, mean, and minimum values of wind force corresponding to the numbers of the Beaufort scale. The pressure conditions were anticyclonic on the continent on May 18 and 19, feebly cyclonic over Britain, France, and Spain on May 16 and 17, and there was a persistent calm to the west of Ireland on May 15 and 16, with prevailing northerly winds from Iceland to west of our islands previous to this. The curves corresponding to the maximum and mean wind values agree very well, both going through the calm to the west of Ireland. The minimum curve did not reach this calm, but was caught in a feeble cyclone between Wales and Ireland, where it performed a loop. The winds were gentle, spent a long time over land, and reached Cambridge in fine warm weather, thus accounting for a large emanation content.

The average amount of Radium Emanation in the Air.

In order to express the quantity of radium emanation in the air in terms of the quantity of radium which would be in radioactive equilibrium with it, it is necessary to carry out comparison experiments, placing a radium solution of known strength in series with one of the tubes. The arrangement of fig. 2 is modified thus :—



The radium solution used was kindly given to me by Prof. Rutherford, and its radium content was $3{\cdot}14 \times 10^{-9}$ gm. in the form of bromide. Before any "exposure" the solution was cleared of all accumulation by bubbling air through it for an hour or two. The same volume of air is sent along each path at the same rate, therefore from the amounts of emanation found from the two tubes we can get by subtraction the value of the ratio

$$\frac{\text{emanation in a known volume of air}}{\text{emanation generated by the solution in a known time.}}$$

The method is a comparative one, and the results are only true if the same fraction of the total emanation is absorbed by the charcoal, whatever be the emanation-content of the air sent through the charcoal-tubes. Experiments made with strong solutions indicated that with strong solutions saturation occcurred, but with solutions giving about the same amounts of emanation as those obtained in the experiments fairly satisfactory results were obtained.

The denominator in the fraction given above is the amount of emanation yielded by a solution containing $3{\cdot}14 \times 10^{-9}$ gm. radium in the known time, t, of the experiment. To find the mass of radium which would be in radioactive equilibrium with this amount of emanation we multiply the denominator by

$$\frac{I_t}{I_0} \text{ i.e. } \frac{I_0(1-e^{-\lambda t})}{I_0} \text{ or } 1-e^{-\lambda t},$$

using the same notation as before (p. 6).

The following table gives the values of $1-e^{-\lambda t}$ required in the experiments :—

TABLE IX.

t (hours) ...	3.	7.	14.	21.	22.	∞.
$1-e^{-\lambda t}$	·0223	·0511	·0997	·146	·152	1·000

Thus the amount of radium that would be in radioactive equilibrium with the amount of emanation that my solution generates in 3 hours is

$$3{\cdot}14 \times 10^{-9} \times {\cdot}0223 \text{ gm.}$$

Five runs of 3 hours each were made with the tubes in parallel, the solution being in series with one of the tubes. The results are given in the following table :—

TABLE X.—Short Runs.

Date 1909.	Air alone.				Air plus Solution.				Emanation generated by solution in 3 hours.
	Tube.	Speed. lit. per min.	Vol. of air.	Emanation caught.	Tube.	Speed. lit. per min.	Vol. of air.	Total emanation caught.	
Mar. 2...	A	·5	92	1·0	B	·58	106	4·9	3·9
July 21.	A	·5	88	·7	B	·5	92	5·2	4·5
„ 23.	A	·5	90	·5	B	·5	90	5·1	4·6
Aug. 27.	A	·5	90	1·1	B	·5	90	5·8	4·7
„ 27.	B	·5	90	1·1	A	·5	90	5·5	4·4

The average amount of emanation caught from the air in 3 hours is ·8, and the average amount caught from the solution (alone) in 3 hours is 4·65 (neglecting the reading on Mar. 2 when the speed of the air-stream rose to ·58).

Therefore on the average the emanation in 90 litres of atmospheric air is equal to that which would be in radioactive equilibrium with

$$\frac{{\cdot}8}{4{\cdot}65} \times 3{\cdot}14 \times 10^{-9} \times {\cdot}0223 \text{ gm. of radium.}$$

The amount of radium which would be in radioactive equilibrium with the emanation in one cubic metre of air is called by Eve the Radium Equivalent. Therefore the average radium equivalent on the days given in Table X. is

$$\frac{1000}{90}\times\frac{\cdot 8}{4\cdot 65}\times 3\cdot 14\times 10^{-9}\times\cdot 0223$$

$$=130\times 10^{-12}\text{ gm.}^{*}$$

In the 1908 experiments the porcelain tubes absorbed in two hours an amount 2·5 from the radium solution. The silica tubes with more than 4 times the cross-section of the porcelain tubes only absorb 4·65 in three hours. This looks as if the charcoal tended to get saturated with the emanation, so that the amount absorbed is not proportional to the time of exposure. The air-readings also tend to give the same conclusion for the average value of the emanation caught from the air in 21 hours (deduced from the results of March, April, May, June, and August) is 2·45, which is much less than 7 times ·8 the average value of the air caught in 3 hours.

These facts suggest that the absorption of the emanation by the charcoal is two-fold, one stage being quick—a surface condensation, and the other much longer—a diffusion into the interior, as has been discovered by McBain† for the absorption of hydrogen by charcoal.

These experiments have led to other experiments on saturation which will be published in due course.

In order to get solution readings to compare with the 21-hours air readings, it is therefore necessary to make solution-exposures of 21 hours. The radium solution used above is too strong for this purpose, as it is wise to keep the amount of emanation from the solution about equal to that from the air, so a solution of one-fifth strength, *i. e.* containing $\frac{3\cdot 14\times 10^{-9}}{5}$ gm. of radium, was made up. In calculating the results of the experiments given in the following table allowance has been made for the fact that the absorptive power of tube B was about 10 per cent. better than that of tube A. (This is shown by the air-results of June and August.) The air-stream was kept practically constant at ·5 litre per minute.

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* The calculation is not quite correct as no allowance is made for the decay of the first portions of the emanation taken from the air, whereas the formula used for the solution allows for this. The error, however, is practically negligible.

† Phil. Mag. Dec. 1909.

TABLE XI.—Long Runs.

Date 1909.	Duration of exposure.	Air alone.			Air plus Solution.			Emanation caught from the Solution.	Radium equivalent of the Air.
		Tube.	Vol. of air.	Emanation caught.	Tube.	Vol. of air.	Emanation caught.		
	hrs.								
Oct. 26-27.	22¼	A	630	1·1	B	660	4·7	4·7−1·2=3·5	52×10^{-12}
„ 27-28.	21	B	610	·9	A	640	4·1	4·1− ·8=3·3	37×10^{-12}
Nov. 2-3...	21	B	650	2·2	A	650	5·2	5·2−2·0=3·2	88×10^{-12}
„ 3-4...	21	A	640	2·6	B	635	6·7	6·7−2·9=3·8	109×10^{-12}

To calculate the mean emanation content of the air for the months March–August we use the mean values 2·45 for the average value of the emanation from 630 litres of air, and 3·45 for the amount of emanation absorbed from a solution containing $\frac{3\cdot14\times10^{-9}}{5}$ gm. of radium in 21 hours.

Therefore the average radium-equivalent of the air

$$=\frac{1000}{630}\times\frac{2\cdot45}{3\cdot45}\times\frac{3\cdot14\times10^{-9}}{5}\times\cdot146$$

$$=105\times10^{-12}\text{ gm.}$$

The lowest value is about 35×10^{-12} gm. and the highest value about 350×10^{-12} gm.

Discussion of the results of experiments made on the variation of the amount of radium emanation in the air with weather conditions.

The only other experiments besides the author's on the measurement of the amount of radium emanation in the air and its association with meteorological phenomena are those of Eve * made at Montreal. The method was the same, but Eve's exposures lasted 2·7 days, whereas mine lasted only 21 hours. Eve found that the ratio of the greatest to the least values was 7 : 1. I get 10 : 1. He found also that the amounts in summer and winter were not widely different; this also agrees with my results.

Eve also found that the approach of a deep cyclone, accompanied by heavy rain or a quick fall of snow, causes an

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* Phil. Mag. Oct. 1908.

increase in the amount of radium emanation in the air, whilst anticyclonic conditions, with dry or very cold weather, give a decrease in the amount of the emanation in the air. This he explains

(1) by the spiral motions of cyclones and anticyclones,
(2) by the suction action of changes of pressure on the emanation in the air lodged in the ground;
(3) by the readier liberation of emanation from moist substances.

My results are opposed to Eve's in this respect. I find that cyclones accompanied by wet weather and strong winds give a decrease in the amount of emanation, whilst anticyclones accompanied by fine weather and light winds give an increase in the amount. There are exceptions, but the above is generally true, and the trajectories I have drawn bear it out.

Of course there is a great difference in the situations of Montreal and Cambridge. The cyclones crossing England come straight from the Atlantic, while those arriving at Montreal have travelled over hundreds of miles of land, and this may explain the whole difference. If my experiments, however, had each lasted 3 days, I should have found much less difference between the maxima and minima values. Ashman *, working at Chicago with the liquid air method, made six measurements of the emanation content, and he gets practically the same results as Eve.

Most of the other workers in this subject have exposed charged wires to the air, and measured the active deposits obtained, the others have measured the atmospheric ionization, &c. Dyke †, working at Cambridge for three weeks in 1906, drew a measured volume of air through a negatively charged metal grid for an hour at a time, and found a greater deposit on still bright days than on cloudy windy days, and a small amount after rain. In California Harvey‡ found the largest deposits occurred when a land wind blew and the humidity was low, and the smallest deposits when an ocean wind blew and the humidity was high. Work has been done on the Continent of Europe by Gockel §, Kohlrausch ||, Schweidler¶, Amaduzzi**, Constanzo††, Simpson‡‡,

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* Amer. Journ. Sci. Aug. 1908.
† Terr. Mag. and Atmos. Elec., Sept. 1906.
‡ *Le Radium*, Aug. 1909.
§ *Phys. Zeitschr.* May 1908.
|| *Akad. Wiss. Wien, Sitz.-Ber.* Oct 1906.
¶ *Ibid.*
** *Accad. Lincei, Atti*, Jan. 1909.
†† *Phys. Zeitschr.* Mar. 1909.
‡‡ Phil. Trans. 1905.

Flemming*, and others. Gockel confirmed the conclusions of Brandes, namely, when the barometer is low there is more active deposit on a wire, and says that rain and gusty weather produce an increase in the amount of emanation. In an earlier paper he says there was more active deposit on fine days than on wet ones. Kohlrausch, working in Vienna on the radioactive induction, found that clouds had a considerable effect, and that there was a decrease after rain and with falling pressure; whereas Schweidler found an increase in the atmospheric ionization on stormy days. Amaduzzi supports Ebert's contention that a fall of the barometer causes an increase in the amount of emanation in the air. Constanzo measured the active deposit over the Mediterranean and found it increased when the wind blew from the land. Some of the best work has been done by Simpson, who carried out a long series of experiments in Lapland in 1905 on the active deposit from atmospheric radioactivity. He found that

(1) On the whole year temperature has a marked effect, but little effect during any one month;
(2) The radioactivity increases as the humidity increases and decreases as the humidity decreases;
(3) The radioactivity decreases as the wind increases in strength;
(4) The radioactivity is greater with a falling barometer than with a rising barometer, but the radioactivity is not necessarily higher with a low barometer than with a high one;
(5) The radioactivity is greater with winds from the land than with winds from the sea. (In Lapland the winds from the land are South winds, and occur when the barometer falls. The winds from the sea are North winds, and occur when the barometer rises.) The wind effect was due to the barometer effect and not *vice versa*.
(6) There is no connexion with the amount of cloud and the radioactivity.
(7) There is no relation between the radioactivity and the potential gradient.

Simpson concluded by saying that all his work supports Elster and Geitel's view that when the atmospheric pressure falls the emanation is sucked out of the ground. He also found that everything which reduces the atmospheric circulation increases the atmospheric radioactivity.

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* *Phys. Zeitschr.* Nov. 1908.

Workers on the ionization in closed vessels include Campbell and Wood[*] at Cambridge, Wulf[†] at Valkenberg in Holland, Strong[‡] at Baltimore, Pacini[§] at Sestola, Wright[‖] and Cline[¶] at Toronto, and many others. Nearly all European observers find a double daily variation in the ionization which is closely parallel to the changes in the atmospheric potential gradient. Wright (*loc. cit.*) and Cline, however, find no evidence of a regular daily variation. Campbell and Wood, Pacini and Cline agree in finding that the ionization is independent of the pressure, temperature, and humidity of the air. When his vessel was not sealed Cline found that the ionization was greatest when the atmospheric pressure was lowest, and this he put down to the emanation sucked out of the earth.

The above results show that at present the subject is in a confused state. It is desirable that instead of isolated observers working on different points of the subject, well equipped bands of observers at several laboratories should thresh out the subject properly. Evidently much depends on the locality at which the observations are made. Exposed wires do not seem to lend themselves to great accuracy in the measurement of atmospheric radioactivity, as there is little knowledge of the actual volume of air which has contributed to the deposit on the wire. Dyke's method seems to be the best for measuring the active deposit, and the charcoal absorption method for measuring the amount of emanation in the air.

Amount of Ionization of the Air due to the Radium Emanation present.

In my former paper I calculated that the radium emanation in the air was, on the average, responsible for the formation of 2·5 ions per c.c. per sec. Eve[**], using later data for the number of α particles shot out per sec. per gm. of radium and its products, reduced this to 1·3 ions per c.c. per sec. Recently Geiger[††] has determined afresh the average number of ions produced by an α particle in its flight. He finds that the average number of ions produced by an α particle

[*] Phil. Mag. Feb. 1907.
[†] *Phys. Zeitschr.* Mar. 1909.
[‡] Phys. Review, Feb. & July 1908.
[§] *Accad. Lincei, Atti*, Feb. 1909.
[‖] Phil. Mag. Feb. 1909.
[¶] Phys. Review, Jan. 1910.
[**] Eve, 'Terrestrial Magnetism,' March 1909.
[††] Geiger, Roy. Soc. Proc. vol. lxxxii., July 1909.

from radium emanation is $1{\cdot}74 \times 10^5$, from Radium A $1{\cdot}87 \times 10^5$, and from Radium C $2{\cdot}37 \times 10^5$. The average for these three products is $2{\cdot}0 \times 10^5$. Hence working on the same lines as before we find that the number of ions produced per sec. per cub. metre of air by the radium emanation, radium A, and radium C in radioactive equilibrium with 105×10^{-12} grm. of radium is

$(105 \times 10^{-12}) \times 3 \times (3{\cdot}4 \times 10^{10}) \times (2{\cdot}0 \times 10^5)$
or $2{\cdot}1 \times 10^6$,
or about 2 per c.c. per sec.

When the emanation content is at its lowest value this would be reduced to ·7, and when at its highest value would be raised to 7.

The average emanation content at Montreal, as measured by Eve, is $\frac{6}{11}$ of the amount in Cambridge, so that the number of ions produced by the emanation at Montreal per c.c. per sec. is about 1·2.

Amount of Ionization of the Air due to the Thorium Emanation present.

W. Wilson[*] has shown that there is about 4000 times as much radium emanation as thorium emanation in the atmosphere near the earth's surface. The radioactive constant of thorium emanation is about 5000 times greater that of radium emanation, hence there are about the same number of thorium emanation atoms and radium emanation breaking up per second in the atmosphere near the earth, and therefore the thorium series of disintegrating products would also be responsible for about 2 ions per c.c. per second.

Therefore in free air the number of ions produced per c.c. per sec. by the emanation of radium and thorium present is about 4. If a vessel were slowly filled with filtered air the thorium products would not enter the vessel, and therefore only 2 of the number of ions produced per c.c. per sec. in a closed vessel are due to emanations, and those 2 to radium emanation.

Apportionment of the ions produced in a metal vessel and in free air to the ionizing agents at work.

The number of ions produced per c.c. per second in a metal vessel has rarely been reduced below 10. This number has

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[*] Phil. Mag. Feb. 1909.

been reached by Cooke*, who got 9·1 in a brass vessel screened by large masses of lead, and by Wright†, who got down to 6·0 in an unscreened zinc vessel on the surface of Lake Ontario, and to 8·6 at the same time in a similar lead vessel. In the calculation of their results all observers have taken the old and small value of *e*, the electronic charge. Wright took $e=3{\cdot}4\times10^{-10}$ E.S.U. If we substitute the correct value $e=4{\cdot}65\times10^{-10}$ E.S.U., Wright's figures for the number of ions become 4·4 and 6·3 respectively. Wright also found 8·2 and 9·8 for the same two vessels in the open air on the ground near the newly erected Physical laboratory at Toronto, and 9·9 and 10·3 in a room within the laboratory. In each case the vessel had been cleaned and filled with filtered air just before the readings were taken, and was unscreened.

McLennan has shown that the water of Lake Ontario is quite free from radioactive matter ‡, and Wright has shown that if the depth of water is greater than four metres it absorbs all the penetrating radiation from the earth below the lake. Hence it follows, considering the zinc vessel alone, that the diminution from 8·2 to 4·4 was due to the cutting off of the penetrating radiation from the earth. Allowing 1 ion per c.c. per sec. to be due to the radium emanation in the air in the vessel, it follows that the remainder must be due to an intrinsic radiation from the walls of the zinc vessel itself. Of the total number 8 produced on the ground near the laboratory, we may therefore say that (*a*) 4 are due to the penetrating radiation from the ground (including any secondary effect this may produce), (*b*) 3 are due to a radiation from the walls of the zinc vessel itself, and (*c*) 1 is due to the radium emanation in the air. In free air (*a*) would be reduced to 1 (see Wright, *loc. cit.* p. 317), (*b*) would be absent, and (*c*) would be raised to 2 by the presence of the thorium products, giving a total of about 3 ions per c.c. per sec. in free air.

Volume of Radium Emanation in the Air.

Rutherford § has shown that the volume of radium emanation in equilibrium with 1 gm. of radium is ·585 cub. mm.

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* Phil. Mag. Oct. 1903.

† Phil. Mag. Feb. 1909.

‡ Eve (Phil. Mag. July 1909) has shown that the radium content of the St. Lawrence at Montreal is $\cdot25\times10^{-12}$ gm. of radium per litre of the water.

§ Proc. Roy. Soc., Aug. 1908.

Hence the average volume of radium emanation in one cubic metre of the atmosphere at Cambridge

$$=(105\times10^{-12})\times(\cdot585\times10^{-3})$$
$$=6\cdot1\times10^{-14}\text{ c.c.}$$

or there is $6\cdot1\times10^{-20}$ c.c. of radium emanation in 1 c.c. of air.

Now there are $2\cdot76\times10^{19}$ molecules of gas in 1 c.c. of gas at 0° C. and 760 mm. Therefore the average number of emanation molecules in 1 c.c. of the atmosphere near the earth's surface

$$=(6\cdot1\times10^{-20})\times(2\cdot76\times10^{19})$$
$$=1\cdot7.$$

Surely it is a triumph to be able to detect the existence of a gas in the atmosphere when there are less than 2 molecules of it present in a cubic centimetre.

Volume of Helium produced from the Emanation in the Air.

Rutherford and Boltwood* have shown that 1 gm. of radium produces helium at the rate of 163 cub. mm. per year. Therefore the amount of helium produced per year from the radium emanation and its products in 1 c.c. of the atmosphere

$$=\tfrac{3}{4}\times\cdot16\times(105\times10^{-12}\times10^{-6})$$
$$=1\cdot3\times10^{-17}\text{ c.c.}$$

Allowing an equal amount to be produced from the thorium products in the atmosphere, and realizing that most of the helium produced by the disintegration of the earlier members of the series in the earth's crust is kept there, it follows that 3×10^{-17} c.c. of helium is produced by radioactive processes per c.c. of the atmosphere per year.

The amount of helium actually present in 1 c.c. of the atmosphere is about 5×10^{-6} c.c., so that these figures hardly afford a method of calculating the age of the earth.

SUMMARY.

(1) The amount of radium emanation in the atmosphere near the earth's surface at Cambridge has been measured at intervals during a year by the coconut charcoal method.

(2) The average radium equivalent per cubic metre is 105×10^{-12} gm. The lowest value is 35×10^{-12} gm., and the highest 350×10^{-12} gm., a ratio of 1 : 10.

(3) The amount of emanation is usually lowest during

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* Manchester Lit. and Phil. Soc. Mem. 54, 1909-1910.

cyclones, *i. e.* during windy, wet weather, when the barometer is low; and usually highest during anticyclones, *i. e.* during dry weather with light variable winds and a high barometer.

(4) In cases where (3) breaks down, a study of the trajectories of the surface air-currents reveals that when air has travelled over the sea to Cambridge or very rapidly over land, the emanation-content is low, while if the air has spent much time over land, the emanation-content is high.

(5) The results of other experiments have been discussed. Eve's results obtained by a similar method at Montreal differ from the author's, but this is probably due to different geographical conditions. Experiments made by measuring the active deposits on exposed wires seem to give misleading and indefinite results.

(6) The number of ions produced per c.c. per sec. in free air at Cambridge due to the radium emanation present is about 2·1 on the average, with a minimum value of ·7 and a maximum value of 7·0.

In conclusion the author wishes to thank Prof. Sir J. J. Thomson for permission to carry out these experiments in the Cavendish Laboratory, and for his stimulating suggestions. The author also wishes to express his thanks to Dr. W. N. Shaw and his assistants at the Meteorological Office for help in tracing the trajectories of the air.

Cavendish Laboratory, Cambridge,
April 1910.

II. *On the Radioactivity of the Rocks of the Transandine Tunnel.* *By* Arnold L. Fletcher, *B.A.I.*[*]

THE following determinations of the Radium content of a series of volcanic rocks from the Andes of South America were made as the result of a suggestion by Professor Joly, that a systematic analysis of some of the larger igneous masses was desirable.

This is the more apparent in view of the various results obtained upon igneous rocks from different localities, and the consequent necessity for a larger number of systematic determinations, with a view to the establishment of some sort of a mean in the case of such materials.

The determinations were made upon a series of rock-specimens taken at various points during the working of the tunnel, and which were obtained by the kindness of Mr. E. Manisty, M.Inst.C.E. They were taken at an average depth of about 1000 feet below surface-level.

[*] Communicated by the Author.

Preparation of Solutions.

Owing to the extreme sensitiveness of the electroscopes used, and the small quantity of material dealt with at each experiment, every possible precaution was taken throughout to avoid the possibility of any errors due to contamination. The work was carried out in a room which had never contained radioactive preparations of any sort. The apparatus was—with few safe exceptions—new, and hitherto unused.

Extreme care was taken to avoid the introduction of radium from the use of impure chemicals, it having been observed in previous work that the commercial alkalies and hydrochloric acid may contain a sufficient quantity of radium to exert a noticeable effect upon the electroscopes. Both the water and the hydrochloric acid used were distilled in the laboratory. In the latter case, the distillation was performed over commercially pure chloride of sodium, so that 100 c.c. of purified acid, evaporated down, showed no trace of sulphuric acid with barium chloride; certain experiments having shown that traces of sulphuric acid are capable of diminishing the emanating radioactive power of rock solutions.

Care was taken in the preparation of the specimens for chemical treatment that they were not exposed to any risks attendant upon handling, but were in nearly all cases manipulated by forceps. The quantities of chemicals used, together with a full description of the electroscopes and of the method employed, may be found in 'Radioactivity and Geology,' chap. xii., and need not therefore be further described.

Considerable difficulty was experienced in obtaining solutions free from precipitate ; often three, and sometimes even four, refusions having been made. It was, however, frequently found that a repetition of the fusion failed to render soluble the original precipitate. It may be noted that those solutions which contained precipitate, and which in the table given below are distinguished with a letter *p*, appear to show no falling off from the general mean.

Calibration of the Electroscopes.

Particular attention was paid to the calibration of the electroscopes. Of these, two were continually in use, "A" being calibrated to an alkaline, and "B" to an acid solution. Both were of about 620 c.c. capacity, and much alike in the dimensions of the gold-leaf system. The earlier calibrations were effected by an observation of the rate of collapse of the leaf, consequent upon the rapid introduction of the emanation, from an aqueous solution containing 1 m.g. uraninite. Subsequently the calibration was effected under conditions more nearly approximating to those obtaining when a rock of low radium content is being examined. To this end a quantity of radium was used, more nearly comparable with the amount found in the solutions examined, and one of the electroscopes was calibrated from an alkaline rock solution, whose radium content had been previously determined; the other similarly from an acid solution.

The following results will show that the calibration of the electroscopes under the new conditions resulted in a marked modification in the constant. The following is a list of the calibrations.

ELECTROSCOPE A.

(1) Standardized from 1 m.g. uraninite (from a standard solution of a uraninite containing 64 per cent. uranium, made by dissolving the mineral in HNO_3, and diluting to a strength of 1 m.g. in 1 c.c.) in about 500 c.c. distilled water; enclosed for 19 hours 25 minutes, involving the accumulation of 14 per cent. of the equilibrium amount of the emanation.

The transference was through a capillary tube and occupied about ten minutes.

Gain = 60 scale-divisions per hour.

From this $C = 0{\cdot}52 \times 10^{-12}$,

where C represents the quantity of radium in grams responsible for a gain of one scale-division per hour.

(2) An earlier experiment of the same character gave

$$C = 0{\cdot}51 \times 10^{-12}.$$

In these experiments the emanation in the electroscope would be equivalent to an amount in equilibrium with $31{\cdot}2 \times 10^{-12}$ gram of radium, *i. e.* a quantity almost four times in excess of the average measured in the experiments, in which the gain was seldom over 20 scale-divisions per hour.

(3) Standardized with ·4 m.g. uraninite in 600 c.c. distilled water. Closed 20 hours, *i. e.* 14·4 per cent. emanation collected. Boiled 36 minutes with talc, using slow admission to electroscope. Emanation present in electroscope equivalent to $12{\cdot}5 \times 10^{-12}$ gram radium in solution.

Gain = 24·5 scale-divisions per hour.

Hence $C = {\cdot}51 \times 10^{-12}$.

(4) Standardized from the alkaline solution derived from 10 grams Keuper Sandstone, fused with 24 grams mixed carbonates, in 600 c.c. distilled water; leached and filtered clear, which when tested gave a gain of 4 scale-divisions per hour. To this was added ·2 m.g. uraninite, standard solution. Closure 14 days, *i. e.* 92·7 per cent. emanation collected.

Gain = 65·5 scale-divisions per hour.

True gain = 70·7 „ „

if closed till radioactive equilibrium was established. Hence

Gain due to added radium = 66·7 scale-divisions per hour,

whence $C = \cdot 61 \times 10^{-12}$.

The constant will be somewhat higher if we assume the normal leak the same for both experiments, when

2nd leak — 1st leak = gain for added radium.

This comes out as 62 scale-divisions per hour, and

$$C = \cdot 65 \times 10^{-12}.$$

(5) Standardized from an alkaline solution obtained by fusing 20 grams basalt in 120 grams carbonates, dissolving in distilled water, leaching and filtering.

This was found to contain 3×10^{-12} gram radium by preliminary experiments, using the constant $0\cdot 6 \times 10^{-12}$.

To this was added ·2 m.g. uraninite from standard solution, so that the total radium present was

$$43\cdot 5 \times 10^{-12} + 3 \times 10^{-12} \text{ gram} = 46\cdot 5 \times 10^{-12} \text{ gram}.$$

Closure 20 days. Gain 63·7 scale-divisions per hour.

Hence $$C = \frac{46\cdot 5 \times 10^{-12}}{63\cdot 7} = 0\cdot 73 \times 10^{-12}.$$

If again we calculated by the difference in gain of rate of discharge in the 1st experiment (5 scale-divisions per hour) and in the 2nd experiment (63·7 scale-divisions per hour), we get the

Gain due to radium = 58·7 scale-divisions per hour.

Hence $$C = \frac{43\cdot 5 \times 10^{-12}}{58\cdot 7} = 0\cdot 74 \times 10^{-12}.$$

ELECTROSCOPE B.

In the case of this electroscope the tests were made throughout with strongly acid solutions.

(1) In this case the test was carried out with the temporary addition of a U tube of $CaCl_2$ and KHO, and with the delivery tube reaching to the bottom of the electroscope.

Standardized with 1 m.g. uraninite in 60 c.c. strong radium-free HCl and 600 c.c. distilled water. Closure 44 hours 30 minutes, *i.e.* 30 per cent. emanation collected.

Gain = 82·4 scale-divisions per hour.

Here the emanation present was equivalent to a quantity in equilibrium with an amount of radium = $65{\cdot}28 \times 10^{-12}$ gram.

Hence $$C = \frac{65{\cdot}28 \times 10^{-12}}{82{\cdot}4} = 0{\cdot}792 \times 10^{-12}.$$

(2) Standardized from an acid solution of 10 grams Keuper Sandstone, consisting of the precipitate insoluble in water after fusion with 24 grams fusion mixture, dissolved in 70 c.c. distilled HCl. Solution very limpid.

Test I. Closure 14 days.

Total leak = 22 scale-divisions per hour

and gain = 16 „ „

Test II. (after adding ·2 m.g. uraninite from standard solution). Closure 14 days. Gain = 65·5 scale-divisions per hour.

Gain due to radium = 65·5 − 16 = 49·5 scale-divisions per hour.

Hence $$C = \frac{40{\cdot}5 \times 10^{-12}}{49{\cdot}5} = 0{\cdot}82 \times 10^{-12}.$$

In this case the emanation present represented $40{\cdot}47 \times 10^{-12}$ gram radium.

(3) Standardized from the acid solution of No. 9 of the Andes rocks. This had already been found to contain 9×10^{-12} gram radium, using the constant ·8. To this was added from a standard uraninite solution $8{\cdot}84 \times 10^{-12}$ gram radium.

Hence

total radium = $17{\cdot}84 \times 10^{-12}$ gram.

Gain (closure 21 days) = 25 scale-divisions per hour.

Hence $$C = \frac{17{\cdot}84 \times 10^{-12}}{25} = {\cdot}71 \times 10^{-12}.$$

(4) Standardized from the acid solution of No. 5 of the Andes rocks. This contained $9{\cdot}17 \times 10^{-12}$ gram radium. To this was added $7{\cdot}07 \times 10^{-12}$ gram radium from standard solution. Closure 21 days.

$$\text{Total radium} = 16{\cdot}24 \times 10^{-12} \text{ gram.}$$
$$\text{Gain} = 19 \text{ scale-divisions per hour.}$$

Hence
$$C = \frac{16{\cdot}24 \times 10^{-12}}{19} = {\cdot}85 \times 10^{-12}.$$

The use of the slow admission capillaries used in the foregoing experiments was continued throughout the rock tests, although comparative experiments in which the admission was made as rapid as was consistent with the safety of the gold leaf, and again with the capillary tube, showed no detectable difference. The construction of the electroscopes were of course also preserved in all particulars alike.

The importance of conducting the calibrating experiment under conditions of the solution as nearly identical as possible with those under which the actual experiments are made, seems immediately apparent from these results. Such a variation in the constant as appears in the above experiments, in the case of electroscope A, might introduce an error of deficiency of as much as 30 per cent. into each experiment.

Effect of Sunlight.

Care was taken to shield the electroscopes from bright daylight, and the discharge rates were read throughout in semi-darkness. A short series of observations showed that the discharge rate might be raised from 5 scale-divisions per hour—the normal leak—to over 80 per hour in direct sunlight, and 30 per hour in bright diffused light. The normal leaks of 10 and 5 scale-divisions per hour for "A" and "B" respectively, were wonderfully constant from day to day, scarcely ever varying over 1 scale-division per hour, three hours after refilling with fresh air. Under these circumstances an increase of 2 or 3 scale-divisions per hour, at an interval of three hours subsequent to the introduction of the emanation, was unmistakably evident.

This would be accounted for by as small a quantity as $3 \times {\cdot}8 \times 10^{-12}$ gram of radium in a solution containing say 10 grams of rock. Hence a quantity of radium of about ${\cdot}24 \times 10^{-12}$ gram per gram was capable of measurement with a fair degree of accuracy.

The method of extraction of the emanation was essentially that described by Professor the Hon. R. J. Strutt, with the modification adopted by Professor Joly, of boiling—for thirty minutes—with talc, *in vacuo*. A slight departure from the method described by Professor Joly was made. At the conclusion of the boiling, the cooling water was cut off, and the ebullition accelerated until steam began to condense in the receiver bulb, when the gas was cut off, and the pinch-cock closed simultaneously. In addition to the possible advantage of a brief violent ebullition, this had the effect of removing any emanation from the flask and condenser, without the addition of any water to the solution; which was then ready for the estimation of contained thorium. A slow transference of the emanation to the electroscopes was then effected through the capillaries—the process occupying about 10 minutes. A glass tube, containing a water-bubble, served to indicate the moment when the electroscope was filled to atmospheric pressure.

The Rocks.

The following representative specimens of the rocks dealt with, were selected, and submitted to microscopic examination :—

Specimen 1.—Large phenocrysts of both soda-lime and lime-soda felspars with rare sanidine, in a turbid ferruginous ground-mass with small tabular felspars, and brownish microliths. Magnetite and red oxide of iron abundant. Many indeterminate iron-stained crystals. No glass. Much augite in yellowish-green phenocrysts. Borders often ferruginous. General appearance of rock highly altered. External colour light grey. Structure trachytic.

An altered Trachyte, with some Andesitic characteristics.

Specimen 4.—Ground-mass consisting of grains of felspar, and turbid glass with indeterminate ferruginous particles. The whole stained red-brown with iron oxide. Many fragments of andesitic lava. External colour brown.

A Felspathic Tuff, much altered.

Specimen 7.—A fine-grained homogeneous ground-mass, consisting mostly of tabular felspar—sometimes banded—with some turbid glass. Considerable calcitic matter developed. Iron-stained particles common. External colour red.

A fine-grained, altered, Andesitic Tuff.

Specimen 8.—Many twinned phenocrysts of soda-lime and lime-soda felspars—oligoclase predominant—in a ground-mass of oligoclase microliths. Magnetite in small grains dusted over the field. No glass, but areas stained green and cryptocrystalline. Colour grey.

An Oligoclase-Trachyte, somewhat decomposed.

Specimen 12.—Phenocrysts of tabular and columnar potash and soda lime felspars, in a ground-mass in which small oligoclase felspars predominate over crystals of soda-lime felspar. Some augite crystals. No glass. Much iron oxide in grains, and irregular areas. Colour red-brown.

An altered Trachyte.

Specimen 13.—A coarse-grained, dark brown rock, partially disintegrated. Consists of irregular grains of different lavas cemented in a nearly opaque matrix, much clouded by iron oxide. A few grains of olivine.

An altered, basic Tuff.

Specimen 14.—A few phenocrysts of columnar lime-soda felspars, and sanidine, in a ground-mass consisting of oligoclase microliths with much calcite in large areas and irregular cracks. No glass; but much green chloritic matter developed—possibly altered glass. Some grains of magnetite. Colour medium grey. Grain fine.

A partially decomposed Sanidine-Oligoclase-Trachyte.

Specimen 17.—Consists of andesitic fragments with calcitic and ferruginous alteration products in a felspathic ground-mass. All constituents in various stages of decomposition. Colour light. Grain medium.

A decomposed Felspathic Tuff.

Specimen 18.—Consists of columnar phenocrysts of sanidine and oligoclase, with more basic felspars, in a ground-mass of oligoclase microliths and calcareous matter. Much chloritic and calcitic matter developed throughout. No magnetite. No glass. Colour light grey.

A Sanidine-Oligoclase-Trachyte, partly decomposed.

It was not considered necessary to examine microscopically the remainder of the specimens, which have been named by comparison with those selected.

The following table shows the radioactivity of the specimens determined. The thorium content was estimated from the same solutions by Professor Joly, using the method described by him (Phil. Mag. May & July, 1909).

No.	Description.	Kilometres from Argentine end.	Radium $\times 10^{-12}$ gram per gram.	Thorium $\times 10^{-5}$ gram per gram.	State of Solution.
1.	Trachyte	2·425	·32	·39	
2.	Tuff	2·425	·80	·43	
3.	Tuff	2·500	·40	0	
4.	Felspathic Tuff	2·650	1·14	·05	
5.	Tuff	2·650	1·40	—	
6.	Tuff	2·725	1·26	·80	
7.	Andesitic Tuff	2·850	·90	—	
8.	Oligoclase Trachyte	2·890	·35	·58	*p.*
9.	Trachyte	3·125	·77	·31	
10.	Trachyte	3·158	·57	·51	*p.*
11.	Andesite	3·200	·52	·41	
12.	Trachyte	3·360	·64	·27	
13.	Tuff	3·466	1·11	·84	*p.*
14.	Sanidine-Oligoclase-Trachyte	3·540	1·07	·71	*p.*
15.	Tuff	3·545	·68	·85	*p.*
16.	Tuff	4·209	·93	1·11	*p.*
17.	Felspathic Tuff	4·409	1·33	·55	*p.*
18.	Sanidine-Oligoclase-Trachyte	3·609	·33	·30	
19.	Tuff	4·709	·58	·83	*p.*
	MEAN		**·79**	**·56**	

It may be noted that the mean ratio borne by the thorium content of these rocks to the radium content, viz. $\cdot 71 \times 10^7$, bears an approximation to that obtained by Professor Joly in a paper on "The Radioactivity of certain Lavas" (Phil. Mag. October, 1909), where the proportion of thorium to radium found was $\cdot 65 \times 10^7$.

The striking feature of these results is their poorness in radioactive matter. This may possibly be referred to the alterations undergone by the rocks, which may have been attended by the removal of all that part of the radium which was soluble in percolating waters. In no case was any trace of radium, and in few cases was any thorium discovered in the alkaline solutions.

The quantities of radioactive matter observed would give rise to very small heating effects. Taking the mean radium content for the rocks in the neighbourhood of the tunnel as $\cdot 79 \times 10^{-12}$ gram per gram, and the thorium content as $\cdot 52 \times 10^{-5}$ gram per gram, we find for the radium the rate of evolution of heat as $201 \cdot 6 \times \cdot 79 \times 10^{-12} = 1 \cdot 6 \times 10^{-10}$ calorie per gram per hour; and for the thorium—allowing that the heat produced per hour per gram of elemental thorium in equilibrium as $2{\cdot}38\times10^{-5}$ calorie per hour—we get for the heat production $2{\cdot}38\times10^{-5}\times{\cdot}56\times10^{-5}=1{\cdot}33\times10^{-10}$ calorie per gram per hour. The total heat evolved is therefore $2{\cdot}9\times10^{-10}$ calorie per gram per hour.

The small thermal effect due to such low quantities of radioactive matter in rocks, has been pointed out by Professor C. H. Lees (Roy. Soc. Proc. A. vol. lxxxiii. p. 344), and we should not expect—nor was there found—any abnormally high degree of temperature in the tunnel.

In conclusion I desire to express my gratitude to Professor Joly, at whose suggestion and under whose directions the work was carried out, and to Professor W. E. Thrift, for his kindness in providing the use of the room in which the experiments were performed.

Geological Laboratory,
Trinity College, Dublin.
May, 1910.

III. *The Interference of the Reflected-Diffracted and the Diffracted-Reflected Rays of a Plane Transparent Grating. and on an Interferometer.* By C. Barus *and* M. Barus [*].

1. *Introductory.*

VII

If parallel light, falling on the front face of a transparent plane grating, is observed through a telescope after reflexion from a rear parallel face (see fig. 1), the spectrum is frequently found to be intersected by strong vertical interference bands. Almost any type of grating will suffice, including the admirable replicas now available, like those of Mr. Ives. In the latter case one would be inclined to refer the phenomenon to the film and give it no further consideration. On closer inspection, however, it appears that the strongest fringes certainly have a different origin and depend essentially on the reflecting face behind the grating. If for instance this face is blurred by attaching a piece of rough wet paper, or by pasting the face of a prism upon it with water, so as to remove most of the reflected light, the fringes all but disappear. If a metal mirror is forced against the rear glass face, whereby a half wave-length is lost at the mirror but not at the glass face in contact, the fringes are impaired, making a rather interesting experiment. With homogeneous light the fringes of the film itself appear to the naked eye as they are usually very large by comparison.

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[*] Communicated by the Authors. Abbreviated from a report to the Carnegie Institute of Washington, D.C., U.S.A.

Granting that the fringes in question depend upon the reflecting surface behind the grating, they must move if the distance between them is varied. Consequently a phenomenon so easily produced and controlled is of much greater interest in relation to micrometric measurements than at first appears, and we have for this reason given it detailed treatment. It has the great advantage of not needing monochromatic light and of being applicable for any wave-length whatever, and admitting of the measurement of small horizontal angles.

When the phenomenon as a whole is carefully studied it is found to be multiple in character. In each order of spectrum there are different groups of fringes of different angular sizes and usually in very different focal planes. Some of these are associated with parallel light, others with divergent or convergent light, so that a telescope is essential to bring out the successive groups in their entirety. At any deviation the diffracted light is necessarily monochromatic; but the fringes need not and rarely do appear in focus with the solar spectrum. If the slit of the spectroscope is purposely slightly inclined to the lines of the grating certain of the fringes may appear inclined in one way and others in the opposite way, producing a cross pattern like a pantograph. The reason for this appears in the equations.

In any case the final evidence is given when the reflecting face behind the grating is movable parallel to it. The interferometer so obtained is subject to the equation (air space e, wave-length λ, angle of incidence i, of diffraction θ'),

$$\delta e = \lambda/2(\cos\theta' - \cos i),$$

and is therefore less unique as an absolute instrument than Michelson's classic apparatus or the device of Fabry and Perot. Its sensitiveness per fringe, δe, depends essentially upon the angle of incidence and diffraction and it admits of but 1 cm. (about) of air space between grating face and mirror before the fringes become too fine to be available. But on the other hand it does not require monochromatic light (a Welsbach burner suffices), it does not require optical plate glass, it is sufficient to use but a square cm. of grating film, and it admits of very easy manipulation, for painstaking adjustments as to normality, &c., are superfluous. In fact, it is only necessary to put the sodium lines in the spectrum reflected from the grating and from the mirror into coincidence both horizontally and vertically with the usual three adjustment screws on grating and mirror. Naturally sunlight is here desirable. Thereupon the fringes will usually appear and may be sharply adjusted upon a second trial at once.

When the air space is small, coarse and fine fringes (fluted fringes) are simultaneously in focus, one of which may be used as a coarse adjustment on the other. Finally, the sensitiveness per fringe to be obtained is easily a length of one half wave-length in the fine fringes and one wave-length in the coarse fringes, though the latter may also be increased almost to the limit of the former.

2. *Observations.*

The following observations were made merely to corroborate the equations used. The general character of the results will become clear on consulting the following abbreviated table chosen at random from many similar data. An Ives replica grating with 15,000 lines to the inch (film between plates of glass ·46 cm. thick) was mounted as usual on a spectrometer admitting of an angular measurement within one minute of arc. Parallel light fell on the grating, fig. 1, *gg*, under different angles of incidence, i, and the spectrum lines were observed by reflexion (after reflexion from *gg* and the rear face *ff*) at an angle of diffraction θ' in air, both in the first and second order of spectra, and so far as possible on both sides of the directly reflected beam. In view of the front plate, the angle i corresponds to an angle of refraction r within the glass, and the angle θ' similarly to an angle of diffraction θ, respectively. Hence $r>\theta_2$ or $\theta_1<r$ denotes the sides of the ordinary ray on which observation is made. As a rule these were as nearly as possible in the region of the *D* line passing toward *E*. Finally, $\delta\theta$ denotes the angle between two consecutive dark fringes, observed and computed as specified. Similarly δe will be reserved for changes of thickness e of the glass and $\delta e'$ for changes of the air space in case of an auxiliary mirror *M*.

For $i=0°$ the number of groups of lines was a single set in each order, but only the end of the spectrum could be seen. Measurements refer (about) to the *C* line. For $i=45°$ several groups were too close together, or too faint for measurement, and the same is true for $i=22°{\cdot}5$. An estimate of divergence is all that could be attempted on the given spectrometer. The case $\theta_1>r$ was usually not available, but for $i=22°{\cdot}5$ two sets were found in the first order, one being the normal set. The fringes in all cases decrease in size from red to violet, but less rapidly than wave-length (§ 7).

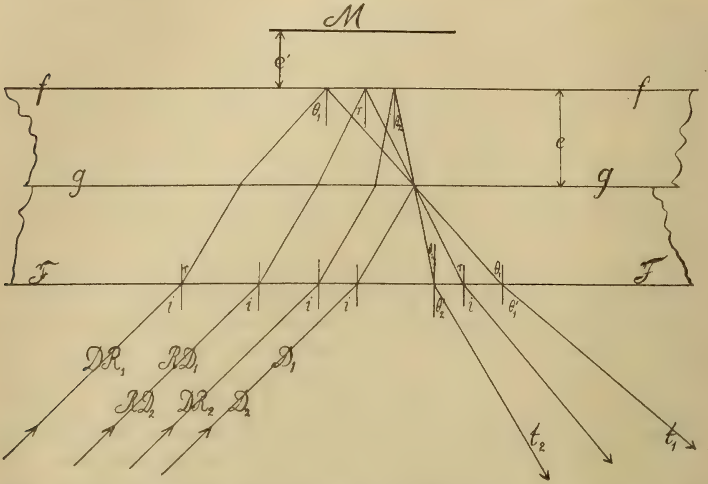
Whether they are convergent or divergent for a given set of fringes, as for instance for the strong set, depends on the position of the grating. Thus the divergent rays become convergent when the grating is rotated 180° about its normal.

It is therefore definitely wedge-shaped. In fact when the auxiliary mirror M is used, the fringes may be put anywhere, either in front of or behind the principal focal plane, by suitably inclining the mirror.

3. *Equations.*

If we suppose the film of the grating gg to be sandwiched in between plates of glass each of thickness e, it will be seen

Fig. 1.



that triplicate rays pass in the direction t_1 ($\theta_1' > i$), or of t_2 ($\theta_2' < i$), which will necessarily produce interference either partial or total. With respect to t_1, the only light received comes either from D_1 by direct diffraction at gg, or from RD_1, by reflexion from the lower face ff, and thereafter by diffraction at gg; or from DR_1, by diffraction at gg and reflexion at ff. Similarly, the light along t_2 comes in like manner either from D_2, or DR_2, or RD_2. With regard to the angles of incidence and refraction or of diffraction within the glass or outside of it, we have the equations for the first and second order of spectra (D being the grating space).

$$\sin i_1 = \mu \sin r_1, \quad \text{(1)}$$

$$\sin \theta_1' = \mu \sin \theta_1, \quad \text{(2)}$$

$$\sin \theta_2' = \mu \sin \theta_2, \quad \text{(3)}$$

$$\sin r - \sin \theta_2 = \lambda/D\mu \text{ or } = 2\lambda/D\mu, \quad \text{(4)}$$

$$\sin \theta_1 - \sin r = \lambda/D\mu \text{ or } = 2\lambda/D\mu, \quad \text{(5)}$$

$$\sin i - \sin \theta_2' = \lambda/D_1, \text{ etc.}, \quad \text{(4')}$$

$$\sin \theta_1' - \sin i = \lambda/D_1, \text{ etc.}, \quad \text{(5')}$$

TABLE I.—INTERFERENCES. Grating between plates of glass each ·48 cm. thick. Additional rear plate (mirror) ·29 cm. thick. Index of refraction of glass $\mu=1·527$.

Side.	Order.	Colour.	Rays.	i.	Mean θ'.	Observed $\delta\theta'$ minutes.	Computed $\delta\theta'$ minutes.	Remarks.
$\theta>r$. $r=0$. $\theta=15° 49'$.	1	* C.	Convergent.	0°	24° 8′	1′·87	1′·81	
	2	......	....	......	......	......	About double divergence but not clear.	
$r>\theta$. $r=27° 35'$. $\theta=13° 35'$.	1	D to E.	Less convergent.	45°	21° 1′	1′·80	1′·70	Strong. Total.
	1	D to E.	Parallel.	45°	21° 21′	·3	....	Estimated **.
	1	Do.	Divergent.	45°	21° 32′	·7	....	Estimated **.
	1	Do.	More divergent.	45°	22° 40′	·87		
$r>0$.	2	Do.	Convergent.	45°	31′	3′·32	....	Clear but faint.
	2	Do.	Convergent.	45°	......	·8	....	Very fine and close.
	2	Do.	Parallel.	45°	31′	1′·20		
	2	Do.	Divergent.	45°	......	......	....	Not clear, $\delta\theta'=2'·0$?
	2	Do.	Very divergent.	45°	......	......	....	Not clear, $\delta\theta'=3'·0$?
$r<\theta$. $r=14° 31'$. $\theta=1° 23'$.	1	D to E.	Very divergent.	22°·5	1° 30′	4·7′	....	Faint but certain.
	1	Do.	Divergent.	22°·5	......	......	....	Faint, $\delta\theta'=2'$?
	1	Do.	Nearly parallel.	22°·5	......	......	....	Faint, $\delta\theta'=1'·5$?
	1	Do.	Parallel.	22°·5	......	......	....	Fine, close, and strong.
	1	Do.	Convergent.	22°·5	2° 6′	1′·85	1′·84	Strong. Total.
Interferometer. Thicknesses e and e' of glass.								
	1	D to E.	....	22°·5		1′·83	1′·84	$e=·48$ cm. Total.
	1	Do.	....	22°·5		1′·13	1′·15	$e'=·77$ cm. Total.

* Colour not definite, only end of red spectrum seen.

** Lines strong but too fine and close together.

where μ is the index of refraction of the glass, found to be equal to 1·5265 for sodium light, by breaking off a small corner of the glass of the grating and using Kohlrausch's total reflectometer.

If the wave fronts be taken in the glass plate *ffgg*, the equations become

$$n\lambda = 2e\mu \cos r, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$n\lambda = 2e\mu \cos \theta_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$n\lambda = 2e\mu(\cos r - \cos \theta_1) \quad . \quad . \quad . \quad . \quad (8)$$

with three other corresponding forms for $\theta < r$.

For an air space between *gg* and *M* the equations would be

$$n\lambda = 2e \cos i,$$

$$n\lambda = 2e \cos \theta',$$

$$n\lambda = 2e(\cos \theta' - \cos i); \text{ \&c.}$$

4. *Differential Equations.*

The quantity measured on the spectrometer is essentially angular and preferably $d\theta'/dn$, the angular distance apart of the fringes, in radians. Later we shall measure δe or the linear displacement of the parallel faces per fringe. In any measurement, however, we meet with embarrassment, inasmuch as n, λ, μ, r, θ, θ', are all variable. The angle i and the thickness e and the grating space D are alone given. Among these the variation of r with μ and λ must be found by experiment. Fortunately, in case of the interferometer, all these variables are eliminated and e alone changes subject to a given i and θ'. The μ used need not be known. See § 7.

For the present purpose, as the variation of μ enters only as a correction, we have been satisfied with the usual results in physical tables. If from the C to the D line

$$(d\mu/\mu)/(d\lambda/\lambda) = -\cdot016,$$

and from the B to the C line, $= -\cdot013$, we may write

$$-\frac{d\mu}{\mu} = \cdot015\,\frac{d\lambda}{\lambda},$$

and therefore

$$d\left(\frac{\lambda}{\mu}\right) = 1\cdot015\,\frac{d\lambda}{\mu}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We shall abbreviate $a = \cdot015$, $b = 1 + a$.

The case $\theta > r$ in the present paper is not of much experimental interest. We may therefore omit it here. For the case of $r > \theta$ we shall have successively, and for the total interferences *RD*, *DR*, equation (8),

$$-\frac{d\lambda}{d\mu} = \frac{\lambda\cos\theta}{\sin r - b\sin\theta}\,\frac{d\theta}{dn}, \quad \dots\dots \quad (11)$$

$$-\frac{dr}{dn} = a\,\frac{\tan r\cos\theta}{\sin r - b\sin\theta}\,\frac{d\theta}{dn}, \quad \dots\dots \quad (12)$$

$$\frac{d\mu}{dn} = \frac{a\mu\cos\theta}{\sin r - b\sin\theta}\,\frac{d\theta}{dn}, \quad \dots\dots \quad (13)$$

$$\frac{d\theta'}{dn} = \frac{\mu\cos\theta(\sin r - \sin\theta)}{\cos\theta'(\sin r - b\sin\theta)}\,\frac{d\theta}{dn}, \quad \dots \quad (14)$$

and finally corresponding to equations (6), (7), (8),

$$\frac{d\theta'}{dn} = \frac{\cos\theta}{2e\cos\theta'}\,\frac{\lambda(\sin r - \sin\theta)}{b - \sin r\sin\theta}, \quad \dots\dots \quad (15)$$

$$\frac{d\theta'}{dn} = \frac{\cos\theta}{2e\cos\theta'}\,\frac{\lambda(\sin r - \sin\theta)}{b\cos r\cos\theta + a\sin r\tan r\cos\theta}, \quad \dots \quad (16)$$

$$\frac{d\theta'}{dn} = \frac{\cos\theta}{2e\cos\theta'}\,\frac{\lambda(\sin r - \sin\theta)}{b\big(1 - \cos(r-\theta)\big) + a\sin r\sin\theta(1 - \cot\theta\tan r)}, \quad (17)$$

the last term in the denominator being corrective. Here $d\theta'/dn$ is the observed angular deviation of two consecutive fringes.

5. *Normal Incidence or Diffraction, &c.*

For the case of normal incidence $i = r = 0$, the equations corresponding to (6), (7), and (8) take a simplified form, and are respectively

$$-\frac{d\theta_0'}{dn} = \frac{\cos\theta}{2be\cos\theta'},\lambda\sin\theta, \quad \dots\dots \quad (15')$$

$$-\frac{d\theta_0'}{dn} = \frac{1}{2be\cos\theta'}\lambda\sin\theta, \quad \dots\dots \quad (16')$$

$$-\frac{d\theta_0'}{dn} = \frac{\cos\theta}{2be\cos\theta'}\,\frac{\lambda\sin\theta}{1 - \cos\theta}. \quad \dots \quad (18')$$

If $\theta' = \theta = 0$ for normal diffraction, which is particularly useful in Rowland's adjustments as well as on the spectrometer

$$-\left[\frac{d\theta'}{dn}\right]_{\theta=0}=\frac{\lambda}{2e}\frac{\sin r}{b(1-\cos r)-a\sin r\tan r}$$

for the case of total interference corresponding to equations (8) and (17). If $i=-\theta'$ or $r=-\theta$,

$$\left[\frac{d\theta'}{dn}\right]_{r=-\theta}=\frac{\lambda}{2e}\frac{1}{\tan\theta\cos\theta'}.$$

6. *Comparison of the Equations of Total Interference with Observation.*

The partial interferences corresponding to equations (6) and (7) are usually too fine to be seen unless e is very small. They amount in cases of equations (15) and (16), where $e=\cdot48$ cm., to the following small angles :—

	(15)	(16)
$i=0°$,	$d\theta'/dn=0'\cdot060$,	$d\theta'/dn=0'\cdot062$;
$22°\cdot5$,	$0'\cdot048$,	$0'\,050$;
$45°$,	$0'\cdot057$,	$0'\cdot058$;

usually less than four seconds of arc and are therefore lost. The origin of the fine interferences actually seen in the table is thus still open to surmise. With small e and the interferometer they are obvious.

The total interferences as computed in the above table agree with the observations to much within ·1 minute of arc, and these are experimental errors ; particularly so, as it was not possible to use both verniers of the spectrometer. The interesting feature of the experiment and calculation is this, that $\delta\theta'$ has about the same value for all incidences i from 0° to 45° and even beyond. The equations do not show this at once owing to the entrance of μ and r. But apart from a and b, equation 17 is nearly

$$\frac{d\theta}{dn}=\frac{\lambda}{2e\mu}\frac{\lambda/D}{1-\cos(r-\theta)},$$

which is independent of r to the extent in which $\cos(r-\theta)$ is constant. The dependence of $d\theta'/dn$ on wave-length is borne out. See § 7.

Finally, $d\theta'/dn$ is independent of μ, except as it occurs in a and b.

If the glass plate *ff gg* is removed and a mirror M used, as in the interferometer, the fringes may be enormously enlarged by decreasing e and the measurements made with any degree of accuracy; but such measurements were originally impracticable and have now little further interest.

7. *Interferometer.*

The final test of the above equation is given by the last part of the table for different thicknesses of *glass*, $e = \cdot 48$ and $e = \cdot 77$ cm. The results are in perfect accord.

These data suffice to state the outlook for the interferometer. In this case n and e are the only variables, so that equation (8) becomes

$$\delta e = \lambda / 2\mu(\cos\theta - \cos r),$$

where δe is the thickness of glass corresponding to the passage of one fringe across the cross-hairs of the telescope.

If instead of glass in the grating above, an air space intervenes between the film of the grating and the auxiliary mirror M (fig. 1), the equation reduces to

$$\delta e = \frac{\lambda}{2(\cos\theta' - \cos i)}, \quad . \quad . \quad . \quad . \quad (20)$$

where i and θ' are the angles of incidence and diffraction in air.

These equations (20) embody a curious circumstance. Inasmuch as θ and θ' change as i increases from 0° to 90° from negative to positive values at about $i = 13°$ and $i = 20°$, respectively, the denominator of either equation (20) will pass through infinity (for air at about $i = 10°$). Hence at this value of i the motion of the mirror M produces no e-effect (stationary fringes), while on either side of it the fringes travel in opposite directions in the telescope when e changes by the same amount. In the negative case the sensitiveness for air spaces passes from $\delta e = -\cdot 000{,}489$ to $\delta e = -\infty$ per fringe. In the positive case from $\delta e = +\infty$ to $\delta e - \cdot 000{,}039$ per fringe, or to a limit of about a half wave-length in case of 15,000 lines to the inch. This limiting sensitiveness may be regarded as practically reached even at $i = 40°$, where $\delta e = \cdot 000{,}155$ cm. per fringe and an angle of about $i = 45°$ is most convenient in practice.

The addition to the large fringes the fine set appears when e is small or not more than a few tenths of a millimetre. The sensitiveness of these is naturally much more marked. In the two cases

$$\delta e = \lambda/2 \cos i \; . \; . \; . \; . \; . \; . \; . \quad (20')$$

and

$$\delta e = \lambda/2 \cos \theta', \; . \; . \; . \; . \; . \; . \quad (20'')$$

so that nearly $\lambda/2$ per fringe is easily attained.

At $i=20°$ about, and in case of an air space, θ' is nearly 0°. We suggested above that these fine fringes may be used as a fine adjustment in connexion with the large fringes, on which they are superimposed. In appearance these large fluted fringes are exceedingly beautiful. The fine fringes have the limiting sensitiveness of the coarse fringes, *i.e.* the cases for $i=90°$ or θ' equal to maximum value. If in different focal planes, both sets of fine fringes may be seen separately for small e (air wedge).

Equation (20) shows that for smaller grating spaces, D, and consequently also in the second order of spectra, there must be greater sensitiveness, *cæt. par.*; but as a rule we have not found these fringes as sharp and useful as those in the first order.

The limiting sensitiveness per fringe, however, follows a very curious rule. If in equation (20) we put $i=90°$,

$$2\delta e = \lambda / \sqrt{r(2-r)}$$

in the first order; if $r=\lambda/D$, and

$$2\delta e = \lambda/2 \sqrt{r(1-r)}$$

in the second order. D is the grating space. Both equations have a minimum, $\delta e=\lambda/2$, at $\lambda/D=1$ in the first order and $\lambda/D=\cdot 5$ in the second order, beyond which it would be *disadvantageous* to decrease the grating space. These minimum conditions are as good as reached even when D corresponds to 15,000 lines to the inch, as above, where roughly $10^6\delta e=38$ cm. in the first order and $10^6\delta e=33$ cm. in the second order.

To view the stationary fringes of the first order was not practicable since they occurred for $i=10°$, whereas the telescopes were in contact at about 20°. In the second order of spectra they may be approached more nearly, as they occur when i is roughly 20°. If the distance e is made small enough so that the three cases of equations (20), (20′), (20″) are visible, the appearance is very peculiar. The fringes of equation (20) are very slow moving. They are intersected by the small fringes of equation (20′), producing the fluted pattern already discussed. Over all travel the rapidly moving fringes of equation (20″), producing a kind of alternation or flickering which it is very difficult to analyse or interpret until e is very small, when all three sets are broad and easily recognized. Sunlight should be used. Nothing like these alternating fringes is seen in the first order.

The above equation shows finally that δe is not exactly proportional to wave-length, though the former decreases with the latter as found above.

The three equations (20) indicate finally that for $i > \theta'$ all fringes travel in the same direction with increasing e; whereas if $\theta' > i$, the set corresponding to equation (20) travel in a direction opposite to that of the set (20′) and (20″). This is strikingly borne out by making the experiment for $\theta' > i$ with a small angle i, both in the first and second order. Flickering in the latter case is accentuated.

Table II. contains a few data obtained by carrying the mirror on a Fraunhofer micrometer, reading to ·0001 cm., toward a stationary grating film. Observations were made in the region of the D lines. The grating was originally between plates of glass $e = \cdot 48$ cm. thick. Finally the plate between grating and mirror was removed, the whole distance now being an air space. This has no effect on δe, but e may then be reduced to zero and the fringes enlarged.

TABLE II.—Interferometer Measurements. Replica grating (collodion film). Air space 0–·25 cm.; total space 0–·9 cm.

i.	θ'.	Coarse fringes.		Fine fringes.	
		$\delta e\times10^6$ obs.	$\delta e\times10^6$ calc.	$\delta e\times10^6$ obs.	$\delta e\times10^6$ calc.
° ′	° ′	cm.	cm.	cm.	cm.
22 30	2 6	390	391	—	—
45 0	21 1	131	130	—	—
67 30	35 1	72	68	—	—
25 0	4 7	322	324	—	—
30 2	8 37	241	240	—	—
Glass removed between mirror and grating.					
22 25	1 40	387	392	34	30 32
45 0	20 49	129	130	33	42 32

These data merely test the equations, as no special pains were taken for accurate measurement, which neither the micrometer screw nor the special adjustments warranted. Usually the micrometer equivalent of 50 fringes was observed on the screw. The maximum distance e between grating and mirror was ·48 cm. of glass and ·25 cm. of air conjointly, or within 1 cm. In the case of fine fringes mere pressure on table or screw impaired the adjustment.

8–9. *Secondary Interferences.*

We come now to the consideration of the minor interferences (Table I.), which are either weaker, finer, or more diffuse than those discussed. In the interpretation of these we have not met with adequate success (assuming that after two reflexions the fringes can no longer be seen) to give it space here. We will therefore dismiss it with the remark that each of the three incident rays of figure 1 corresponds to three emergent rays for $\theta > r$ and three for $\theta < r$. If we call these a, b, c, a', b', c', a'', b'', c'' for either case, the possible partial interferences may be found by grouping the terms of the following determinant in pairs :—

$$\begin{vmatrix} a & b & c \\ a' & b' & c' \\ a'' & b'' & c'' \end{vmatrix}$$

There are 18 cases, most of which, however, are identical in path-difference.

10. *Convergent and Divergent Rays.*

What finally characterizes the above groups of interferences is the difference in position of their focal planes. They rarely coincide with the spectrum (parallel rays), and hence do not always destroy it. If present with the spectrum the latter is wholly wiped out. If the strong fringes are convergent for a given adjustment of grating they become divergent when the grating is rotated 180° about its normal. Hence the plates of glass are sharply wedge-shaped, and to these differences the location of the focal planes is to be referred.

In addition to this the three regular reflexions are not in the same focus which shows the surfaces (collodion film) to be slightly curved. The above experiments succeed best when two of the reflexions are yellowish, which probably means that the grating face is from the observer.

Suppose the remote glass face makes an angle $dr/2$ with the surface of the grating. Then the *DR* ray of the strong interferences has its angle increased by $d\theta = dr$, whereas the *RD* ray receives an increment of but

$$d\theta = \frac{\cos r}{\cos \theta} dr.$$

Hence if the *DR* and *RD* rays were parallel for parallel surfaces, they would be at an angle corresponding to

$$\frac{d\theta - dr}{dr} = \frac{\cos r - \cos \theta}{\cos \theta}, \quad . \quad . \quad . \quad . \quad (24)$$

where $dr/2$ is the angle of the wedge. If *DR* is negative in character, opposite conditions will hold, since dr and $d\theta$ change signs together.

Rays all but parallel will cross each other in front (convergent) or behind (divergent) the grating, depending on their mutual lateral positions. As a ray moves from the right to the left of the normal, the phenomenon may change from divergence to convergence, and *vice versa.*

These relations are very well brought out by the interferometer of which the mirror *M* may be inclined at pleasure. If small values of deviation only are in question, this instrument becomes a means of measuring small horizontal angles γ between mirror and grating as these involve less change of focus.

In fact, if h is the vertical height of the illumination at the mirror *M*, and the corresponding obliquity of fringes is equivalent to an excess of N fringes crossing the bottom of the cross-hairs as compared with the top for a wave-length λ, $\gamma = N\delta e/h$; or

$$\gamma = \frac{N\lambda}{2h(\cos \theta' - \cos i)}.$$

The question next at issue is thus the value of h. It will be noticed that if parallel rays fall upon the slit, they will be brought to a focus by the collimator objective first, and thereafter by the telescope objective placed at a diametral distance D beyond it. Then if S is the vertical length of slit used, and f_c and f_t the focal lengths of the two objectives respectively, it follows that the length $h = S$ is virtually illuminated. Hence

$$\gamma = \frac{N\lambda}{2S(\cos \theta' - \cos i)}. \quad . \quad . \quad . \quad . \quad (25)$$

For since the angle γ, or a ratio, is in question, $N\delta e/h$ is constant, and it makes no difference where the mirror M may be placed, *i. e.* how great the absolute vertical height of the illumination h may be.

In case of this method (parallel light impinging on the slit) the illumination at each point of the image is received from but a single point (nearly) of the mirror, whereas if the light falling on the slit is convergent, the whole vertical extent of the mirror illumination contributes to each point of the image in the ocular. Hence in the latter case the fringes are only sharp when M and the grating are rigorously parallel, and they soon become blurred when this is increasingly less true. The same observation also accounts for the greater difficulty in adjustment when lamp-light is used. In any case, equation (25) furnishes N/S. N may be obtained with an ocular micrometer. The angle γ may also be found by actually measuring the inclination to the vertical, β, of the fringes in the ocular. Here if the height of image s in the ocular corresponds to the vertical length of slit S,

$$\frac{s}{S}=\frac{f_t}{f_c}-2\left(1-\frac{D}{f_c}\right); \quad . \quad . \quad . \quad . \quad . \qquad (26)$$

while

$$\beta=\frac{Nf_t}{s}\frac{d\theta'}{dn},$$

where $d\theta'/dn$ is given by equation (17). Hence s may be eliminated and

$$\beta=\frac{N}{S\left(\frac{1}{f_c}-\frac{2}{f_t}+\frac{2D}{f_cf_t}\right)}\frac{d\theta'}{dn}.$$

If, now, we further eliminate N/S in equation (25) by equation (27), we have finally

$$\gamma=\frac{\beta\lambda(f_t+2(D-f_c))}{2f_cf_t(\cos\theta'-\cos i)\,d\theta'/dn},$$

so that γ is given in terms of β, the observed inclination of fringes in the ocular. To measure β the ocular must be revolvable on its axis so that the cross-hairs may be brought into coincidence with the fringes, and the angles found. To measure N, the D lines, if in focus, may often be used for reference in place of vertical cross-hairs, as they remain vertical.

Using the data of the above experiments, if $i=45°$, $N=1$,

$$f_c=f_t=D \text{ (nearly)}=23 \text{ cm.}, \qquad \cos\theta'-\cos i=\cdot 2264,$$
$$S=\cdot 9 \text{ cm.}, \qquad \lambda=60\times 10^{-6},$$
$$d\theta'/dn=493\times 10^{-6},$$

whence

$$\gamma=146\times 10^{-6} \text{ radian},$$

or about a half minute of arc per fringe, and $\beta=44'$ per fringe. Thus β is about 88 times as large as γ. At $i=22°\cdot 5$, $\gamma=1'\cdot 5$ per fringe, $\beta=45'$ per fringe. Naturally the sensitiveness increases with the angle of incidence i. When the fringes are large 1/10 fringe is easily estimated, so that a horizontal angle γ of a few seconds between mirror and grating should be measurable. An ocular micrometer as suggested would carry the precision beyond this.

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TTI VTR

IV. *On the Lengths of the Focal Lines of Cylindrical Lenses.*

By A. Whitwell, *M.A.*, *A.R.C.Sc.I.*[*]

The following paper is a continuation of one entitled "On Refraction at a Cylindrical Surface," published in the Phil. Mag. for July 1903[†]. In that paper the form of the focal lines or focal areas produced by refraction at a cylindrical surface was investigated, the aperture parallel to the axis of the cylinder being considered to be unlimited.

The object of the present paper is to find the lengths of the focal lines produced by a single cylindrical surface or by one or more cylindrical or sphero-cylindrical lenses, the aperture being so small that the focal lines may be considered to be straight lines. The formulæ arrived at are analogous to the ordinary first-approximation formulæ for thin spherical lenses.

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[*] Communicated by the Author.

[†] There is an error in this paper on p. 54. The two equations at the foot of this page should be

$$\frac{d}{d+\sqrt{a^2+h^2}}=\frac{r}{d''}.$$

$$d''=\sqrt{\mu^2(a-r)^2+(\mu^2-1)h^2}-(a-r).$$

1. *To find the lengths of the focal lines of a single cylindrical surface.*

Fig. 1 represents an elevation and fig. 2 a plan of the system of rays. The light is supposed to pass from left to right and the index of refraction of the second medium $= \mu$.

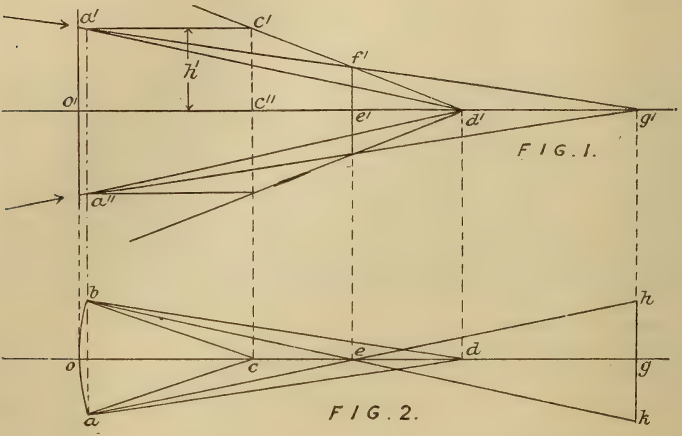

FIG. 1.

FIG. 2.

Distances measured to the right of o or o' are positive. The axis of the cylindrical surface is vertical and the arc b, o, a, represents the trace of the surface on the horizontal plane.

$h_1 = o'a' =$ the semi-aperture parallel to the axis of the cylinder or the axial semi-aperture.

$h_2 = oa = ob =$ the semi-aperture at right angles to the axis of the cylinder or the tangential semi-aperture.

$a'c'$ is the elevation and ac, bc, the plans of two normals to the cylindrical surface.

$r_1 =$ the radius of the surface.

$u = o'd' =$ the distance from o' of the point in which the incident rays cut the axis of x.

(a) *The line parallel to the axis of the cylinder; this may be called the axial focal line.*

Two incident rays symmetrical with respect to the plane of fig. 1 are represented in elevation by the lines $a'd'$ and in plan by the lines $a\,d$, $b\,d$; the corresponding refracted rays are represented in elevation by the line $a'\,f'\,g'$, and in plan by the lines aeh and bek.

The incident ray $a'd'$, the refracted ray $a'g'$, and the normal $a'c'$ are all in one plane, and as was shown in the previous paper, above referred to, the point of intersection f' of the lines $a'g'$ and $c'd'$ is on the focal line; it is in fact the uppermost limit of the focal line corresponding to the semi-aperture h_1.

If $e'f' = l_1$ and $o'e' = v_1$ we have from the triangle $c'c''d'$

$$\frac{l_1}{h_1} = \frac{u-v_1}{u-r_1} \quad \text{or} \quad l_1 = h_1\left(\frac{u-v_1}{u-r_1}\right). \quad . \quad . \quad . \quad (1)$$

Now by the ordinary formula for spherical surfaces we have

$$\frac{1}{r_1} - \frac{1}{u} = \mu\left(\frac{1}{r_1} - \frac{1}{v_1}\right) \quad \text{or} \quad u = \frac{v_1 r_1}{\mu r_1 - (\mu - 1)v_1},$$

and substituting this value of u in (1) we get

$$l_1 = h_1\left(\frac{\mu-1}{\mu r_1}\right)v_1,$$

but

$$\frac{\mu-1}{\mu r_1} = \frac{1}{f_1}$$

where f_1 is the focal length of a spherical surface of radius r_1.

$$\therefore \quad l_1 = \frac{h_1 v_1}{f_1},$$

or, the length of the axial focal line = axial aperture × distance of focal line from the surface × power of the surface.

(b) *The line at right angles to the axis of the cylinder; this may be called the tangential focal line.*

Two incident rays symmetrical with respect to the horizontal plane or the plane of fig. 2 are represented in elevation by the lines $a'd'$ and $a''d'$ and in plan by the line ad, and the corresponding refracted rays in elevation by the lines $a'g'$ and $a''g'$ and in plan by the line ah. The two refracted rays will intersect in the horizontal plane in the point h which is at the extremity of the tangential focal line corresponding to the semi-aperture h_2.

If $hg = gk = l_2$ and $og = v_2$,

we have from the triangles obe and ehg (fig. 2),

$$\frac{l_2}{h_2} = \frac{v_2 - v_1}{v_1} \quad \text{or} \quad l_2 = h_2\left(\frac{v_2 - v_1}{v_1}\right). \quad . \quad . \quad . \quad (2)$$

But $v_2 = \mu u$ and $\dfrac{1}{r_1} - \dfrac{1}{u} = \mu\left(\dfrac{1}{r_1} - \dfrac{1}{v_1}\right)$.

By eliminating u we find

$$v_1 = \frac{\mu r_1 v_2}{v_2(\mu - 1) + \mu r_1}$$

and substituting this value of v_1 in (2) we get

$$l_2 = h_2\left(\frac{\mu - 1}{\mu r_1}\right) v_2 \quad \text{or} \quad l_2 = \frac{h_2 v_2}{f_1},$$

that is the length of the tangential focal line
= the tangential aperture × distance of the line from the surface × power of the surface.

2. *To find the lengths of the focal lines of a spherocylindrical lens.*

Figs. 3 and 4 represent an elevation and a plan of the incident and refracted rays at the second or spherical surface, the corresponding rays at the first or cylindrical surface being represented in figs. 1 and 2.

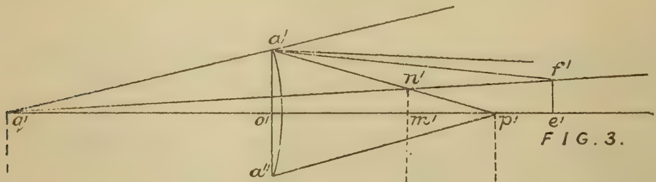

FIG. 3.

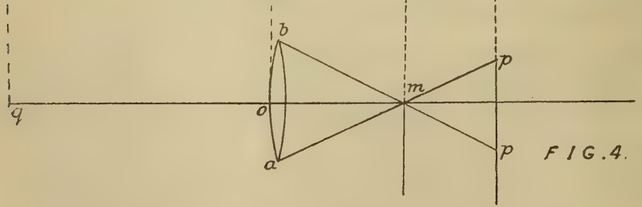

FIG. 4.

Let $q\,q'$ be the centre of the spherical surface the radius of which $= -r_2$.

(a) *The axial focal line.*

The two symmetrical rays, represented in elevation by the line $a'f'$, which were the refracted rays at the cylindrical surface, are now the incident rays. After being refracted at the spherical surface they will intersect at the point n' on the line joining the point f' to the centre q' of the spherical surface. The point n' is at the extremity of the axial focal line.

If $m'n' = l_3$ and $o'm' = v_3$ we have from the triangles $f'e'q'$ and $n'm'q'$ (fig. 3),

$$\frac{l_3}{l_1} = \frac{v_3 - r_2}{v_1 - r_2} \quad \text{or} \quad l_3 = l_1 \frac{v_3 - r_2}{v_1 - r_2}. \quad . \quad . \quad . \quad (3)$$

From the ordinary formula for spherical lenses

$$-\frac{1}{r_2} + \frac{1}{v_3} = \mu\left(\frac{1}{v_1} - \frac{1}{r_2}\right)$$

we have
$$v_1 = \frac{\mu r_2 v_3}{(\mu - 1)v_3 + r_2},$$

and substituting this value of v_1 in (3) we get

$$l_3 = h_1\left(\frac{\mu - 1}{r_1}\right)v_3,$$

or the length of the axial focal line of a sphero-cylindrical lens = axial aperture × distance of the line from the lens × the glass to air power of the cylindrical surface.

$\frac{\mu - 1}{r_1}$ = the glass to air power of the cylindrical surface ;
or the power of a plano-cylindrical lens having a cylindrical surface of radius r_1 ; or the difference of the two principal powers of the sphero-cylindrical lens.

(b) *The tangential focal line.*

Two refracted rays symmetrical with respect to the horizontal plane or the plane of fig. 4 are represented in elevation by the lines $a'n'p'$, and $a''p'$, and in plan by the line amp. These two rays will intersect at a point p in the horizontal plane, and this point will be at the extremity of the tangential focal line pp corresponding to the aperture h_2. If the semi-length of this line $= l_4$ and its distance from $o = v_4$, we have from fig. 4,

$$\frac{l_4}{h_2} = \frac{v_4 - v_3}{v_3} \quad \text{or} \quad l_4 = h_2 \frac{v_4 - v_3}{v_3}. \quad . \quad . \quad . \quad (4)$$

Now

$$-\frac{1}{u}+\frac{1}{v_4}=\frac{\mu-1}{-r_2} \quad \text{and} \quad -\frac{1}{u}+\frac{1}{v_3}=(\mu-1)\left(\frac{1}{r_1}-\frac{1}{r_2}\right).$$

$$\therefore\ \frac{1}{v_3}-\frac{1}{v_4}=\frac{\mu-1}{r_1} \quad \text{and} \quad \frac{v_4-v_3}{v_3}=v_4\left(\frac{\mu-1}{r_1}\right),$$

or

$$l_4=h_2\left(\frac{\mu-1}{r_1}\right)v_4;$$

∴ the length of the tangential focal line of a sphero-cylindrical lens = the tangential aperture × distance of the line from the lens × glass to air power of the cylindrical surface.

The results in 2 of course apply to a plano-cylindrical lens.

3. *To find the lengths of the focal lines of two plano-cylindrical lenses in contact, the axes being crossed at right angles.*

Fig. 5 is an end elevation of the system of rays looking in the direction of propagation of the light, that is from left to right, and fig. 6 is a front elevation. The axis of the first lens is vertical and its focal length $= f_1$. The axis of the second lens is horizontal and its focal length $= f_2$. The semi-apertures are h_1 and h_2 as before. Two rays, symmetrical with respect to the plane of fig. 6, incident at $a'b'$ after refraction by the first lens will intersect at the point c' at a distance from the lenses $= o'v' = v_1$ and at a distance from the axis of $x = c'v' = \frac{h_1 v_1}{f_1}$.

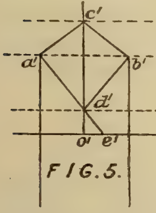

FIG. 5.

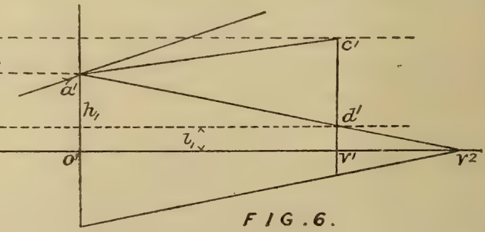

FIG. 6.

The second lens will bend these rays downwards to the position $a'd'$, $b'd'$. The deviation $c'd'$ will be $= \frac{h_1 v_1}{f_2}$ since $\frac{h_1}{f_2}$ is the deviation per unit of length along the axis of x.

(a) *The axial focal line; that is the line parallel to the axis of the first lens.*

If l_1 be the semi-length of the axial focal line,

$$l_1 = d'v' = c'v' - c'd' = \frac{h_1 v_1}{f_1} - \frac{h_1 v_1}{f_2};$$

$$\therefore \quad l_1 = h_1 v_1 \left(\frac{1}{f_1} - \frac{1}{f_2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or the length of the axial focal line of two plano-cylindrical lenses in contact with the axes crossed at 90° = the axial aperture × distance of the line from the lenses × difference of the powers of the lenses.

(b) *The tangential focal line.*

If the line $a'd'$ (fig. 5) be produced to meet the axis of x in e' and if the line $a'd'$ (fig. 6) be produced to meet the axis of x in v^2, $l_2 = o'e'$ is the semi-length of the tangential focal line and $o'v^2 = v_2$ is its distance from the lenses.

From fig. 5 we have

$$\frac{l_2}{l_1} = \frac{h_2}{h_1 - l_1},$$

and from fig. 6 we have

$$\frac{h_1 - l_1}{h_1} = \frac{v_1}{v_2},$$

$$\therefore \quad l_2 = l_1 \frac{h_2}{h_1 - l_1} = l_1 h_2 \frac{v_2}{h_1 v_1} = h_2 v_2 \left(\frac{1}{f_1} - \frac{1}{f_2}\right).$$

If $f_1 = f_2$ both l_1 and $l_2 = 0$, or two plano-cylindrical lenses of the same focal length crossed at right angles are equivalent to a spherical lens.

4. *To find the lengths of the focal lines of two plano-cylindrical lenses in contact of focal lengths f_1 f_2 with axes crossed at an angle θ.*

(a) First we will take the incident light to be parallel.

(1) *The axial line or that within the angle θ.*

Fig. 7 is an end view of the system looking from left to right of fig. 8 which is a front elevation.

The line oc making an angle θ_1 with the vertical line oo' (fig. 7) represents the axis of the first lens of which the focal length is f_1. The line oh making an angle θ_2 with the line oo' represents the axis of the second lens the focal length of which is f_2. Let a, b (fig. 7) be the points of incidence of two horizontal parallel rays symmetrical with respect to the line oo'. The axial semi-aperture $oo' = h_1$; the tangential semi-aperture $o'a = o'b = h_2$.

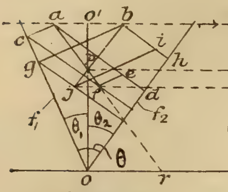

FIG. 7.

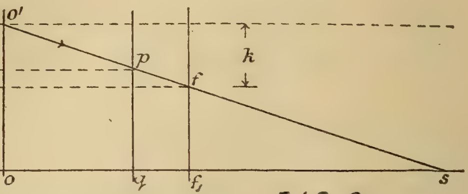

FIG. 8.

Consider first the ray incident at a. The first lens *alone* will deflect the ray in a plane at right angles to the axis f_1. The line ac (fig. 7) will represent the emergent ray, the point c being at a perpendicular distance f_1 from the lens. The second lens *alone* will deflect the ray in a plane at right angles to the axis f_2. The line ad (fig. 7) will represent the emergent ray, the point d being at a perpendicular distance f_2 from the lens. In the line ad take a point e such that

$$\frac{ae}{ad} = \frac{f_1}{f_2}.$$

Then the lines ac, ae, will represent the deviations in the focal plane of the first lens due to the two lenses separately and the diagonal af of the parallelogram $acef$ will represent the deviation due to both lenses acting together *.

The line af also represents in end view the ray after it has emerged from both lenses, and the line $o'f$ (fig. 8) will represent the ray in front elevation; of_1 (fig. 8) being made $= f_1$. The line ff_1 (fig. 8) represents the trace of the focal plane of the first lens.

Consider secondly the ray incident at b. The first lens *alone* will deflect the ray to a point g distant f_1 from the lens; the second lens *alone* will deflect the ray to the point h distant f_2 from the lens.

In the line bh take a point i such that $\frac{bi}{bh} = \frac{f_1}{f_2}$. Then as

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* See Chapter X. Handbook of Optics, by W. N. Suter. Macmillan & Co., 1899.

before the diagonal bj of the parallelogram $bigj$ will represent in end view the ray after emergence from both lenses whilst the line $o'f$ (fig. 8) will represent the ray in front view.

We shall now find what must be the relation between the angles θ_1 and θ_2 when the two emergent rays af and bj intersect on the line oo' or intersect in the central plane of which oo' is the trace in fig. 7 or the plane of the paper in fig. 8.

We have from fig. 7,

$$ac = h_1 \sin\theta_1 - h_2 \cos\theta_1,$$

$$ae = \frac{f_1}{f_2} ad = \frac{f_1}{f_2}(h_1 \sin\theta_2 + h_2 \cos\theta_2),$$

$$bg = h_1 \sin\theta_1 + h_2 \cos\theta_1,$$

$$bi = \frac{f_1}{f_2} bh = \frac{f_1}{f_2}(h_1 \sin\theta_2 - h_2 \cos\theta_2).$$

From these values we can readily obtain the components of the diagonals af and bj resolved along and at right angles to the line oo'.

Let the resolved component of af along $oo' = k$.

" " " af at 90° to $oo' = l$.

" " " bj along $oo' = m$.

" " " bj at 90° to $oo' = n$.

Then

$$k = h_1 \sin^2\theta_1 - h_2 \sin\theta_1 \cos\theta_1 + \frac{f_1}{f_2}(h_1 \sin^2\theta_2 + h_2 \sin\theta_2 \cos\theta_2),$$

$$l = -h_1 \sin\theta_1 \cos\theta_1 + h_2 \cos^2\theta_1 + \frac{f_1}{f_2}(h_1 \sin\theta_2 \cos\theta_2 + h_2 \cos^2\theta_2),$$

$$m = h_1 \sin^2\theta_1 + h_2 \sin\theta_1 \cos\theta_1 + \frac{f_1}{f_2}(h_1 \sin^2\theta_2 - h_2 \sin\theta_2 \cos\theta_2),$$

$$n = h_1 \sin\theta_1 \cos\theta_1 + h_2 \cos^2\theta_1 - \frac{f_1}{f_2}(h_1 \sin\theta_2 \cos\theta_2 - h_2 \cos^2\theta_2).$$

Now, if $k = m$, $l = n$, and $k^2 + l^2 = m^2 + n^2$, the two diagonals will be equal in length and equally inclined to the line oo', and as the points ab are symmetrical with respect to the line oo', the two diagonals will intersect at some point p on this line.

By equating k and m or l and n we get the relation

$$f_1 \sin \theta_2 \cos \theta_2 = f_2 \sin \theta_1 \cos \theta_1,$$

and it will be found that this relation also satisfies the equation $k^2 + l^2 = m^2 + n^2$.

If this relation between θ_1 and θ_2 hold, then every pair of rays incident at symmetrical points such as a and b will, after refraction by both lenses, intersect in the central plane at some point on a line represented in fig. 7 by op, and in fig. 8 by pq. This line pq is therefore the principal focal line.

If we call its semi-length l_1.

From fig. 7 we have $l_1 = op = h_1 - o'p$.

Now $$\frac{o'p}{h_2} = \frac{k}{l}, \quad \therefore\ l_1 = h_1 - h_2 \frac{k}{l}.$$

Substituting the known values of k and l with the condition

$$f_1 \sin \theta_2 \cos \theta_2 = f_2 \sin \theta_1 \cos \theta_1,$$

and simplifying, we get

$$l_1 = h_1 \frac{f_1 \cos 2\theta_2 + f_2 \cos 2\theta_1}{f_1 \cos^2 \theta_2 + f_2 \cos^2 \theta_1}.$$

If F_1 be the principal axial focal length of the combination, we have

$$oq = F_1; \quad \frac{F_1}{f_1} = \frac{o'p}{k}; \quad \text{or } F_1 = \frac{f_1}{k} \cdot \frac{h_2 k}{l} = \frac{f_1 h_2}{l},$$

and substituting the value of l with the condition

$$f_1 \sin \theta_2 \cos \theta_2 = f_2 \sin \theta_1 \cos \theta_1,$$

we have

$$F_1 = \frac{f_1 f_2}{f_1 \cos^2 \theta_2 + f_2 \cos^2 \theta_1} = \frac{1}{\dfrac{\cos^2 \theta_2}{f_2} + \dfrac{\cos^2 \theta_1}{f_1}},$$

and

$$l_1 = h_1 F_1 \left(\frac{\cos 2\theta_2}{f_2} + \frac{\cos 2\theta_1}{f_1} \right).$$

(2) *The tangential line.*

If we produce the line af (fig. 7) to meet the axis of x in r, then or will be the semi-length of the tangential focal line. If $or = l_2$ we have from fig. 7,

$$\frac{l_2}{l_1} = \frac{or}{op} = \frac{h_2}{o'p} = \frac{l}{k},$$

and substituting the values of l and k we get

$$l_2 = h_2 \frac{f_1 \cos 2\theta_2 + f_2 \cos 2\theta_1}{f_2 \sin^2 \theta_1 + f_1 \sin^2 \theta_2}.$$

If F_2 be the principal tangential focal length of the combination, we have from fig. 8,

$$F_2 = os; \quad \frac{F_2}{f_1} = \frac{h_1}{k}; \quad F_2 = \frac{f_1 h_1}{k} = \frac{1}{\dfrac{\sin^2 \theta_1}{f_1} + \dfrac{\sin^2 \theta_2}{f_2}}.$$

$$\therefore \qquad l_2 = h_2 F_2 \left(\frac{\cos 2\theta_2}{f_2} + \frac{\cos 2\theta_1}{f_1} \right).$$

Now

$$\frac{1}{F_1} = \frac{\cos^2 \theta_2}{f_2} + \frac{\cos^2 \theta_1}{f_1},$$

$$\frac{1}{F_2} = \frac{\sin^2 \theta_1}{f_1} + \frac{\sin^2 \theta_2}{f_2},$$

$$\frac{1}{F_1} - \frac{1}{F_2} = \frac{\cos 2\theta_1}{f_1} + \frac{\cos 2\theta_2}{f_2},$$

and

$$l_1 = h_1 F_1 \left(\frac{1}{F_1} - \frac{1}{F_2} \right),$$

$$l_2 = h_2 F_2 \left(\frac{1}{F_1} - \frac{1}{F_2} \right).$$

(*b*) Secondly, we will take the light diverging from a point at a distance $-u$ from the point o (fig. 10).

(1) *The axial focal line.*

Figs. 9 and 10 are end and front elevations respectively, being similar views to figs. 7 and 8, the letters f_1, f_2, h_1, h_2, θ_1, θ_2 having the same meaning as before. Consider first a

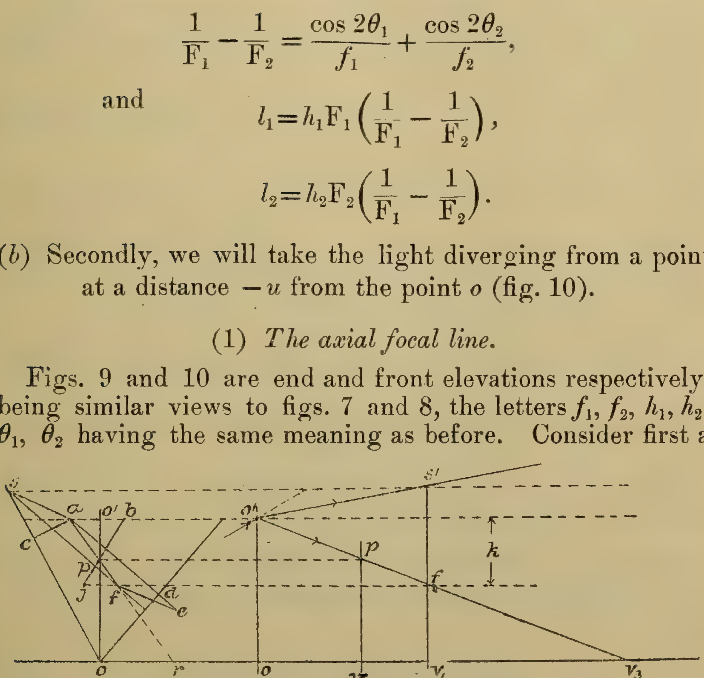


FIG. 9. FIG. 10.

ray incident at a. This ray, after emerging from the first lens, will be represented in end view by the line as (fig. 9), where $os=\frac{v_1}{f_1}oc$, and in front view by the line $o's'$ (fig. 10). The distance from the lens of the point $s=ov_1=v_1$. The point v_1 is conjugate to the point $-u$ with respect to the first lens. The ray as in passing through the second lens is bent towards the axis of the second lens, the deviation sf or ae corresponding to the distance v_1 being $=\frac{ad}{f_2}v_1$, since $\frac{ad}{f_2}$ is the deviation per unit length along the axis of x, this deviation being measured along a line at right angles to the axis od. The line af will therefore represent in end view the ray after emerging from both lenses. The emergent ray is represented in front elevation by the line $o'fv_3$ in fig. 10.

Now

$$os=\frac{v_1}{f_1}oc=\frac{v_1}{f_1}(h_1\cos\theta_1+h_2\sin\theta_1),$$

$$ae=\frac{v_1}{f_2}ad=\frac{v_1}{f_2}(h_1\sin\theta_2+h_2\cos\theta_2).$$

From these values we can get as before the resolved components of the diagonal af along the line $oo'=k$ and at right angles to this line $=l$.

$$k=\frac{v_1}{f_2}(h_1\sin^2\theta_2+h_2\sin\theta_2\cos\theta_2)-\frac{v_1}{f_1}(h_1\cos^2\theta_1+h_2\sin\theta_1\cos\theta_1)+h_1,$$

$$l=\frac{v_1}{f_2}(h_2\cos^2\theta_2+h_1\sin\theta_2\cos\theta_2)-\frac{v_1}{f_1}(h_2\sin^2\theta_1+h_1\sin\theta_1\cos\theta_1)+h_2.$$

The corresponding values m and n for the resolved components of the line bj, obtained by considering a symmetrical ray incident at b and making a similar construction, are

$$m=\frac{v_1}{f_2}(h_1\sin^2\theta_2-h_2\sin\theta_2\cos\theta_2)-\frac{v_1}{f_1}(h_1\cos^2\theta_1-h_2\sin\theta_1\cos\theta_1)+h_1,$$

$$n=\frac{v_1}{f_2}(h_2\cos^2\theta_2-h_1\sin\theta_2\cos\theta_2)-\frac{v_1}{f_1}(h_2\sin^2\theta_1+h_1\sin\theta_1\cos\theta_1)+h_2.$$

By equating k to m and l to n we get the condition under which the lines af and bj intersect on the line oo', viz.,

$$f_1\sin\theta_2\cos\theta_2-f_2\sin\theta_1\cos\theta_1=0. \quad . \quad . \quad . \quad (6)$$

If the semi-length of the axial focal line $=l_1$, from figs. 9 and 10 we have

$$\frac{h_1-l_1}{h_2}=\frac{k}{l}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or

$$l_1=h_1-\frac{k}{l}h_2.$$

If the distance of the point p or v_2 (fig. 10) from the point o or from the lenses be called v_2, we have from fig. 10

$$\frac{v_1}{v_2}=\frac{k}{h_1-l_1}, \text{ but from fig. 9 } \frac{k}{h_1-l_1}=\frac{l}{h_2}.$$

$$\therefore \qquad \frac{v_1}{v_2}=\frac{l}{h_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

From equations 7 and 8, by substituting the values of k and l with the condition (6), we get

$$l_1=h_1v_2\left(\frac{\cos 2\theta_2}{f_2}+\frac{\cos 2\theta_1}{f_1}\right),$$

$$\text{or} \qquad l_1=h_1v_2\left(\frac{1}{\mathrm{F}_1}-\frac{1}{\mathrm{F}_2}\right),$$

an analogous result to that obtained for parallel light.

(2) *The tangential focal line.*

Let the line af be produced to meet the axis of x at r (fig. 9) and the line $o'f$ be produced to meet the axis of x in the point v_3 (fig. 10). The semi-length of the tangential focal line $=or=l_2$, and the distance of the line from the lenses $=ov_3=v_3$. From fig. 9 we have

$$\frac{l_2+h_2}{l}=\frac{h_1}{k}, \quad \text{or } l_2=h_1\frac{l}{k}-h_2, \quad . \quad . \quad . \quad (9)$$

and from fig. 10 we have

$$\frac{v_1}{v_3}=\frac{k}{h_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

From equations 9 and 10, by substituting the values of k and l and putting in the condition (6), we get

$$l_2=v_3h_2\left(\frac{\cos 2\theta_2}{f_2}+\frac{\cos 2\theta_1}{f_1}\right),$$

$$=v_3h_2\left(\frac{1}{\mathrm{F}_1}-\frac{1}{\mathrm{F}_2}\right).$$

5. *The lengths of the focal lines of a number of cylindrical lenses in contact arranged with their axes crossed at any angles.*

The results obtained in the last section are perfectly general. Let the focal lengths of the lenses be f_1, f_2, f_3, &c., and let the angles between the axes of the lenses and any fixed line such as oo', figs. 7 and 9, be θ_1, θ_2, θ_3, &c., the angles being reckoned positive in one direction and negative in the other. The condition that must be fulfilled if two parallel rays symmetrical with respect to the plane containing the line oo' and the optic axis are to be refracted so as to intersect in this plane, is

$$\Sigma \frac{\sin\theta\cos\theta}{f}=0.$$

The principal focal lengths of the system are

$$F_1=\frac{1}{\Sigma \frac{\cos^2\theta}{f}},$$

$$F_2=\frac{1}{\Sigma \frac{\sin^2\theta}{f}}$$

and the semi-lengths of the focal lines are

$$l_1=h_1F_1\Sigma\frac{\cos 2\theta}{f}=h_1F_1\left(\frac{1}{F_1}-\frac{1}{F_2}\right),$$

$$l_2=h_2F_2\Sigma\frac{\cos 2\theta}{f}=h_2F_2\left(\frac{1}{F_1}-\frac{1}{F_2}\right).$$

6. *To find the lengths of the two focal lines of two plano-cylindrical lenses of focal lengths* f_1 *and* f_2 *with axes crossed at* 90°, *the distance between the lenses being* $=\delta$.

Figs. 11 and 12 are elevation and plan respectively of the system of rays.

(a) *The line parallel to the axis of the first lens which is vertical.*

Two rays diverging from a point uu', at a distance $-u$ from the first lens, and incident thereon at symmetrical points a, b, a', b', will, after refraction by the first lens, intersect in the point c' (fig. 11) on the line represented in elevation by $c'v_1'$ (fig. 11), and in plan by the point v_1 in fig. 12.

Let $f_1v_1'=v_1$ and $f_1a'=h_1$.

Then we have

$$v_1'c'=\frac{h_1v_1}{f_1}.$$

The two refracted rays on meeting the second lens in points distant h_3 from the axis of x are bent downwards, the point of intersection being at d', the distance $c'd'$ or the deviation due to the second lens being $=\frac{h_3}{f_2}(v_1-\delta)$, since $\frac{h_3}{f_2}$ is the deviation per unit length along the line f_1v_1', and $v_1-\delta$ is the distance f_2v_1'.

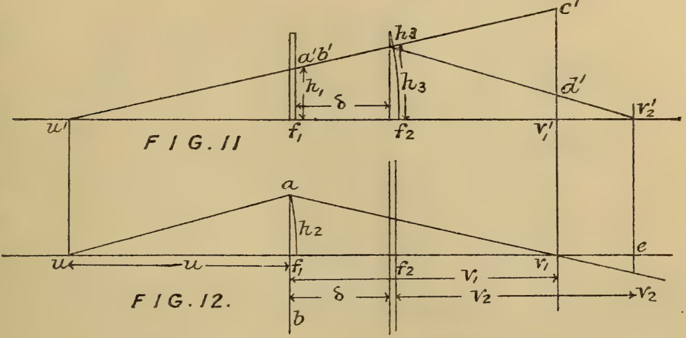


FIG. 11

FIG. 12.

Let l_1 be the semi-length of the line.

From fig. 11 we have

$$l_1=\frac{h_1v_1}{f_1}-\frac{h_3}{f_2}(v_1-\delta)\ , \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and

$$\frac{h_3-h_1}{\delta}=\frac{\frac{h_1v_1}{f_1}-h_1}{v_1},$$

or

$$h_3=h_1\left\{\delta\left(\frac{1}{f_1}-\frac{1}{v_1}\right)+1\right\}.$$

Substituting this value of h_3 in (11) and simplifying, we get

$$l_1=h_1\left\{v_1\left(\frac{1}{f_1}-\frac{1}{f_2}-\frac{\delta}{f_1f_2}\right)+\frac{\delta^2}{f_1f_2}-\frac{\delta^2}{v_1f_2}+\frac{2\delta}{f_2}\right\}.$$

$$=\frac{h_1}{f_1f_2v_1}\left\{v_1^2(f_2-f_1-\delta)+v_1(\delta^2+2\delta f_1)-\delta^2f_1\right\}.$$

If $v_1=f_1$, or the incident line is parallel,

$$l_1=h_1f_1\left(\frac{1}{f_1}-\frac{1}{f_2}+\frac{\delta}{f_1f_2}\right).$$

(b) *The line parallel to the axis of the second lens which is horizontal.*

Produce the refracted ray h_3d' (fig. 11) to meet the horizontal plane in the point v_2, v_2'.

Then $v_2e=l_2$ is the semi-length of the focal line.

From fig. 12 we have

$$\frac{l_2}{h_2}=\frac{v_2+\delta-v_1}{v_1},$$

or

$$l_2=\frac{h_2}{v_1}(v_2+\delta)-h_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Now

$$-\frac{1}{u}+\frac{1}{v_1}=\frac{1}{f_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and

$$\frac{1}{-u+\delta}+\frac{1}{v_2}=\frac{1}{f_2}, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$\therefore \quad \frac{1}{v_1}=\frac{\delta v_2-\delta f_2-v_2f_2+v_2f_1-f_1f_2}{\delta v_2f_1-\delta f_1f_2-v_2f_1f_2}$$

and substituting this value in (12) we get

$$l_2=\frac{h_2\{v_2^2(f_2-f_1-\delta)+v_2(2\delta f_2-\delta^2)+\delta^2f_2\}}{v_2f_1f_2+\delta f_1f_2-\delta v_2f_1}.$$

If $v_2=f_2$,

$$l_2=h_2f_2\left(\frac{1}{f_1}-\frac{1}{f_2}+\frac{\delta}{f_1f_2}\right).$$

From fig. 11 it will be seen that when $c'd'=c'v_1'$, we shall have $v_1=v_2+\delta$ and the lengths of the focal lines $=0$.

This will happen when the points conjugate to $-u$ with respect to the two lenses separately coincide, or when

$$v_1^2(f_2-f_1-\delta)+v_1(\delta^2+2\delta f_1)-\delta^2f_1=0.$$

The form of this equation shows that when f_1 and f_2 are constant there are two values of v_1 corresponding to each value of δ which will make the lengths of the focal lines $=0$.

7. *To find the lengths of the focal lines of a sphero-cylindrical lens when the source of light is not on the optic axis.*

(a) *The axial focal line.*

Fig. 13 is a front elevation of the system. We can regard the lens as made up of a plano-cylindrical lens of focal length f_1 and of a plano-spherical lens of focal length f_2.

The two powers of the combination are $\frac{1}{f_2}$ and $\frac{1}{f_1}+\frac{1}{f_2}$, the latter of which we will call $\frac{1}{f_3}$. Let a be the source of light situated at a distance $au=a$ from the axis ou and at a distance $ou = -u$ from the lens, and let the semi-aperture $= h_1$. Consider first the refraction by the plano-cylindrical

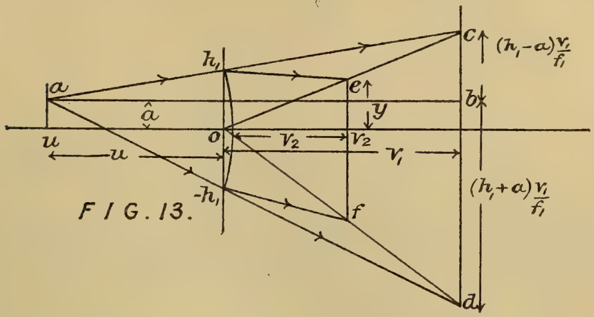


FIG. 13.

lens alone. The part of the lens above the line *ab* will produce a focal line *bc* of length $(h_1 - a)\frac{v_1}{f_1}$ at a distance $ov_1 = v_1$ from the lens. The part of the lens below the line *ab* will produce a focal line *bd* of length $(h_1 + a)\frac{v_1}{f_1}$. The total length of the line is $2h_1\frac{v_1}{f_1}$.

Consider now the refraction by the plano-spherical lens. A pair of rays, symmetrical with respect to the plane of the paper in fig. 13, converging to the point *c*, fig. 13, will be refracted in such a way that their point of intersection will be at *e* on the line *oc*, the distance of *e* from the lens being $= ov_2$ or v_2. Similarly a pair of rays converging to *d* will, after refraction by the spherical lens, intersect at *f* on the line *od*. The axial focal line will therefore be *ef*. If its total length $= 2l_1$, we have from fig. 13

$$\frac{2l_1}{v_2} = \frac{2h_1\frac{v_1}{f_1}}{v_1} \text{ or } l_1 = \frac{h_1}{f_1}v_2,$$

that is the length of the line is the same as when the point *a* or the source of light is on the optic axis *ou*.

If the length of that part of the line above the axis *ou* be called *y* we have

$$\frac{y}{v_2} = \frac{(h_1 - a)\frac{v_1}{f_1} + a}{v_1}$$

$$= \frac{h_1}{f_1} + a\left(\frac{1}{v_1} - \frac{1}{f_1}\right) = \frac{h_1}{f_1} + \frac{a}{u},$$

or

$$y = \frac{h_1}{f_1} v_2 + \frac{a v_2}{u},$$

but

$$-\frac{1}{u} + \frac{1}{v_2} = \frac{1}{f_3} \quad \text{or} \quad \frac{1}{u} = \frac{1}{v_2} - \frac{1}{f_3},$$

$$\therefore \quad y = \frac{h_1}{f_1} v_2 + a - \frac{a v_2}{f_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This is the equation of a line which forms the upper limit of the focal line as its distance from the lens varies. It is represented in fig. 14 by the line ag. The intercept on the axis of $x = og = \frac{af_1 f_3}{af_1 - h_1 f_3}$ and the intercept on the axis of $y = oa = a$. When $v_2 = f_3$, $y = \frac{f_3}{f_1} h_1$.

If in equation 15 we put $h_1 = -h_1$ we get the equation of the line ak, fig. 14, which forms the lower limit of the focal line. The intercept on the axis of $y = a$ and that on the axis of $x = ok = \frac{af_1 f_3}{af_1 + h_1 f_3}$. When $v_2 = f_3$, $y = -\frac{f_3}{f_1} h_1$.

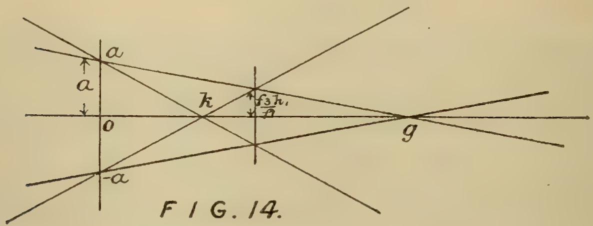


FIG. 14.

If in equation 15 we put $a = -a$ and $h_1 = h_1$ and $-h_1$ we get the equations of the two lines $-ag$ and $-ak$ which form the limits of the focal lines when the source is at $-a$.

Fig. 14 shows that if we have two sources of light at a distance $2a$ apart the axial focal lines will coincide at the principal focus, their lengths being $= 2h_1 \frac{f_3}{f_1}$, and will overlap if their distance from the lens lies between the values

$$og = \frac{af_1 f_3}{af_1 - h_1 f_3} \quad \text{and} \quad ok = \frac{af_1 f_3}{af_1 + h_1 f_3}.$$

(b) *The tangential focal line.*

Fig. 15 shows a plan view of the system. A pair of rays symmetrical with respect to the plane of fig. 15 diverging from a point a_1 at a distance $a_1u = a_1$ from the axis ou and at

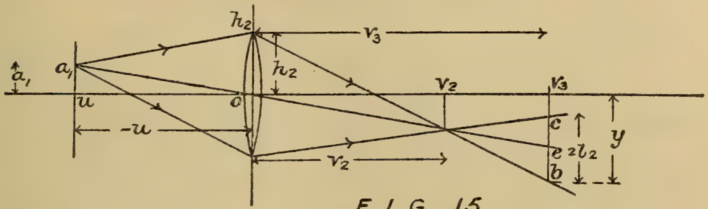


FIG. 15.

a distance $ou = -u$ from the lens, and incident at a point h_2 at a distance $oh_2 = h_2$ from the axis ou will, after refraction by both surfaces, intersect in the plane of the paper fig. 15, at a point b the distance of which from the lens $= ov_3 = v_3$. A similar pair of rays incident at the corresponding point $-h_2$ will intersect at c and bc will be the tangential focal line. Let the length $bc = 2l_2$.

Now

$$-\frac{1}{u} + \frac{1}{v_2} = \frac{1}{f_3}$$

$$-\frac{1}{u} + \frac{1}{v_3} = \frac{1}{f_2}.$$

Subtracting one equation from the other we get

$$\frac{1}{v_2} - \frac{1}{v_3} = \frac{1}{f_3} - \frac{1}{f_2} \qquad \therefore \frac{v_3 - v_2}{v_2 v_3} = \frac{1}{f_3} - \frac{1}{f_2} = \frac{1}{f_1}.$$

From fig. 15 we have

$$\frac{2l_2}{2h_2} = \frac{v_3 - v_2}{v_2},$$

$$\therefore \quad \frac{l_2}{h_2} = \frac{v_3}{f_1} \quad \text{or} \quad l_2 = \frac{v_3 h_2}{f_1},$$

that is the length of the tangential focal line is the same as when the source of light is on the axis ou.

The equations to the two lines which form the upper and lower limits of the tangential focal line when its distance from the lens varies are

$$y = v_3 e \pm l_2.$$

Now

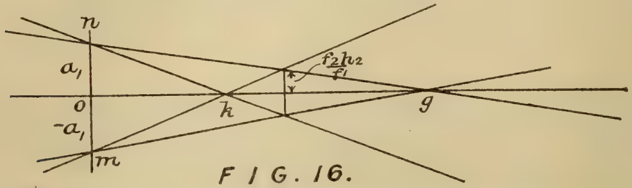
$$\frac{-v_3 e}{v_3} = \frac{a_1}{-u} \quad \text{or} \quad v_3 e = \frac{a_1 v_3}{u},$$

$$\therefore \quad y = \frac{a_1 v_3}{u} \pm l_2 = a_1 v_3 \left(\frac{1}{v_3} - \frac{1}{f_2}\right) \pm \frac{v_3 h_2}{f_1},$$

or

$$y = a_1 - \frac{a_1 v_3}{f_2} \pm \frac{v_3 h_2}{f_1}.$$

These lines are shown on fig. 16 by ng and nk.



F I G. 16.

When a_1 is made $= -a_1$ we get the equations of lines mg, mk (fig. 16).

The intercepts on the axis of y are $\pm a_1$ and those on the axis of x are

$$\frac{a_1 f_1 f_2}{a_1 f_1 \pm h_2 f_2}.$$

Fig. 16 shows that if we have two sources of light at a distance $2a$ apart the tangential focal lines will be distinct if their distance from the lens is less than

$$ok = \frac{a_1 f_1 f_2}{a_1 f_1 + h_2 f_2}$$

or greater than

$$og = \frac{a_1 f_1 f_2}{a_1 f_1 - h_2 f_2},$$

but will overlap if they are formed anywhere between these two distances.

8. *The image produced by a sphero-cylindrical lens of an object consisting of narrow parallel horizontal and vertical bands or slits of light.*

(1) *The images of the horizontal bands.*

Let the distance between the centres of the object bands be a and the width of the bands be w. Each point of each horizontal band will produce an axial and a tangential focal line. At the tangential focus all the tangential focal lines due to one of the object bands will together form a horizontal image band the width of which parallel to the axis of the cylindrical surface of the lens will be $\frac{wv_3}{-u}$, and the distance between the centres of the image bands will be $\frac{av_3}{-u}$, where v_3 is the distance of the image and $-u$ the distance of the object from the lens.

Consider now what will happen at the axial focus. Every point in one of the horizontal object bands will produce an axial focal line of which the length $= \frac{2h_1v_2}{f_1}$, where v_2 is the distance of the image from the lens h_1 the axial semi-aperture, and f_1 the focal length of the plano-cylindrical part of the lens. The horizontal image bands will have a width parallel to the axis of the cylindrical surface of the lens

$$= \frac{wv_2}{-u} + 2h_1\frac{v_2}{f_1},$$

the first term being the width which the image band would have if the lens were spherical. The distance between the centres of the image bands will be $\frac{av_2}{-u}$. Fig. 17 (p. 80) is a similar view to fig. 14 but showing the limits of the focal lines due to five narrow object bands, the distance apart being $=a$ and the width w being small enough to be neglected. The lines A, B, C, D are drawn at distances from the lens by putting $a=1$, 2, 3, or 4 in the formula

$$og = \frac{af_1f_3}{af_1 - 2f_3h_1},$$

and the lines I, H, G, F at distances obtained by making $a=1$, 2, 3, or 4 in the formula

$$ok = \frac{af_1f_3}{af_1 + 2f_3h_1}.$$

If the object be placed at such a distance from the lens that the image is formed at the line A or I, the edges of adjacent image bands will coincide and there will appear to be no image at all; a screen placed at A or I will be very nearly uniformly illuminated. If the images are formed nearer to the lens than I or further away than A, five separate and distinct image bands will be formed. Again, if the images be formed at the lines B or H it will be seen that the edges of the image bands due to the object bands 1, 3 and 2, 4 and 3, 5 coincide, and we shall get the central part of the screen almost uniformly illuminated from two slits whilst the top and bottom will be illuminated from one slit only. Again, if the images are formed at C or G the edges of the image bands due to slits 1, 4 and 2, 5 coincide and we get the centre of the screen illuminated by three slits, the outer parts being illuminated from two slits and the edges from one slit only. Similarly, if the images are formed at D or F the edges of the image bands due to slits 1 and 5 coincide and the centre of the screen is illuminated from four slits, the light fading off towards the top and bottom edges as the screen is illuminated from three, two, and one slit only. When the object is at a great distance all the images coincide at F the principal axial focus.

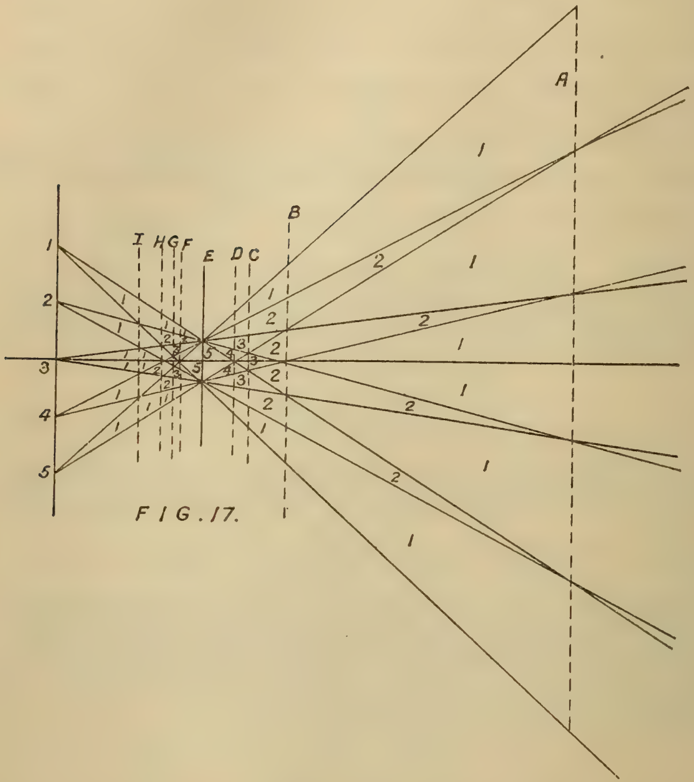
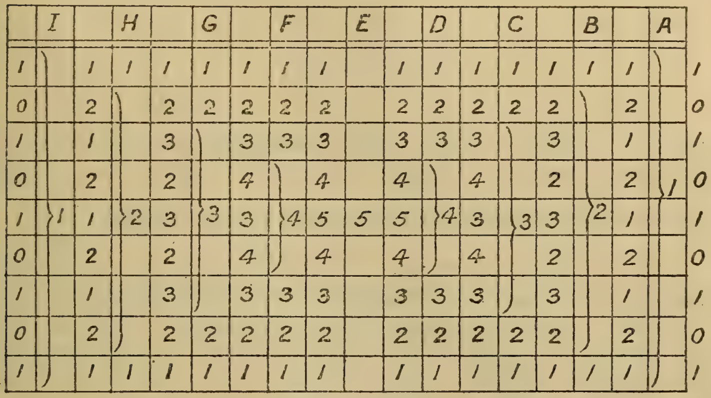


FIG. 17.

The table, fig. 18, shows the number and amount of illumination of the image bands due to five object bands, the



	I		H		G		F		E		D		C		B		A	
1		1	1	1	1	1	1	1		1	1	1	1	1	1	1		1
0		2		2	2	2	2	2		2	2	2	2	2		2		0
1		1		3		3	3	3		3	3	3		3		1		1
0		2		2		4		4		4		4		2		2	1	0
1	1	1	2	3	3	3	4	5	5	5	4	3	3	3	2	1		1
0		2		2		4		4		4		4		2		2		0
1		1		3		3	3	3		3	3	3		3		1		1
0		2		2	2	2	2	2		2	2	2	2	2		2		0
1		1	1	1	1	1	1	1		1	1	1	1	1	1	1		1

FIG. 18.

letters representing the same lines as in fig. 17 and the numerals the number of slits which illuminate the particular image bands; for instance, if the image bands are formed at some point between the lines B and C there will appear to be three bands illuminated from three slits separated by bands illuminated from two slits, the edges of the screen being illuminated from one slit.

(2) *The images of the vertical slits.*

Each point of each vertical object band or slit will form an axial and a tangential focal line. At the axial focus all the axial focal lines due to the points on one vertical object band will together form one vertical image band, and if $-u$ and v_2 be the distances of object and image from the lens the distance between the vertical image bands will be $=\frac{av_2}{-u}$, and their width in a horizontal direction will be $=\frac{wv_2}{-u}$. Consider now what will happen at the tangential focus. Every point on one of the vertical object bands will form a tangential focal line of which the length will be $=\frac{2h_2v_3}{f_1}$, v_3 being the distance of the line from the lens, h_2

the tangential semi-aperture, and f_1 the focal length of the plano-cylindrical component of the lens. The vertical image bands formed at the tangential focus will have a horizontal width

$$=\frac{wv_3}{-u}+\frac{2h_2v_3}{f_1},$$

the first term being the width the bands would have were the lens spherical. The distances between the centres of the vertical image bands at the tangential focus will be $\frac{av_3}{-u}$.

If fig. 17 be regarded as a plan view analogous to fig. 16 instead of an elevation analogous to fig. 14, then all that has been said about the images of the horizontal bands at the axial focus will apply to the images of the vertical bands at the tangential focus. The lines A to I are, however, to be obtained by putting $a=1$, 2, 3, or 4 in the formula

$$\frac{af_1f_2}{af_1\pm 2h_2f_2}.$$

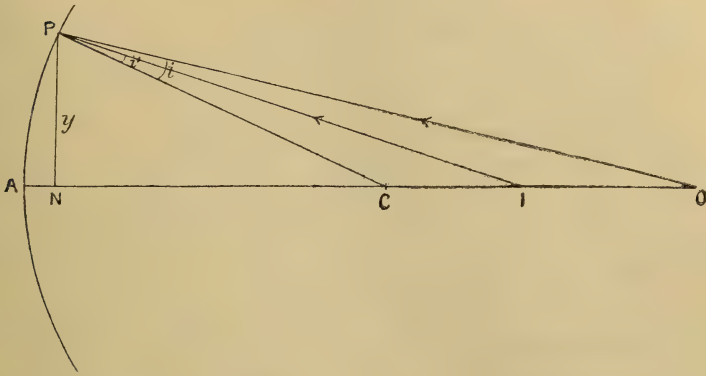
V. *A Formula for the Spherical Aberration in a Lens-System correct to the Fourth Power of the Aperture.* By E. HOWARD SMART, *M.A., Head of Mathematical Department, Birkbeck College**.

THE ordinary formulæ as given in the text-books for central spherical aberration are computed to the square of the aperture only,—a degree of approximation which is insufficient for the purpose of the practical optician in the design of photographic and other objectives. In the following work a formula will be given for the longitudinal aberration for a system of coaxial spherical surfaces separating media of refractive indices $\mu_0 \ldots \mu_\kappa$ which is correct to the fourth power of the aperture. A greater degree of accuracy than this is usually undesirable, the complexity of the additional corrections being out of all proportion to their usefulness.

Let the spherical surface AP of radius r_i separate media of refractive indices μ_{i-1} and μ_i. Let the ray OP be incident

* Communicated by the Author.

at a distance y_i from the axis. If s_i and s_i' denote the distances (measured from the vertex positively to the right) of the intermediate point images formed by paraxial rays



respectively before and after refraction, and Δ_{i-1}, Δ_i the corresponding spherical aberrations for the rays OP, PI, we have $AO = s_i + \Delta_{i-1}$, $AI = s_i' + \Delta_i$. Then C being the centre of the surface AP we have as usual

$$\mu_{i-1} \sin i = \mu_i \sin i',$$

whence accurately

$$\frac{\mu_{i-1} \cdot CO}{OP} = \frac{\mu_i CI}{IP}.$$

$$\therefore \quad \frac{\mu_{i-1}(AO - r_i)}{\sqrt{AO^2 - 2(AO - r_i)AN}} = \frac{\mu_i(AI - r)}{\sqrt{AI^2 - 2(AI - r)AN}}.$$

Let $AN = \lambda$, then

$$\frac{\mu_{i-1}(s_i + \Delta_{i-1} - r_i)}{\sqrt{(s_i + \Delta_{i-1})^2 - 2\lambda(s_i + \Delta_{i-1} - r_i)}} = \frac{\mu_i(s_i' + \Delta_i - r_i)}{\sqrt{(s_i' + \Delta_i)^2 - 2\lambda(s_i' + \Delta_i - r_i)}}.$$

Expanding each side in powers of the Δ's by Taylor's theorem we have

$$\mu_{i-1}\left\{f(s_i) + \Delta_{i-1} f'(s_i') + \frac{1}{2!}\Delta_{i-1}^2 f''(s_i) \ldots\right\}$$

$$= \mu_i\left\{f(s_i') + \Delta_i f'(s_i') + \frac{1}{2!}\Delta_i^2 f''(s_i') \ldots\right\},$$

where

$$f(s_i)=\frac{s_i-r_i}{\sqrt{s_i^2-2\lambda(s_i-r_i)}}\,;$$

$$f'(s_i)=\frac{\lambda(r_i-s_i)+s_ir_i}{\{s_i^2-2\lambda(s_i-r_i)\}^{3/2}}\,;$$

$$f''(s_i)=\frac{\lambda^2(5s_i-2r_i)+2\lambda(s_i^2-r_is_i+r_i^2)-2r_is_i^2}{\{s_i^2-2\lambda(s_i-r_i)\}^{5/2}}\,;$$

with similar expressions for the dashed letters.

Expanding these in powers of λ

$$f(s_i)=\left(1-\frac{r_i}{s_i}\right)+\frac{\lambda}{s_i}\left(1-\frac{r_i}{s_i}\right)^2+\frac{3}{2}\frac{\lambda^2}{s_i^2}\left(1-\frac{r_i}{s_i}\right)^3+\ldots$$

Since $$\frac{\lambda}{r_i}=\frac{1}{2}\left(\frac{y_i}{r_i}\right)^2+\frac{1}{8}\left(\frac{y_i}{r_i}\right)^4$$

to the fourth power of (y/r),

$$f(s_i)=\left(1-\frac{r_i}{s_i}\right)+\frac{r_i}{2s_i}\left(1-\frac{r_i}{s_i}\right)^2\left(\frac{y_i}{r_i}\right)^2$$
$$+\frac{1}{8}\frac{r_i}{s_i}\left(1-\frac{r_i}{s_i}\right)^2\left(1+\frac{3r_i}{s_i}\left(1-\frac{r_i}{s_i}\right)\right)\left(\frac{y_i}{r_i}\right)^4.$$

Similarly

$$f'(s_i)=\frac{r_i}{s_i^2}\left\{1-\frac{\lambda}{r_i}\left(1-\frac{r_i}{s_i}\right)\left(1-\frac{3r_i}{s_i}\right)\right.$$
$$\left.-\frac{3}{2}\left(\frac{\lambda}{r_i}\right)^2\left(\frac{r_i}{s_i}\right)\left(1-\frac{r_i}{s_i}\right)^2\left(2-\frac{r_i}{s_i}\right)\ldots\right\}$$
$$=\frac{r_i}{s_i^2}\left\{1-\frac{1}{2}\left(\frac{y_i}{r_i}\right)^2\left(1-\frac{r_i}{s_i}\right)\left(1-\frac{3r_i}{s_i}\right)\right.$$
$$\left.-\frac{1}{8}\left(\frac{\lambda}{r_i}\right)^4\left(1-\frac{r_i}{s_i}\right)\left(1+\frac{3r_i}{s_i}-9\left(\frac{r_i}{s_i}\right)^2+3\left(\frac{r_i}{s_i}\right)^3\right)\right\}.$$

$$f''(s_i)=-\frac{2r}{s_i^3}\left\{1-\left(\frac{\lambda}{r_i}\right)\left(1-\frac{6r_i}{s_i}+\frac{6r_i^2}{s_i^2}\right)\right.$$
$$\left.+\left(\frac{\lambda}{r_i}\right)^2\left(-\frac{15}{2}\left.\overline{\frac{r_i}{s_i}}\right|+37\left.\overline{\frac{r_i}{s_i}}\right|^2-40\left.\overline{\frac{r_i}{s_i}}\right|^3+\frac{25}{2}\left.\overline{\frac{r_i}{s_i}}\right|^4\right)\right\}$$
$$=-\frac{2r}{s_i^3}\left\{1-\frac{1}{2}\left(\frac{y_i}{r_i}\right)^2\left(1-\frac{6r_i}{s_i}+\frac{6r_i^2}{s_i^2}\right)\right.$$
$$\left.-\frac{1}{8}\left(\frac{y_i}{r_i}\right)^4\left(1+9\left.\overline{\frac{r_i}{s_i}}\right|-68\left.\overline{\frac{r_i}{s_i}}\right|^2+80\left.\overline{\frac{r_i}{s_i}}\right|^3-25\left.\overline{\frac{r_i}{s_i}}\right|^4\right)\right\}$$

these correct to the fourth power of $\frac{y_i}{r_i}$.

The expansion therefore takes the form

$$\mu_{i-1}\Bigg[\Bigg\{1-\frac{r_i}{s_i}\Bigg)+\frac{1}{2}\left(\frac{r_i}{s_i}\right)\left(1-\frac{r_i}{s_i}\right)^2\left(\frac{y_i}{r_i}\right)^2+\frac{1}{8}\frac{r_i}{s_i}\left(1-\frac{r_i}{s_i}\right)^2\left(1+3\frac{r_i}{s_i}\left(1-\frac{r_i}{s_i}\right)\right)\left(\frac{y_i}{r_i}\right)^4\Bigg\}$$

$$+\frac{\Delta_{i-1}r_i}{s_i^{\,2}}\Bigg\{1-\frac{1}{2}\left(1-\frac{r_i}{s_i}\right)\left(1-\frac{3r_i}{s_i}\right)\left(\frac{y_i}{r_i}\right)^2-\frac{1}{8}\left(1-\frac{r_i}{s_i}\right)\Bigg(1+3\frac{r_i}{s_i}-9\left(\frac{r_i}{s_i}\right)^2$$

$$+3\left(\frac{r_i}{s_i}\right)^3\Bigg)\left(\frac{y_i}{r_i}\right)^4\Bigg\}$$

$$-\frac{\Delta_{i-1}^2 r_i}{s_i^{\,3}}\Bigg\{1-\frac{1}{2}\left(1-\frac{6r_i}{s_i}\left(1-\frac{r_i}{s_i}\right)\right)\left(\frac{y_i}{r_i}\right)^2-\frac{1}{8}\Bigg(1+9\left(\frac{r_i}{s_i}\right)-68\left(\frac{r_i}{s_i}\right)^2$$

$$+80\left(\frac{r_i}{s_i}\right)^3-25\left(\frac{r_i}{s_i}\right)^4\Bigg)\left(\frac{y_i}{r_i}\right)^4\Bigg\}\Bigg]$$

= a similar expression in μ_i, Δ_i, and s_i'.

To a first approximation neglecting $\left(\frac{y_i}{r_i}\right)^2$ and Δ we get of course

$$\mu_{i-1}\left(1-\frac{r_i}{s_i}\right)=\mu_i\left(1-\frac{r_i}{s_i}\right).$$

Let each of these be denoted by Q_{s_i}.

To a second approximation

$$\mu_{i-1}\left\{\frac{1}{2}\frac{r_i}{s_i}\left(1-\frac{r_i}{s_i}\right)^2\left(\frac{y_i}{r_i}\right)^2+\frac{r_i\Delta_{i-1}}{s_i^2}\right\}$$

$$=\mu_i\left\{\frac{1}{2}\frac{r_i}{s_i'}\left(1-\frac{r_i}{s_i'}\right)^2\left(\frac{y_i}{r_i}\right)^2+\frac{r_i\Delta_i}{s_i'^2}\right\}.$$

Whence

$$\frac{\mu_i\Delta_i}{s_i'^2}-\frac{\mu_{i-1}\Delta_{i-1}}{s_i^2}=\frac{1}{2}y_i^2Q^2_{s_i}\left(\frac{1}{\mu_{i-1}s_i}-\frac{1}{\mu_i s_i'}\right).$$

And if θ_i be the inclination of the ray to the axis in the medium whose refractive index is μ_i

$$\theta_{i-1}s_i=\theta_i s_i'=y_i$$

to this degree of accuracy, and therefore summing the series of difference equations (as in E. T. Whittaker's tract on the 'Theory of Optical Instruments')

$$\mu_\kappa\Delta_\kappa\theta_\kappa^2=\frac{1}{2}\sum_{p=1}^{p=\kappa}Q^2_{sp}y_p^4\left(\frac{1}{\mu_{p-1}s_p}-\frac{1}{\mu_p s_p'}\right),$$

$$\frac{\mu_\kappa\Delta_\kappa y_\kappa^2}{s_\kappa'^2}=\frac{1}{2}\sum_{p=}^{p=\kappa}Q^2_{sp}y_p^4\left(\frac{1}{\mu_{p-1}s_p}-\frac{1}{\mu_p s_p'}\right).$$

Proceeding to a third approximation we may assume Δ as of the order Ay^2 and neglecting powers of $\frac{y_i}{r_i}$ above the fourth,

$$\mu_{i-1}\left[\frac{1}{2}\frac{r_i}{s_i}\left(1-\frac{r_i}{s_i}\right)^2\left(\frac{y_i}{r_i}\right)^2+\frac{1}{8}\frac{r_i}{s_i}\left(1-\frac{r_i}{s_i}\right)^2\left(1+\frac{3r_i}{s_i}\left(1-\frac{r_i}{s_i}\right)\right)\left(\frac{y_i}{r_i}\right)^4\right.$$

$$\left.+\frac{\Delta_{i-1}r_i}{s_i^2}\left\{1-\frac{1}{2}\left(1-\frac{r_i}{s_i}\right)\left(1-\frac{3r_i}{s_i}\right)\left(\frac{y_i}{r_i}\right)^2\right\}-\frac{\Delta_{i-1}^2 r_i}{s_i^3}\right]$$

$=$ a similar expression in μ_i, Δ_i, and s_i'.

We can use the relation $\theta_{i-1}s_i = \theta_i s_i' = y_i$ again correct to this order of approximation.

$$\mu_i\Delta_i\theta_i^2-\mu_{i-1}\Delta_{i-1}\theta_{i-1}^2=\frac{1}{2}y_i^4 Q_{s_i}^2\left(\frac{1}{\mu_{i-1}s_i}-\frac{1}{\mu_i s_i'}\right)$$

$$+\frac{1}{8}\frac{y_i^5}{r_i^2}Q_{s_i}^2\left(\frac{1}{\mu_{i-1}s_i}-\frac{1}{\mu_i s_i'}\right)+\frac{3}{8}y_i^6 Q_{s_i}^3\left(\frac{1}{\mu_{i-1}^2 s_i^2}-\frac{1}{\mu_i^2 s_i'^2}\right)$$

$$-\frac{1}{2}\frac{y_i^4}{r_i^2}\left[\frac{\Delta'_{i-1}\mu_{i-1}}{s_i^2}\left(1-\frac{r_i}{s_i}\right)\left(1-\frac{3r_i}{s_i}\right)-\frac{\Delta'_i\mu_i}{s_i'^2}\left(1-\frac{r_i}{s_i'}\right)\left(1-\frac{3r_i}{s_i}\right)\right]$$

$$+y_i^2\left[\frac{\mu_i\Delta_i'^2}{s_i'^3}-\frac{\mu_{i-1}\Delta_{i-1}'^2}{s_i^3}\right]$$

where Δ' denotes the value of Δ as obtained from the last approximation.

Summing the difference equations for the system of refracting surfaces and putting Θ_i for

$$Q_{s_i}^2\left(\frac{1}{\mu_{i-1}s_i}-\frac{1}{\mu_i s_i'}\right),$$

we get

$$\mu_\kappa\Delta_\kappa\theta_\kappa^2=\frac{1}{2}\sum_{i=1}^{i=\kappa}y_i^4\Theta_i+\frac{1}{8}\sum_{i=1}^{i=\kappa}\frac{y_i^6}{r_i^2}\Theta_i+\frac{3}{8}\sum_{i=1}^{i=\kappa}y_i^6 Q_{s_i}\Theta_i\left(\frac{1}{\mu_{i-1}s_i}+\frac{1}{\mu_i s_i'}\right)$$

$$+\frac{1}{2}\sum_{i=1}^{i=\kappa}\frac{y_i^4}{r_i^2}\left(\frac{\Delta'_i\mu_i}{s_i'^2}-\frac{\Delta'_{i-1}\mu_{i-1}}{s_i^2}\right)-2\sum_{i=1}^{i=\kappa}\frac{y_i^4}{r_i}\left(\frac{\Delta'_i\mu_i}{s_i'^3}-\frac{\Delta'_{i-1}\mu_{i-1}}{s_i^3}\right)$$

$$+\frac{3}{2}\sum_{i=1}^{i=\kappa}y_i^4\left(\frac{\Delta'_i\mu_i}{s_i'^4}-\frac{\Delta'_{i-1}\mu_{i-1}}{s_i^4}\right)+\sum_{i=1}^{i=\kappa}y_i^2\left[\frac{\mu_i\Delta_i'^2}{s_i'^3}-\frac{\mu_{i-1}\Delta'^2_{i-1}}{s_i^3}\right].$$

Substituting for

$$\frac{\Delta'_i\mu_i}{s_i^2}-\frac{\Delta'_{i-1}\mu_{i-1}}{s_i^2}$$

the value

$$\frac{1}{2}y_i^2Q_{s_i}^2\left(\frac{1}{\mu_{i-1}s_i}-\frac{1}{\mu_i s_i}\right),$$

or $\frac{1}{2}y_i^2\Theta$ before obtained, the expression takes the final shape

$$\mu_\kappa\Delta_\kappa\theta_\kappa^2=\frac{1}{2}\sum_{i=1}^{i=\kappa}y_i^4\Theta_i+\frac{3}{8}\sum_{i=1}^{i=\kappa}\frac{y_i^6}{r_i^2}\Theta_i+\frac{3}{8}\sum_{i=1}^{i=\kappa}y_i^6Q_{s_i}\Theta_i\left(\frac{1}{\mu_{i-1}s_i}+\frac{1}{\mu_i s_i}\right)$$

$$-2\sum_{i=1}^{i=\kappa}\frac{y_i^4}{r_i}\left(\frac{\Delta'_i\mu_i}{s_i'^3}-\frac{\Delta'_{i-1}\mu_{i-1}}{s_i^3}\right)+\frac{3}{2}\sum_{i=1}^{i=\kappa}y_i^4\left(\frac{\Delta'_i\mu_i}{s_i'^4}-\frac{\Delta'_{i-1}\mu_{i-1}}{s_i^4}\right)$$

$$+\sum_{i=1}^{i=\kappa}y_i^2\left(\frac{\mu_i\Delta_i'^2}{s_i'^3}-\frac{\mu_{i-1}\Delta_{i-1}'^2}{s_i^3}\right),$$

or $\Delta_\kappa=\frac{s_\kappa^2}{\mu_\kappa y_\kappa^2}$ × above expression.

(the last five terms being required by the higher order of approximation).

To test this let us apply it to the case of a single thin lens of radii r and s in air, and let u, s, v be the distances of the object and its successive images from the lens. We have

$$Q_1=\frac{1}{r}-\frac{1}{u}=\mu\left(\frac{1}{r}-\frac{1}{s_1}\right),\quad \Theta_1=\left(\frac{1}{r}-\frac{1}{u}\right)^2\left(\frac{\mu+1}{u}-\frac{1}{r}\right)\frac{\mu-1}{\mu^2},$$

$$\Delta'_1=\frac{s_1^2}{2\mu}Q_1^2y^2\left(\frac{1}{u}-\frac{1}{\mu s_1}\right)=\frac{1}{2}\frac{s_1^2}{\mu}y^2\Theta_1,$$

$$Q_2=\frac{1}{s}-\frac{1}{v}=\mu\left(\frac{1}{s}-\frac{1}{s_1}\right),\quad \Theta_2=\left(\frac{1}{s}-\frac{1}{v}\right)^2\left(\frac{1}{s}-\frac{\mu+1}{v}\right)\frac{\mu-1}{\mu^2},$$

$$\Delta'_2=\frac{1}{2}v^2y^2(\Theta_1+\Theta_2).$$

Also

$$\frac{1}{u}+\frac{1}{\mu s_1}=\frac{\mu^2+1}{\mu^2 u}+\frac{\mu-1}{\mu^2 r},$$

$$\frac{1}{\mu s_1}+\frac{1}{v}=\frac{\mu^2+1}{\mu^2 v}+\frac{\mu-1}{\mu^2 s}.$$

The formula reduces in this case to

$$v^2\Bigl[\frac{1}{2}(\Theta_1+\Theta_2)y^2+\frac{3}{8}\Bigl(\frac{\Theta_1}{r^2}+\frac{\Theta_2}{s^2}\Bigr)y^4+\frac{3}{8}\Bigl(Q_1\Theta_1\Bigl(\frac{1}{u}+\frac{1}{\mu s_1}\Bigr)$$

$$+Q_2\Theta_2\Bigl(\frac{1}{\mu s_1}+\frac{1}{v}\Bigr)\Bigr)y^4-2\Bigl\{\frac{\mu\Delta'_1}{rs_1{}^3}+\frac{1}{s}\Bigl(\frac{\Delta'_2}{v^3}-\frac{\mu\Delta'_1}{s_1{}^3}\Bigr)\Bigr\}y^4$$

$$+\frac{3}{2}y^4\frac{\Delta'_2}{v^4}+\frac{y^2\Delta'_2{}^2}{v^3}\Bigr],$$

or

$$\frac{1}{2}(\Theta_1+\Theta_2)y^2v^2+\frac{1}{8}y^4v^2\Bigl[3\Bigl(\frac{\Theta_1}{r^2}+\frac{\Theta_2}{s^2}\Bigr)+\frac{3}{\mu^2}\Bigl\{\Theta_1\Bigl(\frac{1}{r}-\frac{1}{u}\Bigr)\Bigl(\frac{\mu^2+1}{u}+\frac{\mu-1}{r}\Bigr)$$

$$+\Theta_2\Bigl(\frac{1}{s}-\frac{1}{v}\Bigr)\Bigl(\frac{\mu^2+1}{v}+\frac{\mu-1}{3}\Bigr)\Bigr\}-8\Bigl\{\frac{\Theta_1}{s_1}\Bigl(\frac{1}{r}-\frac{1}{s}\Bigr)+\frac{1}{sv}(\Theta_1+\Theta_2)\Bigr\}$$

$$-\frac{6}{v^2}(\Theta_1+\Theta_2)\Bigr]+\frac{1}{4}y^4v^3(\Theta_1+\Theta_2)^2.$$

The first term gives the previous approximation. Dealing with the second the coefficient of $\frac{1}{8}y^4v^2$ is

$$\Theta_1\Bigl\{\frac{3}{r^2}+\frac{3}{\mu^2}\Bigl(\frac{1}{r}-\frac{1}{u}\Bigr)\Bigl(\frac{\mu^2+1}{u}+\frac{\mu-1}{r}\Bigr)-\frac{8}{s_1}\Bigl(\frac{1}{r}-\frac{1}{s}\Bigr)\Bigr\}$$

$$+\Theta_2\Bigl\{\frac{3}{s_2}+\frac{3}{\mu^2}\Bigl(\frac{1}{s}-\frac{1}{v}\Bigr)\Bigl(\frac{\mu^2+1}{v}+\frac{\mu-1}{s}\Bigr)\Bigr\}-2(\Theta_1+\Theta_2)\Bigl(\frac{4}{sv}-\frac{3}{v^2}\Bigr).$$

Since $$\frac{\mu}{s_1}=\frac{\mu-1}{r}+\frac{1}{u}=\frac{\mu-1}{s}+\frac{1}{v}$$

and $$\mu\Bigl(\frac{1}{r}-\frac{1}{s}\Bigr)=\Bigl(\frac{1}{r}-\frac{1}{u}\Bigr)-\Bigl(\frac{1}{s}-\frac{1}{v}\Bigr);$$

this may be written

$$\frac{\Theta_1}{\mu^2}\Bigl\{\frac{\mu^2-\mu+3}{r^2}+\frac{3\mu^2+\mu-6}{ru}-\frac{3(\mu^2-1)}{u^2}\Bigr\}$$

$$+\frac{\Theta_2}{\mu^2}\Bigl\{\frac{\mu^2-\mu+3}{s^2}+\frac{3\mu^2+\mu-6}{sv}-\frac{3(\mu^2-1)}{v^2}\Bigr\}$$

$$+\frac{2\Theta_1}{\mu^2}\Bigl\{\Bigl(\frac{\mu-1}{r}+\frac{1}{u}\Bigr)^2+4\Bigl(\frac{\mu-1}{s}+\frac{1}{v}\Bigr)\Bigl(\frac{1}{s}-\frac{1}{v}\Bigr)-\frac{4\mu^2}{sv}+\frac{3\mu^2}{v^2}\Bigr\}$$

$$+\frac{2\Theta_2}{\mu^2}\Bigl\{\frac{\mu^2+2\mu-3}{s^2}-\frac{4\mu^2+2\mu-6}{sv}+\frac{3(\mu^2-1)}{v^2}\Bigr\}.$$

Substituting for $\frac{\mu-1}{r}+\frac{1}{u}$ as above in terms of s and v the coefficients of $2\Theta_1/\mu^2$ and $2\Theta_2/\mu^2$ are easily seen to be equal and each may be written

$$(\mu-1)\left(\frac{1}{s}-\frac{1}{v}\right)\left(\overline{\mu+1}\left(\frac{1}{s}-\frac{1}{v}\right)+2\left(\frac{1}{s}-\frac{\mu+1}{v}\right)\right).$$

The whole expression for the longitudinal aberration is thus

$$\begin{aligned}\frac{1}{2}(\Theta_1+\Theta_2)y^2v^2+\frac{1}{8\mu^2}y^4v^2\Big[\Theta_1&\left\{\frac{(\mu^2-\mu+3)}{r^2}+\frac{(3\mu^2+\mu-6)}{ru}-\frac{3(\mu^2-1)}{u^2}\right\}\\ &+\Theta_2\left\{\frac{\mu^2-\mu+3}{s^2}+\frac{(3\mu^2+\mu-6)}{sv}-\frac{3(\mu^2-1)}{v^2}\right\}\\ &+2(\mu-1)(\Theta_1+\Theta_2)\left\{(\mu+1)\left(\frac{1}{s}-\frac{1}{v}\right)^2+2\left(\frac{1}{s}-\frac{\mu+1}{v}\right)\left(\frac{1}{s}-\frac{1}{v}\right)\right\}\\ &+\frac{1}{4}y^4v^3(\Theta_1+\Theta_2)^2,\end{aligned}$$

where Θ_1 and Θ_2 have the values given above.

Some writers give the spherical aberration as a correction to $\frac{1}{v}$ instead of v. Assuming this correction to be

$$-(Ay^2+By^4),$$

the longitudinal aberration for a thin lens is

$$1\Big/\left(\frac{1}{v}-Ay^2-By^4\right)-v \quad \text{or} \quad (Ay^2+By^4)v^2+A^2y^4v^3$$

to this order of approximation. Comparing with the above the result for a thin lens (allowing for the necessary changes in notation) is seen to agree with Messrs. Herman and Dennis Taylor's formula as given in the latter's 'System of Applied Optics' (Appendix, pp. 6 and 13).

In applying the formula to any lens system a relation between successive y's is needed.

If d_i is the distance between the ith and $(i+1)$th surfaces, P_iN_i, $P_{i+1}N_{i+1}$ the successive ordinates, A_i, A_{i+1} the vertices of the surfaces, it is easily seen that

$$\frac{y_{i+1}}{y_i}=1+\frac{d_i+A_iN_i-A_{i+1}N_{i+1}}{s_i'+\Delta'_i-A_iN_i}=1+\frac{d_i+\frac{1}{2}\frac{y_i^2}{r_i}-\frac{1}{2}\frac{y_{i+1}^2}{r_{i+1}}}{s_i'+\Delta'_i-\frac{1}{2}\frac{y_i^2}{r_i}}$$

to the 2nd power of the y's.

Expanding and remembering that Δ'_i is of the order y_i^2 we get easily

$$\frac{y_{i+1}}{y_i} = 1 + \frac{d_i}{s_i'} - \frac{d_i\Delta'_i}{s_i'^2} + \frac{y_i^2}{2s_i'r_i}\left(1+\frac{d_i}{s_i}\right) - \frac{y_i^2}{2s_i'r_{i+1}}\left(1+\frac{d_i}{s_i}\right)^2,$$

using the first approximation for y_{i+1} in terms of y_i.

In our formula, therefore, it will be usually sufficient to substitute

$$y_i\left(1+\frac{d_i}{s_i}\right) \quad \text{for} \quad y_{i+1}.$$

We shall conclude the paper by applying the formula to a thick double convex lens on which is incident a beam parallel to the axis. Let r_1 r_2 be the radii of the surfaces. Then $s_1=\infty$, and it must be remembered that successive s's are measured from the vertices of the respective surfaces, and let $s_2'=v$. The formula takes the form :—

$$\frac{v^2}{y_2^2}\left[\frac{1}{2}(y_1^4\Theta_1+y_2^4\Theta_2)+\frac{3}{8}\left(\frac{y_1^6}{r_1^2}\Theta_1+\frac{y_2^6}{r_2^2}\Theta_2\right)\right.$$
$$+\frac{3}{8}\left\{y_1^6Q_1\Theta_1\left(\frac{1}{u}+\frac{1}{\mu s_1'}\right)+y_2^6Q_2\Theta_2\left(\frac{1}{\mu s_2}+\frac{1}{v}\right)\right\}$$
$$-2\left\{\frac{y_1^4}{r_1}\frac{\mu\Delta'_1}{s_1^3}+\frac{y_2^4}{r_2}\left(\frac{\Delta'_2}{v^3}-\frac{\mu\Delta'_1}{s_2^3}\right)\right\}+\frac{3}{2}\left\{y_1^4\frac{\Delta'_1\mu}{s_1'^4}+y_2^2\left(\frac{\Delta'_2}{v^4}-\frac{\mu\Delta'_1}{s_2^4}\right)\right\}$$
$$\left.+\left\{y_1^2\frac{\mu\Delta'^2_1}{s_1'^3}+y_2^2\left(\frac{\Delta'^2_2}{v^3}-\frac{\mu\Delta'^2_1}{s_2^3}\right)\right\}\right].$$

Take the following numerical values

$\left\{\begin{matrix} r_1=-1 \\ r_2=+3 \end{matrix}\right\}$, t (the lens-thickness at the middle) ·75, $y_1=\cdot 4$,

then by calculation $s_1'=-3$, $s_2=-2\cdot 25$, $s_2'=v=-1\cdot 2$, $y_2=\cdot 3$,

$Q_1=-1$, $Q_2=7/6$, $\Theta_1=2/9$, $\Theta_2=\dfrac{7^2\times 29}{8\times 3^5}$, $\mu\Delta'_1=\cdot 16$,

$$\frac{\Delta'_2}{v^2}=\frac{1}{2y_2^2}(y_1^4\Theta_1+y_2^4\Theta_2) = \cdot 064{,}498.$$

The rest of the numerical work may be arranged as follows :—

			+	−
2nd order corrections	$\frac{1}{2} y_1^4\Theta_1$	=	·002,844	
	$\frac{1}{2} y_2^4\Theta_2$	=	·002,960	
			·005,804	
3rd order corrections	$\frac{3}{8}\frac{y_1^6}{r_1^2}\Theta_1$	=	·000,341	
	$\frac{3}{8}\frac{y_2^6}{r_2^2}\Theta_2$	=	·000,022	
	$\frac{3}{8} y_1^6 Q_1\Theta_1\left(\frac{1}{u}+\frac{1}{\mu s_1'}\right)$	=	·000,076	
	$\frac{3}{8} y_2^6 Q_2\Theta_2\left(\frac{1}{\mu s_2}+\frac{1}{v}\right)$	=		·000,353
	$-2\frac{y_1^4}{r_1}\frac{\mu\Delta'_1}{s_1'^3}$	=		·000,303
	$-2\frac{y_2^4}{r_2}\left(\frac{\Delta'_2}{v^3}-\frac{\mu\Delta'_1}{s_2^3}\right)$	=	·000,234	
	$\frac{3}{2} y_1^4\frac{\Delta'_1\mu}{s_1'^4}$	=	·000,076	
	$\frac{3}{2} y_2^4\left(\frac{\Delta'_2}{v^4}-\frac{\mu\Delta'_1}{s_2^4}\right)$	=	·000,489	
	$y_1^2\frac{\mu\Delta'^2}{s_1'^3}$	=		·000,101
	$y_2^2\left(\frac{\Delta'^2_2}{v^3}-\frac{\mu\Delta'^2_1}{s_2^3}\right)$	=		·000,082
			·007,042	·000,839
			·000,839	
			+·006,203	

To get the final value of Δ_2 this must be multiplied by $\frac{v^2}{y_2^2}$ or 16. This gives +·099,248.

An accurate tracing of the extreme ray through this lens by a trigonometrical method gave for the longitudinal aberration +·099,37, showing a negligible discrepancy of ·00012 approximately.

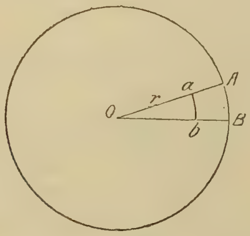
Feb. 3, 1910.

VI. *The Problem of Uniform Rotation treated on the Principle of Relativity.*

By G. STEAD, *B.A., and* H. DONALDSON, *B.Sc., Cavendish Laboratory, Cambridge**.

EHRENFEST (*Phys. Zeit.* Nov. 1909, Science Abstracts, Jan. 1910) advances the problem of the rotation of a solid cylinder about its axis, in connexion with the Principle of Relativity. He suggests that a contradiction is involved from the facts that any element of *circumference*, which must be moving in the direction of its length, tends to contract in the usual ratio $\sqrt{1-\frac{v^2}{c^2}}:1$, where c is the velocity of light and v the velocity of the element, whereas any *radius* tends to remain unaltered, because it moves in a direction perpendicular to its own length. A quantitative solution of the problem in the simpler case in which the rotating cylinder is reduced to a rotating disk has led to rather interesting conclusions, and is here given.

Consider the disk rotating about an axis through its centre perpendicular to its plane. In a small sector AOB of angle $\delta\theta$, any length ab, at a distance r from O, will contract from $r\,.\,\delta\theta$ to $r\,.\,\delta\theta\sqrt{1-\frac{v^2}{c^2}}$ when the disk is rotating, so that ab is moving with linear velocity v.



As Ehrenfest pointed out, the Oa will have no tendency to change, and if this condition is to be fulfilled it is impossible for the disk to remain in the plane form. It must assume a cup-like form, whose horizontal sections will, from symmetry, be circles, and whose shape is such that ab has contracted to $ab\sqrt{1-\frac{v^2}{c^2}}$, while O$a$ is unaltered.

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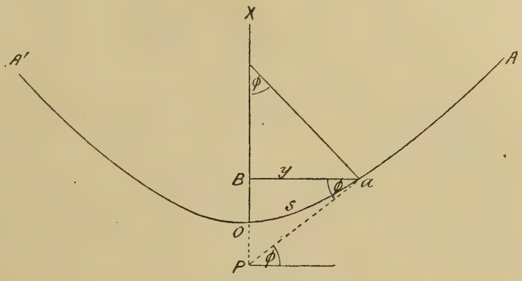
* Communicated by the Authors.

If, therefore, A′OA represent the vertical section of the final form of the disk containing the axis of rotation OX,



we shall have Oa measured along the arc equal to r, while aB measured perpendicular to OB will be $r\sqrt{1-\frac{v^2}{c^2}}$. In this way both the conditions demanded by the relativity principle will be satisfied.

Writing O$a = s$ and $a\text{B} = y$, according to the usual notation, we have

$$y = s\sqrt{\frac{c^2-v^2}{c^2}} = s\sqrt{\frac{c^2-y^2\omega^2}{c^2}},$$

ω being the angular velocity of the disk.

$$\therefore\quad y^2c^2 = s^2c^2 - y^2s^2\omega^2. \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

Differentiating, and arranging terms, we have

$$(c^2+\omega^2s^2)\,y\frac{dy}{ds} = s\,(c^2-y^2\omega^2)$$

or
$$(c^2+\omega^2s^2)y\cos\phi = s(c^2-y^2\omega^2). \quad . \quad . \quad . \quad \text{(ii.)}$$

Substituting in (ii.) the value of y from (i.) we have, taking the positive root of the equation,

$$(c^2+\omega^2s^2)\frac{sc\cos\phi}{\sqrt{c^2+\omega^2s^2}} = \left(c^2-\frac{\omega^2s^2c^2}{c^2+\omega^2s^2}\right)s,$$

whence

$$\underline{(c^2+\omega^2s^2)^{3/2}\cos\phi = c^3.} \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

This gives the intrinsic equation of a section of the disk when rotating with angular velocity ω, and contains no approximations.

Case I.—When the velocity of any point on the disk is small compared with the velocity of light, we have

$$\cos\phi = \frac{c^3}{c^3\left(1+\frac{\omega^2 s^2}{c^2}\right)^{3/2}}.$$

The conditions of this case will be satisfied if ωs is small compared with c.

Thus we may write

$$\cos\phi = 1 - 3/2\,\frac{\omega^2 s^2}{c^2},$$

whence

$$\underline{s = \frac{2}{\sqrt{3}}\,\frac{c}{\omega}\sin\frac{\phi}{2}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv.)}$$

This indicates that the form of the vertical section in this case is a curve of the cycloid family, an epicycloid.

Case II.—When the velocity of a point on the outer part of the disk approaches the velocity of light, since we have

$$y = \frac{sc}{\sqrt{c^2+\omega^2 s^2}}$$

and

$$v = y\omega,$$

we get

$$v = \frac{sc\omega}{\sqrt{c^2+\omega^2 s^2}} = \frac{c}{\sqrt{\frac{c^2}{s^2\omega^2}+1}}. \quad . \quad . \quad . \quad . \quad \text{(v.)}$$

From this we see that for all values of s which differ from zero by any finite quantity, $v=c$ when ω is infinite. Thus no point on the disk can be made to move with a velocity greater than that of light, which is exactly what would be expected from relativity principles.

Further, from the equation

$$\cos\phi = \frac{1}{\left(1+\frac{\omega^2 s^2}{c^2}\right)^{3/2}}$$

we see that, when ω becomes very large, $\cos\phi$ is small, and is also sensibly independent of s, unless s is very small. Hence, when the angular velocity becomes very large, the disk approaches the form of a right circular cone of small angle, except near the centre of the disk.

When ω is infinite, all points at a finite distance from the centre of the disk are at zero distance from the axis of rotation, *i. e.* the disk has become a straight line coinciding with the axis of rotation and of length equal to the original radius of the disk.

This straight line, of infinite density, is analogous to the plane of infinite density obtained by moving a solid body in a straight line with the velocity of light.

The difficulty of experimentally discriminating between this solution of the problem and the solution which considers the rotating disk as contracting but still remaining in one plane would be great. If we assume that light is reflected from a mirror fixed normally to the disk, and assume that we can detect a deflexion of 1 mm. in the position of the reflected beam received on a scale 10 metres distant, *i. e.* a value of ϕ equal to $\frac{1}{20,000}$, it will still be necessary to have a frequency of revolution of about 1000 per second to produce this effect.

In conclusion, it would seem probable that, for a disk of any appreciable thickness, the plane position would be maintained during the rotation, the material of the disk being strained, in which case Ehrenfest's contention, that we have here a contraction of a line in a direction perpendicular to its direction of motion, is valid. On the other hand the above theory does away with this difficulty, but involves a change of form of the disk, which does not, however, lead to any conclusions not in perfect accordance with relativity principles.

VII. *A Rational Formula for the Discharge over a Broad-crested Weir.* *By* Professor A. H. Gibson, *D.Sc.*, *University College, Dundee* *.

As was first pointed out by Dr. W. C. Unwin, an expression for the flow over a broad-crested weir may be deduced from first principles if it be assumed that the crest is so wide in the direction of flow, that the water settles down before leaving the crest, to form a parallel stream of thickness t, and that in this stream the pressure at any point is that corresponding to its depth. Thus, assuming the velocity in the surface, and at every point in this stream to be given by $\sqrt{2g(\mathrm{H}-t)}$ ft. per second, where H is the up-stream head measured above the crest, the discharge is given by $\mathrm{Q}=bt\sqrt{2g(\mathrm{H}-t)}$ cub. ft. per second, where b is the breadth of the stream.

As the stream will adjust itself so as to give maximum discharge under given conditions, t can be determined by

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* Communicated by the Author.

equating $\frac{dQ}{dt}$ to zero. This gives $t = \frac{2}{3}H$, and on substituting this value we get $Q = \cdot 385 b\sqrt{2g} \,.\, H^{\frac{3}{2}}$ C.F.S. Writing this in the usual form, $Q = \frac{2}{3} Cb\sqrt{2g}H^{\frac{3}{2}} = KbH^{\frac{3}{2}}$ we have $C = \cdot 578$ and $K = 3\cdot 087$.

This method of treatment becomes more rational if account be taken of the fact that in a parallel stream flowing in an open channel, the distribution of velocity over any vertical is not uniform, being a maximum at or near the surface and a minimum at the bottom.

Experiments show that the ratio of the mean velocity over the section of such a stream, to the maximum surface velocity, while varying with the depth, width, and roughness of the bottom of the channel, lies between the limits ·82 and ·87 for such surfaces and depths as are common on the crests of such weirs, this ratio increasing with the depth of water.

Assuming, as is practically the case, that the maximum surface velocity in the case of the weir is equal to $\sqrt{2g(H-t)}$, the mean velocity will equal $k\sqrt{2g(H-t)}$, and the discharge will be given by

$$k \,.\, K \,.\, bH^{\frac{3}{2}} = 3\cdot 087 kbH^{\frac{3}{2}} = K' bH^{\frac{3}{2}} \text{ cub. ft. sec.}$$

Thus corresponding to the values ·82 and ·87 of k, the values of K' become 2·53 and 2·69.

The validity of this formula receives remarkable confirmation from the results of a large series of tests on such weirs, carried out in 1903 at Cornell University for the U. S. Geological Survey *. From a summary of these tests it appears that on broad weirs, for depths between 1 and 5 feet, the coefficient K' is sensibly uniform, increasing slightly with H. With weirs from 5 to 16 feet wide K' lies between 2·62 and 2·64, while with heads between ·5 foot and 1·0 foot, K' varies from 2·73 to 2·64. Experiments at Cornell University in 1899, on a weir having a crest 6·56 feet wide, with a sharp upstream edge †, show the following results:—

Value of H	·5	1·0	1·5	2·0	5·0
Value of K′	2·49	2·59	2·53	2·47	2·69

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* Water Supply and Irrigation Paper, No. 200. U. S. Geological Survey.

† Trans. American Soc. Civil Engineers, 1900.

VIII. *Partial Pressures in Liquid Mixtures.*

By William Edward Story *.

LAST summer Professor Rosanoff called my attention to an investigation of the partial pressures in certain binary mixtures that he was making by the application of the Duhem-Margules equation to experiments carried on in the Chemical Laboratory of Clark University, and to analogous applications that had been made by others. The mathematical aspect of the problem interested me ; I studied it carefully and found that it was possible not only to improve the method, from a mathematical point of view, by the use of more convergent series than those heretofore employed, but also to extend it to mixtures of any number of components. Incidentally it appeared that the coefficients of the new series are more readily calculated from actual observations than those of the former series, that Raoult's law holds for any number of components, that this law is an immediate consequence of the Duhem-Margules equation, and that Margules' formulæ for the partial pressures in a binary mixture involve no assumption other than those involved in the equation just mentioned. The present paper describes my method in general, and its application to binary and ternary mixtures in particular.

Contents.

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1. This investigation is restricted exclusively to such a liquid mixture and its variations as satisfy the following conditions :—

a. All variations of the mixture shall take place isothermally, that is at a constant temperature.

b. Each component shall have a vapour, and therefore a pressure of its own.

c. The partial pressure of any component of the mixture at the temperature in question shall depend solely on the composition of the mixture—that is on the molar proportions of the several components,—and shall vary continuously when the composition varies continuously, being finite for all compositions.

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* Communicated by the Author.

d. The partial pressure of any component shall be 0 if the proportion of that component is 0—that is, if the component in question is absent from the mixture, and only then.

e. The rate at which the partial pressure of any component changes as the proportion of that or any other component changes continuously shall be finite; and the rate at which the partial pressure of any component increases from 0 as that component is added gradually to any mixture of the other components alone shall not be 0.

f. Any component by itself shall have a perfectly definite pressure at the temperature in question.

g. A possible association or dissociation of the molecules of any component shall be regarded as producing a corresponding change in the molar proportion of that component.

It is important to observe the distinction between the partial pressure of a component of the mixture (to which conditions *c*, *d*, and *e* refer) and the pressure of the same substance in liquid form at the same temperature when existing by itself (see condition *f*). In the latter case the component by itself may be regarded as the whole mixture; its pressure is then the total pressure of the mixture. Otherwise the total pressure of the mixture is the sum of the partial pressures of its components; it is in this sense that the partial pressure of an absent component is 0 (as in condition *d*), because such a component contributes nothing to the total pressure of the mixture. These two cases—that in which the component in question is absent and that in which it constitutes the whole mixture—are the two extremes, as far as that component is concerned.

2. The molar proportion of any component of the mixture is the ratio of the number of "mols" of that component present to the total number of mols of all the components present. Let κ be the number of components under consideration (not necessarily all present in the mixture), $n_1, n_2, n_3, \ldots n_\kappa$ the numbers of mols of the several components in the mixture, $x_1, x_2, x_3, \ldots x_\kappa$ their molar proportions, and $p_1, p_2, p_3, \ldots p_\kappa$ their partial pressures, respectively. Let

$$\mathrm{N} = n_1 + n_2 + n_3 + \ldots + n_\kappa ; \quad \ldots . \quad (1)$$

then

$$x_r = \frac{n_r}{\mathrm{N}}, \quad n_r = \mathrm{N}x_r, \quad (r = 1, 2, 3, \ldots \kappa), \quad . \quad (2)$$

and

$$x_1 + x_2 + x_3 + \ldots + x_\kappa = 1. \quad . \quad . \quad . \quad . \quad (3)$$

Furthermore, if dx_1, dx_2, dx_3, . . , dx_κ are the infinitesimal changes in the x's that correspond to any infinitesimal variation of composition of the mixture, we have, by (3)

$$dx_1 + dx_2 + dx_3 + \ldots + dx_\kappa = 0. \quad . \quad . \quad . \quad (4)$$

On account of (3) the x's are not all independent, as is also implied by (4), but when the values of any $\kappa - 1$ of the x's, positive or 0 and having a sum not greater than 1, are given, the value of the remaining x will be determined by (3). In particular, if any x has the value 1, all the other x's have the common value 0, and, if all but one of the x's are 0, that one is 1. If $x_r = 0$, we have, by (2), $n_r = 0$ and *vice versa*, and the rth component is absent. If $x_r = 1$, the rth component is the only one present, and constitutes the whole mixture; then every n is 0 excepting n_r. When we speak hereafter of "all values of the x's," we shall mean all sets of values that satisfy (3).

By condition *c*, each of the partial pressures p is a continuous singly-valued function of the x's, finite for all values of the x's. In consequence of (3) it may be expressed as a function of any $\kappa - 1$ of the x's, and, on replacement of the x's by their values from (2), it may be expressed as a function of the n's. It will be convenient to represent p_s, the partial pressure of the sth component, by $p_s^{(n)}$ when expressed as a function of the n's, by $p_s^{(\bar{x})}$ when expressed as a function of all the x's by substitution of the n's in the terms of the x's from (2) in $p_s^{(n)}$ (N falls out and the result of the substitution is just the same as if each n in $p_s^{(n)}$ were replaced by the corresponding x, because $p_s^{(n)}$ is a homogeneous function of the n's of degree 0), and by $p_s^{(x)}$ when expressed as a function of x_1, x_2, x_3, . . . $x_{\kappa-1}$ (without x_κ). It is to be observed that $p_s^{(n)}$, $p_s^{(\bar{x})}$, and $p_s^{(x)}$ are perfectly definite expressions; but p_s can be expressed in many ways as a function of all the x's, on account of the relation (3). Then, because $p_s^{(n)}$ is a homogeneous function of the n's of degree 0,

$$n_1 \frac{\partial p_s^{(n)}}{\partial n_1} + n_2 \frac{\partial p_s^{(n)}}{\partial n_2} + n_3 \frac{\partial p_s^{(n)}}{\partial n_3} + \ldots + n_\kappa \frac{\partial p_s^{(n)}}{\partial n_\kappa} = 0. \quad . \quad (5)$$

Also, by (2),

$$\frac{\partial p_s^{(\bar{x})}}{\partial x_r} = \mathrm{N}\frac{\partial p_s^{(n)}}{\partial n_r} \quad (r = 1, 2, 3, \ldots, \kappa), \quad . \quad . \quad (6)$$

and, by (3),

$$\frac{\partial p_s^{(x)}}{\partial x_r} = \frac{\partial p_s^{(\bar{x})}}{\partial x_r} - \frac{\partial p_s^{(\bar{x})}}{dx_\kappa} = \mathrm{N}\left(\frac{\partial p_s^{(n)}}{\partial n_r} - \frac{\partial p_s^{(n)}}{\partial n_\kappa}\right) \quad (r = 1, 2, 3, \ldots, \kappa - 1). \quad . \quad (7)$$

From (7), (2), (3), and (5) follows

$$\begin{aligned} & x_1\frac{\partial p_s^{(x)}}{\partial x_1} + x_2\frac{\partial p_s^{(x)}}{\partial x_2} + x_3\frac{\partial p_s^{(x)}}{\partial x_3} + \ldots + x_{\kappa-1}\frac{\partial p_s^{(x)}}{\partial x_{\kappa-1}} \\ &= \mathrm{N}\left[\left(x_1\frac{\partial p_s^{(n)}}{\partial n_1} + x_2\frac{\partial p_s^{(n)}}{\partial n_2} + x_3\frac{\partial p_s^{(n)}}{\partial n_3} + \ldots + x_{\kappa-1}\frac{\partial p_s^{(n)}}{\partial n_{\kappa-1}}\right)\right. \\ &\qquad\qquad \left. - (x_1 + x_2 + x_3 + \ldots + x_{\kappa-1})\frac{\partial p_s^{(n)}}{\partial n_\kappa}\right] \\ &= n_1\frac{\partial p_s^{(n)}}{\partial n_1} + n_2\frac{\partial p_s^{(n)}}{\partial n_2} + n_3\frac{\partial p_s^{(n)}}{\partial n_3} + \ldots + n_{\kappa-1}\frac{\partial p_s^{(n)}}{\partial n_{\kappa-1}} - (1 - x_\kappa)\mathrm{N}\frac{\partial p_s^{(n)}}{\partial n_\kappa} \\ &= -\mathrm{N}\frac{\partial p_s^{(n)}}{\partial n_\kappa}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8) \end{aligned}$$

Furthermore, considering $p_s^{(n)}$ as derived from $p_s^{(x)}$ by substituting the values of $x_1, x_2, x_3, \ldots, x_{\kappa-1}$ in terms of the n's from (2), we have, by (8),

$$\left.\begin{aligned} \frac{\partial p_s^{(n)}}{\partial n_r} &= \frac{1}{\mathrm{N}}\left[\frac{\partial p_s^{(x)}}{\partial x_r} - \left(x_1\frac{\partial p_s^{(x)}}{\partial x_1} + x_2\frac{\partial p_s^{(x)}}{\partial x_2} + x_3\frac{\partial p_s^{(x)}}{\partial x_3} + \ldots\right.\right. \\ &\qquad\qquad \left.\left. + x_{\kappa-1}\frac{\partial p_s^{(x)}}{\partial x_{\kappa-1}}\right)\right] \\ &= \frac{1}{\mathrm{N}}\frac{\partial p_s^{(x)}}{\partial x_r} + \frac{\partial p_s^{(n)}}{\partial n_\kappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \end{aligned}\right\} \quad (9)$$

as also by (7).

By condition d, we have

$$p_s = 0 \text{ for } x = 0 \text{ or } n_s = 0 \quad (s = 1, 2, 3, \ldots, \kappa). \quad (10)$$

By condition *e*,

$$\frac{\partial p_s^{(n)}}{\partial n_r} \text{ is finite for all values of the } n\text{'s} \quad (r, s = 1, 2, 3, \ldots, \kappa) \quad (11)$$

and
$$\frac{\partial p_s^{(n)}}{\partial n_s} \text{ is not 0 for } n_s = 0. \quad . \quad . \quad . \quad . \quad (12)$$

From condition *d* or (10) and (9) follows

$$\left.\begin{aligned} &\frac{\partial p_s^{(n)}}{\partial n_r} = 0 \text{ for } n_s = 0 \quad (r, s = 1, 2, 3, \ldots, \kappa \text{ and } r \lesseqgtr s), \\ &\frac{\partial p_s^{(x)}}{\partial x_r} = 0 \text{ for } x_s = 0 \quad (r, s = 1, 2, 3, \ldots, \kappa - 1 \text{ and } r \lesseqgtr s), \\ &\frac{\partial p_\kappa^{(x)}}{\partial x_r} = -\mathrm{N}\frac{\partial p_\kappa^{(n)}}{\partial n_\kappa} \text{ for } x_\kappa = 0 \quad (r = 1, 2, 3, \ldots, \kappa - 1)\,; \end{aligned}\right\} \quad (13)$$

so that

$$\frac{\partial p_\kappa^{(x)}}{\partial x_r} \text{ is neither 0 nor infinite for } x_\kappa = 0 \quad (r = 1, 2, 3, \ldots, \kappa - 1).$$

From (9) follows

$$\frac{\partial p_s^{(n)}}{\partial n_s} = \frac{1 - x_s}{\mathrm{N}}\frac{\partial p_s^{(x)}}{\partial x_s} = \frac{1}{\mathrm{N}}\frac{\partial p_s^{(x)}}{\partial x_s} \text{ for } x_s = 0 \quad (s = 1, 2, 3, \ldots, \kappa - 1), \quad (14)$$

so that, by (11),

$$\frac{\partial p_s^{(x)}}{\partial x_s} \text{ is finite and not 0 for } x_s = 0 \quad (s = 1, 2, 3, \ldots, \kappa - 1). \quad . \quad (15)$$

From (7) and (11) follows that

$$\frac{\partial p_s^{(x)}}{\partial x_r} \text{ is finite for all values of the } x\text{'s} \quad \left.\begin{matrix} (r = 1, 2, 3, \ldots, \kappa - 1\,; \\ s = 1, 2, 3, \ldots, \kappa). \end{matrix}\right\} (16)$$

By condition *f*, we have

$$p_s = \mathrm{P}_s \text{ for } x_s = 1 \quad (s = 1, 2, 3, \ldots, \kappa), \quad . \quad (17)$$

where P_s, for each value of s, is a perfectly definite constant for the temperature in question.

3. For any liquid mixture that satisfies conditions a–g of paragraph 1, we have the generalized Duhem-Margules equation

$$n_1 d \ln p_1 + n_2 d \ln p_2 + n_3 d \ln p_3 + \ldots + n_\kappa d \ln p_\kappa = 0, \quad (18)$$

where "ln" denotes "natural logarithm," that is logarithm to the base $e = 2{\cdot}718\ldots$, and the differentials refer to any infinitesimal changes in the molar proportions of the components and the corresponding infinitesimal changes in their partial pressures, at the given temperature. This equation was originally given * only for a binary mixture, but the method of proof is applicable to any number of components. This equation may or may not hold for other mixtures, but we regard it as *proved* only for mixtures that satisfy conditions a–g.

On account of (2), equation (18) may be written

$$x_1 d \ln p_1 + x_2 d \ln p_2 + x_3 d \ln p_3 + \ldots + x_\kappa d \ln p_\kappa = 0, \quad (19)$$

or, by (3),

$$x_1 d \ln \frac{p_1}{p_\kappa} + x_2 d \ln \frac{p_2}{p_\kappa} + x_3 d \ln \frac{p_3}{p_\kappa} + \ldots + x_{\kappa-1} d \ln \frac{p_{\kappa-1}}{p_\kappa} + d \ln p_\kappa = 0, \quad (20)$$

which is a convenient form to use when $x_1, x_2, x_3, \ldots, x_{\kappa-1}$ are taken for the independent variables. This equation, being a homogeneous linear differential equation in the κ functions $p_1, p_2, p_3, \ldots, p_\kappa$ of $\kappa - 1$ independent variables, is equivalent to a system of $\kappa - 1$ homogeneous linear partial differential equations in these functions and therefore suffices, with the conditions (10) and (17), to determine all the κ functions when one of them is known. But we shall find it more convenient to derive them all from another function to be determined by experiment.

Because $p_s = 0$ for $x_s = 0$, by (10), there exists a definite positive power of x_s, say $x_s^{\epsilon_s}$,—where ϵ_s is a positive integer or fraction,—such that $p_s : x_s^{\epsilon_s}$ is neither 0 nor infinite for $x_s = 0$; so that, by conditions c and d, this ratio is neither 0

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* Duhem, *Ann. de l'Ecole normale sup.* (3) vol. iv. p. 9 (1887); "Dissolutions et Mésures, 3 mém., Les mélanges doubles," *Trav. et Mém. de la Faculté de Lille*, iii. D (1894): *Traité élémentaire de mécanique chimique*, vol. iv. book 8, chap. 7 (1899).

Margules, *Sitzungsber. der Wiener Akad.* vol. civ. p. 1243 (1895).

See also Ostwald, *Allgemeine Chemie* (2 Aufl.), p. 636 ff., and Nernst, *Theoretische Chemie* (2 Aufl.), p. 118.

A simple deduction of the equation by Luther is given in Ostwald's work, p. 639.

nor infinite for any values of the x's. Regarding the p's as functions of all the x's, put

$$\ln\left(\frac{p_s}{x_s^{\epsilon_s}}\right) = u_s \quad (s = 1, 2, 3, \ldots, \kappa)\,; \quad . \quad . \quad (21)$$

then u_s is, by condition c, a continuous singly-valued function of the x's, finite for all values of the x's. From (21) follows *

$$p_s = x_s^{\epsilon_s}\, e^{u_s} \quad (s = 1, 2, 3, \ldots, \kappa), \; . \quad . \quad . \quad (22)$$

where, by (17),

$$u_s = \ln \mathrm{P}_s \text{ for } x_s = 1 \quad (s = 1, 2, 3, \ldots, \kappa). \; . \quad (23)$$

Now let x_κ, the p's, and the u's be expressed in terms of $x_1, x_2, x_3, \ldots, x_{\kappa-1}$. Then, for

$$x_s = 0 \; (s = 1, 2, 3, \ldots, \kappa - 1),$$

we have, by definition of the derivative, (22), and (15), that

$$\frac{dp_s}{dx_s} = \frac{p_s}{x_s} = x_s^{\epsilon_s - 1} e^{u_s} \text{ is neither 0 nor infinite :} \qquad (24)$$

therefore, because u_s is finite, by (21),

$$\epsilon_s = 1 \quad (s = 1, 2, 3, \ldots, \kappa - 1) \quad . \quad . \quad . \quad (25)$$

Also, for $x_\kappa = 0$, that is

$$x_1 + x_2 + x_3 + \ldots + x_{\kappa-1} = 1 \text{ and } n_\kappa = 0,$$

we have, by definition of the derivative, (13), (2), (22), (11), and (12),

$$-\frac{dp_\kappa}{dx_r} = \mathrm{N}\frac{dp_\kappa^{(n)}}{dn_\kappa} = \mathrm{N}\frac{p_\kappa}{n_\kappa} = \frac{p_\kappa}{x_\kappa} = x_\kappa^{\epsilon_\kappa - 1} e^{u_\kappa} \text{ is neither 0 nor infinite ;} (26)$$

therefore, because u_κ is finite . . . ., by (21),

$$\epsilon_\kappa = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

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* This is substantially Margules' formula, $p_1 = \mathrm{P}_1 x^{\alpha_0} e^u$, where $u = 0$ for $x = 1$ (see *loc. cit.*). There seems to be an idea in the minds of some that this formula involves an assumption; but, clearly, (21) simply defines the use of the symbol u_s. The only assumption that Margules makes in the formula as he gives it is that u can be developed according to positive integral powers of $1 - x$.

By virtue of (25) and (27), (22) becomes

$$p_s = x_s e^{u_s} \quad (s = 1, 2, 3, \ldots, \kappa), \quad . \quad . \quad (28)$$

where, of course, (23) still holds. From (28) follows

$$dp_s = (dx_s + x_s du_s) e^{u_s} \quad (s = 1, 2, 3, \ldots, \kappa) \quad . \quad (29)$$

and, therefore

$$x_s d \ln p_s = dx_s + x_s du_s \quad (s = 1, 2, 3, \ldots, \kappa),$$

so that (19) becomes, when we take account of (4),

$$x_1 du_1 + x_2 du_2 + x_3 du_3 + \ldots + x_\kappa du_\kappa = 0, \quad . \quad (30)$$

or, by (3),

$$x_1 d(u_1 - u_\kappa) + x_2 d(u_2 - u_\kappa) + x_3 d(u_3 - u_\kappa) + \ldots + x_{\kappa-1} d(u_{\kappa-1} - u_\kappa) + du_\kappa = 0, \quad . \quad . \quad . \quad (31)$$

if we express everything in terms of $x_1, x_2, x_3, \ldots, x_{\kappa-1}$.

On changing the signs of all terms of (31), distributing $-du_\kappa$ equally among the other terms, and adding

$$\frac{1}{\kappa-1}(du_1 + du_2 + du_3 + \ldots + du_{\kappa-1})$$

to both members of the equation, we obtain

$$\left.\begin{array}{l} \left(\frac{1}{\kappa-1} - x_1\right) d(u_1 - u_\kappa) + \left(\frac{1}{\kappa-1} - x_2\right) d(u_2 - u_\kappa) + \left(\frac{1}{\kappa-1} - x_3\right) d(u_3 - u_\kappa) \\ \quad + \ldots + \left(\frac{1}{\kappa-1} - x_{\kappa-1}\right) d(u_{\kappa-1} - u_\kappa) = \frac{1}{\kappa-1} d(u_1 + u_2 + u_3 + \ldots + u_{\kappa-1}). \end{array}\right\} (32)$$

Putting

$$x_s = \frac{1}{\kappa-1} - z_s \quad \text{or} \quad z_s = \frac{1}{\kappa-1} - x_s \quad (s = 1, 2, 3, \ldots, \kappa-1). \quad (33)$$

and

$$\frac{1}{\kappa-1}(u_1 + u_2 + u_3 + \ldots + u_{\kappa-1}) = \omega, \quad . \quad . \quad (34)$$

taking $z_1, z_2, z_3, \ldots, z_{\kappa-1}$ for new independent variables, in terms of which the x's, u's, p's, and the new function ω are to be expressed, we have*, from (32),

$$z_1 d(u_1 - u_\kappa) + z_2 d(u_2 - u_\kappa) + z_3 d(u_3 - u_\kappa) + \dots + z_{\kappa-1} d(u_{\kappa-1} - u_\kappa) = d\omega. \quad (35)$$

As $x_s (s = 1, 2, 3, \dots, \kappa - 1)$ may have any value from 0 to 1, z_s may have any value from $-\frac{\kappa-2}{\kappa-1}$ to $+\frac{1}{\kappa-1}$, so that the *absolute* value of z_s is always less than 1, which is decidedly advantageous when we have to do with infinite series in the variables. Namely, the smaller the absolute values of the variables the more readily is the convergency of such a series determined and the fewer terms will it probably be necessary to use in calculating its value to any given degree of accuracy. Further on we have given a special method for treating a binary mixture, which is practically equivalent to that mentioned in the last footnote; by means of which we have calculated the formulæ (26) from actual observations of several binary mixtures. We have also calculated these same formulæ in terms of the x's, and the special method not only has the advantage of using variables with smaller absolute values, but gives series for the u's with more rapidly diminishing coefficients than the former. It does not, however, seem possible to predict that the series for the u's will always be more convergent, or have more rapidly diminishing coefficients, the smaller the absolute values of the variables involved.

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* The method we are going to apply to (35) to determine $u_1, u_2, u_3, \dots, u_\kappa$ from ω as functions of the z's may be applied to (31) to determine $u_1, u_2, u_3, \dots, u_{\kappa-1}$ from u_κ as functions of the x's. Also, if, after changing the signs of all terms of (31), we had distributed only $\kappa - 1$ κ-ths of $-du_\kappa$ among the other terms, had added $\frac{1}{\kappa}(du_1 + du_2 + du_3 + \dots + du_\kappa)$ to both members, and had put

$$x_s = \frac{1}{\kappa} - z_s (s = 1, 2, 3, \dots, \kappa - 1) \quad \text{and} \quad \frac{1}{\kappa}(u_1 + u_2 + u_3 + \dots + u_\kappa) = \omega,$$

we should have had the same equation (35) with the new variables z and the new function ω. The determination of $u_1, u_2, u_3, \dots, u_\kappa$ and this function ω in terms of the new z's will follow the same lines as in the text. For a binary mixture ($\kappa = 2$) this method is preferable to that given above, because here the absolute value of any z never exceeds $\frac{1}{2}$, while above it may amount to 1 (for the corresponding $x = 0$). But for values of $\kappa \geqq 3$, the method of the text gives the smaller maximum absolute value of any z, namely $\frac{\kappa-2}{\kappa-1}$ instead of $\frac{\kappa-1}{\kappa}$ (for the corresponding $x = 1$).

4. For $x_r = 0$ $(r = 1, 2, 3, \ldots, \kappa-1)$ we have, by (29) and (24),

$$\frac{\partial p_r}{\partial x_r} = \left(1 + x_r \frac{\partial u_r}{\partial x_r}\right) e^{u_r} = e^{u_r},$$

$$\frac{\partial p_r}{\partial x_k} = x_r \frac{\partial u_r}{\partial x_k} e^{u_r} = 0 \quad (k = 1, 2, 3, \ldots, \kappa-1 \text{ and } k \lesseqgtr r),$$

so that, by (16),

$$x_r \frac{\partial u_r}{\partial x_k} = 0 \quad (k = 1, 2, 3, \ldots, \kappa-1),$$

and, therefore,

$$x_r du_r = 0 \, ; \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

also, for $x_\kappa = 0$ we have, by (29), (4), and (26),

$$\frac{\partial p_\kappa}{\partial x_k} = \left(-1 + x_\kappa \frac{\partial u_\kappa}{\partial x_k}\right) e^{u_\kappa} = -e^{u_\kappa} \quad (k = 1, 2, 3, \ldots, \kappa-1),$$

so that, by (16),

$$x_\kappa \frac{\partial u_\kappa}{\partial x_k} = 0 \quad (k = 1, 2, 3, \ldots, \kappa-1)$$

and, therefore,

$$x_\kappa du_\kappa = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

It is not self-evident that $x_r du_r = 0$ for $x_r = 0$, because one or more of the derivatives of u_r might be infinite, but (36) and (37) here proved show that even if $\frac{\partial u_r}{\partial x_k}$ is infinite for $x_r = 0$, it is infinite of so low an order that its product by x_r is 0.

If, now, $x_s = 1$ $(s = 1, 2, 3, \ldots, \kappa)$ all the other x's are 0, by (3), and, therefore, by (36) and (37), equation (30) reduces to

$$du_s = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Therefore, by (27) and (23),

$$dp_s = \mathrm{P}_s \, dx_s \text{ for } x_s = 1 \quad (s = 1, 2, 3, \ldots, \kappa), \tag{39}$$

that is, by (4),

$$\left.\begin{array}{l} \left.\begin{array}{l} \dfrac{\partial p_s}{\partial x_s} = \mathrm{P}_s \\ \dfrac{\partial p_s}{\partial x_r} = 0 \end{array}\right\} \text{ for } x_s = 1 \quad (r, s = 1, 2, 3, \ldots, \kappa-1 \text{ and } r \gtrless s), \\ \dfrac{\partial p_\kappa}{\partial x_r} = -\,\mathrm{P}_\kappa \text{ for } x_\kappa = 1 \quad (r = 1, 2, 3, \ldots, \kappa-1). \end{array}\right\} \tag{40}$$

Equations (40) express Raoult's law, which is thus seen to hold for a mixture of any number of components and to be independent of any assumptions excepting those made in conditions *a–g* *.

5. Going back to equation (35), we assume that the functions u can be developed according to positive integral powers of the z's ; this is equivalent, by (33), to the assumption that the u's can be developed according to positive integral powers of the x's. Then, by (34), ω can be similarly developed. Any term of such a development is of the form

$$z_1^{g_1} \; z_2^{g_2} \; z_3^{g_3}, \ldots z_{\kappa-1}^{g_{\kappa-1}}$$

multiplied by a constant coefficient, where each of the exponents $g_1, g_2, g_3, \ldots, g_{\kappa-1}$ is any positive integer or 0. Let the coefficient of the product of powers of the z's just written in u_r be denoted by $a^{(r)}_{g_1, g_2, g_3, \ldots, g_{\kappa-1}}$ and the coefficient

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* Gahl (*Zeitschr. für physikalische Chemie*, vol. xxxiii. pp. 192–195) has considered what might happen if the last part of our condition *e* were not satisfied,—but his cases are purely hypothetical. Considering only a binary mixture, he assumes that the partial pressure p of one component is proportional to a power of the corresponding molar fraction x whose exponent is an integer as great as 2,—whereas it is not certain even that this pressure can be developed according to integral powers of x. He says that it often happens that $\frac{\partial p}{\partial x} = 0$ for $x = 0$, but cites no specific case. It may be well doubted whether a mixture can have any component for which this condition is satisfied unless $p = 0$ for every value of x, in which case the component has no pressure of its own and the Duhem-Margules equation is not proved for any mixture that contains it.

of the same product of powers of the z's in ω be denoted by $c_{g_1, g_2, g_3, \dots, g_{\kappa-1}}$. Then

$$u_r = \Sigma_g\, a^{(r)}_{g_1, g_2, g_3, \dots, g_{\kappa-1}} z_1^{g_1} z_2^{g_2} z_3^{g_3} \dots z_{\kappa-1}^{g_{\kappa-1}}, \tag{41}$$

and

$$\omega = \Sigma_g\, c_{g_1, g_2, g_3, \dots, g_{\kappa-1}} z_1^{g_1} z_2^{g_2} z_3^{g_3} \dots z_{\kappa-1}^{g_{\kappa-1}}, \tag{42}$$

where Σ_g denotes the sum of the terms following it for all possible combinations of all possible numbers $g_1, g_2, g_3, \dots, g_{\kappa-1}$ of which each is a positive integer or 0. For the sake of brevity, we shall write $a^{(r)}_{\dots\dots}$ instead of $a^{(r)}_{g_1, g_2, g_3, \dots, g_{\kappa-1}}$, and $c_{\dots\dots}$ instead of $c_{g_1, g_2, g_3, \dots, g_{\kappa-1}}$. Any coefficient with a g written among the suffixed dots with $+1$ or -1 attached shall denote the result of increasing or diminishing that particular suffix by 1, without altering the other suffixes. Thus, $a^{(r)}_{\dots g_k-1\dots}$ denotes the coefficient of u_r that is derived from $a^{(r)}_{g_1, g_2, g_3, \dots, g_{\kappa-1}}$ by writing g_k-1 instead of g_k for the k-th suffix, and $c_{\dots g_k+1\dots}$ denotes the coefficient of ω that is derived from $c_{g_1, g_2, g_3, \dots, g_{\kappa-1}}$ by writing g_k+1 instead of g_k for the k-th suffix.

Equation (35) is equivalent to the set of $\kappa-1$ homogeneous linear partial differential equations

$$\left.\begin{array}{c} z_1 \dfrac{\partial(u_1-u_\kappa)}{\partial z_r} + z_2 \dfrac{\partial(u_2-u_\kappa)}{\partial z_r} + \dots + z_{\kappa-1} \dfrac{\partial(u_{\kappa-1}-u_\kappa)}{\partial z_r} = \dfrac{\partial \omega}{\partial z_r} \\ (r = 1, 2, 3, \dots, \kappa-1). \end{array}\right\} \tag{43}$$

Substituting the expressions (41) and (42) for the u's and ω and equating the coefficients of like products of powers of the z's in the two members of each of the equations (43), we have, for *each* set of values of $g_1, g_2, g_3, \dots, g_{\kappa-1}$,

$$\left.\begin{array}{c} \sum\limits_{k=1}^{k=\kappa-1} g_r\left(a^{(k)}_{\dots g_k-1\dots} - a^{(\kappa)}_{\dots g_k-1\dots}\right) = g_r\, c_{\dots\dots} \\ (r = 1, 2, 3, \dots, \kappa-1), \end{array}\right\}. \tag{44}$$

where $\sum\limits_{k=1}^{k=\kappa-1}$ denotes the sum of the terms following it for all values of k from 1 to $\kappa-1$. Namely, the term actually written in the left member of (44) is the coefficient of

$$z_1^{g_1} z_2^{g_2} z_3^{g_3} \ldots z_r^{g_r - 1} \ldots z_{\kappa-1}^{g_{\kappa-1}}$$

in the k-th term of the left number of the r-th equation (43) and the right member of (44) is the coefficient of the same product of powers of the z's in the right member of the r-th equation (43). But it is to be observed that the numerical multiplier of the r-th term of the r-th equation (44) (the term for which $k = r$) is $g_r - 1$ and not g_r, and that the k-th term of the left member of the r-th equation (44) is to be omitted if the k-th g of the set in question (that is g_k) is 0. The r-th equation (44) falls out if $g_r = 0$ for the set in question.

The left members of equations (43) have no constant terms and, therefore, the derivatives of ω with respect to $z_1, z_2, z_3, \ldots, z_{\kappa-1}$ have no constant terms; that is

$$c_{1(k)} = 0 \quad (k = 1, 2, 3, \ldots, \kappa - 1) \;.\;\;.\;\;. \quad (45)$$

where $c_{1(k)}$ denotes the coefficient of z_k in ω (the c whose suffixes are all 0 except the k-th and that is 1). Furthermore, if $a_0^{(r)}$ and c_0 are used for brevity to denote the constant terms of u_r and ω, respectively, we have, by (34),

$$a_0^{(1)} + a_0^{(2)} + a_0^{(3)} + \ldots a_0^{(\kappa-1)} = (\kappa - 1) c_0. \;\;.\;\;.\;\; \quad (46)$$

If we write, for any *given* set of values of $g_1, g_2, g_3, \ldots, g_{\kappa-1}$,

$$g_1 + g_2 + g_3 + \ldots + g_{\kappa-1} = \mathrm{G} \quad .\;\;.\;\;. \quad (47)$$

and add the system of r equations (44) for this set, remembering what we said about the numerical coefficient of the term of each equation that corresponds to the number of that equation in the system, we find

$$(\mathrm{G} - 1) \sum_{k=1}^{k=\kappa-1} \left(a^{(k)}_{\,\cdot\cdot g_k - 1\cdot\cdot} - a^{(\kappa)}_{\,\cdot\cdot g_k - 1\cdot\cdot} \right) = \mathrm{G}\, c_{\cdot\cdot\cdot\cdot} \qquad (48)$$

On subtracting $\mathrm{G} - 1$ times the r-th equation (44) from g_r times equation (48) we have

$$(\mathrm{G} - 1)\left(a^{(r)}_{\,\cdot\cdot g_r - 1\cdot\cdot} - a^{(\kappa)}_{\,\cdot\cdot g_r - 1\cdot\cdot} \right) = g_r\, c_{\cdot\cdot\cdot\cdot\cdot}$$

or, writing $g_r + 1$ instead of g_r, preserving the notation (47),

$$\mathrm{G}\left(a^{(r)}_{\cdot\cdot\cdot\cdot\cdot} - a^{(\kappa)}_{\cdot\cdot\cdot\cdot\cdot} \right) = (g_r + 1)\, c_{\cdot\cdot g_r + 1\cdot\cdot} \quad (r = 1, 2, 3, \ldots, \kappa - 1) \;. \quad (49)$$

for any set of values of $g_1, g_2, g_3, \ldots, g_{\kappa-1}$ that are not all 0. Namely, it is evident that the constant terms of the u's will not occur in equations (43), being driven out by differentiation; they will be determined later. It may be remarked that the notation (47) enables us to write equations (45) thus:

$$c_{\cdot\cdot\cdot\cdot\cdot} = 0 \quad \text{if} \quad \mathrm{G} = 1. \quad . \quad . \quad . \quad . \qquad (50)$$

The $\kappa-1$ equations (49) may be written

$$a^{(r)}_{\cdot\cdot\cdot\cdot\cdot} - a^{(\kappa)}_{\cdot\cdot\cdot\cdot\cdot} = \frac{g_r+1}{\mathrm{G}} c_{\cdot\cdot g_r+1\cdot\cdot} \quad (r = 1, 2, 3, \ldots, \kappa-1 \text{ and } 1 \overset{=}{<} \mathrm{G}), \qquad (51)$$

whose sum, by (34), is

$$(\kappa-1)\, c_{\cdot\cdot\cdot\cdot\cdot} - (\kappa-1)\, a^{(\kappa)}_{\cdot\cdot\cdot\cdot\cdot} = \frac{1}{\mathrm{G}} \sum_{k=1}^{k=\kappa-1} (g_k+1)\, c_{\cdot\cdot g_k+1\cdot\cdot},$$

from which follows

$$a^{(\kappa)}_{\cdot\cdot\cdot\cdot\cdot} = c_{\cdot\cdot\cdot\cdot\cdot} - \frac{1}{(\kappa-1)\mathrm{G}} \sum_{k=1}^{k=\kappa-1} (g_k+1)\, c_{\cdot\cdot g_k+1\cdot\cdot} \qquad (52)$$

for any set of values of $g_1, g_2, g_3, \ldots, g_{\kappa-1}$ that are not all 0. Substituting $a^{(\kappa)}_{\cdot\cdot\cdot\cdot\cdot}$ from (52) in (51) we have

$$\left. \begin{array}{c} a^{(r)}_{\cdot\cdot\cdot\cdot\cdot} = c_{\cdot\cdot\cdot\cdot\cdot} - \dfrac{1}{(\kappa-1)\mathrm{G}} \displaystyle\sum_{k=1}^{k=\kappa-1} (g_k+1)\, c_{\cdot\cdot g_k+1\cdot\cdot} + \dfrac{g_r+1}{\mathrm{G}} c_{\cdot\cdot g_r+1\cdot\cdot} \\ (r = 1, 2, 3, \ldots, \kappa-1) \end{array} \right\} (53)$$

for any set of values of $g_1, g_2, g_3, \ldots, g_{\kappa-1}$ that are not all 0. It will be observed that the aggregate multiplier of $c_{\cdot\cdot g_r+1\cdot\cdot}$ in (53) is

$$-\frac{g_r+1}{(\kappa-1)\mathrm{G}} + \frac{g_r+1}{\mathrm{G}} = \frac{\kappa-2}{\kappa-1}\,\frac{g_r+1}{\mathrm{G}}. \quad . \quad . \quad (54)$$

The coefficients of the u's are all given in terms of the coefficients of ω by (52) and (53), excepting the constant terms.

We have, by (23), $u_r = \ln \mathrm{P}_r$ for $x_r = 1$, that is, by (33), for $z_r = -\dfrac{\kappa-2}{\kappa-1}$ and $z_s = \dfrac{1}{\kappa-1}$ $(r, s = 1, 2, 3, \ldots, \kappa-1$

and $s \leqq r$); but $u_\kappa = \ln P_\kappa$ for $x_\kappa = 1$, that is, by (3),

$$\text{for} \qquad x_1 = x_2 = x_3 = \ldots = x_{\kappa-1} = 0$$

$$\text{or for} \qquad z_r = \frac{1}{\kappa-1} (r = 1, 2, 3, \ldots, \kappa-1).$$

Substituting these values of the z's in (41), we have

$$\ln P_r = \Sigma_g (-1)^{g_r} \frac{(\kappa-2)^{g_r}}{(\kappa-1)^{G}} a^{(r)}_{\ldots\ldots} \qquad (r = 1, 2, 3, \ldots, \kappa-1)$$

and

$$\ln P_\kappa = \Sigma_g \frac{1}{(\kappa-1)^G} a^{(\kappa)}_{\ldots\ldots};$$

that is, if $\sum\limits_{1 \leqq G}$ denotes the same summation as Σ_g with the omission of the term for which $G=0$,

$$a_0^{(r)} = \ln P_r - \sum_{1 \leqq G} (-1)^{g_r} \frac{(\kappa-2)^{g_r}}{(\kappa-1)^G} a^{(r)}_{\ldots\ldots} \quad (r=1, 2, 3 \ldots, \kappa-1) \qquad (55)$$

and

$$a_0^{(\kappa)} = \ln P_\kappa - \sum_{1 \leqq G} \frac{1}{(\kappa-1)^G} a^{(\kappa)}_{\ldots\ldots} \ldots \ldots \ldots \qquad (56)$$

Substituting the expressions for $a^{(r)}_{\ldots\ldots} (1 \leqq G)$ from (53) in (55), using $\sum\limits_{2 \leqq G}$ to denote the same summation as Σ_g with the omission of the terms for which $G=0$ or 1, and taking account of (50), we find

$$a_0^{(r)} = \ln P_r + \sum_{2 \leqq G} (-1)^{g_r} \frac{(\kappa-2)^{g_r}}{(\kappa-1)^G} c_{\ldots\ldots} \left[-1 + \frac{G-g_r}{G-1} - \frac{g_r}{(\kappa-2)(G-1)} + \frac{(\kappa-1)\, g_r}{(\kappa-2)(G-1)} \right]$$

$$= \ln P_r + \sum_{2 \leqq G} (-1)^{g_r} \frac{(\kappa-2)^{g_r}}{(\kappa-1)^G (G-1)} c_{\ldots\ldots} \quad (r=1, 2, 3, \ldots, \kappa-1). \qquad (57)$$

Substituting the expressions for $a^{(\kappa)}_{\ldots\ldots} (1 \leqq G)$ from (52) in (56), taking account of (50), we find

$$a_0^{(\kappa)} = \ln P_\kappa + \sum_{2 \leqq G} \frac{1}{(\kappa-1)^G} c_{\ldots\ldots} \left[-1 + \frac{G}{G-1} \right]$$

$$= \ln P_\kappa + \sum_{2 \leqq G} \frac{1}{(\kappa-1)^G (G-1)} c_{\ldots\ldots} \ldots \ldots \qquad (58)$$

From (41) and (51) follows

$$\left.\begin{array}{l} u_r - u_\kappa = a_0^{(r)} - a_0^{(\kappa)} + \sum\limits_{1 \leqq \mathrm{G}} \dfrac{g_r+1}{\mathrm{G}}\, c_{\ldots g_r+1\ldots}\, z_1^{g_1} z_2^{g_2} z_3^{g_3} \ldots z_{\kappa-1}^{g_{\kappa-1}} \\ \qquad\qquad\qquad\qquad (r=1, 2, 3, \ldots, \kappa-1), \end{array}\right\} \quad (59)$$

where, by (57) and (58), the constant term of the right member is

$$a_0^{(r)} - a_0^{(\kappa)} = \ln \frac{\mathrm{P}_r}{\mathrm{P}_\kappa} + \sum_{2 \leqq \mathrm{G}} \frac{(-1)^{g_r} (\kappa-2)^{g_r} - 1}{(\kappa-1)^{\mathrm{G}} (\mathrm{G}-1)}\, c \ldots\ldots \quad (60)$$

Also, by (28) and (33),

$$u_r - u_\kappa = \ln \left(\frac{p_r x_\kappa}{p_\kappa x_r}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

Equations (59) and (61) serve to determine ω and ultimately u_r $(r=1, 2, 3, \ldots, \kappa-1)$ and the formulæ (28) for the partial pressures in mixtures of any given components from actual observations of mixtures of those components in different proportions. Such an observation is supposed to give the values of $x_1, x_2, x_3, \ldots, x_\kappa, p_1 : p_\kappa, p_2 : p_\kappa, p_3 : p_\kappa, \ldots, p_{\kappa-1} : p_\kappa$. From these values are determined $u_r - u_\kappa$ $(r=1, 2, 3, \ldots, \kappa-1)$ by (61) and z_k $(k=1, 2, 3, \ldots, \kappa-1)$ by (33). On substituting the value of $u_r - u_\kappa$ for any value of r and the values of the z's in (59) we obtain a linear equation in the coefficients $c_{,\ldots\ldots}$ for $2 \leqq \mathrm{G}$ and in the constant $a_0^{(r)} - a_0^{(\kappa)}$; each observation gives $\kappa-1$ such equations in the c's and in the $\kappa-1$ constants, corresponding to the $\kappa-1$ values of r. So far as we know, ω is an *infinite* series in the z's, but in practice we must suppose that it is convergent and that we shall get a sufficiently close approximation to it by taking a certain number of terms of it. As there will generally be no reason to assume that there is any difference in the order of magnitude of the different x's and, therefore, of the different z's, the terms of ω that are of one magnitude are those that are of one degree in the z's, that is those for which G, in the notation of (47), has one value. The natural mode of procedure will, then, be to take the aggregate of terms of ω whose degree does not exceed a certain number as a sufficiently close approximation to the whole expression. In other words, we agree to neglect every coefficient $c_{\cdots\cdots}$ the sum of whose suffixes exceeds a certain number. What the limit of the degree of terms considered shall be will depend on the accuracy and number of the observations. The number of observations must be at least sufficient to furnish as many equations (59) ($\kappa-1$ for each observation) as there are coefficients of ω to be determined plus $\kappa-1$ (for the $\kappa-1$ constants $a_0^{(r)}-a_0^{(\kappa)}$). It is preferable, however, to use a much larger number of observations and to solve the equations (59) by the method of least squares. The larger the number of observations the more accurate the values of the coefficients calculated from them may be expected to be. In fact, by increasing the number of observations, formulæ can be obtained from which the partial pressures for given molar proportions of the components can be calculated much more accurately than they can be observed. But, to effect this increase of accuracy, it will be necessary to carry out the numerical computations to several places more than are given by the observations.

When the c's for $2\leqq G$ have been determined from (59), the a's for $1\leqq G$ can be calculated from (52) and (53), with due regard to (50), and then, by (28) and (41), $a_0^{(r)}$ $(r=1, 2, 3, \ldots, \kappa)$ can be found from any one observation as

$$a_0^{(r)}=\ln\left(\frac{p_r}{x_r}\right)-\sum_{1\leqq G} \overset{(r)}{a}_{\cdots\cdots}\, z_1^{g_1} z_2^{g_2} z_3^{g_3} \ldots z_{\kappa-1}^{g_{\kappa-1}} (r=1, 2, 3, \ldots, \kappa). \quad (62)$$

Finally, P_r $(r=1, 2, 3, \ldots, \kappa-1)$ and P_κ are found from (57) and (58).

After the values of the a's have been calculated, the partial pressures for any composition of the mixture can be easily found from (62) without going back to (28).

The constant term of ω plays no part in the determination, but, if wanted, its value, by (46) and (57), is

$$c_0=\frac{1}{\kappa-1}\ln(P_1 P_2 P_3 \ldots P_{\kappa-1})$$

$$+\sum_{2\leqq G}\frac{c_{\cdots\cdots}}{(\kappa-1)^{G+1}(G-1)}\sum_{k=1}^{k=\kappa-1}(-1)^{g_k}(\kappa-2)^{g_k}. \quad (63)$$

Special Method for Binary Mixtures.

6. For a binary mixture, the alternative method given in the footnote to (35) is preferable to the general method developed above, but we give still another method for this

case. So far as they correspond, we designate the formulæ by the same numbers as in the general method, with an accent attached.

By (28) and (23) we have

$$p_1 = x_1\, e^{u_1},\quad p_2 = x_2\, e^{u_2}, \quad . \quad . \quad . \quad (28')$$

where

$$u_1 = \ln \mathrm{P}_1 \text{ for } x_1 = 1,\; u_2 = \ln \mathrm{P}_2 \text{ for } x_2 = 1. \quad . \quad (23')$$

Put

$$x_1 = \frac{1}{2} + z,\quad x_2 = \frac{1}{2} - z \quad . \quad . \quad . \quad (33')$$

and

$$u_1 - u_2 = \omega \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34')$$

Then

$$\left(\frac{1}{2} + z\right) du_1 + \left(\frac{1}{2} - z\right) du_2 = 0, \quad . \quad . \quad . \quad (30')$$

so that

$$du_1 = \left(\frac{1}{2} - z\right) d\omega,\; du_2 = -\left(\frac{1}{2} + z\right) d\omega \quad . \quad . \quad (64)$$

Put

$$u_1 = \sum\nolimits_g a_g^{(1)} z^g,\; u_2 = \sum\nolimits_g a_g^{(2)} z^g, \quad . \quad . \quad . \quad (41')$$

$$\omega = \sum\nolimits_g c_g z^g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42')$$

Then, by (64),

$$\sum_{1\leqq g} g\, a_g^{(1)} z^{g-1} = \frac{1}{2} \sum_{1\leqq g} g\, c_g z^{g-1} - \sum_{1\leqq g} g\, c_g\, z^g,$$

$$\sum_{1\leqq g} g\, a_g^{(2)} z^{g-1} = -\frac{1}{2} \sum_{1\leqq g} g\, c_g z^{g-1} - \sum_{1\leqq g} g\, c_g z^g,$$

so that

$$\left.\begin{aligned} a_g^{(1)} &= \frac{1}{2} c_g - \frac{g-1}{g} c_{g-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (53') \\ a_g^{(2)} &= -\frac{1}{2} c_g - \frac{g-1}{g} c_{g-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (52') \end{aligned}\right\} (1 \leqq g),$$

and, in particular,

$$a_1^{(1)} = \frac{1}{2} c_1, \quad a_1^{(2)} = -\frac{1}{2} c_1.$$

Also, by (23′) and (41′), because $z = \frac{1}{2}$ corresponds to $x_1 = 1$

and $z=-\frac{1}{2}$ to $x_2=1$, by (33′),

$$a_0^{(1)}=\ln \mathrm{P}_1-\sum_{1\leqq g} a_g^{(1)}\frac{1}{2^g}=\ln \mathrm{P}_1-\sum_{1\leqq g}\frac{c_g}{2^{g+1}}+\sum_{1\leqq g}\frac{gc_g}{(g+1)2^{g+1}}$$

$$=\ln \mathrm{P}_1-\sum_{1\leqq g}\frac{c_g}{2^{g+1}\,(g+1)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (57')$$

$$a_0^{(2)}=\ln \mathrm{P}_2-\sum_{1\leqq g}(-1)^g\,a_g^{(2)}\frac{1}{2^g}=\ln \mathrm{P}_2+\sum_{1\leqq g}(-1)^g\frac{c^g}{2^{g+1}}-\sum_{1\leqq g}(-1)^g\frac{gc_g}{(g+1)2^{g+1}}$$

$$=\ln \mathrm{P}_2+\sum_{1\leqq g}(-1)^g\frac{c_g}{2^{g+1}\,(g+1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58')$$

Now, by (42′), (34′), and (28′),

$$\Sigma_g c_g z^g=\ln\left(\frac{p_1\,x_2}{p_2\,x_1}\right) \quad . \quad . \quad . \quad . \quad . \quad (61')$$

by which any desired number of the coefficients c_g can be calculated from a sufficient number of sets of corresponding values of x_1, x_2, z, p_1, and p_2. From these values of the c's the values of $a_g^{(1)}$ and $a_g^{(2)}$ for g as great as 1, and not greater than the greatest suffix of any c by more than 1, can be calculated by (53′) and (52′). Then, from any *one* set of corresponding values of z, p_1, and p_2, we have, by (28′) and (41′),

$$a_0^{(1)}=\ln\frac{p_1}{x_1}-\sum_{1\leqq g} a_g^{(1)}z^g, \quad a_0^{(2)}=\ln\frac{p_2}{x_2}-\sum_{1\leqq g} a_g^{(2)}z^g, \quad . \quad (62')$$

where, by (53′), (52′), and (61′),

$$\sum_{1\leqq g} a_g^{(1)}z^g=\frac{1}{2}\sum_{1\leqq g} c_g z^g-\sum_{1\leqq g}\frac{g}{g+1}c_g\,z^{g+1}=\left(\frac{1}{2}-z\right)\sum_{1\leqq g} c_g\,z^g+z\sum_{1\leqq g}\frac{c_g}{g+1}z^g$$

$$=x_2\left[\ln\left(\frac{p_1\,x_2}{p_2\,x_1}\right)-c_0\right]+z\sum_{1\leqq g}\frac{c_g}{g+1}z^g,$$

$$\sum_{1\leqq g} a_g^{(2)}z^g=-\frac{1}{2}\sum_{1\leqq g} c_g\,z^g-\sum_{1\leqq g}\frac{g}{g+1}c_g\,z^{g+1}=-\left(\frac{1}{2}+z\right)\sum_{1\leqq g} c_g z^g+z\sum_{1\leqq g}\frac{c_g}{g+1}z^g$$

$$=-x_1\left[\ln\left(\frac{p_1\,x_2}{p_2\,x_1}\right)-c_0\right]+z\sum_{1\leqq g}\frac{c_g}{g+1}z^g\,;$$

so that

$$\left.\begin{aligned} a_0^{(1)} &= x_1 \ln\left(\frac{p_1}{x_1}\right) + x_2\left[\ln\left(\frac{p_2}{x_2}\right) + c_0\right] - z \sum_{1 \leqq g} \frac{c_g}{g+1} z^g, \\ a_0^{(2)} &= x_1\left[\ln\left(\frac{p_1}{x_1}\right) - c_0\right] + x_2 \ln\left(\frac{p_2}{x_2}\right) - z \sum_{1 \leqq g} \frac{c_g}{g+1} z^g, \end{aligned}\right\} \quad . \quad (65)$$

from which follows, by (33′) and (34′),

$$a_0^{(1)} + a_0^{(2)} = 2\left[x_1 \ln\left(\frac{p_1}{x_1}\right) + x_2 \ln\left(\frac{p_2}{x_2}\right)\right] - 2z\Sigma_g \frac{c_g}{g+1} z^g, \quad . \quad . \quad . \quad (66)$$

$$a_0^{(1)} - a_0^{(2)} = c_0 . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

Then $a_0^{(1)}$ and $a_0^{(2)}$ are determined from a single observation by (65), or by (66) and (67). Finally, P_1 and P_2 are determined by (57′) and (58′).

Ternary Mixtures.

7. For the sake of showing how the general method works out in practice, we give the formulæ and equations for the case of a ternary mixture ($\kappa = 3$), neglecting terms of ω that are of higher than the fourth degree in the z's. This implies, by (52) and (53), that terms of u_1, u_2, u_3 that are of higher degree than the fourth in the z's are also to be neglected. The formulæ shall be numbered as in the general method, with two accents attached to each number to distinguish this particular case.

$$p_1 = x_1 e^{u_1}, \quad p_2 = x_2 e^{u_2}, \quad p_3 = x_3 e^{u_3}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28'')$$

$$u_1 = \ln P_1 \text{ for } x_1 = 1, \quad u_2 = \ln P_2 \text{ for } x_2 = 1, \quad u_3 = \ln P_3 \text{ for } x_3 = 1; \; (23'')$$

$$x_1 = \frac{1}{2} - z_1, \quad x_2 = \frac{1}{2} - z_2, \quad x_3 = z_1 + z_2; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33'')$$

$$\frac{1}{2}(u_1 + u_2) = \omega; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34'')$$

$$\left.\begin{aligned} u_1 = {} & a_0^{(1)} + a_{10}^{(1)} z_1 + a_{01}^{(1)} z_2 + a_{20}^{(1)} z_1^2 + a_{11}^{(1)} z_1 z_2 + a_{02}^{(1)} z_2^2 + a_{30}^{(1)} z_1^3 + a_{21}^{(1)} z_1^2 z_2 \\ & + a_{12}^{(1)} z_1 z_2^2 + a_{03}^{(1)} z_2^3 + a_{40}^{(1)} z_1^4 + a_{31}^{(1)} z_1^3 z_2 + a_{22}^{(1)} z^2 z_2^2 + a_{13}^{(1)} z_1 z_2^3 + a_{04}^{(1)} z_2^4, \\ u_2 = {} & a_0^{(2)} + a_{10}^{(2)} z_1 + a_{01}^{(2)} z_2 + a_{20}^{(2)} z_1^2 + a_{11}^{(2)} z_1 z_2 + a_{02}^{(2)} z_2^2 + a_{30}^{(2)} z_1^3 + a_{21}^{(2)} z_1^2 z_2 \\ & + a_{12}^{(2)} z_1 z_2^2 + a_{03}^{(2)} z_2^3 + a_{40}^{(2)} z_1^4 + a_{31}^{(2)} z_1^3 z_2 + a_{22}^{(2)} z_1^2 z_2^2 + a_{13}^{(2)} z_1 z_2^3 + a_{04}^{(2)} z_2^4, \\ u_3 = {} & a_0^{(3)} + a_{10}^{(3)} z_1 + a_{01}^{(3)} z_2 + a_{20}^{(3)} z_1^2 + a_{11}^{(3)} z_1 z_2 + a_{02}^{(3)} z_2^2 + a_{30}^{(3)} z_1^3 + a_{21}^{(3)} z_1^2 z_2 \\ & + a_{12}^{(3)} z_1 z_2^2 + a_{03}^{(3)} z_2^3 + a_{40}^{(3)} z_1^4 + a_{31}^{(3)} z_1^3 z_2 + a_{22}^{(3)} z_1^2 z_2^2 + a_{13}^{(3)} z_1 z_2^3 + a_{04}^{(3)} z_2^4; \end{aligned}\right\} (41'')$$

$$\left.\begin{array}{l}\omega=c_0+c_{10}z_1+c_{01}z_2+c_{20}z_1^2+c_{11}z_1z_2+c_{02}z_2^2+c_{30}z_1^3+c_{21}z_1^2z_2\\ \quad+c_{12}z_1z_2^2+c_{03}z_2^3+c_{40}z_1^4+c_{31}z_1^3z_2+c_{22}z_1^2z_2^2+c_{13}z_1z_2^3+c_{04}z_2^4\,;\end{array}\right\}(42'')$$

$$c_{10}=c_{01}=0\,;\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(45''),\ (50'')$$

$$g_1+g_2=\mathrm{G}\,;\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(47'')$$

$$\left.\begin{array}{lllll}
a_{10}^{(1)}=c_{20}-\frac{1}{2}c_{11}, & & a_{01}^{(1)}=\frac{1}{2}c_{11}-c_{02}, & & a_{20}^{(1)}=c_{20}+\frac{3}{4}c_{30}-\frac{1}{4}c_{21},\\
a_{11}^{(1)}=c_{11}+\frac{1}{2}c_{21}-\frac{1}{2}c_{12}, & & a_{02}^{(1)}=c_{02}+\frac{1}{4}c_{12}-\frac{3}{4}c_{03}, & & a_{30}^{(1)}=c_{30}+\frac{2}{3}c_{40}-\frac{1}{6}c_{31},\\
a_{21}^{(1)}=c_{21}+\frac{1}{2}c_{31}-\frac{1}{3}c_{22}, & & a_{12}^{(1)}=c_{12}+\frac{1}{3}c_{22}-\frac{1}{2}c_{13}, & & a_{03}^{(1)}=c_{03}+\frac{1}{6}c_{13}-\frac{2}{3}c_{04},\\
a_{40}^{(1)}=c_{40}, & a_{31}^{(1)}=c_{31}, & a_{22}^{(1)}=c_{22}, & a_{13}^{(1)}=c_{13}, & a_{04}^{(1)}=c_{04}\,;\\
a_{10}^{(2)}=-c_{20}+\frac{1}{2}c_{11}, & & a_{01}^{(2)}=-\frac{1}{2}c_{11}+c_{02}, & & a_{20}^{(2)}=c_{20}-\frac{3}{4}c_{30}+\frac{1}{4}c_{21},\\
a_{11}^{(2)}=c_{11}-\frac{1}{2}c_{21}+\frac{1}{2}c_{12}, & & a_{02}^{(2)}=c_{02}-\frac{1}{4}c_{12}+\frac{3}{4}c_{03}, & & a_{30}^{(2)}=c_{30}-\frac{2}{3}c_{40}+\frac{1}{6}c_{31},\\
a_{21}^{(2)}=c_{21}-\frac{1}{2}c_{31}+\frac{1}{3}c_{22}, & & a_{12}^{(2)}=c_{12}-\frac{1}{3}c_{22}+\frac{1}{2}c_{13}, & & a_{03}^{(2)}=c_{03}-\frac{1}{6}c_{13}+\frac{2}{3}c_{04},\\
a_{40}^{(2)}=c_{40}, & a_{31}^{(2)}=c_{31}, & a_{22}^{(2)}=c_{22}, & a_{13}^{(2)}=c_{13}, & a_{04}^{(2)}=c_{04}\,;
\end{array}\right\}(53'')$$

$$\left.\begin{array}{lllll}
a_{10}^{(3)}=-c_{20}-\frac{1}{2}c_{11}, & & a_{01}^{(3)}=-\frac{1}{2}c_{11}-c_{02}, & & a_{20}^{(3)}=c_{20}-\frac{3}{4}c_{30}-\frac{1}{4}c_{21},\\
a_{11}^{(3)}=c_{11}-\frac{1}{2}c_{21}-\frac{1}{2}c_{12}, & & a_{02}^{(3)}=c_{02}-\frac{1}{4}c_{12}-\frac{3}{4}c_{03}, & & a_{30}^{(3)}=c_{30}-\frac{2}{3}c_{40}-\frac{1}{6}c_{31},\\
a_{21}^{(3)}=c_{21}-\frac{1}{2}c_{31}-\frac{1}{3}c_{22}, & & a_{12}^{(3)}=c_{12}-\frac{1}{3}c_{22}-\frac{1}{2}c_{13}, & & a_{03}^{(3)}=c_{03}-\frac{1}{6}c_{13}-\frac{2}{3}c_{04},\\
a_{40}^{(3)}=c_{40}, & a_{31}^{(3)}=c_{31}, & a_{22}^{(3)}=c_{22}, & a_{13}^{(3)}=c_{13}, & a_{04}^{(3)}=c_{04}\,;
\end{array}\right\}(52'')$$

$$\left.\begin{array}{l}
a_0^{(1)}=\ln \mathrm{P}_1+\frac{1}{4}(c_{20}-c_{11}+c_{02})-\frac{1}{16}(c_{30}-c_{21}+c_{12}-c_{03})+\frac{1}{48}(c_{40}-c_{31}+c_{22}-c_{13}+c_{04}),\\
a_0^{(2)}=\ln \mathrm{P}_2+\frac{1}{4}(c_{20}-c_{11}+c_{02})+\frac{1}{16}(c_{30}-c_{21}+c_{12}-c_{03})+\frac{1}{48}(c_{40}-c_{31}+c_{22}-c_{13}+c_{04}),
\end{array}\right\}(57'')$$

$$a_0^{(3)}=\ln \mathrm{P}_3+\frac{1}{4}(c_{20}+c_{11}+c_{02})+\frac{1}{16}(c_{30}+c_{21}+c_{12}+c_{03})+\frac{1}{48}(c_{40}+c_{31}+c_{22}+c_{13}+c_{04});\ (58'')$$

putting

$$a_0^{(1)} - a_0^{(3)} = b_0^{(1)}, \quad a_0^{(2)} - a_0^{(3)} = b_0^{(2)}, \quad \ldots \ldots \qquad (68)$$

$$\left.\begin{aligned} & b_0^{(1)} + 2c_{20}z_1 + c_{11}z_2 + \frac{3}{2}c_{30}z_1^2 + c_{21}z_1z_2 + \frac{1}{2}c_{12}z_2^2 + \frac{4}{3}c_{40}z_1^3 + c_{31}z_1^2z_2 \\ & \qquad + \frac{2}{3}c_{22}z_1z_2^2 + \frac{1}{3}c_{13}z_2^3 = \ln\left(\frac{p_1x_3}{p_3x_1}\right), \qquad (59'') \\ & b_0^{(2)} + c_{11}z_1 + 2c_{02}z_2 + \frac{1}{2}c_{21}z_1^2 + c_{12}z_1z_2 + \frac{3}{2}c_{03}z_2^2 + \frac{1}{3}c_{31}z_1^3 + \frac{2}{3}c_{22}z_1^2z_2 \\ & \qquad + c_{13}z_1z_2^2 + \frac{4}{3}c_{04}z_2^3 = \ln\left(\frac{p_2x_3}{p_3x_2}\right); \qquad (61'') \end{aligned}\right\}$$

$$\left.\begin{aligned} b_0^{(1)} &= \ln\left(\frac{P_1}{P_3}\right) - \frac{1}{2}c_{11} - \frac{1}{8}(c_{30}+c_{12}) - \frac{1}{24}(c_{31}+c_{13}), \\ b_0^{(2)} &= \ln\left(\frac{P_2}{P_3}\right) - \frac{1}{2}c_{11} - \frac{1}{8}(c_{21}+c_{03}) - \frac{1}{24}(c_{31}+c_{13}); \end{aligned}\right\} \quad \ldots \qquad (60'')$$

$$c_0 = \frac{1}{2}\ln(P_1P_2) + \frac{1}{4}(c_{20} - c_{11} + c_{02}) + \frac{1}{48}(c_{40} - c_{31} + c_{22} - c_{13} + c_{04}); \qquad (63'')$$

$$u_1 = \ln\left(\frac{p_1}{x_1}\right), \quad u_2 = \ln\left(\frac{p_2}{x_2}\right), \quad u_3 = \ln\left(\frac{p_3}{x_3}\right). \qquad (21'')$$

Equations (59) and (61) are here combined into one set with the double number (59″) (61″). Each observation furnishes a pair of such equations. Together they involve 14 constants to be determined, namely,

$$b_0^{(1)},\ c_{20},\ c_{30},\ c_{40},\ b_0^{(2)},\ c_{02},\ c_{03},\ c_{04},\ c_{11},\ c_{21},\ c_{12},\ c_{31},\ c_{22},\ c_{13};$$

and seven observations will, therefore, suffice to determine these constants. But it is better to use a much larger number of observations and to solve these equations by the method of least squares. This solution is effected as follows.

For any given values of g_1 and g_2 put

$$\sum_{\text{obs.}} z_1^{g_1}z_2^{g_2} = [g_1g_2], \quad \sum_{\text{obs.}} z_1^{g_1}z_2^{g_2}\ln\left(\frac{p_1x_3}{p_3x_1}\right) = [g_1g_2]_1, \quad \sum_{\text{obs.}} z_1^{g_1}z_2^{g_2}\ln\left(\frac{p_2x_3}{p_3x_2}\right) = [g_1g_2]_2.$$

where $\sum\limits_{\text{obs.}}$ denotes the sum of the expression that follows

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N

$b_0^{(1)}$.	c_{20}.	c_{30}.	c_{40}.	$b_0^{(2)}$.	c_{02}.	c_{03}.	c_{04}.	c_{11}
n	2[10]	$\frac{3}{2}$[20]	$\frac{4}{3}$[30]					[01
2[10]	4[20]	3[30]	$\frac{8}{3}$[40]					2[1
$\frac{3}{2}$[20]	3[30]	$\frac{9}{4}$[40]	2[50]					$\frac{3}{2}$[2
$\frac{4}{3}$[30]	$\frac{8}{3}$[40]	2[50]	$\frac{16}{9}$[60]					$\frac{4}{3}$[3
				n	2[01]	$\frac{3}{2}$[02]	$\frac{4}{3}$[03]	[10
				2[01]	4[02]	3[03]	$\frac{8}{3}$[04]	2[11
				$\frac{3}{2}$[02]	3[03]	$\frac{9}{4}$[04]	2[05]	$\frac{3}{2}$[12
				$\frac{4}{3}$[03]	$\frac{8}{3}$[04]	2[05]	$\frac{16}{9}$[06]	$\frac{4}{3}$[13
[01]	2[11]	$\frac{3}{2}$[21]	$\frac{4}{3}$[31]	[10]	2[11]	$\frac{3}{2}$[12]	$\frac{4}{3}$[13]	[02
[11]	2[21]	$\frac{3}{2}$[31]	$\frac{4}{3}$[41]	$\frac{1}{2}$[20]	[21]	$\frac{3}{4}$[22]	$\frac{2}{3}$[23]	[12
$\frac{1}{2}$[02]	[12]	$\frac{3}{4}$[22]	$\frac{2}{3}$[32]	[11]	2[12]	$\frac{3}{2}$[13]	$\frac{4}{3}$[14]	$\frac{1}{2}$[03
[21]	2[31]	$\frac{3}{2}$[41]	$\frac{4}{3}$[51]	$\frac{1}{3}$[30]	$\frac{2}{3}$[31]	$\frac{1}{2}$[32]	$\frac{4}{9}$[33]	[22
$\frac{2}{3}$[12]	$\frac{4}{3}$[22]	[32]	$\frac{8}{9}$[42]	$\frac{2}{3}$[21]	$\frac{4}{3}$[22]	[23]	$\frac{8}{9}$[24]	$\frac{2}{3}$[13
$\frac{1}{3}$[03]	$\frac{2}{3}$[13]	$\frac{1}{2}$[23]	$\frac{4}{9}$[33]	[12]	2[13]	$\frac{3}{2}$[14]	$\frac{4}{3}$[15]	$\frac{1}{3}$[04]

it for all the observations. In particular, if n is the number of observations,

$$[00] = n, \quad [g_1 0] = \sum_{\text{obs.}} z_1^{g_1}, \quad [0 g_2] = \sum_{\text{obs.}} z_2^{g_2},$$

$$[00]_1 = \sum_{\text{obs.}} \ln\left(\frac{p_1 x_3}{p_3 x_1}\right), \quad [g_1 0]_1 = \sum_{\text{obs.}} z_1^{g_1} \ln\left(\frac{p_1 x_3}{p_3 x_1}\right), \quad [0 g_2]_1 = \sum_{\text{obs.}} z_2^{g_2} \ln\left(\frac{p_1 x_3}{p_3 x_1}\right),$$

$$[00]_2 = \sum_{\text{obs.}} \ln\left(\frac{p_2 x_3}{p_3 x_2}\right), \quad [g_1 0]_2 = \sum_{\text{obs.}} z_1^{g_1} \ln\left(\frac{p_2 x_3}{p_3 x_2}\right), \quad [0 g_2]_2 = \sum_{\text{obs.}} z_2^{g_2} \ln\left(\frac{p_2 x_3}{p_3 x_2}\right).$$

In addition to $[00] = n$ there are 47 of these sums to be calculated from the observations, namely, 27 sums $[g_1 g_2]$ for all values of g_1 and g_2 whose sum does not exceed 6, 10 sums $[g_1 g_2]_1$ and 10 sums $[g_1 g_2]_2$ for all values of g_1 and g_2 whose sum does exceed 3,—as is indicated in the adjoined table of normal equations.

Each line of this table corresponds to one of the 14 normal equations; each of the first 14 columns contains the multipliers of the constant that stands at the top of that column in the 14 equations, and the last column (after the sign of equality) contains the right members of the several equations. The first 27 sums mentioned above occur only in the left members, and the 20 other sums only in the right members. The multiplier of any one of the last 6 constants in any one of the last 6 equations is the sum of two terms, as is also the right member of each of the last 6 equations. It will be noticed that the first four constants do not occur in the second four equations, nor the second four constants in the first four equations. The simplest mode of solving these equations is, therefore, to eliminate the first four constants successively from the first four and the last six equations, and then the second four constants successively from the second four equations and the six equations resulting from the previous elimination. When the last six constants have been found from the six resulting equations, their substitution in the equations previously obtained by elimination from the first four and the second four equations will give the first four and the second four constants. The advantage of this order of elimination is that we never have to deal with more than ten equations at once, and that we do not have to introduce any constant into an equation in which it did not previously occur in order to eliminate another constant.

When the c's have been thus found, the a's are easily calculated by (53″) and (52″), excepting $a_0^{(1)}$, $a_0^{(2)}$, and $a_0^{(3)}$, which are found from (41″) and (21″) by means of the other a's

NORMAL EQUATIONS.

$b_0^{(1)}$.	c_{20}.	c_{30}.	c_{40}.	$b_0^{(2)}$.	c_{02}.	c_{03}.	c_{04}.	c_{11}.	c_{21}.	c_{12}.	c_{31}.	c_{22}.	c_{13}.		
n	$2[10]$	$\frac{3}{2}[20]$	$\frac{4}{3}[30]$					$[01]$	$[11]$	$\frac{1}{2}[02]$	$[21]$	$\frac{2}{3}[12]$	$\frac{1}{3}[03]$	=	$[00]_1$
$2[10]$	$4[20]$	$3[30]$	$\frac{8}{3}[40]$					$2[11]$	$2[21]$	$[12]$	$2[31]$	$\frac{4}{3}[22]$	$\frac{2}{3}[13]$	=	$2[10]_1$
$\frac{3}{2}[20]$	$3[30]$	$\frac{9}{4}[40]$	$2[50]$					$\frac{3}{2}[21]$	$\frac{3}{2}[31]$	$\frac{3}{4}[22]$	$\frac{3}{2}[41]$	$[32]$	$\frac{1}{2}[23]$	=	$\frac{3}{2}[20]_1$
$\frac{4}{3}[30]$	$\frac{8}{3}[40]$	$2[50]$	$\frac{16}{9}[60]$					$\frac{4}{3}[31]$	$\frac{4}{3}[41]$	$\frac{2}{3}[32]$	$\frac{4}{3}[51]$	$\frac{8}{9}[42]$	$\frac{4}{9}[33]$	=	$\frac{4}{3}[30]_1$
				n	$2[01]$	$\frac{3}{2}[02]$	$\frac{4}{3}[03]$	$[10]$	$\frac{1}{2}[20]$	$[11]$	$\frac{1}{3}[30]$	$\frac{2}{3}[21]$	$[12]$	=	$[00]_2$
				$2[01]$	$4[02]$	$3[03]$	$\frac{8}{3}[04]$	$2[11]$	$[21]$	$2[12]$	$\frac{2}{3}[31]$	$\frac{4}{3}[22]$	$2[13]$	=	$2[01]_2$
				$\frac{3}{2}[02]$	$3[03]$	$\frac{9}{4}[04]$	$2[05]$	$\frac{3}{2}[12]$	$\frac{3}{4}[22]$	$\frac{3}{2}[13]$	$\frac{1}{2}[32]$	$[23]$	$\frac{3}{2}[14]$	=	$\frac{3}{2}[02]_2$
				$\frac{4}{3}[03]$	$\frac{8}{3}[04]$	$2[05]$	$\frac{16}{9}[06]$	$\frac{4}{3}[13]$	$\frac{2}{3}[23]$	$\frac{4}{3}[14]$	$\frac{4}{9}[33]$	$\frac{8}{9}[24]$	$\frac{4}{3}[15]$	=	$\frac{4}{3}[03]_2$
$[01]$	$2[11]$	$\frac{3}{2}[21]$	$\frac{4}{3}[31]$	$[10]$	$2[11]$	$\frac{3}{2}[12]$	$\frac{4}{3}[13]$	$[02]+[20]$	$[12]+\frac{1}{2}[30]$	$\frac{1}{2}[03]+[21]$	$[22]+\frac{1}{3}[40]$	$\frac{2}{3}[13]+\frac{2}{3}[31]$	$\frac{1}{3}[04]+[22]$	=	$[01]_1+[10]_2$
$[11]$	$2[21]$	$\frac{3}{2}[31]$	$\frac{4}{3}[41]$	$\frac{1}{2}[20]$	$[21]$	$\frac{3}{4}[22]$	$\frac{2}{3}[23]$	$[12]+\frac{1}{2}30]$	$[22]+\frac{1}{4}[40]$	$\frac{1}{2}[13]+\frac{1}{2}[31]$	$[32]+\frac{1}{6}[50]$	$\frac{2}{3}[23]+\frac{1}{3}[41]$	$\frac{1}{3}[14]+\frac{1}{2}[32]$	=	$[11]_1+\frac{1}{2}[20]_2$
$\frac{1}{2}[02]$	$[12]$	$\frac{3}{4}[22]$	$\frac{2}{3}[32]$	$[11]$	$2[12]$	$\frac{3}{2}[13]$	$\frac{4}{3}[14]$	$\frac{1}{2}[03]+[21]$	$\frac{1}{2}[13]+\frac{1}{2}[31]$	$\frac{1}{4}[04]+[22]$	$\frac{1}{2}[23]+\frac{1}{3}[41]$	$\frac{1}{3}[14]+\frac{2}{3}[32]$	$\frac{1}{6}[05]+[23]$	=	$\frac{1}{2}[02]_1+[11]_2$
$[21]$	$2[31]$	$\frac{3}{2}[41]$	$\frac{4}{3}[51]$	$\frac{1}{3}[30]$	$\frac{2}{3}[31]$	$\frac{1}{2}[32]$	$\frac{4}{9}[33]$	$[22]+\frac{1}{3}[40]$	$[32]+\frac{1}{6}[50]$	$\frac{1}{2}[23]+\frac{1}{3}[41]$	$[42]+\frac{1}{9}[60]$	$\frac{2}{5}[33]+\frac{2}{9}[51]$	$\frac{1}{3}[24]+\frac{1}{3}[42]$	=	$[21]_1+\frac{1}{3}[30]_2$
$\frac{2}{3}[12]$	$\frac{4}{3}[22]$	$[32]$	$\frac{8}{9}[42]$	$\frac{2}{3}[21]$	$\frac{4}{3}[22]$	$[23]$	$\frac{8}{9}[24]$	$\frac{2}{3}[13]+\frac{2}{3}[31]$	$\frac{2}{3}[23]+\frac{1}{3}[41]$	$\frac{1}{3}[14]+\frac{2}{3}[32]$	$\frac{2}{3}[33]+\frac{2}{9}[51]$	$\frac{4}{9}[24]+\frac{4}{9}[42]$	$\frac{2}{9}[15]+\frac{2}{3}[33]$	=	$\frac{2}{3}[12]_1+\frac{2}{3}[21]_2$
$\frac{1}{3}[03]$	$\frac{2}{3}[13]$	$\frac{1}{2}[23]$	$\frac{4}{9}[33]$	$[12]$	$2[13]$	$\frac{3}{2}[14]$	$\frac{4}{3}[15]$	$\frac{1}{3}[04]+[22]$	$\frac{1}{3}[14]+\frac{1}{2}[32]$	$\frac{1}{6}[05]+[23]$	$\frac{1}{3}[24]+\frac{1}{3}[42]$	$\frac{2}{9}[15]+\frac{2}{3}[33]$	$\frac{1}{9}[06]+[24]$	=	$\frac{1}{3}[03]_1+[12]_2$

and the z_1, z_2, p_1, p_2, p_3 that belong to any one observation. Finally, P_1, P_2, P_3 are determined by (57′) and (58″).

If wanted, c_0 is calculated from (63″).

The most laborious part of the calculation is the determination of the 47 sums that enter into the normal equations. This is best effected according to the following scheme.

For each observation, find

$$z_1, \quad z_2, \quad \ln x_1, \quad \ln x_2, \quad \ln x_3, \quad \ln\frac{x_3}{x_1}, \quad \ln\frac{x_3}{x_2}, \quad \ln\frac{p_1}{p_3}, \quad \ln\frac{p_2}{p_3},$$

$$\ln\left(\frac{p_1x_3}{p_3x_1}\right) = l_1, \quad \ln\left(\frac{p_2x_3}{p_3x_2}\right) = l_2\,;$$

next, by successive multiplications by z_1,

$$\begin{array}{ll}
z_1^2,\ z_1^3,\ z_1^4,\ z_1^5,\ z_1^6 & \left[\text{test } z_1^6 = z_1^3 \times z_1^3\right], \\
z_1l_1,\ z_1^2l_1,\ z_1^3l_1 & \left[\text{test } z_1^3l_1 = z_1^3 \times l_1\right], \\
z_1l_2,\ z_1^2l_2,\ z_1^3l_2 & \left[\text{test } z_1^3l_2 = z_1^3 \times l_2\right];
\end{array}$$

then, by successive multiplications by z_2,

$$\begin{array}{ll}
z_2^2,\ z_2^3,\ z_2^4,\ z_2^5,\ z_2^6 & \left[\text{test } z_2^6 = z_2^3 \times z_2^3\right], \\
z_1z_2,\ z_1z_2^2,\ z_1z_2^3,\ z_1z_2^4,\ z_1z_2^5 & \left[\text{test } z_1z_2^5 = z_1 \times z_2^5\right], \\
z_1^2z_2,\ z_1^2z_2^2,\ z_1^2z_2^3,\ z_1^2z_2^4 & \left[\text{test } z_1^2z_2^4 = z_1 \times z_1z_2^4\right], \\
z_1^3z_2,\ z_1^3z_2^2,\ z_1^3z_2^3 & \left[\text{test } z_1^3z_2^3 = z_1 \times z_1^2z_2^3\right], \\
z_1^4z_2,\ z_1^4z_2^2 & \left[\text{test } z_1^4z_2^2 = z_1 \times z_1^3z_2^2\right], \\
z_1^5z_2 & \left[\text{test } z_1^5z_2 = z_1 \times z_1^4z_2\right]. \\
z_2l_1,\ z_2^2l_1,\ z_2^3l_1 & \left[\text{test } z_2^3l_1 = z_2^3 \times l_1\right], \\
z_1z_2l_1,\ z_1z_2^2l_1 & \left[\text{test } z_1z_2^2l_1 = z_1 \times z_2^2l_1\right], \\
z_1^2z_2l_1 & \left[\text{test } z_1^2z_2l_1 = z_1 \times z_1z_2l_1\right], \\
z_2l_2,\ z_2^2l_2,\ z_2^3l_2 & \left[\text{test } z_2^3l_2 = z_2^3 \times l_2\right], \\
z_1z_2l_2,\ z_1z_2^2l_2 & \left[\text{test } z_1z_2^2l_2 = z_1 \times z_2^2l_2\right], \\
z_1^2z_2l_2 & \left[\text{test } z_1^2z_2l_2 = z_1 \times z_1z_2l_2\right].
\end{array}$$

If the calculation of these numbers is carried out in tabular form, like functions in one column and functions belonging to the same observation in one line, the

47 sums wanted can be found by simple addition of the numbers in the 47 columns (omitting the third to the ninth columns,—whose sums are not wanted, and which may be written on a sheet by themselves; as these seven numbers have to be combined by addition and subtraction, it may be most convenient to arrange them in columns corresponding to the several observations, to effect their combinations in these columns, and to transfer the values of l_1 and l_2 thus found to the main sheets).

Worcester, Mass., U.S.A.,
January 1, 1909.

IX. *On the Statistical Theory of Heat Radiation. By* Prof. HAROLD A. WILSON, *F.R.S., McGill University, Montreal* [*]

THE theory of the distribution of the energy in the spectrum of full radiation which we owe to Planck has recently been presented in a new and more general form by Sir J. Larmor [†]. In Planck's theory the energy is taken to be emitted by "resonators" contained in the body which are supposed to only gain and lose energy by certain finite increments the magnitude of which is proportional to the frequency of vibration. On this view it is not absolutely necessary to regard the radiation itself as made up of finite elements; but Einstein and others have shown that Planck's theory can be so interpreted. Larmor considers the radiation itself as made up of "elements of disturbance" which are regarded as definite entities possessing energy, but the energy in an element can vary continuously.

Larmor states that on his view "it would be the limiting differential ratio of energy element to extent of cell that is somehow predetermined, but now without any implication that energy is itself constituted on an atomic basis." I find that Larmor's theory seems to require the radiation to be made up of finite elements of the same magnitude as those contemplated by Planck and Einstein. This does not mean that energy itself has an atomic constitution, but it does appear to require some such sort of constitution for the radiation.

Larmor obtains the equation $\epsilon\theta=\log\left(1+\frac{\mathrm{N}}{n}\right)$, where ϵ denotes the energy per element of disturbance of a particular wave-length, n the number of such elements, and N the

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[*] Communicated by the Author.

[†] Proc. Roy. Soc. A. vol. lxxxiii., 1909.

number of "cells" into which the æther is supposed divided for radiation of the wave-length under consideration. θ is a function of the temperature, and is the same for all the different sets of cells.

To determine the relation between θ and the temperature (t) on the conventional absolute scale we have Boltzmann's expression for the entropy $S = k \log W$, where W denotes the number of ways in which the system can be arranged in its actual state. Hence

$$\frac{dS}{dn} = k\frac{d(\log W)}{dn} = k\log\left(1+\frac{N}{n}\right)$$

for the system consisting of the n elements distributed among N cells. If n is increased by unity, the increase of entropy is ϵ/t, so that

$$\frac{\epsilon}{t} = k\log\left(1+\frac{N}{n}\right) = k\epsilon\theta.$$

Hence
$$\theta = \frac{1}{kt}.$$

Larmor shows that $N \propto 1/\lambda^3$ and $\epsilon \propto 1/\lambda$; so that after multiplying by $1/\lambda$ to allow for the variation of $d\lambda$ we get, putting $\epsilon = hc/\lambda$,

$$e_\lambda = \mathcal{C}\lambda^{-5}\left(e^{\frac{hc}{\lambda kt}}-1\right)^{-1},$$

where e_λ denotes the energy density per unit range of wave-length and c the velocity of light. To get $\mathcal{C}$ we can make use of the value of e_λ for long wave-lengths calculated by H. A. Lorentz and Jeans, viz., $e_\lambda = 8\pi kt/\lambda^4$. Hence

$$\frac{\mathcal{C}}{\lambda^5}\frac{\lambda kt}{hc} = \frac{8\pi kt}{\lambda^4};$$

so that
$$\mathcal{C} = 8\pi hc \text{ and } e_\lambda = \frac{8\pi hc}{\lambda^5}\left(e^{\frac{hc}{\lambda kt}}-1\right)^{-1}$$

which is Planck's formula.

In the formula $n\epsilon = \dfrac{N\epsilon}{e^{\epsilon/kt}-1}$ if we suppose ϵ indefinitely diminished while λ is kept constant, we get $n\epsilon = Nkt$, so that the energy per cell is kt and is the same for all the sets of cells. This is merely equipartition of energy and corresponds with $e_\lambda = 8\pi kt/\lambda^4$. It seems therefore that ϵ cannot be made indefinitely small on Larmor's theory any more than on Planck's*.

The total number of elements of energy per c.c. ($\mathcal{N}$) is given by the equation

$$\mathcal{N}=\int_0^\infty \frac{8\pi hc\lambda}{hc\lambda^5}\left(e^{\frac{hc}{k\lambda t}}-1\right)^{-1}d\lambda.$$

Hence

$$\mathcal{N}=16\pi\left(\frac{kt}{ch}\right)^3\left(1+\frac{1}{2^3}+\frac{1}{3^3}+\ldots\right).$$

The series in brackets is equal to $1{\cdot}20\ldots=\alpha'$ say.

The total energy per c.c. is

$$\mathrm{E}=\frac{48\pi\alpha k^4t^4}{c^3h^3},$$

where $\alpha=1+\frac{1}{2^4}+\frac{1}{3^4}+\ldots=1{\cdot}0823$.

Let $\bar{\epsilon}$ denote the average energy per element so that

$$\bar{\epsilon}=\frac{\mathrm{E}}{\mathcal{N}}=3kt\frac{\alpha}{\alpha'}.$$

Now $3kt/2$ is the average translational energy of a molecule of a gas, and

$$\frac{2\bar{\epsilon}}{3kt}=2\frac{\alpha}{\alpha'}=1{\cdot}80\ldots$$

It appears, therefore, that the average energy per element of disturbance in the radiation is equal to 1·80 times the energy of a monatomic gas molecule. This result, it will be observed, is independent of the absolute values of the constants in Planck's formula.

The pressure (p) of the radiation is equal to E/3, so that

$$p=\mathcal{N}kt\frac{\alpha}{\alpha'}.$$

For a gas we have $p=\mathcal{N}kt$ if $\mathcal{N}$ now denotes the number of molecules per c.c. Thus for a given pressure and temperature a gas contains 0·90 times as many molecules per c.c. as full radiation contains elements of energy. The elements of disturbance have on the average as much energy as if each possessed 5·4 degrees of freedom and equipartition held good. For a gas each molecule of which has six degrees of freedom

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* The value of ϵ for any wave-length is of course given by $\epsilon=hc/\lambda$, using the value of h required by the observed values of e_λ.

we have $p=\frac{E}{3}$, where E denotes the total energy of the gas per c.c. Also for an adiabatic expansion of such a gas $pv^{4/3}=\text{const.}$ These two equations also hold for full radiation, which suggests that the elements of disturbance ought to have energy corresponding to six degrees of freedom instead of only 5·4, but the energy is not distributed among the elements in the same way as among the gas molecules.

Consider the free expansion of full radiation from a volume v_1 to a volume v_2. The chance that an element is in v_1 when the volume is v_2 is v_1/v_2. Thus the chance that all the $\mathcal{N}v_1$ elements are in v_1 is $\left(\frac{v_1}{v_2}\right)^{Nv_1}$; hence the increase of entropy S_2-S_1 due to the free expansion is $k\mathcal{N}v_1\log\frac{v_2}{v_1}$. If v_2-v_1 is very small, say dv, this becomes $k\mathcal{N}dv=dS$. Now

$$dS=\frac{dU+pdv}{t};$$

so that for an infinitesimal free expansion, if for the moment we regard t as unaffected, we have

$$dS=\frac{pdv}{t}=\frac{\mathcal{N}\bar{\epsilon}dv}{3t}.$$

Hence
$$k\mathcal{N}dv=\frac{\mathcal{N}\bar{\epsilon}}{3t}dv,$$

or
$$\bar{\epsilon}=3kt \text{ instead of } \bar{\epsilon}=3kt\frac{\alpha}{\alpha'}.$$

This makes $\bar{\epsilon}$ equal to the energy of six degrees of freedom, but the supposed infinitesimal free expansion alters the temperature of the radiation by different infinitely small amounts for the energy of different wave-lengths. Consequently it is not clear that even after only an infinitesimal free expansion the radiation can be regarded as having a definite temperature differing infinitely little from t.

In the case of the gas we have in the same way for a free expansion

$$dS=k\mathcal{N}dv=\frac{pdv}{t}=\frac{1}{3}\frac{\mathcal{N}mu^2dv}{t},$$

where m is the mass of a molecule and u^2 the average square of the velocity of the molecules. Hence $\frac{3}{2}kt=\frac{1}{2}mu^2$, which gives the value of k due to Planck. The known equation

$\lambda_m t = \frac{ch}{4{\cdot}965k}$, where λ_m is the wave-length for which e_λ has its maximum value, gives with the expression found for $\mathscr{N}$

$$\mathscr{N} = \frac{16\pi\alpha'}{(4{\cdot}965\lambda_m)^3}.$$

Consequently the number of elements of disturbance per c.c. can be calculated from λ_m without knowing the density of the energy. Since $\lambda_m t = 0{\cdot}294$, we get approximately

$$\mathscr{N} = 19{\cdot}5t^3.$$

Thus at 2000° on the absolute scale there are $1{\cdot}56 \times 10^{11}$ elements per c.c. in full radiation according to the theory considered here.

Montreal, April 13, 1910.

X. *The Amount of Thorium in Sedimentary Rocks.— I. Calcareous and Dolomitic Rocks.* By J. Joly, *F.R.S.*[*]

THE systematic determination of the amount of thorium in sedimentary rocks does not seem to have been hitherto attempted. Using a method already fully described by me (Phil. Mag., May and July 1909) I have recently measured the thorium content of calcareous and dolomitic rocks from various parts of the world and of various geological ages. The results are given below.

In all cases, the rock after being brought to a coarse powder was treated with 100 ccs. of HCl diluted to a bulk of 200 ccs. with distilled water. A test applied to 500 ccs. of the acid used showed no trace of thorium. After the first violent effervescence had ceased, the whole was heated for a couple of hours on the water-bath. The undissolved part was then filtered off, dried, and fused with about twice its weight of the usual fusion-mixture of the carbonates of sodium and potassium. The melt was then leached with water and acidified with sufficient acid rapidly stirred up with it. In most cases a clear or almost clear solution resulted, which could be added to the solution containing the soluble part of the rock. In a few cases, where the insoluble residue, obtained after treating the rock with HCl, was large, the

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[*] Communicated by the Author.

residue was, after fusion, divided into an acid and an alkaline solution; the former being alone added to the original acid solution, and the alkaline solution reserved for a separate test.

It was thought best to determine the constant of the electroscope by an experiment in which a known amount of a standard solution of thorianite was added to one of the acid rock solutions which had been already tested for thorium. Throughout the experiments all the solutions were boiled in the same flask and brought to the same bulk. These conditions, as well as those of velocity of air-current &c., were preserved unchanged when finding the constant of the electroscope. It was found that when one cubic centimetre of a standard thorianite solution containing $6{\cdot}977 \times 10^{-4}$ gram thorium per cc. was added to the rock solution, the rate of discharge of the electroscope increased from a quite steady rate of 7·3 scale-divisions per hour to 50 scale-divisions per hour, a gain of 42·7 scale-divisions. Consequently one scale-division per hour increase corresponds to $1{\cdot}63 \times 10^{-5}$ gram thorium, which is the required constant. A previous determination of the constant of this electroscope under the same conditions, but effected by adding the thorianite to the solution of a trachyte of the Andes, gave the constant as $1{\cdot}68 \times 10^{-5}$ gram. The first value was used throughout.

The figures in the brackets, given in the table which follows, refer to the weight in grams of the amount of rock dealt with.

It will be noticed that in most cases the quantity of thorium present is so small that it could not be certainly determined in the quantity of rock used. The major limit, in such cases, is obtained by dividing the constant of the electroscope by the weight of rock taken; it being assumed that a change in rate of discharge of one scale-division per hour is readable. This assumption is certainly justifiable.

It would appear from these results that thorium is not abstracted in any considerable degree from waters in which calcareous materials are formed. This may be due to a process of organic selection among the dissolved materials. I have obtained, in the case of a sample of sea-water from the Indian Ocean, $0{\cdot}9 \times 10^{-8}$ gram thorium per gram of water (Phil. Mag. July 1909). If this approximates to the average thorium content of sea-water, by far the greater part of the thorium accompanying a given amount of calcium salts in sea-water must be rejected in the organic processes attending the abstraction of the lime.

TABLE.

			THORIUM. (gr. per grm. $\times 10^{-5}$).
1.	Littorina Limestone (Pleistocene). Rhein Hesse. (45)		0·13
2.	Nummulite Limestone. loc.? (50)		0·08
3.	Marsupites Chalk. loc.? (32)	less than	*0·06*
4.	Upper Chalk. Co. Antrim. (50)	less than	*0·03*
5.	Lower Chalk. Isle of Wight. (34)	less than	*0·05*
6.	Earthy Limestone (Upper Cretaceous). Were, Westphalia. (30)		0·22
7.	Dolomitic Flagstone (Portlandian). Embeckhausen, Hannover. (30)	less than	*0·05*
8.	Oolite. Isle of Portland, Dorset. (50)	less than	*0·03*
9.	Lithographic Slate (Kimmeridgian). Solenhofen, Bavaria. (30)	less than	*0·05*
10.	Limestone (Jura). Hohenstein, Saxony. (30)	less than	*0·05*
11.	Limestone (Jura). Schnaitheim, Ulm. (30)	less than	*0·05*
12.	Red Marble. Italy. (30)	less than	*0·05*
13.	Limestone (Malm). Untergletcher, Grindelwald. (40)	less than	*0·04*
14.	Limestone (Dogger). Sandfirn, Tödi. (40)	less than	*0·04*
15.	White Marble (Trias). Carrara, Italy. (30)	less than	*0·05*
16.	Muschelkalk. Heidelberg. (50)	less than	*0·03*
17.	Limestone (Zechstein). Tettenborn, Hartz. (30)	less than	*0·05*
18.	Limestone (Upper Carboniferous). Co. Kildare. (30)	less than	*0·05*
19.	Limestone (Carboniferous). Armagh, Ireland. (22·5)	less than	*0·10*
20.	Oolite (Carboniferous). Ballina, Co. Mayo. (50)	less than	*0·03*
21.	Limestone (Carboniferous). Nuttlar, Westphalia. (30)	less than	*0·05*
22.	Limestone (Carboniferous). Dusseldorf. (30)	less than	*0·05*
23.	Limestone (Lower Carboniferous). Co. Kildare. (30)		0·14
24.	Lower Limestone Shale. Co. Kildare. (30)		0·33
25.	Grey Marble (Upper Devonian). Namur, Belgium. (30)	less than	*0·05*
26.	Black Marble (Devonian). Shuppach, Nassau. (30)	less than	*0·05*
27.	Dolomite (Devonian). Gerolstein, Eifel. (30)		0·16
28.	Favosites Limestone (Devonian). Torquay, Devon. (30)	less than	*0·05*
29.	Coral Limestone (Upper Silurian). Aymestry. (35)	less than	*0·05*
30.	Porites Limestone (Middle Silurian). Wenlock. (35)	less than	*0·05*
31.	White Marble (Lower Silurian). Boda, Norway. (30)	less than	*0·05*
32.	Cheirurus Limestone (Ordovician). Chair of Kildare. (40)		0·05
33.	White Marble (Archæan). Pentelicon, Greece. (30)	less than	*0·05*
34.	Dolomite. Fichtel Erzgebirge; Sayda, Saxony. (30)	less than	*0·05*

In the case of two rocks dealt with (Nos. 6 and 24) there were at once very considerable insoluble residues, and a thorium content greater than was generally indicated. It seemed of interest to find if the thorium was in these cases in the soluble or in the insoluble part of the rock. The soluble part of 42 grams of No. 6 was tested separately and found to contain $5{\cdot}3 \times 10^{-5}$ gram thorium. The total thorium in 42 gram is $9{\cdot}1 \times 10^{-5}$. Hence there is no special concentration of the thorium in the insoluble part, which in this case was found to be very nearly 40 per cent. by weight of the rock. In the case of No. 24 the soluble part of 50 grams was found to contain $5{\cdot}05\times10^{-5}$ gram thorium. As the entire 50 grams should contain $16{\cdot}3\times10^{-5}$ gram thorium, and the soluble part was found to be just 71 per cent. of the rock, there is here a considerable concentration in the insoluble residue.

It may be remarked as regards the geological significance of these results, that the calcareous rocks have been estimated as constituting about 5 per cent. of the bulk of the total sedimentaries upon the land*, and although somewhat higher estimates have been made, they certainly constitute a small fraction of the sedimentaries.

Soils derived from such rocks consist largely of the insoluble residues, and hence the influence of the surface materials in ionizing the atmosphere over calcareous districts cannot be directly inferred from such results as the foregoing.

Geological Laboratory, Trinity College, Dublin,
May 13, 1910.

XI. *On an Oscillation Detector actuated solely by Resistance-temperature Variations.* *By* W. H. Eccles, *D.Sc.*†

In a recent communication to the Physical Society ‡ the properties of a type of iron-oxide coherer were discussed. The paper described experiments on coherers made by dipping a slightly oxidised iron wire into clean mercury, or by pressing a fine iron wire against a thinly oxidized iron plate, and the results were discussed mathematically. It was shown that in the case of the iron point and oxidized plate the whole of the experiments could be explained qualitatively on the assumption that the only electrical phenomena at play were the Joule effect and the resistance-temperature changes in the small mass of oxide between the metal electrodes. The hypothesis that was put forward must be summarized here. Let ρ be the resistance of that part of the detector where the current flow is so constricted that the Joule effect produces rise of temperature, and r the resistance of the remainder of the circuit. The resistance ρ is usually localized at the contact of the conductors that form the detector, and it varies with the temperature of the minute mass of matter at the contact; let α be the coefficient of decrease of resistance with rise of temperature. The resistance r includes that of the bulk of the substances forming the detector, the leads

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* Van Hise, 'Treatise on Metamorphism,' p. 940.

† Communicated by the Physical Society: read May 27, 1910.

‡ W. H. Eccles, "On Coherers," Phil. Mag. June 1910; Proc. Phys. Soc. vol. xxii. 1910.

and the telephone; it is supposed constant. Let c be the current when the electromotive force applied to the detector is ϵ. Assume that the rate of loss of heat from the warmed contact is $m\theta$, where θ is the temperature of the contact above that of the surroundings. Then it was shown that in the steady state

$$\epsilon=\left(\frac{\rho_0}{1+q\alpha c^2}+r\right)c, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ρ_0 is the resistance of the contact when cold and q is a constant. If the curve $\epsilon=\rho_0 c/(1+q\alpha c^2)$ be plotted with ϵ as abscissæ and c as ordinates, it is seen to rise from the origin of coordinates with an increasing gradient till at a definite value of ϵ it becomes vertical. Then as c increases, the curve bends towards the axis of c and approaches it asymptotically. Along this latter part of the curve, increasing current is associated with decreasing electromotive force—an unstable state of affairs. Any conductor possessing a negative temperature-coefficient of resistance exhibits these properties. In such conductors an increase of current produces, in accordance with Joule's law, an increase of temperature, and consequently a diminution of the resistance. The curve shows that after a certain stage is passed the diminution of the resistance which accompanies increasing current is great enough to lead to a catastrophe. Stability can, however, be obtained by introducing into the circuit of the variable resistance ρ a sufficiently large constant resistance r. The phenomenon resembles that of the electric arc. The unstable portion of the above curve corresponds, in fact, to the "falling characteristic" of the arc.

If the resistance r is large the ϵ, c curve has a positive gradient throughout, and the gradient has a maximum at some value of ϵ. Near this point the contact is found to work best as a detector of oscillations. The hypothesis put forward by the author supposes that a train of oscillations, by yielding its energy as heat to the contact, raises the temperature there and disturbs the existing equilibrium of current and voltage. The dissipation of a train of oscillations is accomplished in a time of the order of a fifty-thousandth of a second; the ensuing fluctuation of the current causes the sound in the telephone. In the paper cited, the energy w given to the telephone circuit was shown to be connected with the energy W delivered by the train of waves by the equation

$$w=m(\mathrm{W}-a), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

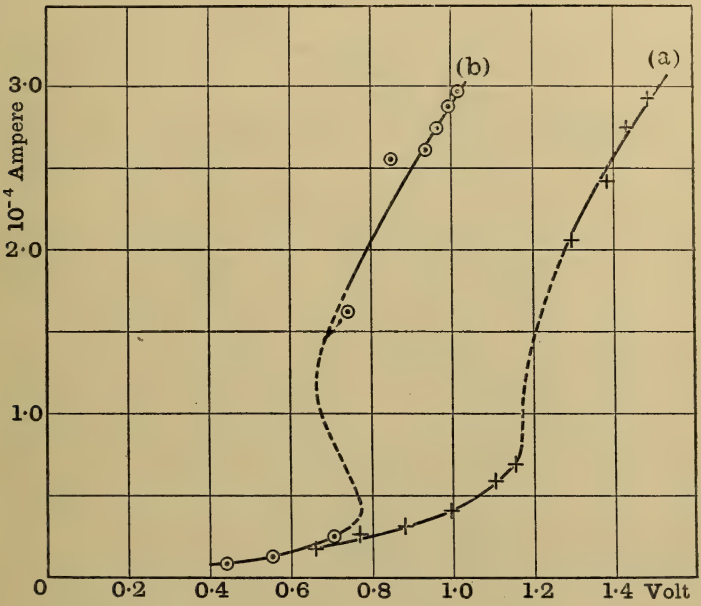
where m and a are constants for any fixed value of the current. This theoretical conclusion agreed well with the experiments on an iron oxide coherer. The object of the present paper is to show that the above hypothesis holds good for a very different type of detector.

All the well-known forms of "contact" detector consist of a contact between two substances that stand well apart in the thermoelectric series; and the thermoelectric force plays a very important part in their operation. They are usually classed as "rectifying detectors" to distinguish them from such detectors as the coherers. In seeking a "rectifying detector" that would illustrate the above hypothesis, substances that stand far apart in the thermoelectric series must be avoided, for such substances would introduce Peltier effects that would tend to mask the resistance-temperature phenomena we wish to isolate. Even in the iron : iron-oxide : iron coherer it is possible that thermoelectric forces arise owing to unequal heating of the two iron to iron-oxide junctions. It occurred to me, therefore, to construct a detector out of one substance only. Accordingly a search was made for a substance possessing high, but not too high, resistivity, with large negative temperature-coefficient. Several such substances were found among the native crystalline oxides and sulphides. Most of these are ælotropic, and must on that account be avoided. Fortunately galena, the native sulphide of lead, has fairly high resistivity, a very large negative resistance coefficient, and crystallizes in the cubic system. A galena-galena detector was therefore constructed. Two pieces of galena cut from the same crystal were embedded in solder, mounted in a clamp, and brought into gentle contact. It was put into a wireless telegraph receiving set and was found to yield excellent signals when a current of proper magnitude was passed through it.

A few preliminary experiments showed that it was not easy to find two pieces of galena, which when placed together and submitted to positive and negative voltages in turn, exhibited perfect symmetry. The asymmetry is always small, and is probably due to the rise of thermoelectric forces at the contact when it becomes heated by the steady current, and these forces are probably caused by slight variations in the chemical composition of the galena from point to point in the crystal. When a contact that gives symmetrical voltage-current curves is found, it constitutes a detector that operates only when a current is passing through it. The efficiency of the detector is the same for each direction of the current, and appears to be practically independent of the shape of the galena surfaces at the contact.

The experiments now to be described were made on selected galena-galena combinations in precisely the same way as the earlier experiments on the iron-oxide detectors. The diagram of the apparatus employed is shown in fig. 1 of the previous paper (Phil. Mag. June 1910, p. 872). The mutual inductance between L and L′ was 2500 cm. in obtaining the results described below.

Fig. 1.



The detector was placed at D and submitted to an electromotive force from P_2, which was varied in steps from zero to about one volt positive or negative. At each step an observation was made of the steady current through the detector, and of the intensity of the sound produced in the telephone by electrical oscillations of amplitude fixed by the position of the jockey on P_1. The steady current observation was made by means of a shunted galvanometer kept connected in series with the telephone. The intensity of the sound was measured by balancing the sound from the detector against that from the interrupter and the potential-divider P_3. Thus were obtained the curves of figs. 1 and 2. Fig. 3 was obtained by applying oscillations of various amplitudes to the detector

Fig. 2.

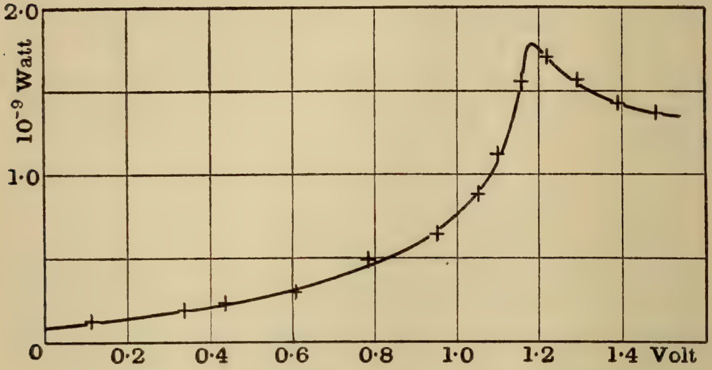
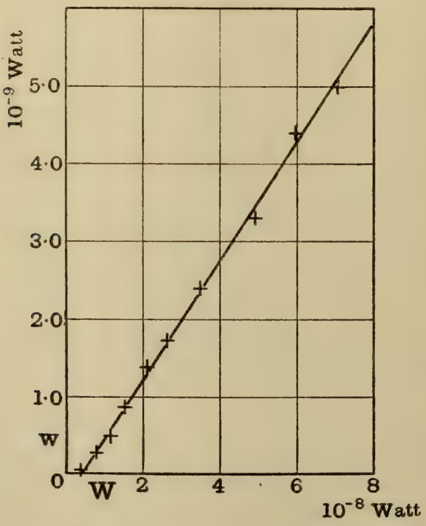


Fig. 3.



while it is traversed by a suitable steady current, and measuring the intensities of the resulting sounds; and therefore expresses the relation between the energy given to the detector and that appearing in the telephone circuit. The curves given here are selected out of a number as representative ones. The absolute values of the energy quantities involved in the results given in this paper were determined in the same way as in the former paper, and are therefore subject to the same errors ; the errors in the *absolute* values of the energy delivered to the telephone circuit may be large.

The most difficult observations to make were the steady current ones. The current-voltage curves obtained with increasing currents are very different from those got with decreasing currents unless certain precautions are observed. Usually a decreasing-current curve lies above an increasing-current curve. The difference between the curves was found to depend greatly on the time allowed for a set of measurements. If, with decreasing currents, the electromotive force be held constant, the galvanometer reading slowly diminishes, till in about half an hour it has fallen as a rule to the value it would have at the same voltage with increasing currents. On the other hand, if the voltage be raised suddenly from zero to a fairly large value, the reading of the galvanometer increases as time elapses, at first quickly and then slowly, rising perhaps fifty per cent. in five minutes, and asymptotically approaching a limit. All these things are due to the temperature at the contact lagging behind the changes of current. This may be understood as follows:—At any stated value of the steady current the mass of galena surrounding the heated contact must be cooler when the current is being increased than when it is being decreased—for the reason that in the former case the conductor has just previously been carrying smaller currents, in the latter case larger currents, than the particular current considered. The rate of loss of heat from the heated matter at the contact to its surroundings is thus greater on the rising curve than on the falling curve, and, in consequence, at corresponding points on the two curves the resistance is higher in the former than in the latter case. This temperature lag may be expected to be more pronounced in detectors made wholly of substances of low thermal conductivity than in detectors consisting of a very thin film of oxide between metal electrodes. The phenomenon is very prominent in this new galena detector though it escaped observation in the iron-oxide detectors, and therefore the former may be expected to work well as a rectifier of alternating currents of moderate frequency.

Once the slow movements of heat through the galena had been observed the difficulties were overcome by allowing time for thermal equilibrium to be attained before the final galvanometer reading was taken. At places near the point of inflexion of the steady current curve the time necessary may be several minutes.

Each setting of the two pieces of galena gives a different contact resistance and therefore a different curve. Since very slight accidental vibrations can cause relative motion of the pieces of galena, it is almost impossible to perform a series of measurements yielding sufficient data for all the curves of figs. 1, 2, 3, with full confidence that the contact has not varied.

Curve *a* of fig. 1 follows the equation.

$$\epsilon=\left(\frac{3\cdot 1\times 10^{4}}{1+2\cdot 95\times 10^{8}c^{2}}+4\cdot 0\times 10^{3}\right)c \quad . \quad . \quad (3)$$

with fair accuracy ; curve *b* obtained with another setting of the crystals has the equation

$$\epsilon=\left(\frac{4\cdot 0\times 10^{4}}{1+8\cdot 3\times 10^{8}c^{2}}+2\cdot 5\times 10^{3}\right)c. \quad . \quad . \quad . \quad (4)$$

The curve of fig. 2 was obtained with the same setting of the crystal that gave curve *a* of fig. 1. It was shown in the previous paper that the ordinates of this curve should be proportional to *m* the coefficient of W in equation (2) above, and that *m* contained the gradient of the steady current curve as its principal factor. A comparison of figs. 1 and 2 confirm the deduction. The line of fig. 3 has the equation

$$w=0\cdot 077\ (\mathrm{W}-0\cdot 4\times 10^{6}),$$

where W is the power in watts given to the detector in the form of oscillations, and *w* the power transformed by the detector and passed to the telephone circuit.

The galena detector here investigated proves very good in practical wireless telegraphy. It has shown itself to be better than any coherer * known to me. This superiority is, according to the hypothesis here advocated, to be ascribed chiefly to the large negative temperature-coefficient of resistivity of galena. By direct measurement of a cube of galena clamped between pieces of tinfoil the resistance was found to fall from 0·33 ohm at 12° C. to 0·10 ohm at 99° C. —a negative coefficient of 0·0079 per degree centigrade. Pyrites has a coefficient about 0·006. Iron oxide has a coefficient somewhat lower than this last.

The cost of a portion of the apparatus used in these experiments was defrayed out of a grant from funds at the disposal of the Royal Society.

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* But not so good as certain "thermoelectric" detectors.

XII. *On the Theory of Surface Forces.—V. Thermodynamics of the Capillary Layer between the Homogeneous Phases of the Liquid and the Vapour.* *By* G. Bakker[*].

§ 1. *Some definitions and mathematical significations.*

THE surface-tension of Laplace may be conceived in two ways. Firstly, as the increase of the available energy, when a part of the liquid- and vapour-phase is converted isothermally into the matter of the capillary layer, in consequence of which the surface of the latter has increased by a unit of surface. The contributions of both homogeneous phases to the formation of the capillary layer are here completely determined, as we assume that liquid and vapour are present in abundance, while the influence of the walls of the vessel is not considered. We imagine the process to be very slow.

What we call a unit of surface for a *plane* capillary layer is evident. For a spherical capillary layer we determine it as follows. The spherical capillary layer lies between two concentric spheres. The radius of the smaller sphere we call R_1 and that of the larger one R_2. We take as the "surface" of the capillary layer that of the sphere the radius of which has the value $R=\frac{R_1+R_2}{2}$. The capillary energy that belongs to one unit of this spherical surface we call the capillary energy or constant of Laplace. If the curvature of the capillary layer is small (*e. g.* measurable) it is unnecessary to distinguish R_1, R_2, and R. However, if the curvature is very large (R_2-R_1 and R may be of the same order of magnitude[†]) we conceive a great many *parts* of spherical capillary layers of *equal* curvature, the collective surface of the resp. spherical surfaces with radius R being unity. The surface energy or the available energy, produced at the formation of the capillary layer per unit of surface (radius R) we represent by H. Fuchs proposed another conception for the surface-tension of Laplace. He perceived that the cohesion in directions respectively perpendicular and parallel to the surface of the capillary layer has not the same value. The difference between these cohesions he considered as the cause of the surface-tension. He has however in this way not *calculated* the surface energy[‡].

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[*] Communicated by the Author.

[†] G. Bakker, Phil. Mag. March 1909, p. 346.

[‡] K. Fuchs, *Wiener Ber.* xcviii. 2 Nov. 1889.

If we consider the thermic (kinetic) pressure as independent of the direction, we may assume the difference between *the hydrostatic pressures* in a point of the capillary layer to be equal to the difference of *the cohesions* both in directions resp. perpendicular and parallel to the capillary layer. If p_N and p_T are the pressures in a point of the capillary layer respectively in directions perpendicular and parallel to the surface of the capillary layer, I have called $p_N - p_T$ the departure from the law of Pascal at the considered point. The capillary constant of Laplace thus becomes the integral of the expression $p_N - p_T$, or, if $\bar{p}_N$ and $\bar{p}_T$ represent average values, we have for a *plane* capillary layer

$$H = (\bar{p}_N - \bar{p}_T)\zeta,$$

in which ζ represents the thickness of the capillary layer. (For a plane capillary layer $\bar{p}_N = p_N$ = ordinary vapour-pressure.) By integration of the expression $p_N - p_T$ Hulshof and Bakker calculated the capillary constant of Laplace. Bakker deduced the *complete* expression of Rayleigh, and has given also an *elementary* proof of the exactness of the conception of Fuchs[*]. As p_T at a definite temperature (about $\frac{4}{5} T_K$) has the value zero[†], we have for that temperature:

$$\zeta = \frac{\text{capillary constant}}{\text{vapour pressure}}.$$

We may thus, at least for the mentioned temperature, consider this quotient as the value of the thickness of the *plane* capillary layer.

If we consider such a large surface of the body, that the total mass of the capillary layer is unity, we call its surface S and consider $S\zeta = v$ as the specific volume of the capillary layer if it is plane. For the spherical capillary layer (see above) the thickness is expressed by $(R_2 - R_1)$; we represent it again by ζ. It will easily be understood that in this case:

$$v = S\zeta + \frac{1}{3}\frac{S\zeta^2}{R}.$$

For the cylindric capillary layer on the contrary we have again $v = S\zeta$, in which S belongs to the radius $R = \frac{R_1 + R_2}{2}$.

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[*] H. Hulshof, *Koninkl. Akad. v. Wetensch.* at Amsterdam, 29 Jan. 1900. G. Bakker, *Zeitschrift f. phys. Chem.* xxxiii. p. 499 (1900); and Phil. Mag. for Dec. 1906, pp. 563 & 569. See Rayleigh, "On the Theory of Surface Forces II.," Phil. Mag. Feb. 1892, formula (22).

[†] G. Bakker, Phil. Mag. Oct. 1907, p. 522, and *Zeitschr. f. phys. Chem.* i. 1905, p. 359.

The pressures in the homogeneous phases we call resp. p_l and p_v or p_1 and p_2. The specific volume of these phases we represent by v_1 and v_2.

Upon the whole we have the following significations:

ζ = Thickness of the capillary layer; dh = differential of ζ, or $\int_1^2 dh = \zeta$.

S = Surface of the plane capillary layer per unit of mass.

R_1 and R_2 = Radii of the two spheres which limit the spherical capillary layer; $R_2 > R_1$.

$R = \frac{R_1 + R_2}{2}$; S = Collective surface of the spheres with radius R, the total mass of the spherical capillary layers being unity. We call S the surface of the spherical capillary layer per unit of mass.

v = Specific volume of the capillary layer or total volume of the capillary layers of equal curvature per unit of mass.

$\frac{1}{v} = \bar{\rho}$ = Mean value of the density of the capillary layer.

p_1 or p_l = Hydrostatic pressure of the homogeneous liquid phase.

p_2 or p_v = Hydrostatic pressure of the homogeneous vapour phase.

v_1 = Spec. volume of the liquid phase; ρ_1 = its density.

v_2 = Spec. volume of the vapour phase; ρ_2 = its density.

$v_2 - v_1 = u$; $\mathfrak{p} = \frac{p_1 + p_2}{2}$; p' = pressure of the theoretical isotherm.

$p = \frac{1}{u}\int_1^2 p'dv$ = Mean value of the pressure $= \frac{p_2 v_2 - p_1 v_1}{v_2 - v_1}$;

r = latent heat of vaporization.

$r_i = r - pu$.

ϵ_1 and ϵ_2 = resp. the energy of the liquid and vapour phase. Thus: $r_i = \epsilon_2 - \epsilon_1$.

η_1 and η_2 = resp. the entropy of the liquid and vapour phase. Thus: $r = T(\eta_2 - \eta_1)$.

μ_1 and μ_2 = resp. the thermodynamic potentials.

ϵ and η = resp. the energy and entropy of the capillary layer per unit of mass.

R_K = Radius of the equation of Kelvin: $p_1 - p_2 = \frac{2H}{R_K}$.

H = Available energy, total departure of the law of Pascal per unit of surface, constant of Laplace or surface-tension.

p_N = Hydrostatical pressure in a point of the capillary layer in a direction perpendicular to its surface.

p_T = Hydrost. pressure in a direction parallel to the surface of the capillary layer.

$$p_N=\frac{1}{\zeta}\int_1^2 p_N dh;\ \bar{p}_T=\frac{1}{\zeta}\int_1^2 p_T dh;\ p_N'=\frac{1}{\zeta^2}\int_1^2 p_N dh^2; p_T'=\frac{1}{\zeta^2}\int_1^2 p_T dh^2.$$

§ 2. *The radius of curvature of a capillary layer and the equation of Kelvin.*

The thickness of a capillary layer that limits a spherical liquid mass of *measurable* curvature may be neglected with respect to the radius of the liquid mass, and it is therefore indifferent whether we consider R_1, R_2, or R.

Quite otherwise is it on the contrary if the value of R lies *e. g.* between one micron and the *minimal value* of the radius of the spherical liquid mass. In a preceding article I found that the minimum value of the radius of a liquid drop is of the same order of magnitude as the thickness of the capillary layer[*].

If R_1 and R_2 are resp. the radii of the spheres which limit the considered spherical capillary layer, we put $R=\frac{R_1+R_2}{2}$ and call R the radius of the drop. The matter within the sphere of radius R_1 should be considered as a liquid. If we call p_l the pressure in the liquid mass of the drop, p_v the pressure of the vapour which limits the drop, H the surface-tension, and R_K a value between R_1 and R_2, Kelvin found as is known:

$$p_l-p_v=\frac{2H}{R_K}. \quad \ldots \ldots \quad (1)$$

Meanwhile R_K has for very little drops a rather complicated signification. If for a point in the capillary layer we call p_N the pressure in a direction perpendicular to the surface (radial), and p_T the pressure in a direction parallel to the surface, we have:

$$\frac{dp_N}{dh}=-\frac{2(p_N-p_T)}{R'}, \quad \ldots \ldots \quad (2)^{\dagger}$$

in which dh represents the differential of the normal to the

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[*] Phil. Mag. March 1909, p. 346.

[†] G. Bakker, Phil. Mag. April 1908, p. 422, formula (17).

surface of the capillary layer, while R′ signifies the radius of the sphere we construct through the considered point concentric to the surface of the little drop. By integration of (2) I found:

$$p_l - p_v = 2\int_1^2 \frac{(p_N - p_T)dh}{R'} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The quantity R_K of Kelvin is at curvatures not too strong* consequently represented by:

$$\frac{1}{R_K}\int_1^2 (p_N - p_T)dh = \int_1^2 \frac{(p_N - p_T)dh}{R'} .$$

Generally R_K is not identical with $R = \frac{R_1 + R_2}{2}$.

We now wish to bring R_K and R into connexion with each other. For that reason we consider the equilibrium of the spherical capillary layer under the influence of the pressures resp. of the liquid (inside R_1) and of the vapour around the little drop in the same way as the hemispheres in the celebrated experiment of Otto von Guericke on the atmospherical pressure. If the thickness of the capillary layer is represented by ζ, and the pressure *parallel* to the surface for a point of the capillary layer is denoted by p_T, we find as the condition for the equilibrium:

$$\pi(R - \tfrac{1}{2}\zeta)^2 p_l - \pi(R + \tfrac{1}{2}\zeta)^2 p_v = -2\pi\int_1^2 p_T R' dh$$

$$= -2\pi\int_1^2 p_T(R - \tfrac{1}{2}\zeta + h)dh. \quad . \quad . \quad (4)$$

As the thickness of a capillary layer only amounts to few millimicrons, we may, in the case when R is of the order of a micron or larger, neglect the terms with ζ^2/R^2, and have:

$$p_l - p_v = \frac{2\zeta\left(\frac{p_l + p_v}{2} - \bar{p}_T\right)}{R}\dagger .$$

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* The surface-tension being the integral of the departure from Pascal's law with respect to the *volume* elements, and not with respect to *dh*.

† If $\int_1^2 p_T dh^2$ is represented by $p_T'\zeta^2$, the complete equation is

$$(p_l - p_v)\left(1 + \frac{\zeta^2}{4R^2}\right) = \frac{2\zeta(\mathfrak{p} - \bar{p}_T)}{R} + (p_T - p_T')\frac{\zeta^2}{R^2}; \text{ where } \mathfrak{p} = \frac{p_l + p_v}{2} .$$

If we neglect the quantities of the order $\frac{\zeta^2}{R^2}$ with respect to unity, and put $\frac{p_l+p_v}{2}=\mathfrak{p}$, we can conclude from (3) and (4):

$$R : R_K=(\mathfrak{p}-\bar{p}_T) : (p_N-\bar{p}_T). \quad . \quad . \quad . \quad . \quad (5)$$

In this consideration we might express the surface-tension of Laplace by the integral:

$$H=\int_1^2 (p_N-p_T)dh.$$

However, if we wish to be perfectly exact, we are to determine what is to be understood by surface and unity of surface of a curved capillary layer, and it is self-evident to point out the sphere of radius R as "surface of the capillary layer." The capillary energy H depends consequently at very strong curvature on so many spherical capillary layers of equal curvature that the mentioned surfaces have a total surface of unity. Let us call the surface per unit of mass of the capillary layer, S.

Through each point of the spherical capillary layer we imagine a sphere, concentric to the adequate little drops. We call points, for which the R of these spheres in the different capillary layers has the same value, homologous ones. If the totality of the surfaces of these spheres per unit of mass is S′, and R′ the corresponding radius, we have:

$$S' : S_1=(R_1+h)^2 : R_1^2,$$

if S_1 represents the total surface of the spheres with radius R_1. If we now consider the capillary energy as the volume integral of the departures from the law of Pascal, we have consequently:

$$HS=\int_1^2 S'(p_N-p_T)dh. \quad . \quad . \quad . \quad . \quad (6)$$

If we put $R'=R_1+h$, then $S' : S_1=(R_1+h)^2 : R_1^2$ or:

$$S'=S_1\left(1+\frac{2h}{R_1}+\frac{h^2}{R_1^2}\right),$$

and the capillary energy per unit *of mass* becomes:

$$HS=S_1\int_1^2 (p_N-p_T)dh+\frac{S_1}{R_1}\int_1^2 (p_N-p_T)dh^2+\frac{S_1}{3R_1^2}\int_1^2 (p_N-p_T)dh^3. \quad . \quad . \quad . \quad . \quad (7)$$

If we put:

$$\int_1^2 p_{\mathrm{N}} dh^2 = p_{\mathrm{N}}'\zeta^2, \int_1^2 p_{\mathrm{T}} dh^2 = p_{\mathrm{T}}'\zeta^2, \int_1^2 p_{\mathrm{N}} dh^3 = p_{\mathrm{N}}''\zeta^3 \text{ and } \int_1^2 p_{\mathrm{T}} dh^3 = p_{\mathrm{T}}''\zeta^3,$$

the expression for H becomes $\left(\text{because } \frac{S_1}{R_1^2} = \frac{S_2}{R_2^2}\right)$

$$H = (\bar{p}_{\mathrm{N}} - \bar{p}_{\mathrm{T}})\zeta - \frac{\zeta^2}{R}\{\bar{p}_{\mathrm{N}} - \bar{p}_{\mathrm{T}} - (p_{\mathrm{N}}' - p_{\mathrm{T}}')\}$$
$$+ \frac{\zeta^3}{R^2}\left\{\frac{\bar{p}_{\mathrm{N}} - \bar{p}_{\mathrm{T}}}{4} + \frac{p_{\mathrm{N}}'' - p_{\mathrm{T}}''}{3} - \frac{p_{\mathrm{N}}' - p_{\mathrm{T}}'}{2}\right\} \quad . \ . \ . \quad (8)$$

For the value $R=1$ micron $\frac{\zeta}{R} = \frac{1}{500}$ (about) for water at ordinary temperature, and so $\frac{\zeta^2}{R^2} = 4.10^{-6}$. If α is a quantity of the order $\bar{p}_{\mathrm{N}} - \bar{p}_{\mathrm{T}}$, we have thus for values of R to the order of the wave-length of light:

$$H = (\bar{p}_{\mathrm{N}} - \bar{p}_{\mathrm{T}})\zeta - \frac{\alpha\zeta^2}{R}. \quad . \ . \ . \ . \ . \ . \quad (9)$$

The equation of Kelvin gives thus:

$$p_l - p_v = \frac{2(\bar{p}_{\mathrm{N}} - \bar{p}_{\mathrm{T}})\zeta}{R_{\mathrm{K}}} - \frac{2\alpha\zeta^2}{R_{\mathrm{K}}R}. \quad . \ . \ . \ . \quad (10)$$

As R_{K} has a complicate signification, we wish to express $p_l - p_v$ by means of a formula, where R_{K} is replaced by

$$R.\left\{R = \frac{R_1 + R_2}{2}\right\}.$$

To this end we put the equation (2) into the form:

$$(R_1 + h)dp_{\mathrm{N}} = -2(p_{\mathrm{N}} - p_{\mathrm{T}})dh, \quad . \ . \ . \quad (2\,a)$$

and integrate with respect to h between 0 and ζ. In this way we find:

$$p_l - p_v = \frac{(\mathfrak{p} + \bar{p}_{\mathrm{N}} - 2\bar{p}_{\mathrm{T}})\zeta}{R} \quad . \ . \ . \ . \ . \ . \quad (11)$$

In this equation $\mathfrak{p} = \frac{p_l + p_v}{2}$ and $\bar{p}_{\mathrm{N}}$ and $\bar{p}_{\mathrm{T}}$ are resp. the average values of p_{N} and p_{T}; *i. e.*:

$$\frac{1}{\zeta}\int_1^2 p_{\mathrm{N}} dh \quad \text{and} \quad \frac{1}{\zeta}\int_1^2 p_{\mathrm{T}} dh.$$

For small curvatures we may put $\mathfrak{p}=\bar{p}_N$, and (11) becomes:

$$p_l-p_v=\frac{2(\bar{p}_N-\bar{p}_T)\zeta}{R},$$

whereas (10) in this case changes into:

$$p_l-p_v=\frac{2(\bar{p}_N-p_T)\zeta}{R_K}.$$

Really we may put in the latter case $R=R_K$.

§ 3. *Latent heat of vaporization and surface-tension.*

We conceive such a number of spherical capillary layers of equal curvature that they form together a unit of mass. We assume these capillary layers to be parts of spherical capillary layers that limit little drops of liquid of equal R. If the quantities which are considered refer to the homogeneous liquid phase, we denote them by the index 1, whereas we take for the homogeneous vaporous phase the index 2. If the thermodynamic potential is represented by μ, we have as the condition for the equilibrium of the capillary layer:

$$\mu_1=\mu_2 \quad \text{or} \quad \epsilon_1-T\eta_1+p_1v_1=\epsilon_2-T\eta_2+p_2v_2. \quad . \quad (12)$$

If r signifies the latent heat of vaporization, we have:

$$r=T(\eta_2-\eta_1)=\epsilon_2-\epsilon_1+p_2v_2-p_1v_1. \quad . \quad . \quad . \quad (13)$$

The matter of the equally curved capillary layers is determined by two parameters. For one of these parameters we take the temperature, while we leave the second provisionally undetermined. We differentiate while the second parameter remains constant and get:

$$\frac{dr}{dT}=\frac{d\epsilon_2}{dT}-\frac{d\epsilon_1}{dT}+p_2\frac{dv_2}{dT}-p_1\frac{dv_1}{dT}+v_2\frac{dp_2}{dT}-v_1\frac{dp_1}{dT}. \quad (14)$$

If we denote the spec. heat *at constant second parameter* by c, we have:

$$c_1=\frac{d\epsilon_1}{dT}+p_1\frac{dv_1}{dT}, \text{ and } c_2=\frac{d\epsilon_2}{dT}+p_2\frac{dv_2}{dT},$$

consequently:

$$\frac{dr}{dT}=c_2-c_1+v_2\frac{dp_2}{dT}-v_1\frac{dp_1}{dT}. \quad . \quad . \quad . \quad (15)$$

On the other hand from

$$\frac{r}{\mathrm{T}}=\eta_2-\eta_1 \text{ follows } \frac{dr}{d\mathrm{T}}-\frac{r}{\mathrm{T}}=c_2-c_1\,; \quad . \quad . \quad . \quad (16)$$

(15) and (16) give in this way:

$$\frac{r}{\mathrm{T}}=v_2\frac{dp_2}{d\mathrm{T}}-v_1\frac{dp_1}{d\mathrm{T}}. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

In the particular case when the curvature is zero $p_2=p_1$ and we get from (17) the known equation:

$$\frac{r}{v_2-v_1}=\mathrm{T}\frac{dp_1}{d\mathrm{T}},$$

in which p_1 represents the ordinary vapour pressure.

The equation (17) may be written in this way:

$$\frac{2r}{(v_2-v_1)\mathrm{T}}=\frac{dp_1}{d\mathrm{T}}+\frac{dp_2}{d\mathrm{T}}+\frac{v_1+v_2}{v_2-v_1}\left(\frac{dp_2}{d\mathrm{T}}-\frac{dp_1}{d\mathrm{T}}\right). \quad . \quad (18)$$

After Kelvin we have further:

$$p_1-p_2=\frac{2\mathrm{H}}{\mathrm{R_K}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

If we differentiate at constant $\mathrm{R_K}$ and take $\mathrm{R_K}$ in the equation (18) as second parameter we find from (19):

$$\frac{dp_1}{d\mathrm{T}}-\frac{dp_2}{d\mathrm{T}}=\frac{2}{\mathrm{R_K}}\frac{d\mathrm{H}}{d\mathrm{T}}, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and (18) becomes:

$$r=(v_2-v_1)\mathrm{T}\frac{d\mathfrak{p}}{d\mathrm{T}}-\frac{v_1+v_2}{\mathrm{R_K}}\mathrm{T}\frac{d\mathrm{H}}{d\mathrm{T}}, \quad . \quad . \quad . \quad (21)$$

in which

$$\mathfrak{p}=\frac{p_1+p_2}{2}=\frac{p_l+p_v}{2}.$$

For $\mathrm{R_K}=\infty$, *i. e.* if liquid and vapour are separated by a plane capillary layer, $p_1=p_2=\mathfrak{p}$, and the last member of (21) disappears, and we get the known equation:

$$r=(v_2-v_1)\,\mathrm{T}\frac{dp_1}{d\mathrm{T}}.$$

If p' represents the pressure of the theoretical isotherm, we put

$$p=\frac{1}{v_2-v_1}\int_1^2 p'dv,$$

or as

$$p_2v_2-p_1v_1=\int_1^2 p'dv,$$

we have

$$\frac{p_2v_2-p_1v_1}{v_2-v_1}=p.$$

We can easily prove the identity:

$$\mathfrak{p}-p=\frac{v_1+v_2}{v_2-v_1}\frac{p_1-p_2}{2}.$$

Consequently, if v_2-v_1 is replaced by u:

$$\mathfrak{p}u-pu=(v_1+v_2)\frac{\mathrm{H}}{\mathrm{R}_{\kappa}}.$$

By substitution in (21):

$$r_i=r-pu=u\left(\mathrm{T}\frac{d\mathfrak{p}}{d\mathrm{T}}-\mathfrak{p}\right)+\frac{v_1+v_2}{\mathrm{R}_{\kappa}}\left(\mathrm{H}-\mathrm{T}\frac{d\mathrm{H}}{d\mathrm{T}}\right). \quad . \quad (22)$$

If a is the coefficient of the Laplace expression for the molecular pressure $a\rho^2$ and the thermic pressure of the form $\mathrm{T}f(v)$, I have found:

$$r_i=\left(a-\mathrm{T}\frac{da}{d\mathrm{T}}\right)(\rho_1-\rho_2)^*.$$

In the case when the equation of state is of the form:

$$p=\mathrm{T}f(v)-\frac{a}{v^2},$$

where a represents a temperature function, we have thus:

$$\left(a-\mathrm{T}\frac{da}{d\mathrm{T}}\right)\rho_1\rho_2=\mathrm{T}\frac{d\mathfrak{p}}{d\mathrm{T}}-\mathfrak{p}+\frac{v_1+v_2}{\mathrm{R}_{\kappa}}\left(\mathrm{H}-\mathrm{T}\frac{d\mathrm{H}}{d\mathrm{T}}\right).$$

The identity:

$$\mathfrak{p}-p=\frac{v_1+v_2}{v_2-v_1}\frac{p_1-p_2}{2}$$

gives by differentiation with respect to T, with second parameter constant:

$$\frac{d(\mathfrak{p}-p)}{d\mathrm{T}}=\frac{v_1+v_2}{v_2-v_1}\frac{d}{d\mathrm{T}}\left(\frac{p_1-p_2}{2}\right)+\frac{p_1-p_2}{2}\frac{d}{d\mathrm{T}}\left(\frac{v_1+v_2}{v_2-v_1}\right), \quad (23)$$

(23) and (18) consequently give in general:

$$\frac{r}{u}-\mathrm{T}\frac{dp}{d\mathrm{T}}=\frac{\mathrm{H}}{\mathrm{R}_{\kappa}}\mathrm{T}\frac{d}{d\mathrm{T}}\left(\frac{v_1+v_2}{v_2-v_1}\right). \quad . \quad . \quad . \quad (24)$$

These relations we shall use in § 4.

§ 4. *The equation of energy of the capillary layer.*

If x and $1-x$ are resp. the quantities of the liquid and vapour, which have formed the capillary layer without

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* *Zeitschrift f. phys. Chemie*, xii. p. 283 (1893).

changing volume and mass, and v the specific volume of the capillary layer, we have:

$$\frac{x}{\rho_1}+\frac{1-x}{\rho_2}=v, \text{ or } x=\frac{\rho_1-v\rho_1\rho_2}{\rho_1-\rho_2}, \text{ and } 1-x=\frac{v\rho_1\rho_2-\rho_2}{\rho_1-\rho_2}.$$

Per unit of mass of the capillary layer the available energy, which the homogeneous phases have engendered, becomes:

$$\frac{\rho_1-v\rho_1\rho_2}{\rho_1-\rho_2}(\mu_1-p_1v_1)+\frac{v\rho_1\rho_2-\rho_2}{\rho_1-\rho_2}(\mu_1-p_2v_2)$$
$$=\mu_1+\frac{p_2-p_1}{\rho_1-\rho_2}+v\frac{p_1v_1-p_2v_2}{v_2-v_1}.$$

As we mentioned above we have:

$$\frac{p_2v_2-p_1v_1}{v_2-v_1}=\frac{1}{v_2-v_1}\int_1^2 p'dv=p.$$

So the last expression becomes

$$\mu_1-\frac{p_1-p_2}{\rho_1-\rho_2}-pv. \quad . \quad . \quad . \quad . \quad . \quad (25)$$

If, consequently, the surface of the capillary layer per unity of mass is S, the available energy of the capillary layer is given by:

$$\epsilon-\mathrm{T}\eta=\mu_1-\frac{p_1-p_2}{\rho_1-\rho_2}-pv+\mathrm{HS}. \quad . \quad . \quad . \quad (26)$$

For, what we *usually* call the capillary energy per unity of mass and represent by HS is the *difference* between $\epsilon-\mathrm{T}\eta$ and the expression (25). Further we have:

$$\mu_1=\frac{\epsilon_1+\epsilon_2}{2}-\mathrm{T}\frac{\eta_1+\eta_2}{2}+\frac{p_1v_1+p_2v_2}{2}.$$

After a simple deduction (26) becomes therefore:

$$\epsilon-\frac{\epsilon_1+\epsilon_2}{2}-\mathrm{T}\left(\eta-\frac{\eta_1+\eta_2}{2}\right)+p\left(v-\frac{v_1+v_2}{2}\right)=\mathrm{HS}^{*}. \qquad (27)$$

For a *plane* capillary layer p becomes the ordinary vapour pressure, and we find the equation for this case, as I have found already in a preceding paper[†].

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[*] $p=\frac{1}{v_2-v_1}\int_1^2 p'dv$, where p' denotes the pressure of the theoretical isotherm (see above).

[†] *Ann. d. Phys.* xvii. p. 492 (1905).

A second thermodynamic relation we find in the following manner. If we evaporate a quantity of the liquid phase given by the expression

$$1-x=\frac{v\rho_1\rho_2-\rho_2}{\rho_1-\rho_2} \quad \text{(see above)},$$

we get precisely the complex of the two homogeneous phases, which can form unit of mass of the capillary layer. The corresponding heat of vaporization is expressed by

$$\frac{v\rho_1\rho_2-\rho_2}{\rho_1-\rho_2}\,.\,r=(v-v_1)\frac{r}{u}.$$

If we further convert the complex into the matter of the capillary layer, we must still add a quantity of heat per unit of mass, expressed by $-\mathrm{T}\frac{d\mathrm{H}}{d\mathrm{T}}\mathrm{S}$. We have therefore:

$$\eta-\eta_1=-\mathrm{S}\frac{d\mathrm{H}}{d\mathrm{T}}+(v-v_1)\frac{r}{u\mathrm{T}}\,^{*}.$$

In the same manner we have:

$$\eta_2-\eta=\mathrm{S}\frac{d\mathrm{H}}{d\mathrm{T}}+(v_2-v)\frac{r}{u\mathrm{T}}.$$

Hence:

$$\eta-\frac{\eta_1+\eta_2}{2}=-\mathrm{S}\frac{d\mathrm{H}}{d\mathrm{T}}+\left(v-\frac{v_1+v_2}{2}\right)\frac{r}{u\mathrm{T}}, \quad . \quad . \quad (28)$$

where $u=v_2-v_1$ represents the difference between the specific volumes of the liquid and vapour.

From the equations (27) and (28) we can now deduce the equation of energy in the following way: by differentiation of (27) we find:

$$d\epsilon-\mathrm{T}d\eta-\tfrac{1}{2}(d\epsilon_1-\mathrm{T}d\eta_1)-\tfrac{1}{2}(d\epsilon_2-\mathrm{T}d\eta_2)-\left(\eta-\frac{\eta_1+\eta_2}{2}\right)d\mathrm{T}$$
$$+d\left\{p\left(v-\frac{v_1+v_2}{2}\right)\right\}=\mathrm{H}d\mathrm{S}+\mathrm{S}d\mathrm{H}. \quad . \quad (29)$$

By substitution of the expression (28) for $\eta-\frac{\eta_1+\eta_2}{2}$, and as:

$$d\epsilon-\mathrm{T}d\eta_1=-p_1dv_1 \qquad \text{and} \qquad d\epsilon_2-\mathrm{T}d\eta_2=-p_2dv_2:$$

$$d\epsilon_1-\mathrm{T}d\eta-\mathrm{H}d\mathrm{S}=-\tfrac{1}{2}\,p_1dv_1-\tfrac{1}{2}\,p_2dv_2+\left(v-\frac{v_1+v_2}{2}\right)$$
$$\left(\frac{r}{u\mathrm{T}}d\mathrm{T}-dp\right)-pd\left(v-\frac{v_1+v_2}{2}\right).$$

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* In another way I have deduced this relation in *Ann. d. Phys.* xvii. p. 496 (1905), formula (37).

We had:

$$\frac{r}{u\mathrm{T}}-\frac{dp}{d\mathrm{T}}=\frac{p_1-p_2}{2}\frac{d}{d\mathrm{T}}\left(\frac{v_1+v_2}{v_2-v_1}\right) \text{ (see above).} \quad . \quad . \quad (24)$$

Consequently:

$$d\epsilon-\mathrm{T}d\eta-\mathrm{H}d\mathrm{S}=\tfrac{1}{2}(p-p_1)dv_1+\tfrac{1}{2}(p-p_2)dv_2+\frac{p_1-p_2}{2}vd\left(\frac{v_1+v_2}{v_2-v_1}\right)$$
$$-\frac{p_1-p_2}{2}\,\frac{v_1+v_2}{2}d\frac{v_1+v_2}{v_2-v_1}+\frac{p_1-p_2}{2}\,\frac{v_1+v_2}{v_2-v_1}dv-pdv.$$

We have

$$p_1-p=\frac{v_2}{v_2-v_1}(p_1-p_2) \quad \text{and} \quad p_2-p=\frac{v_1}{v_2-v_1}(p_1-p_2),$$

and we get therefore:

$$\mathrm{T}d\eta=d\epsilon+pdv-\mathrm{H}d\mathrm{S}-\frac{p_1-p_2}{2}d\left\{v\frac{v_1+v_2}{v_2-v_1}\right\}$$
$$+\frac{p_1-p_2}{2}\left\{\frac{v_2dv_1+v_1dv_2}{v_2-v_1}+\frac{v_1+v_2}{2}d\frac{v_1+v_2}{v_2-v_1}\right\}.$$

Further we have:

$$\frac{v_2dv_1+v_1dv_2}{v_2-v_1}+\frac{v_1+v_2}{2}d\frac{v_1+v_2}{v_2-v_1}=\frac{2v_2^2dv_1-2v_1^2dv_2}{(v_2-v_1)^2}=d\frac{2v_1v_2}{v_2-v_1}.$$

So the equation of energy of the capillary layer becomes:

$$\mathrm{T}d\eta=d\epsilon+pdv-\mathrm{H}d\mathrm{S}+\frac{p_1-p_2}{2}d\left\{\frac{2v_1v_2}{v_2-v_1}-v\frac{v_1+v_2}{v_2-v_1}\right\}^*. \quad (30)$$

In the equation (28) the differential quotient $\frac{d\mathrm{H}}{d\mathrm{T}}$ is partial, the second parameter being constant. In the equation (30) we must conceive R is the constant. The state of the *plane* capillary layer is completely determined by one parameter. This parameter is in the present consideration the temperature, and we may now state for the *plane* capillary layer:

$$\mathrm{T}d\eta=d\epsilon+pdv-\mathrm{H}d\mathrm{S}, \quad . \quad . \quad . \quad . \quad (31)$$

in this case: $p_1=p_2=$ ordinary vapour pressure.

The equation (31) is also easily to be deduced directly. For if ζ is the thickness of the plane capillary layer and

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* The general equation of energy of the capillary layer becomes:

$$\mathrm{T}d\eta=d\epsilon+pdv-\mathrm{H}ds-\mathrm{S}\left(\frac{d\mathrm{H}}{d\mathrm{R}}\right)_{\mathrm{T}}d\mathrm{R}+\frac{p_1-p_2}{2}d\left\{\frac{2v_1v_2}{v_2-v_1}-v\frac{v_1+v_2}{v_2-v_1}\right\}.$$

$\mathfrak{p}$ represents the ordinary vapour pressure, $S\mathfrak{p}d\zeta$ is the work done by $\mathfrak{p}$, and $\bar{p}_T\zeta dS$ that done by $\bar{p}_T$. So we have:

$$Td\eta = d\epsilon + S\mathfrak{p}d\zeta + \bar{p}_T\zeta dS.$$

Now, however,

$$H = (\bar{p}_N - \bar{p}_T)\zeta \quad \text{and} \quad v = \zeta S.$$

So we get:

$$Td\eta = d\epsilon + \mathfrak{p}dv - \mathfrak{p}\zeta dS + \bar{p}_T\zeta dS.$$

Further, for the *plane* capillary layer:

$$p_1 = p_2 = \mathfrak{p} = \bar{p}_N = \text{ordinary vapour pressure.}$$

Hence $$Td\eta = d\epsilon + \mathfrak{p}dv - (\bar{p}_N - \bar{p}_T)\zeta dS,$$

or $$Td\eta = d\epsilon + \mathfrak{p}dv - HdS. \quad \ldots\ldots \quad (31)$$

For the curved capillary layer we may also deduce the equation of energy without having recourse to the equations (27) and (28).

If as above S_1, S, and S_2 are the total surface, which refer to the radii R_1, R, and R_2 (per unit of mass of the capillary layer), we have for the work done by p_1 and p_2:

$$S_2 p_2(dR + \tfrac{1}{2}d\zeta) - S_1 p_1(dR - \tfrac{1}{2}d\zeta).$$

For unchanged R consequently:

$$\tfrac{1}{2}S_2 p_2 p\zeta + \tfrac{1}{2}S_1 p_1 d\zeta.$$

Further we have:

$$S_1 = \left(1 - \frac{\zeta}{R} + \frac{\zeta^2}{4R^2}\right)S \quad \text{and} \quad S_2 = \left(1 + \frac{\zeta}{R} + \frac{\zeta^2}{4R^2}\right)S.$$

The work done by p_1 and p_2 becomes consequently:

$$\mathfrak{p}S\left(1 + \frac{\zeta^2}{4R^2}\right)d\zeta - \tfrac{1}{2}(p_1 - p_2)\frac{\zeta S}{R}d\zeta.$$

For values of R of the order of a micron $p_1 - p_2$ is of the order $\frac{1}{1000}$ against $\mathfrak{p}$. For values of R of the order of a wave-length of light or larger, we may thus put for the work done by p_1 and p_2:

$$\mathfrak{p}Sd\zeta.$$

The work done by the pressure $\bar{p}_T$ (in a direction parallel to the surface of the capillary layer) becomes:

$$\Sigma\, dS_1\, p_T dh\left(1 + \frac{2h}{R_1} + \frac{h^2}{R_1{}^2}\right) = dS_1\zeta\bar{p}_T + \frac{dS_1}{R_1}\zeta^2 p_T', \quad (32)$$

where $$p_T' = \frac{1}{\zeta^2}\int_1^2 p_T\, dh^2.$$

The members with $\frac{\zeta^2}{R^2}$ are again neglected.

To find an expression for p_T', we multiply the equation ($2\,a$) with h and integrate with respect to h. In this way we find

$$R_1\zeta p_2 - R_1\bar{p}_N\zeta + \zeta^2 p_2 = p_T'\zeta^2,$$

or as: $R_1 = R - \frac{1}{2}\zeta,$

$$p_T'\zeta^2 = R\zeta\left(1+\frac{\zeta}{2R}\right)p_2 - R\zeta\left(1-\frac{\zeta}{2R}\right)\bar{p}_N.$$

By substitution in (32) the expression for the work done by $\bar{p}_T$ becomes:

$$dS_1\zeta\bar{p}_T + \frac{dS_1}{R_1}R\zeta\left(1+\frac{\zeta}{2R}\right)p_2 - \frac{dS_1}{R_1}R\zeta\left(1-\frac{\zeta}{2R}\right)\bar{p}_N.$$

Further we have: $\frac{R_1}{R} = 1 - \frac{\zeta}{2R}$. Neglecting the terms with $\frac{\zeta^2}{4R^2}$, we have for the work done by $\bar{p}_T$:

$$p_2\zeta\, dS - \left(1-\frac{\zeta}{R}\right)\zeta(\bar{p}_N - \bar{p}_T)\, dS,$$

and the total work becomes:

$$\mathfrak{p}S d\zeta + p_2\zeta\, dS - \left(1-\frac{\zeta}{R}\right)\zeta(\bar{p}_N - \bar{p}_T)\, dS. \quad . \quad (33)$$

If we had written the equation ($2\,a$) in the form:

$$(R_2 - h)\, dp_N = 2(p_N - p_T)\, dh,$$

and had taken dh in the opposite sense to that adopted above, we should have found (by substitution of the expression for p_T' in (32)) for the work done by $\bar{p}_T$:

$$dS\left(1+\frac{\zeta}{R}\right)\zeta\bar{p}_T + p_1\zeta\, dS - dS\zeta\bar{p}_N\left(1+\frac{\zeta}{R}\right).$$

The total work may be expressed thus by:

$$\mathfrak{p}S d\zeta + p_1\zeta\, dS - \left(1+\frac{\zeta}{R}\right)\zeta(\bar{p}_N - \bar{p}_T)\, dS, \quad . \quad (34)$$

or if we take half the sum of (33) and (34) the work is expressed by:

$$\mathfrak{p}(S d\zeta + \zeta\, dS) - \zeta(\bar{p}_N - \bar{p}_T)\, dS\,^{*}, \quad . \quad . \quad . \quad (35)$$

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* For the *plane* capillary layer we have: $v = s\zeta$ and $H = (\bar{p}_N - \bar{p}_T)\zeta$. The expression (35) becomes, therefore, for the *plane* capillary layer: $\mathfrak{p}dv - H dS$.

The equation of energy of the curved capillary layer becomes, therefore, for values of R of the order of a wavelength of light or greater:

$$Td\eta = d\epsilon + \mathfrak{p}(Sd\zeta + \zeta dS) - \frac{p_1 - p_2}{2} RdS, \quad . \quad . \quad (36)$$

where R must be conceived as constant.

If R is measurable or has a value not smaller than a micron, we have:

$$Sd\zeta + \zeta dS = dv \quad \text{and} \quad \frac{p_1 - p_2}{2} R = H,$$

and (36) becomes:

$$Td\eta = d\epsilon + \mathfrak{p}dv - HdS.$$

The equation (30), however, is contrary to (36) quite exact.

§ 5. *The plane capillary layer considered as the limit of a cylindrical.*

The formulæ simplify when we consider a cylindrical capillary layer instead of a spherical one. The condition for the equilibrium *e. g.* gives instead of the equation (11, § 2) the more simple one:

$$p_l - p_v = \frac{(\mathfrak{p} - \bar{p}_T)\zeta}{R}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

in the case when the liquid is inside the capillary layer (liquid drop).

If, however, the cylindrical capillary turns its concave side to the vapour (bubble of vapour), we get:

$$p_v - p_l \frac{(\mathfrak{p} - \bar{p}_T)\zeta}{R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

In order to deduce the equation (37) we consider the cylindrical capillary layer simply like a tube under the influence of an inward pressure p_l and an outward one p_v. Instead of p_v and p_l, we put as above: p_2 and p_1. If the corresponding quantities are represented by the same letters as in the consideration of the spherical layer, and z denote the total length of the cylindrical capillary layers of equal curvature, the condition for the equilibrium gives immediately:

$$2R_1 z p_1 - 2R_2 z p_2 = -z \int_1^2 p_T \, dh, \quad . \quad . \quad . \quad (39)$$

or:

$$p_1 - p_2 = \frac{\zeta(\mathfrak{p} - \bar{p}_T)}{R}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

where R represents again half the sum $\frac{R_1 + R_2}{2}$ of the inner and outer radii.

As for a cylindrical capillary layer the curvature is $\frac{1}{R}$ and only the half of the curvature of a spherical capillary layer with the same R, we have instead of the equation (2*a*)(§ 2):

$$dp_N(R_1+h)=-(p_N-p_T)\,dh. \quad . \quad . \quad . \quad (41)$$

By integration with respect to h:

$$R_1(p_2-p_1)+\zeta p_2-\int_1^2 p_N\,dh=-\int_1^2 p_N\,dh+\int_1^2 p_T\,dh,$$

$$\text{or:} \qquad p_1-p_2=\frac{\zeta(\mathfrak{p}-\bar{p}_T)}{R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

In order to deduce the equation of energy we calculate firstly the work done by the pressure p_l, p_v, and p_T.

The capillary layer (per unit of mass) is determined by two parameters, and we consider the temperature to be variable while R = constant.

The work done by p_2 and p_1 becomes:

$$\tfrac{1}{2}S_2p_2d\zeta+\tfrac{1}{2}S_1p_1d\zeta,$$

or, whereas $S_2=S\left(1+\frac{\zeta}{2R}\right)$ and $S_1=S\left(1-\frac{\zeta}{2R}\right)$,

$$\mathfrak{p}Sd\zeta+\frac{\zeta}{4R}Sd\zeta(p_2-p_1).$$

The work done by the pressure p_T parallel to the capillary layer becomes further:

$$\Sigma dS_1\,p_Tdh\left(1+\frac{h}{R_1}\right)=dS_1\zeta\bar{p}_T+\frac{dS_1}{2R_1}p_T'\zeta^2$$
$$=dS\left(1-\frac{\zeta}{2R}\right)\zeta\bar{p}_T+\frac{dS}{2R}p_T'\zeta^2\,{}^*.$$

The total work becomes consequently:

$$\mathfrak{p}Sd\zeta-\frac{\zeta}{4R}Sd\zeta\,(p_1-p_2)+dS\left(1-\frac{\zeta}{2R}\right)\zeta\bar{p}_T+\frac{dS}{2R}p_T'\zeta^2. \quad (42)$$

By multiplication of (41) by h and integration, we find easily:

$$R(p_2-\bar{p}_N)+\tfrac{1}{2}\zeta\bar{p}_N+\tfrac{1}{2}\zeta p_2=\tfrac{1}{2}p_N'\zeta+\tfrac{1}{2}p_T'\zeta, \quad . \quad (43)$$

where

$$p_N'=\frac{1}{\zeta^2}\int_1^2 p_N\,dh^2.$$

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* For $dS'=2\pi R'dz$, consequently $\Sigma\, 2\pi R'dh\,p_T\,dz=\Sigma\, dS'\,p_T\,dh$.

The capillary energy per unit of mass, or the volume integral of the departure $p_N - p_T$ from the law of Pascal is:

$$HS = \int_1^2 S' (p_N - p_T)\, dh = S_1 \int_1^2 \left(1 + \frac{h}{R_1}\right)(p_N - p_T)\, dh$$

$$= S\left(1 - \frac{\zeta}{2R}\right)\zeta\,(\bar{p}_N - \bar{p}_T) + \frac{S}{2R}\zeta^2\,(p^{N\prime} - p_T{}'),$$

or: $$H = \zeta\,(\bar{p}_N - \bar{p}_T) - \frac{\zeta^2}{2R}\{(\bar{p}_N - \bar{p}_T) - (p_N{}' - p_T{}')\}. \quad (44)$$

From (43) and (44) we easily find by elimination of $p_N{}'$:

$$\zeta p_T{}' = (R + \tfrac{1}{2}\zeta)\, p_2 - (R - \tfrac{1}{2}\zeta)\, \bar{p}_T - \frac{R}{\zeta} H. \quad . \quad (45)$$

The expression for the work done by the pressures p_1, p_2, and p_T becomes therefore:

$$\mathfrak{p} S d\zeta + \tfrac{1}{2} dS \zeta p_2 + \tfrac{1}{2} dS \zeta \bar{p}_T - \tfrac{1}{2} H dS + \frac{\zeta}{4R} S d\zeta\,(p_2 - p_1)$$

$$+ \frac{\zeta\, dS}{2R}\{\tfrac{1}{2}\zeta p_2 - \tfrac{1}{2}\zeta \bar{p}_T\}. \quad . \quad . \quad (46)$$

Now we have: $$\bar{p}_T \zeta = (R + \tfrac{1}{2}\zeta) p_2 - (R - \tfrac{1}{2}\zeta)\, p_1. \quad . \quad (37)$$

By substitution in (46):

$$\mathfrak{p}(S d\zeta + \zeta dS) - \tfrac{1}{2} H dS - \tfrac{1}{2} R dS (p_1 - p_2) - \frac{\zeta}{8R}(p_1 - p_2)\{2 S d\zeta + \zeta dS$$

$$. \quad . \quad . \quad . \quad (47).$$

Further we have:

$$v = \pi(R_2{}^2 - R_1{}^2)z = \pi\zeta\,(R_1 + R_2)z = 2\pi\zeta R z = S\zeta;$$

hence: $$dv = S\, d\zeta + \zeta\, dS.$$

The expression for the work done by the capillary layer becomes therefore:

$$\mathfrak{p} dv - \tfrac{1}{2} H \left(1 + \frac{R}{R_K}\right) dS - \frac{p_1 - p_2}{2} \cdot \frac{1}{4R} d\,(\zeta v)\ *.$$

The equation of energy of the cylindrical capillary layer per unit of mass becomes consequently:

$$T d\eta = d\epsilon + \mathfrak{p} dv - \tfrac{1}{2} H \left(1 + \frac{R}{R_K}\right) dS - \frac{p_1 - p_2}{8R} d\,(\zeta v). \quad (48)$$

* For $\zeta\,(2 S d\zeta + \zeta dS) = \zeta\,(dv + S d\zeta) = \zeta dv + v d\zeta = d(v\zeta)$.

The considerations, which the equations (27) and (28) produced, may be applied also to a cylindrical capillary layer. Quite in the same way as in § 4, we find again :

$$\mathrm{T}d\eta = d\epsilon + \mathfrak{p}dv - \mathrm{H}d\mathrm{S} + \frac{p_1-p_2}{2}\, d\left\{\frac{2v_1v_2}{v_2-v_1} - v\frac{v_1+v_2}{v_2-v_1}\right\}, \quad (30)$$

(48) and (30) give :

$$(\mathrm{R}_{\mathrm{K}}-\mathrm{R})\, d\mathrm{S} = d\left\{\frac{2v_1v_2}{v_2-v_1} - v\frac{v_1+v_2}{v_2-v_1}\right\} + \frac{1}{4\mathrm{R}}\, d\,(\zeta v). \quad (49)$$

On the other hand we have :

$$2v\frac{\dot{p}_{\mathrm{N}}-\mathfrak{p}}{p_1-p_2} = \frac{2v_1v_2}{v_2-v_1} - v\frac{v_1+v_2}{v_3-v_1}, \quad . \quad . \quad . \quad (50)$$

where $\dot{p}_{\mathrm{N}}v$ denotes the volume integral of the pressure p_{N}, or :

$$\dot{p}_{\mathrm{N}} = \frac{1}{\zeta\mathrm{S}}\int_1^2 \mathrm{S}'p_{\mathrm{N}}\, dh.$$

This relation (50) we prove in the following way :—

At the formation of the unit of mass of the capillary layer the quantities of liquid and vapour which have produced the matter of the capillary layer, were :

$$\frac{\rho_1-v\rho_1\rho_2}{\rho_1-\rho_2} \quad \text{and} \quad \frac{v\rho_1\rho_2-\rho_2}{\rho_1-\rho_2} \quad \text{(see above § 4).}$$

The available energy which has *disappeared* is consequently:

$$-\left\{\frac{\rho_1-v\rho_1\rho_2}{\rho_1-\rho_2}p_1v_1 + \frac{v\rho_1\rho_2-\rho_2}{\rho_1-\rho_2}p_2v_2\right\} = -\left\{\frac{p_1-p_2}{\rho_1-\rho_2} + pv\right\}. \quad . \quad . \quad . \quad . \quad (51)$$

If $\bar{\rho}$ represents the average value of the density of the capillary layer, we have for the last expression :

$$-\left\{p + \frac{\bar{\rho}}{\rho_1-\rho_2}(p_1-p_2)\right\}v.$$

If $\dot{p}_{\mathrm{T}} = \frac{1}{\zeta\mathrm{S}}\int_1^2 \mathrm{S}'p_{\mathrm{T}}\, dh$, we may consider $-\dot{p}_{\mathrm{T}}v$ as the available energy which is *gained* at the formation of a unit of mass of the capillary layer.

The change of the available energy at the formation of the capillary layer per unit of mass, *i.e.* the capillary energy HS, consequently becomes :

$$\mathrm{HS} = \left\{p + \frac{\bar{\rho}}{\rho_1-\rho_2}(p_1-p_2) - \dot{p}_{\mathrm{T}}\right\}v. \quad . \quad . \quad (52)$$

On the other hand we have:

$$\mathrm{HS}=(\dot{p}_{\mathrm{N}}-\dot{p}_{\mathrm{T}})v,$$

and therefore:

$$\dot{p}_{\mathrm{N}}-p=\frac{\bar{\rho}}{\rho_1-\rho_2}(p_1-p_2). \quad . \quad . \quad . \quad . \quad . \qquad (53)$$

By means of the identity:

$$\mathfrak{p}=p+\frac{\rho_1+\rho_2}{\rho_1-\rho_2}\left(\frac{p_1-p_2}{2}\right),$$

we find immediately:

$$\frac{\dot{p}_{\mathrm{N}}-\mathfrak{p}}{p_1-p_2}=\frac{\bar{\rho}-\dfrac{\rho_1+\rho_2}{2},}{\rho_1-\rho_2} \quad . \quad . \quad . \quad . \quad . \qquad (50')$$

which is the equation (50).

Now we have:

$$v\,\dot{p}_{\mathrm{N}}=\int_1^2 \mathrm{S}'\,p_{\mathrm{N}}\,dh=\mathrm{S}\zeta\left(1-\frac{\zeta}{2\mathrm{R}}\right)\bar{p}_{\mathrm{N}}+\mathrm{S}\frac{\zeta^2}{2\mathrm{R}}\,p_{\mathrm{N}}'. \qquad (54)$$

Further we found

$$\mathrm{R}(p_2-\bar{p}_{\mathrm{N}})-\tfrac{1}{2}\zeta\,\bar{p}_{\mathrm{N}}+\tfrac{1}{2}\zeta\,p_2-\tfrac{1}{2}p_{\mathrm{N}}'\zeta+p_{\mathrm{T}}'\zeta, \quad . \qquad (43)$$

and

$$\mathrm{H}=\zeta(\bar{p}_{\mathrm{N}}-p_{\mathrm{T}})-\frac{\zeta^2}{2\mathrm{R}}\{\bar{p}_{\mathrm{N}}-\bar{p}_{\mathrm{T}}-(p_{\mathrm{N}}'-p_{\mathrm{T}}')\}. \qquad (44)$$

From (54), (43), (44), and (37) we easily find:

$$\zeta\mathrm{S}\,\dot{p}_{\mathrm{N}}=\int_1^2 \mathrm{S}'\,p_{\mathrm{N}}\,dh=\tfrac{1}{2}\mathrm{HS}+\frac{\zeta\mathrm{S}}{2}\bar{p}_{\mathrm{T}}\left(1-\frac{\zeta}{2\mathrm{R}}\right)+\frac{\zeta\mathrm{S}}{2}p_2\left(1+\frac{\zeta}{2\mathrm{R}}\right);$$
$$. \quad . \quad . \quad . \quad . \qquad (55)$$

or by substitution of $\dot{p}_{\mathrm{N}}$ in (50):

$$\mathrm{H}-(p_1-p_2)\left(\mathrm{R}+\frac{\zeta^2}{4\mathrm{R}}\right)=(p_1-p_2)\,\zeta\frac{2\bar{\rho}-(\rho_1+\rho_2)}{\rho_1-\rho_2}. \qquad (56)$$

Further we have: $\dfrac{\mathrm{H}}{p_1-p_2}=\mathrm{R}_{\mathrm{K}}$. So the equation (56) becomes:

$$\mathrm{R}_{\mathrm{K}}-\mathrm{R}=\zeta\frac{2\bar{\rho}-(\rho_1+\rho_2)}{\rho_1-\rho_2}+\frac{\zeta^2}{4\mathrm{R}}, \quad . \quad . \quad . \qquad (57)$$

or

$$\mathrm{S}(\mathrm{R}_{\mathrm{K}}-\mathrm{R})=\frac{\zeta v}{4\mathrm{R}}+\frac{2v_1v_2}{v_2-v_1}-v\frac{v_1+v_2}{v_2-v_1}. \quad . \qquad (58)$$

By differentiation of (58):

$$S d(R_K - R) + (R_K - R) dS = d \frac{\zeta v}{4R} + d\left\{ \frac{2v_1 v_2}{v_2 - v_1} - v \frac{v_1 + v_2}{v_2 - v_1} \right\}. \quad . \quad . \quad . \quad . \quad (59)$$

Now we had:

$$(R_K - R) dS = \frac{1}{4R} d(\zeta v) + d\left\{ \frac{2v_1 v_2}{v_2 - v_1} - v \frac{v_1 + v_2}{v_2 - v_1} \right\}. \quad (55)$$

I. e., if the temperature is changed by *constant* value of R, we have:

$$S d(R_K - R) = S dR_K = 0.$$

If $R = \frac{R_1 + R_2}{2}$ remains unchanged so does also the Kelvin quantity R_K. At the critical temperature:

$$\bar{\rho} = \frac{\rho_1 + \rho_2}{2} \quad \text{and} \quad \rho_1 - \rho_2 = 0.$$

Hence:

$$\frac{\bar{\rho} - \frac{\rho_1 + \rho_2}{2}}{\rho_1 - \rho_2} = \frac{0}{0} = \frac{\frac{d}{dT}\left\{ \bar{\rho} - \frac{\rho_1 + \rho_2}{2} \right\}}{\frac{d(\rho_1 - \rho_2)}{dT}}.$$

In the neighbourhood of the critical temperature the difference $\bar{\rho} - \frac{\rho_1 + \rho_2}{2}$ is *always* small, and $\frac{d}{dT}\left(\bar{\rho} - \frac{\rho_1 + \rho_2}{2}\right)$ is therefore *at* the critical temperature null or finite. Further we have at the critical temperature:

$$\frac{d\rho_1}{dT} = -\infty \quad \text{and} \quad \frac{d\rho_2}{dT} = \infty.$$

Hence:

$$\lim. \frac{\bar{\rho} - \frac{\rho_1 + \rho_2}{2}}{\rho_1 - \rho_2} = \frac{\frac{d}{dT}\left\{ \bar{\rho} - \frac{\rho_1 + \rho_2}{2} \right\}}{\frac{d(\rho_1 - \rho_2)}{dT}} = \frac{\text{null or finite}}{-\infty - \infty} = 0.$$

The equation (57) becomes, therefore, at the critical temperature:

$$R_K - R = \frac{\zeta_K^2}{4R}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

where ζ_K denotes the thickness of the capillary layer at the critical temperature.

The equation (57) becomes thus :

$$\frac{\bar{\rho}-\frac{\rho_1+\rho_2}{2}}{\rho_1-\rho_2}=\frac{\zeta_K{}^2-\zeta^2}{8R\zeta}. \quad . \quad . \quad . \quad . \quad (61)$$

If we now consider the plane capillary layer as a limit-case of the cylindrical of small curvature, we must take in (61) $R=\infty$. As $\zeta_K{}^2-\zeta^2$ always remains small, we have

$$\lim. \frac{\bar{\rho}-\frac{\rho_1+\rho_2}{2}}{\rho_1-\rho_2}=0 \quad \text{for } R=\infty.$$

So we have for the *plane* capillary layer $\bar{\rho}=\frac{\rho_1+\rho_2}{2}$.

I.e.: if we have a *plane* capillary layer the volume of which amounts to one cm^3*, this capillary layer contains as much matter as the totality of half a cm^3 of liquid and half a cm^3 of vapour.

For the contribution of the liquid resp. vapour at the formation of the capillary layer (per unit of mass) (see § 4) we found :

$$x=\frac{\rho_1-v\rho_1\rho_2}{\rho_1-\rho_2} \quad \text{and} \quad 1-x=\frac{v\rho_1\rho_2-\rho_2}{\rho_1-\rho_2}.$$

For the *plane* capillary layer these quantities are thus :

$$\left(\frac{1}{v}=\bar{\rho} \text{ being } \frac{\rho_1+\rho_2}{2}\right)$$

$$\frac{\rho_1}{\rho_1+\rho_2} \quad \text{and} \quad \frac{\rho_2}{\rho_1+\rho_2}.$$

Liquid and vapour contribute consequently to the plane capillary layer quantities resp. proportional to their densities.

In consequence of the law of Cailletet and Mathias (the so-called law of the rectilinear diameter) $\rho_1+\rho_2$ is in the case when the homogeneous phases of the liquid and the vapour are separated by a *plane* capillary layer a decreasing linear function of the temperature, or

$$\frac{\rho_1+\rho_2}{2}=\rho_K+\alpha(T_K-T),$$

where α represents a constant, ρ_K the critical density, and T_K the critical temperature.

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* For water at ordinary temperature the surface of the considered capillary layer becomes about 500 m^2.

We have thus for the plane capillary layer in the case when the law of Cailletet and Mathias applies:

$$\bar{\rho} = \rho_{\mathrm{K}} + \alpha(\mathrm{T}_{\mathrm{K}} - \mathrm{T}),$$

or:

The average density of a plane capillary layer is a decreasing linear function of the temperature.

XIII. *On the Bending of Electric Waves round a Large Sphere*: II. *By* J. W. Nicholson, *M.A.*, *D.Sc.*[*]

Investigation of the transitional region.

IN the section immediately preceding, the extent of the region of transition between brightness and shadow, when a radial oscillator is placed close to the surface of a perfectly conducting sphere, was examined. The present section is devoted to a discussion of the nature of this region. On reference to an earlier section this region, being the continuation on one side of that of brightness, will contain a magnetic force which, on this side, may be derived like (44) in the form

$$\gamma\rho = \Sigma_1^\infty u(1 + e^{2\iota\chi_n}) \sin(m\theta - \tfrac{1}{4}\pi)\, e^{\iota(\phi_n - \phi_{nr})}, \quad (66)$$

where

$$u = \iota m(2m \sin\theta\, \mathrm{R}_n \mathrm{R}_{nr}/\pi k^2 a^4)^{\frac{1}{2}},$$

provided that we neglect points in the immediate vicinity of the oscillator, so that θ is not small, and the use of an asymptotic formula for the zonal harmonic is legitimate. A different type of solution is valid for such points, which must be deferred for the present.

Again, in the region of brightness, it was shown that the above series could be expressed as the sum of four others of the exponential type, such that two only could have a vanishing derivate of an exponent. This property will continue to hold in the initial part of the transitional region. Since χ_n is not of an order capable of causing oscillation in an exponent involving it, the exponents of the four series may be regarded as $\phi_n - \phi_{nr} \pm m\theta$, whose derivates when x is not too nearly equal to unity are, with respect to m, or zx,

$$\sin^{-1} x - \sin^{-1} cx \pm \theta.$$

Only the lower sign of the ambiguity leads to a zero point at the boundary of the region of brightness. Accordingly,

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[*] Communicated by the Author; for Part I. see Phil. Mag. April 1910.

the zero point in the continuation of that region is still determined from

$$zv=\phi_n-\phi_{nr}-m\theta, \quad . \quad . \quad . \quad . \quad . \quad (67)$$

while it exists, and we may write, with this value

$$\gamma = \Sigma_1^\infty u(1+e^{2\iota\chi_n})\,e^{\iota zv},$$

where on reduction,

$$u=-e^{\frac{1}{4}\iota\pi}\,(k\mathrm{R}_n\mathrm{R}_{nr}\,/\,2\,\pi ar^2\sin\theta)^{\frac{1}{2}}. \quad . \quad . \quad (68)$$

In this formula $m=z$ has been inserted, for they now begin to differ by a quantity of lower order than z, and u is not oscillatory. The zero point, except in oscillating functions, is now sufficiently given by $x=1$. But χ_n can no longer be written as zero, for when $x=1$, it reaches the value $\frac{1}{6}\pi$. At the zero point it has a certain finite value χ_0 not quite of order unity in this case. Again, under the same circumstances,

$$v=v_0+\tfrac{1}{2}v_0''\,(x-x_0)^2,$$

neglecting higher terms near the zero point x_0.

The most significant part of the magnetic force becomes therefore

$$\gamma=u_0(1+e^{2\iota\chi_0})z\,e^{\iota zv_0}\int_{-\infty}^{\infty}d\xi\,e^{\frac{1}{2}\iota zv_0''\xi^2}$$

$$=u_0(1+e^{2\iota\chi_0})\,(2\pi z/v_0'')^{\frac{1}{2}}\,e^{\iota zv_0+\frac{1}{4}\iota\pi}, \quad . \quad . \quad (69)$$

but its further examination is not important. It is a solution of the same type as in the region of brightness, but no longer represents the oscillator in the presence of a plane reflector.

But on passing further into the transitional region, with θ still not small, $\partial\phi_n/\partial n$ and $\partial\phi_{nr}/\partial n$ become of order $m^{-\frac{1}{3}}$, and can no longer balance θ. The zero point therefore ceases to exist, and we enter upon the region more truly defined as that of transition in which we may expect, from ordinary considerations, to find bands of alternate maximum and minimum intensity, which, on the other side, merge into a continuous shadow. These bands will now be shown to occur, but before $\partial\phi_n/\partial n$ is of order $m^{-\frac{1}{3}}$.

In order that a set of harmonic terms in the series should become of supreme importance, it is not necessary that the derivate of an exponent should be zero, but only that it be small. Hitherto it has not been possible for this to occur without the zero value being attained. But in the present case, we have just passed from a region in which the derivate can be zero to one in which it cannot. Although v' cannot now become zero, it must attain a certain minimum value ϵ

for the component series which formerly had a zero point. On moving further across the transitional region towards the shadow, this minimum becomes larger, and the region of shadow may be designated as that for which this minimum is no longer a small quantity. This will appear subsequently. Meanwhile it may be shown that when ϵ is small, diffraction bands must be present.

The harmonic term whose order n is such that its exponent has the minimum derivative ϵ will obviously be the "centre" of a cluster of important harmonics. The name "minimum point" already suggested in an earlier section will be given to this, by analogy with the theory of the zero point. Denoting it by a suffix zero, it is evident that

$$v_0'=\epsilon, \quad v_0''=0, \quad v=v_0+\epsilon(x-x_0)+\tfrac{1}{6}v_0'''(x-x_0)^3$$

in its vicinity, and the magnetic force will be derived from

$$\gamma = \Sigma_1^\infty u(1+e^{2\iota\chi_n})e^{\iota zv},$$

where u has the value in (66), and

$$zv=\phi_n-\phi_{nr}-m\theta.$$

In the calculation of v_0 and u_0 the expansions of the Bessel functions suitable for the case in which argument and order are nearly equal must be employed. These have been given by the writer[*] as follows:—

If

$$\left.\begin{aligned} f_1 &= \int_0^\infty dw \cos(w^3+\rho w) \\ f_2 &= \int_0^\infty dw \sin(w^3+\rho w) \\ f_3 &= \int_0^\infty dw\, e^{-w^3+\rho w} \end{aligned}\right\}, \quad . \quad . \quad . \quad (70)$$

so that f_1 is an Airy's integral[†].

Then if $\rho=(m-z)(6/z)^{\frac{1}{3}}$, and $m-z$ is not of order z,

$$\left.\begin{aligned} J_m(z) &= \pi^{-1}(6/z)^{\frac{1}{3}} f_1(\rho) \\ J_{-m}(z) &= \pi^{-1}(6/z)^{\frac{1}{3}} \{f_1(\rho)\cos m\pi+(f_2+f_3)\sin m\pi\} \end{aligned}\right\}, \quad (71)$$

and in the present case, since $m=n+\frac{1}{2}$ where n is an integer,

$$J_{-m}(z)=(-)^n\pi^{-1}(6/z)^{\frac{1}{3}}(f_2+f_3), \quad . \quad . \quad (72)$$

the functions f having an argument ρ.

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[*] Phil. Mag. Aug. 1908.

[†] Airy, Camb. Phil. Trans. vi. p. 379; viii. p. 595. Stokes, Math. and Phys. Papers, ii. p. 329 *et seq.*

Again, $2\sin m\pi K_m(z)\, e^{\frac{1}{2}\iota m\pi}/\pi = J_{-m}(z) - e^{\iota m\pi} J_m(z)$,

leading on reduction, m being half an odd integer, to

$$K_m(z) = 2^{-1}(6/z)^{\frac{1}{3}}(f_2+f_3-\iota f_1)\, e^{-\frac{1}{2}\iota m\pi}. \quad . \quad (73)$$

Comparing with the usual substitution in terms of R_n and ϕ_n, it follows that

$$\left.\begin{aligned} R_n &= (2\pi)^{-1}\, 6^{\frac{2}{3}}\, z^{-\frac{1}{3}}(f_1^2+f_4^2) \\ \phi_n &= \tan^{-1} f_1/f_4 \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad (74)$$

where f_4 stands for f_2+f_3. If the functions F correspond to the functions f with argument $\rho_1 = (m-kr)(6/kr)^{\frac{1}{3}}$, then if $z_1 = kr$

$$\left.\begin{aligned} \tan\phi_{nr} &= F_1/F_4, \\ R_{nr} &= (2\pi)^{-1}\, 6^{\frac{2}{3}}\, z_1^{-\frac{1}{3}}(F_1^2+F_4^2). \end{aligned}\right\}. \quad . \quad . \quad . \quad (75)$$

If an accent applied to any function denote differentiation with respect to its argument ρ or ρ_1 as the case may be,

$$v' = \partial v/\partial x = (6/z)^{\frac{1}{3}}\, \phi'_n - (6/z_1)^{\frac{1}{3}}\, \phi'_{nr} - \theta,$$

since $$z^{-1}\,\partial\rho/\partial x = \partial\rho/\partial m = (6/z)^{\frac{1}{3}}.$$

Thus $$v' = \left(\frac{6}{z}\right)^{\frac{1}{3}} \frac{f_4 f_1' - f_1 f_4'}{f_1^2+f_4^2} - \left(\frac{6}{z_1}\right)^{\frac{1}{3}} \frac{F_4 F_1' - F_1 F_4'}{F_1^2+F_4^2} - \theta, \quad (76)$$

which may be reduced to a simpler form as follows:—

The integral equivalent to $u = f_2 - \iota f_1$ has been shown by Stokes to satisfy

$$u'' - \tfrac{1}{3}\rho u = \tfrac{1}{3}\iota,$$

where the accent means $\partial/\partial\rho$. Thus separating real and imaginary elements,

$$f_1'' - \tfrac{1}{3}\rho f_1 = 0$$

$$f_2'' - \tfrac{1}{3}\rho f_2 = -\tfrac{1}{3}.$$

Again, it is not difficult to show that

$$f_3'' - \tfrac{1}{3}\rho f_3 = \tfrac{1}{3},$$

and by addition, since $f_4 = f_2 + f_3$

$$f_4'' - \tfrac{1}{3}\rho f_4 = 0,$$

so that f_4 and f_1 satisfy the same equation, from which

$$f_4 f_1'' - f_1 f_4'' = 0,$$

and therefore $f_4 f_1' - f_1 f_4'$ is independent of ρ.

But when $\rho=0$,

$$f_1=\int_0^{\infty} dw \cos w^3=\frac{1}{2\sqrt{3}}\Gamma\left(\frac{1}{3}\right),$$

$$f_1'=\int_0^{\infty} w\,dw \sin w^3=-\frac{1}{2\sqrt{3}}\Gamma\left(\frac{2}{3}\right),$$

$$f_4=\int_0^{\infty} dw\,(\sin w^3+e^{-w^3})=\frac{1}{2}\Gamma\left(\frac{1}{3}\right),$$

$$f_4'=\int_0^{\infty} w\,dw\,(\cos w^3+e^{-w^3})=\frac{1}{2}\Gamma\left(\frac{2}{3}\right),$$

so that, by use of a property of the Gamma functions,

$$f_1f_4'-f_4f_1'=\tfrac{1}{3}\pi=\mathrm{F}_1\mathrm{F}_4'-\mathrm{F}_4\mathrm{F}_1' \quad . \quad . \quad , \qquad (77)$$

in a similar manner, and thus from (74–76)

$$v'=\mathrm{R}_{nr}^{-1}-\mathrm{R}_n^{-1}-\theta. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (78)$$

Otherwise, it is a known property of the asymptotic substitution in R_n and ϕ_n that

$$\partial\phi_n/\partial z=\mathrm{R}_n^{-1},$$

and since $$\rho=(m-z)(6/z)^{\frac{1}{3}}$$

$$z^{-1}\partial\phi_n/\partial x=\partial\phi_n/\partial m=(6/z)^{\frac{1}{3}}\phi_n',$$

the accent denoting differentiation with respect to ρ, and

$$\partial\phi_n/\partial z=-(6/z)^{\frac{1}{3}}(1-n-z/3z)\phi_n',$$

and since the second term of this formula may be neglected if $n-z$ is of lower order than z, even though ρ have the highest order consistent with this, it follows that

$$z^{-1}\partial\phi_n/\partial x=-\mathrm{R}_n^{-1},$$

and the value of v' in (78) follows at once.

The comparison of these two modes of proof supplies an interesting indication of the degree of accuracy possessed by the formulæ (70 *et seq.*). It appears that even if ρ is of higher order than unity, provided that $n-z$ is of *any* lower order than z, they may be used in the present case.

This paper does not propose to tabulate the effect in the transitional region, for in the present state of our knowledge of the subject, the main interest attaches to a determination of the nature of the effect. The formulæ are therefore left in a somewhat undeveloped state for the present.

Let n_0 denote the value of n at the minimum point, and $m_0=n_0+\frac{1}{2}$.

Writing $\rho_0=(m_0-z)(6/z)^{\frac{1}{3}}, \qquad \rho_{10}=(m_0-kr)(6/kr)^{\frac{1}{3}}$. (79)

Then
$$\epsilon=\mathrm{R}_{nr}^{-1}-\mathrm{R}_n^{-1}-\theta,$$
$$\mathrm{R}_n=(2\pi)^{-1}\,6^{\frac{2}{3}}\,z^{-\frac{1}{3}}\,(f_1{}^2+f_4{}^2),$$
$$\mathrm{R}_{nr}=(2\pi)^{-1}\,6^{\frac{2}{3}}\,(kr)^{-\frac{1}{3}}\,(\mathrm{F}_1{}^2+\mathrm{F}_4{}^2),$$
$$zv_0=\tan^{-1}f_1/f_4-\tan^{-1}\mathrm{F}_1/\mathrm{F}_4-\theta m,$$
$$v_0{}'''=z^2\frac{\partial^2}{\partial n^2}\left(\frac{1}{\mathrm{R}_{nr}}-\frac{1}{\mathrm{R}_n}\right),$$
$$u_0=-e^{\frac{1}{4}\iota\pi}\,(k\mathrm{R}_n\mathrm{R}_{nr}/2\pi ar^2\sin\theta)^{\frac{1}{2}},$$
$$u_{10}=u_0\,e^{2\iota\chi_0}$$
$$\tan\chi_0=-\tfrac{1}{2}\,\partial\mathrm{R}_n/\partial z=(3/\pi)(f_1f_1{}'+f_4f_4{}'), \quad . \quad . \quad . \quad (80)$$

with the minimum point substituted in each. With these values,

$$\gamma=e^{\iota zv_0}\,\Sigma_1^\infty\,(u+u_1)\,e^{\iota z(v-v_0)}$$
$$=z\,e^{\iota zv_0}\int_{-\infty}^{\infty}d\xi\,.\,\frac{\iota\epsilon+\ldots}{\rho^{\iota\epsilon+\ldots}-1}\cdot(u+u_1)\,e^{\iota z\epsilon\xi+\frac{1}{6}\iota zv_0{}'''\xi^3},$$

by the usual summation formula, where the limits have been taken as infinite. Actually, they are not even of order z for the harmonics of the type contributing mainly to the sum, but owing to the rapid oscillation of the exponential they may be regarded as infinite in the usual way. Again, to the same order, the multiplier of the exponential in the integrand may be taken as corresponding to the value of ξ making the exponent a minimum, or $\xi=0$. Thus

$$\gamma=\frac{\iota\epsilon z}{e^{\iota\epsilon}-1}\,(u_0+u_{10})e^{\iota zv_0}\int_{-\infty}^{\infty}d\xi\;e^{\iota z\epsilon\xi+\frac{1}{6}\iota zv_0{}'''\xi^3}, \quad . \quad (81)$$

and the integral is identical with

$$\left(\frac{6}{zv_0{}'''}\right)^{\frac{1}{3}}\int_0^\infty dw\,\cos\,(w^3+\sigma w), \quad . \quad . \quad . \quad (82)$$

where
$$\sigma=z\epsilon\,(6/zv_0{}''')^{\frac{1}{3}},$$

and γ is therefore proportional to an Airy's integral. The transitional region therefore exhibits maxima and minima after the manner customary in such problems when treated by the ordinary methods, provided that this integral is of the type which oscillates. Now ϵ is positive, and therefore for oscillation to take place it is sufficient that v_0''' should be negative. This condition is evidently satisfied, for v_0'' has decreased from its positive value in the region of brightness to a zero value, so that its derivate is continuously negative. Otherwise, the result follows from (80). The existence of maxima and minima is therefore demonstrated. But on passing further into the region, towards the geometrical shadow, ϵ tends to increase, and the terms near the minimum point no longer have a preponderant sum. Moreover, χ_n tends to behave like ϕ_n. The oscillation between maximum and minimum ceases, and in fact the whole effect becomes of a smaller order of magnitude, the series hitherto neglected contributing to an equal extent. When ϵ is of higher order than $z^{-\frac{2}{3}}$, the term of the exponential involving v_0''' becomes unimportant, and the sum is at once of lower order in so far as it depends on the series hitherto most important. It will appear later that the series tend to cancel one another in a remarkable way.

The above investigation is restricted to points in the transitional region not too far away from the obstacle, for ϕ_{nr} has been assumed to be of the same type as ϕ_n for a given value of n. Thus the bands will disappear at a sufficient distance. The investigation for the small values of θ is postponed, and the succeeding sections take up the problem of the geometrical shadow.

Preliminary discussion of the geometrical shadow.

In the geometrical shadow, as we have seen, it is not possible for the derivate of an exponent, in any of the series for the magnetic force, to vanish or become small. No group of terms, therefore, becomes of supreme importance after the manner of previous sections. Moreover, as was pointed out earlier, it follows that the harmonics of low order may contribute substantially to the sum, and thus the asymptotic expansion of the zonal harmonic must not be used even for a finite orientation from the transmitter. The proper formula was given in (48) and becomes

$$\gamma\rho = \mathrm{G}\,(\theta) \sum_{n=1}^{\infty} m(\mathrm{R}_n \mathrm{R}_{nr})^{\frac{1}{2}} (1 + e^{2\iota\chi_n}) \sin m\phi \, e^{\iota(\phi_n - \phi_{nr})},$$

where $\mathrm{G}\,(\theta)$ is an operation defined by

$$\mathrm{G}\,(\theta) \,.\, w = \frac{2\iota \sin^2\theta}{ka^2\pi} \frac{d}{d\theta} \int_\theta^\pi \frac{w\,d\phi}{\sqrt{2}\sqrt{(\cos\theta - \cos\phi)}}, \quad . \qquad (83)$$

and χ_n does not lead to finite oscillation in the manner of ϕ_u in an exponential. This series becomes

$$\gamma\rho = \mathrm{G}(\theta)\,\Sigma_0^\infty\, u\,(e^{\iota z v_1} - e^{\iota z v_2}), \quad . \quad . \quad . \quad (84)$$

where

$$u = m(\mathrm{R}_n \mathrm{R}_{nr})^{\frac{1}{2}}\,(1 + e^{2\iota\chi_n})/2\iota, \qquad z(v_1, v_2) = \phi_n - \phi_{nr} \pm m\phi.$$

Since $\mathrm{G}(\theta)$ annihilates the first harmonic, $n=0$ is taken as the starting point instead of $n=1$. We restrict the investigation for the present to points actually *on* the surface of the sphere for this is the case to which controversy has hitherto related and which moreover has a much simpler analysis. Thus

$$u = m\mathrm{R}_n\,(1 + e^{2\iota\chi_n})/2\iota, \qquad z(v_1, v_2) = \pm\phi m. \quad . \quad (85)$$

Recalling the formula of summation*, which in the present case is very simple, since derivates of v higher than the first are all zero, the series

$$\mathrm{S} = \Sigma_{n_0}^\infty\, u\left(\frac{n}{z}\right) e^{\iota z v\left(\frac{n}{z}\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (86)$$

has a sum

$$\mathrm{S} = z\int_\epsilon^\infty dx\left(\mathrm{U}_0 + \frac{\mathrm{U}_1}{z} + \frac{\mathrm{U}_2}{z^2} + \ldots\right) e^{\iota z v}, \,. \qquad (87)$$

where

$$\epsilon = n_0/z, \qquad x = n/z$$

$$\mathrm{U}_r = \frac{1}{r\,!}\,\mathrm{D}^r u_r \,.\, \psi_r, \qquad \mathrm{D} = \partial/\partial x,$$

$$\psi_r = \frac{d^r}{d\omega^r}\left(\frac{\omega}{e^\omega - 1}\right)_{\omega = \iota v'}$$

In the present case, n is to be replaced by $n+\frac{1}{2}$ or m, so that n_0 is replaced by $\frac{1}{2}$. With the values of R_n and χ_n developed in an earlier section when n is not comparable with z,

$$u = \frac{zx}{\iota}\left(1 + \frac{x^2}{2}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

where $zx = n + \frac{1}{2}$. More accurate values of the functions are found to introduce a correction which is only of order zx^3/z or x^3, and cannot affect the argument of this or of the next section. There is no necessity to give the analysis of this point, which can readily be supplied from the higher approximations already given. It will be necessary later to use

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* Messenger of Math. Oct. 1907.

these higher approximations in a more extended investigation of the region of brightness.

Before proceeding further at this point, it is necessary to make some remarks about the sum of the series. Although there is no group of terms of supreme importance on account of a vanishing derivate of the function v, it might be thought that since u rises in order in the neighbourhood of any pole which it may have, terms in such a region might supply the important part of the sum. But the poles of u must arise from the zeros of the function

$$d/dz \,.\, z^{\frac{1}{2}} \mathrm{K}_m(z),$$

none of which are real. Moreover, their imaginary parts are all large, so that such terms will necessarily have an exponential factor in their sum, of large real argument. This argument cannot be positive from elementary physical considerations, and therefore it is negative, and the sum of any such set of terms decreases in a rapid exponential manner round the surface, and may be ignored in comparison with the terms considered in this section. The rigorous analysis of this point will follow later, these rough indications being enough for the present.

Since in the integral of (87) there is no zero point, and no difficulty introduced by poles of the function u, an integration by parts is legitimate. This is taken between the limits ϵ and infinity, corresponding to $n=0$ and $n=\infty$, and ϵ is in this case $(2z)^{-1}$. The term at infinity may be neglected as corresponding to harmonics of infinite order, which have been dealt with already, and for the term at $x=1/2z$, the value of u in (88) may be used.

The order of the integral thus becomes that of

$$\mathrm{U}_\epsilon z \int_\epsilon e^{\iota z v}\, dx \quad \text{or} \quad \left[\mathrm{U}_\epsilon \frac{e^{\iota z v}}{\iota v'}\right]_\epsilon,$$

where $\quad zv_\epsilon = \pm\iota\phi, \quad$ and $\quad \mathrm{U}_\epsilon = u_\epsilon = (2\iota)^{-1},$

rejecting z^{-1} throughout. The integral thus has zero order in z at most, and by an inspection of the operation $\mathrm{G}(\theta)$, $\gamma\rho$ would therefore not be of greater order in linear magnitudes than $(ka^2)^{-1}$. When the sphere is absent, the corresponding order of this quantity is known to be k, as found in the investigation of the region of brightness. Accordingly, the magnetic force when the sphere is present is at most of order $(ka)^{-2}$ relatively to its value when the sphere is absent, and this is approximately 10^{-12} in the numerical case typical of wireless telegraphy.

The shadow produced by the sphere is therefore very complete, and in fact much too complete to admit diffraction as an explanation of the experimental results. For *very* small orientations, of course, the exponential portions of the sum could be of greater order than this, and they are not included in this remark.

The integration by parts remains valid for harmonics in the vicinity of $m = z$, although R_n, and therefore u, is of higher order in this case. For the change in R_n is continuous, and it is only necessary to break up the integration from ϵ to ∞ into several stages in which different formulæ for R_n are used. The continuity of the values of R_n and ϕ_n is demonstrated in a paper on the asymptotic expansions of Bessel functions [*]. Since the term neglected in the integration is necessarily of the same order relatively to that retained, in each part of the range, a series of integrations by parts is sufficient to show that the terms near $m = z$ are already fully taken into account. Their main effect is in fact exponential, as will appear later. This investigation is sufficient to give an upper limit to the value of the diffracted effect, and is complete enough to decide the main point of controversy on this subject. It will be noticed that even when points not *on* the surface are treated, and $\phi_n - \phi_{nr}$ is therefore not zero, the effect cannot be of a greater order than above, so that the use of a receiver not very close to the surface cannot, with diffraction alone as an aid, furnish an effect sufficiently great to be perceptible, for finite orientations.

But for other purposes, it is necessary to carry the calculation further, and to obtain an actual formula for the effect, and it will be shown in the next section that the actual effect is much smaller than the limit assigned above.

Further examination.

We proceed to collect the terms of the order which is apparently most significant in the expression for the magnetic force. Since by (88)

$$u = \frac{zx}{\iota}\left(1 + \frac{x^2}{2}\right),$$

neglecting x^3 and zx^5, therefore

$$\begin{aligned} u_\epsilon &= (u)_{zx=\frac{1}{2}} = 1/2\iota, \\ Du_\epsilon &= (z/\iota)\left(1 + \tfrac{3}{2}x^2\right) = z/\iota, \\ D^2 u_\epsilon &= 3/2\iota\,; \end{aligned}$$

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[*] Phil. Mag. Feb. 1910.

and on examination, no further derivate is of higher order than z. Thus to order zero in z, from (87)

$$\mathrm{U}_0+\frac{\mathrm{U}_1}{z}+\frac{\mathrm{U}_2}{z^2}+\ldots=u_\epsilon\psi_0+\mathrm{D}u_\epsilon\,.\,\psi_1+\mathrm{D}^2u_\epsilon\,.\,\frac{\psi_2}{2\,!}+\ldots$$

or $(\psi_0+2\psi_1)/2\iota$. This becomes, in terms of v', on reduction,

$$(v'\cos\tfrac{1}{2}v'-2\sin\tfrac{1}{2}v')/4\sin^2\tfrac{1}{2}v'\,.\,e^{-\frac{1}{2}\iota v'},$$

and therefore from (84, 85), if $(v_1, v_2)=\pm\phi x$,

$$\gamma\rho=\mathrm{G}(\theta)z\int_\epsilon^\infty dx\left(\mathrm{U}_0+\frac{\mathrm{U}_1}{z}+\ldots\right)(e^{\iota z v_1}-e^{\iota z v_2})$$

$$=\mathrm{G}(\theta)\left[\left(\mathrm{U}_0+\frac{\mathrm{U}_1}{z}+\ldots\right)\left(\frac{e^{\iota z v_1}}{\iota v_1'}-\frac{e^{\iota z v_2}}{\iota v_2'}\right)\right]_\epsilon^\infty$$

$$=\mathrm{G}(\theta)\,.\,\frac{\phi\cos\frac{1}{2}\phi-2\sin\frac{1}{2}\phi}{4\iota\sin^2\frac{1}{2}\phi}\left(\frac{1}{\phi}+\frac{1}{-\phi}\right)=0,$$

so that the term of this order in the magnetic force vanishes. Moreover, it may be shown at once that whenever

$$\mathrm{U}_0+\frac{\mathrm{U}_1}{z}+\frac{\mathrm{U}_2}{z^2}+\ldots$$

is the product of $e^{-\frac{1}{2}\iota v'}$ and an odd function of v', the same result must occur. A further examination of the magneti force indicates in this way that the set of terms of order z^{-1} contributes zero when $v''=0$, or when the point at which the effect is desired is on the surface of the sphere, so that $\phi_n=\phi_{nr}$. The magnetic force is thus at least two orders higher than was shown in the last section.

These results indicate that the vanishing of these terms of successive orders is general, and this will now be shown to be the case, by an independent method.

Consider u as a function of m or $n+\frac{1}{2}$. It may be shown * that if R_n is derived from Bessel functions of real order m, without any restriction of m to half integral values,

$$\mathrm{R}_n=\frac{4z}{\pi}\int_0^\infty \mathrm{K}_0(2z\sinh t)\cosh 2mt\,dt. \quad . \quad . \quad (89)$$

This integral is an *even* function of m, and so also therefore is R_n. Moreover, χ_n is also an even function because

$$\tan\chi_n=-\tfrac{1}{2}\partial\mathrm{R}_n/\partial z.$$

Thus u, which is proportional to $m\mathrm{R}_n(1+e^{2\iota\chi_n})$, is an *odd*

* Phil. Mag. Feb. 1910, p. 234.

function of m, and may be expanded in an asymptotic series in the form

$$mA_0 + m^3A_1 + m^5A_2 + \ldots$$

so that

$$\gamma\rho = G(\theta)\,\Sigma_1^\infty\,(mA_0 + m^3A_1 + \ldots)\sin m\phi,$$

where the coefficients A are independent of m.

Now it is known that, when convergent, the series

$$\sum_{m=0}^{\infty} m^{2p+1}\sin m\phi = 0 \quad . \quad . \quad . \quad . \quad . \quad (90)$$

if p is an integer.

Now near the lower limit ϵ of the integration in the previous section, it is known that the coefficients A decrease in order of z, from the form of R_n as a function of m when m is small. It follows that the terms of $\gamma\rho$ expressed as a series in descending powers of z will continue to vanish, and this shows that the actual value of $\gamma\rho$ must be of an exponential form for points on the surface of the sphere. Thus the result of M. Poincaré's revised investigation, and that given by the method of this paper, are not at variance for surface points, and the effect in this special case is entirely exponential.

But this line of argument is liable to failure when the magnetic series contains an oscillating exponential of argument proportional to $\phi_n - \phi_{nr}$, and it is therefore not yet shown that the effect at other points in the shadow is determined by an exponential law. M. Poincaré's mode of proof also fails, in its present form, for other than surface points, as it definitely assumes the absence of oscillation.

In the next section, a preliminary discussion of the exponential sum is given, and the investigation for other than surface points is postponed for the present.

Determination of the exponential sum.

As the sum of the harmonic series, for points on the surface, is now shown to be mainly caused by terms in the neighbourhood of singularities of the function u, it is simpler to proceed otherwise at this point, as a direct summation may be effected. Let ν be a typical value of m making

$$d/dz \,.\, z^{\frac{1}{2}}K_m(z) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

Then $m=\nu$ is a pole of the function u, and this must be a simple pole because u is proportional to the ratio of $z^{\frac{1}{2}}K_m(z)$ to its derivate. Again, on reference to the original expansions in R_n and ϕ_n for the Bessel functions, it is seen that the poles are given by the solution of the equation in m,

$$\partial R_n/\partial z = 2\iota, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (92)$$

and since, whether m be real or not [*],

$$R_n = \frac{4z}{\pi}\int_0^\infty K_0(2z \sinh t) \cosh 2mt \, dt,$$

we note that R_n is an even function, so that $m=-\nu$ is also a pole. The poles thus occur in pairs. Moreover, an inspection of (89) shows at once that it cannot be satisfied for real values of m when z is real. Thus there are no real poles. Now when m, even though complex, is not nearly equal in modulus to z, although less,

$$R_n = z/(z^2-m^2)^{\frac{1}{2}}$$

and it is found to be impossible to satisfy (92) within the limits of validity of this formula. The poles therefore correspond to values of m of order z at least.

We may assume, at once, the justification appearing in the result, that the poles contributing mainly to the sum are those whose imaginary parts are least. Moreover, it is fairly evident from the above reasoning that the least order the imaginary part can have is that of $z^{\frac{1}{3}}$, since there are no poles in the first region of expansions of the Bessel functions. In the section following, the first pole is determined and found to be of the form

$$m = z - \iota z^{\frac{1}{3}}\beta_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (93)$$

where β_0 is a numerical quantity approximately equal to 1/3, and its contribution to the sum is of supreme importance. We shall also, for the present, assume that the imaginary part of the poles is negative. If a_ν be the residue of the function

$$z^{\frac{1}{2}}K_m(z) \Big/ \frac{d}{dz} \cdot z^{\frac{1}{2}}K_m(z) = \tfrac{1}{2}\iota R_n(1+e^{2\iota\chi_n})$$

at the pole ν, then the corresponding terms in its development by Cauchy's theorem, including the pole $-\nu$, become

$$a_\nu\left(\frac{1}{m-\nu} - \frac{1}{m+\nu}\right) = \frac{2\nu a_\nu}{m^2-\nu^2}.$$

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[*] *Vide* Phil. Mag. Feb. 1910 for the case of m real. The proof there given can obviously be extended.

Thus again defining $G(\theta)$ by the operation

$$G(\theta)\,.\,w=\frac{2\iota\sin^2\theta}{ka^2\pi}\,\frac{d}{d\theta}\int_\theta^\pi\frac{w\,d\phi}{\sqrt{2}\sqrt{(\cos\theta-\cos\phi)}}. \qquad (94)$$

Then for points on the surface, by (83),

$$\gamma\rho=G(\theta)\sum_{n=1}^{\infty}mR_n(1+e^{2\iota\chi_n})\sin m\phi$$

$$=-2\iota G(\theta)\sum_{n=1}^{\infty}\Sigma_\nu\frac{2\nu a_\nu}{m^2-\nu^2}\,.\,m\sin m\phi,$$

and as $m\sin m\phi/m^2-\nu^2$ is an even function of m, the summation may be replaced by half that from $-\infty$ to ∞. Therefore

$$\gamma\rho=-\iota G(\theta)\,\Sigma_\nu 2\nu a_\nu\sum_{m=-\infty}^{m=\infty}\frac{m\sin m\phi}{m^2-\nu^2}, \quad . \quad . \quad . \quad (95)$$

where $2m$ takes all possible integral values, positive or negative. But the last summation may be effected. For consider the function $f(\nu)\sec\pi\nu$, where $f(\nu)$ has no poles. The poles of the function are given by $\cos\pi\nu=0$ or

$$\pi\nu=\pm\,(n+\tfrac{1}{2})\pi=\pm\,m\pi,$$

where m is a typical value of m in the desired summation. The residues at these poles are $f(\pm m)/\pi\sin m\pi$, so that

$$f(\nu)\sec\pi\nu=\sum_{-\infty}^{\infty}\frac{1}{\pi\sin m\pi}\left(\frac{f(m)}{\nu-m}+\frac{f(-m)}{\nu+m}\right),$$

m taking half integral values. Identifying this with the series

$$\sum_{-\infty}^{\infty}\frac{m\sin m\phi}{m^2-\nu^2}=\frac{1}{2}\sum_{-\infty}^{\infty}\left(\frac{\sin m\phi}{\nu+m}-\frac{\sin m\phi}{\nu-m}\right),$$

we find at once that

$$\sum_{-\infty}^{\infty}\frac{m\sin m\phi}{m^2-\nu^2}=\frac{\pi\cos\nu(\pi-\phi)}{\cos\nu\pi}, \quad . \quad . \quad . \quad . \quad (96)$$

and therefore

$$\gamma\rho=-2\pi\iota\,\Sigma_\nu\nu a_\nu G(\theta)\,.\,\sec\nu\pi\cos\nu(\pi-\phi).$$

Assuming the result of the next section, that the first pole is one for which $\nu=z-\iota z^{\frac{1}{3}}\beta$, where β is an ordinary numerical quantity, we have, ϕ being less than π throughout the operation of $G(\theta)$,

$$\frac{\cos\nu(\pi-\phi)}{\cos\nu\pi}=\frac{e^{\iota\nu(\pi-\phi)}}{e^{\iota\pi\nu}}=e^{-\iota\nu\phi},$$

and is very small, containing an exponential of large real negative argument. Thus

$$\gamma\rho = -2\pi\iota\,\Sigma_\nu \nu a_\nu \mathrm{G}(\theta)e^{-\iota\nu\phi}$$

$$= \frac{4\sin^2\theta}{ka^2}\,\frac{d}{d\theta}\Sigma_\nu \nu a_\nu \int_\theta^\pi \frac{d\phi e^{-\iota\nu\phi}}{\sqrt{2}\sqrt{(\cos\theta-\cos\phi)}},$$

and the important part of the integral is contributed near the lower limit. Writing $\phi=\theta+\xi$ and neglecting square and higher powers, the integral becomes

$$\int_0^\infty \frac{d\xi}{\sqrt{(2\xi\sin\theta)}}e^{-\iota\nu(\theta+\xi)} = \frac{e^{-\iota\nu\theta}}{\sqrt{(2\sin\theta)}}\cdot\sqrt{\frac{\pi}{\nu}}\cdot e^{-\frac{1}{4}\iota\pi},$$

and taking the leading term in the differentiation with respect to θ, we finally obtain

$$\gamma\rho = \frac{-2\sin\theta}{ka^2}(2\pi\sin\theta)^{\frac{1}{2}}\Sigma_\nu \nu^{\frac{3}{2}} a_\nu e^{-\iota\nu\theta+\frac{1}{4}\iota\pi}, \quad . \quad (97)$$

and it is now necessary to determine the residue a_ν.

It is already obvious from the last equation that the poles whose imaginary part has an order greater than $z^{\frac{1}{3}}$ are not important, and they will henceforward be neglected, and the summation restricted to those poles which are of type

$$\nu = z - \iota z^{\frac{1}{3}}\beta,$$

β being of zero order and numerical.

Now near $m=\nu$, by definition of a_ν,

$$z^{\frac{1}{2}}\mathrm{K}_m(z)\Big/\frac{d}{dz}\cdot z^{\frac{1}{2}}\mathrm{K}_m(z) = \frac{a_\nu}{m-\nu},$$

and therefore

$$a_\nu = z^{\frac{1}{2}}\mathrm{K}_m(z)\Big/\frac{\partial^2}{\partial m\partial z}z^{\frac{1}{2}}\mathrm{K}_m(z)$$

with $m=\nu$ substituted after the differentiation. But ν being of the above form, the Bessel function is proportional to, by results referred to earlier,

$$z^{-\frac{1}{3}}f(\rho),$$

where $\rho=(m-z)(6/z)^{\frac{1}{3}}$, and $f(\rho)$ does not otherwise contain m or z. Thus $\partial/\partial m=(6/z)^{\frac{1}{3}}\partial/\partial\rho$, and moreover, so far as the term of highest order is concerned, $\partial/\partial z=-(6/z)^{\frac{1}{3}}\partial/\partial\rho$. For in this term, differentiation only lowers the order by $z^{\frac{1}{3}}$, and in others, by z. Thus we may write near $m=\nu$,

$$\partial/\partial z = -\partial/\partial m,$$

and accordingly,

$$a_\nu = -z^{\frac{1}{2}}\mathrm{K}_m(z) \Big/ \frac{\partial^2}{\partial z^2} z^{\frac{1}{2}}\mathrm{K}_m(z)$$

$$= (1-m^2-\tfrac{1}{4}\,.\,/z^2)^{-1}_{m=\nu}$$

by the use of the differential equation satisfied by the function K. This result is very elegant. To the same order, we may write

$$a_\nu = z^2/(z^2-\nu^2) = z^{2/3}/2\iota\beta \quad . \quad . \quad . \quad . \quad (98)$$

on reduction, and therefore

$$\gamma = k^2(ka)^{-\frac{7}{3}}(2\pi \sin\theta)^{\frac{1}{2}}\,\Sigma_\nu \beta^{-1}\nu^{\frac{3}{2}}e^{-\iota\nu\theta+\frac{3}{4}\iota\pi}.$$

But in non-oscillating terms, we may write $\nu=ka$ to the order already retained, so that finally

$$\gamma = k^2(ka)^{-\frac{5}{6}}(2\pi \sin\theta)^{\frac{1}{2}}\,\Sigma_\nu \beta^{-1}e^{-(ka)^{\frac{1}{3}}\beta\theta-\iota ka\theta+\frac{3}{4}\iota\pi}, \quad (99)$$

and only the first term of the summation is really important.

For an undisturbed oscillator, the corresponding formula becomes

$$\gamma_0 = -\tfrac{1}{2}k^2(ka)^{-1}\cot\tfrac{1}{2}\theta e^{-2\iota ka\sin\frac{1}{2}\theta+\frac{1}{2}\iota\pi}, \quad . \quad (100)$$

and the ratio of the amplitudes in the two cases is therefore

$$(8\pi\sin\theta)^{\frac{1}{2}}(ka)^{\frac{1}{6}}\tan\tfrac{1}{2}\theta\,.\,\beta^{-1}e^{-(ka)^{\frac{1}{3}}\beta\theta}, \quad . \quad . \quad (101)$$

and the exponential factor is of the same form as that derived otherwise by M. Poincaré, who does not give the other factors nor the value of β. The impossibility of explaining the experimental results by means of diffraction is now evident. In the next section, a determination of β is made, and an examination of the formula numerically is given. Succeeding sections deal with the remaining problems hitherto postponed, viz., the effect at *any* point in the geometrical shadow, the effect in the neighbourhood of the oscillator, and the determination of a second approximation for points in the region of brightness.

XIV. *The Heat developed during the Absorption of Electrons by Platinum.* *By* O. W. Richardson, *M.A., D.Sc., Professor of Physics, and* H. L. Cooke, *M.A., Assistant Professor of Physics, Princeton University*[*].

[Plate III.]

§ 1. IN 1901[†] one of the writers showed that the phenomena attending the emission of negative electricity by hot metals could be explained on the assumption that the electrons which, on the electron theory of metallic conduction, move freely inside the metal, attain sufficient kinetic energy at high temperatures to enable them to overcome the forces tending to keep them inside the metal, and so escape. From the way in which the thermionic current varied with the temperature it was shown that the difference, w, in the value of the potential energy when outside and when inside a metal could be calculated. Somewhat later[‡] it was shown that the existence of this difference in the potential energy would involve a loss of thermal energy by the substance when the electrons were being given off, and it was pointed out that this effect would increase very rapidly with the temperature; so that at sufficiently high temperatures the loss of energy due to this cause would be greater than that arising from thermal emission. An effect of this character has recently been discovered by Wehnelt and Jentzsch[§].

Another consequence of the existence of this difference of potential energy is that when electrons possessing negligible kinetic energy pass into a metal an amount of heat should be developed which is equal in magnitude to the difference in potential energy for each electron multiplied by the number of electrons entering the metal. The present experiments show that this effect exists, and is of the expected order of magnitude.

On this view of thermionic emission, the loss of energy when the electrons escape will consist of two parts:—(1), that due to the thermal kinetic energy of agitation of the escaping electrons, and (2), that required to overcome the work function, w. Recent experiments show that the former is equal to the kinetic energy of thermal agitation of a molecule of gas at the temperature of the metal, and corresponds, at any temperature which is available experimentally, to the energy which would be acquired by falling through a

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[*] Communicated by the Authors.

[†] O. W. Richardson, Camb. Phil. Proc. vol. xi. p. 286.

[‡] O. W. Richardson, Phil. Trans. A. vol. cci. p. 497.

[§] *Ann. der Physik* [3] vol. xxviii. p. 537.

potential difference of a fraction of a volt. The precise value of the fraction depends, of course, on the absolute temperature, to which it is proportional. The first loss appears to be small compared with the second at all available temperatures.

The heating effect which should occur, on this view, when electrons enter a metal is made up similarly of two parts: one proportional to the kinetic energy, k, which the electrons possess immediately before entering the metal, and two, a part which depends upon the difference of potential energy of the electron when inside and outside of a metal. This will be equal to the work, $w=e\phi$, done by the surface forces on the entering electrons. Here e is the charge on an electron and ϕ is the difference of potential energy per unit charge. Hence, if n electrons enter the metal in unit time, the rate at which kinetic energy is transported into the metal will be equal to $n(e\phi+k)$. In general, k will consist of two parts, the first due to the energy, $\alpha\theta$, of thermal agitation of the hot metal from which they are emitted, and the second, due to the potential difference, V, driving them from the hot metal to the cold. If the conditions are steady, the current will be continuous and there will be a flow of an equal number of electrons out of the cold metal, each of which will transport on the average an amount of kinetic energy $\alpha\theta_0$ with it, where θ_0 is the temperature of the cold metal. The total quantity of heat developed by the n electrons when they flow into the cold metal is, therefore, equal to

$$n(e\phi+e\mathrm{V}+\alpha(\theta_1-\theta_0)),$$

so that the rate of production of heat by a current, i, will be equal to

$$i\left(\phi+\mathrm{V}+\frac{\alpha}{e}(\theta_1-\theta_0)\right).$$

For constant values of θ_1 and θ_0 the rate of production of heat will thus be a linear function of V which takes the value

$$\phi+\frac{\alpha}{e}(\theta_1-\theta_0),\text{ when } \mathrm{V}=0.$$

This development of heat is clearly analogous to the heat liberated during the condensation of a vapour to a liquid.

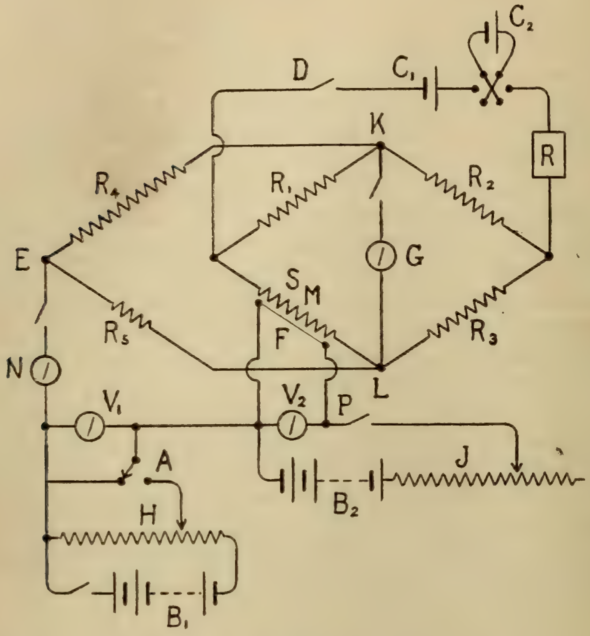
§ 2. *Method of Experimenting.*

To detect and measure this heating effect an electrical method was used. The electrons were obtained by heating osmium filaments which were kindly presented to us by the *Deutsche Gasglühlicht Aktiengesellschaft* of Berlin, to whom we are glad to be able to take this opportunity of expressing our thanks. Osmium is a very refractory substance, and when a filament of it is heated it emits a copious supply of negative electrons which can very easily be regulated by adjusting the heating current through it. A long narrow strip of thin platinum foil was wound in the form of a grid on glass supports so that the different strands were nearly in one plane. Two osmium filaments (see below) were suitably supported, one on each side of the grid, and insulated from it. The filaments were heated by means of an electric current, and an adjustable difference of potential could be applied between the filaments and the grid, causing the electrons emitted by the filament to flow into the grid. The ensuing rise in temperature of the platinum grid was determined by measuring its resistance by a Wheatstone's bridge method. The present arrangement differs from the usual Wheatstone's bridge problem, however, in one important respect. In addition to the usual battery current flowing through the four arms, we have also the thermionic current, which flows from the filament into the strip which forms the other arm Unless the effect of this is compensated, there will be a deflexion of the galvanometer, even when the resistances are in the proper proportion for a balance to be obtained under the usual conditions. This compensation was effected by introducing two auxiliary resistances into the bridge in the manner described below.

In addition to measuring the change in the resistance of the strip produced by the electrons, it was also necessary to measure the thermionic current which produced it. This was done by means of a micro-ammeter suitably inserted between the bridge system and the positive terminal of the cells which were used to maintain the applied difference of potential between the heated filaments and the strip.

The rest of the arrangement will be made clear by referring to the accompanying diagram (fig. 1, p. 176). The electric current which heated the osmium filament, F, was supplied by the battery B_2 and could be regulated by means of the rheostat J. The voltmeter V_2 served to measure the potential drop along the filament. The strip, indicated by S, forms one arm of the Wheatstone's bridge of which $R_1R_2R_3$ are the other arms. G is the galvanometer, and D, C_1, C_2 the battery arm, R_4 and R_5 are the compensating resistances which are respectively connected to the ends of the galvanometer arms .The junction between R_4 and R_5 is connected through a switch to the micro-ammeter N, which serves to measure the thermionic current. The other terminal of this was connected to the positive end of the battery B_1, which supplied the potential difference necessary to drive the electrons from the

Fig. 1.



filament F to the strip S. B_1 was in series with the rheostat H and the potential could be tapped off from various points of this by means of a sliding contact. The switch A enabled the sliding contact to be connected with the negative end of the filament F and the potential thus applied between F and S was measured by means of the voltmeter V_1. The rocking switch A was introduced so that this potential difference could be changed from zero to any desired value almost instantaneously, and thus the flow of the electrons into the grid could be started or stopped when desired.

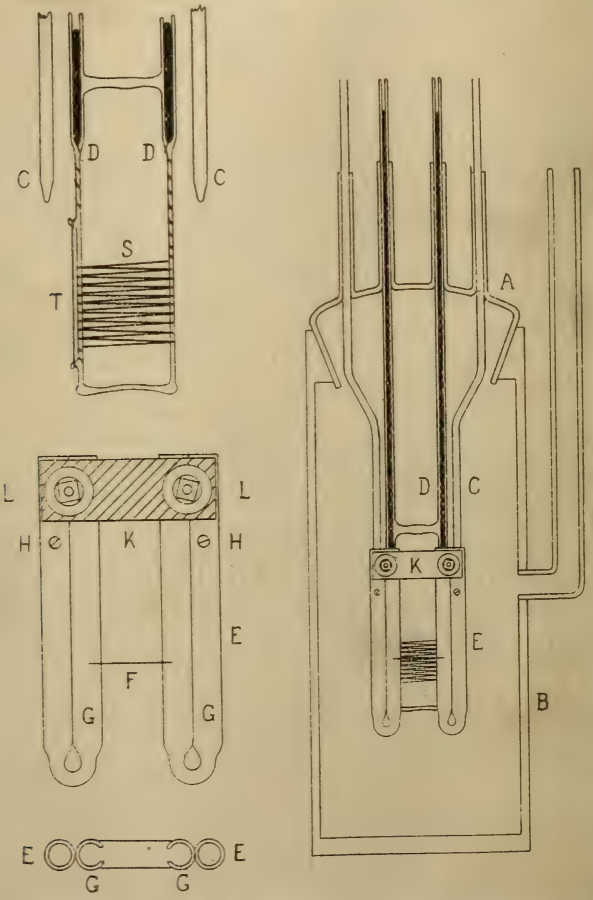
The mechanism of the compensating device needs a little further consideration. Imagining for a moment the thermionic current from F to S to be turned off, it will be seen that the condition that the battery C_1, C_2 should produce no deflexion in the galvanometer G is the usual relation $S : R_1 = R_3 : R_2$. Now suppose the thermionic current to be turned on. There will be a current flowing into various parts of the resistance S. The result will be that in general the two points K and L will no longer be at the same potential.

There will be a point M in S such that at this point the current along S which arises from the thermions is zero. The thermionic current will flow from M towards R_1, and towards L, and from those points along the various possible connexions to the point, wherever it may be, (in the present case at E) where the thermionic current is led out of the circuit. It will be seen that if the resistances R_4 and R_5 are introduced as shown, provided the resistance from M through R_1 to K is to the resistance from M to L as R_4 is to R_5, K and L will still be at the same potential even when the thermionic current is flowing.

The method thus involves a double adjustment which was carried on as follows:—First of all the switch A was put to the left, so that the thermionic current was off. The resistance R_1 was then adjusted until no current with the battery C_1C_2 on flowed through the galvanometer G, involving the usual condition of proportionality between the arms S, R_1, R_2, and R_3. The battery C_1C_2 was then put out of commission, and one of the resistances R_4, R_5 was adjusted until no deflexion of the galvanometer occurred when the thermionic current was turned on. It might be thought that if the battery circuit DC_2 was broken when the second adjustment was made, the adjustment would not hold when the switch D was subsequently closed, owing to the resistance in this arm being different under the two sets of circumstances. To avoid this objection two separate batteries C_1, C_2 were used, and it was arranged by means of a commutating switch that they could either be put in series or opposed to one another. In the one case the potential in this circuit would thus be twice that of a single battery while in the other case it would be zero, but in either case the resistance of the arm DC_1C_2 would be the same. In carrying out the first adjustment the batteries C_1 C_2 were in series and produced the bridge current, while in carrying out the second adjustment they were opposed to one another, so that there was no current actuating the bridge circuit. As a matter of fact, we were not able to satisfy ourselves that it made any difference whether the switch D was open or closed when the second adjustment was made.

In order to be quite certain that this method of compensating for the effect of the thermionic current flowing into the arm S was free from objection, we made dummy experiments with a resistance in the arm S provided with a sliding contact, so that small differences of potential from a battery could be introduced between the contact and the point E. The operations were then repeated with this arrangement. First the resistance R_1 was adjusted with the cells C_1, C_2 on, so that no current flowed through the galvanometer G. The cells C_1, C_2 were then made to oppose one another, and it was found, as was to be expected, that when the battery between E and the sliding contact was turned on there was a deflexion of the galvanometer G which could be stopped by suitably adjusting R_4. It was now found that after putting C_1 and C_2 in series there was no deflexion in the galvanometer G, whether the potential difference between E and the sliding contact was on or off, showing that the method of compensating worked satisfactorily.

Fig. 2.



The construction of the part of the apparatus containing the grid and filaments is shown in detail in figure 2. The whole was in a cylindrical brass box B connected through a side tube with a McLeod gauge and Gaede pump. The supports of the grid and filament were fixed air-tight with sealing-wax through four tubes in a glass stopper A which was ground to fit a conical hole in the top of the brass box. This was found to make a perfectly satisfactory air-tight joint if the two surfaces were carefully ground and suitably greased. The glass tubes DD supported a glass framework on which the strip S was wound in the manner shown. By twisting the glass rods which formed the framework very quickly while they were being drawn out it was found possible to produce a thread on them in which the strip could be laid, and which prevented the possibility of its slipping about after it had been wound. The return end T of the strip was prevented from touching the intermediate portions by being wound around two glass projections as shown. The ends of the strip were soldered onto two platinum wires sealed through the tubes, which were filled with mercury, and thus made contact with the outside.

The osmium filaments F were soldered onto the outside of two bent brass tubes which were clamped together by two glass plates K, bolted at L. The inner side of the brass tube was cut and opened out as shown in section below. The outer tubes were made so as to just slide on the brass rods C. This arrangement carrying the filaments was placed around the closed framework carrying the strip and slid onto the brass rods C, being fixed in position by the screws H. It was adjusted so that the two filaments F were opposite the middle of the grid S. The object of the inner tubes G was to shield the glass supports so that the electrons did not flow onto them. It was thought that if this happened some of the heating effect might be lost.

§ 3. *Method of taking Observations.*

In taking the observations it was found necessary first of all to wait for a considerable length of time for the temperature of the system to become steady. This was usually a matter of two or three hours after the heating current had been turned on. Up to that time the resistance of the strip S gradually increased. In fact, it was generally found that no matter how long one waited there was a slow drift in the direction of increasing temperature and in any case there were apt to be small slow alterations one way or the other. After the lapse of an hour or two, however, they would be so small as to be of no serious consequence with the method of taking galvanometer readings described below. When the conditions had become satisfactory the resistance R_1 was adjusted first of all, so that there was no deflexion of the galvanometer when the Wheatstone's bridge E.M.F. was operative. Then the cell C_2 was reversed and the balancing resistance R_4 adjusted until there was no deflexion of the galvanometer. The battery C_2 was now reversed so that C_1 and C_2 were in series, and since the direct effect of the thermionic current on the galvanometer has been compensated for, any deflexion produced when the thermionic current is turned on can only arise from the alteration its heating effect produces in the resistance of the strip S. There will, of course, be some heating effect due to the increase of the current flowing through the strip on account of its Joule effect. It is easy to show that with the current used in the previous experiments this effect was small compared with the effects measured, and the correction for this will be considered later. On turning on the thermionic current it was found that the balance of the galvanometer was disturbed, the deflexion being very rapid at first but gradually dying away to a small drift which was difficult to distinguish from the gradual drift of the galvanometer. Preliminary experiments showed that much the greater part of the heating effect occurred in the first half minute. It is difficult to be certain exactly how much, but, with a thin strip, 90 per cent., and probably more, of the total change of resistance developed took place within this time. Presumably, in different experiments under similar conditions the same fraction of the final rise of temperature would be developed in equal times, so that the method was adopted of always measuring the increase of temperature, or the change of resistance, to which it is proportional, developed in a given interval. This was usually 30 seconds, but in some of the earlier experiments only 15 seconds, while more recently intervals of one or two minutes have been used. As a matter of experience, however, it seems that 30 seconds is the best interval to use as it is long enough to obtain the bulk of the effect, and to enable the periodic oscillations of the galvanometer to die down, while avoiding to a very considerable extent the errors arising from the drifting of the temperature to which the heatings with longer intervals are more subject. We have made several experiments to test the point, but have not been able to convince ourselves that there is any difference in the values obtained when different times are employed, except such as might arise from casual fluctuations. In order to eliminate the effect of these as far as possible, long series of readings were taken, first with the thermionic current on for the given interval, then with the thermionic current off for the same interval, and so on in succession. In this manner the effect of the drift and casual fluctuations could be eliminated.

In the first experiments the heating effect of the thermionic current was compared with the heating effect arising from an increase in the current produced by the batteries C_1, C_2 of the Wheatstone's bridge. This current could be increased or diminished at will by altering the resistance in the box R in the bridge arm of the circuit. The heating effect produced in this way in the strip S is equal, of course, to the resistance of the strip multiplied by the difference of the squares of the current passing through it, and could thus be calculated, the currents through the bridge being measured by a suitable milliammeter. It was found, however, that the change of resistance thus produced did not vary with the time in quite the same way as that due to the thermionic current, but got up to its maximum value somewhat less rapidly. There is an important difference in the mode of liberation of heat in the two cases. That due to the thermionic current is developed at the surface of the metal, whereas the other is a volume effect. On these grounds we should expect the final state of equilibrium to be reached in different times in the two cases, so that there is an objection to the measurement of the heating effect by comparison of the effects produced in equal times in the two cases.

There is, however, a simple method of deducing the heating effect arising from the difference of potential energy of the electrons inside and outside of the metal, which appears to be free from this objection. We have seen that if a difference of potential is applied so as to drive the electrons from the filament F to the strip S, their kinetic energy will be increased by a calculable amount, which is proportional to this difference of potential. So that if we compare the effect produced by the electrons when they fall through no voltage with that produced when they fall through a voltage V, we shall at once be able to determine the difference in the potential energy in terms of the kinetic energy gained by an electron when it falls through a potential difference of one volt. When the difference of potential driving the electrons is zero, the thermionic current is so small that it is impossible to measure the heating effect to which it gives rise with accuracy. But this difficulty can be avoided if we compare the heating effect produced by the thermionic current with two different voltages. On the view developed at the beginning of this paper, the effect per unit current will be a linear function of the voltage, and from the position of the point at which the heating effect produced by unit thermionic current cuts the voltage axis, on the diagram in which this effect is plotted against the voltage, we can at once deduce the difference of potential energy in terms of the work done on the electron when it falls through one volt. All that is necessary, then, is to measure simultaneously both the thermionic current and the change it produces in the resistance of the strip S for a series of different voltages. This method has the advantage that in every case the heating effect is produced at the surface of the strip, so that the conditions are more comparable than when the heating effect of the thermionic current is compared with the heat production due to an increase of current in the Wheatstone's bridge.

It is also simpler to work with, because the sensitiveness of the galvanometer depends on the current actuating the Wheatstone's bridge; so that in measuring the heating effect of an increase in this current, it is necessary to determine the sensitiveness of the bridge for each current used. The experiments made with this method of standardizing the effect agreed as to order of magnitude with those which depend on a direct comparison of the effects of the different voltages. There was, however, a definite difference in the magnitude given by the two methods, which we believe to be due to the fact that the mode of liberation of the heat is different in the two cases.

It was stated above that when there is no voltage driving the thermionic current the effect is too small to measure with accuracy. It can, however, be detected and measured, and it is found to agree with the value determined by the less direct experiments within the order of accuracy of its measurement.

Another point which was tested in the preliminary experiments was whether the change of resistance in the strip produced in a given time was proportional to the energy supplied to it. Measurements of this were made by varying the current in the Wheatstone's bridge circuit. The measurements gave the following numbers :—

(1) Change of resistance in 15 seconds......... (Scale-divisions.)	30	66	103
(2) Watts $\times 10^4$	4·55	9·9	14·7
(1) ÷ (2)	6·60	6·66	7·00

The change of resistance is proportional to the watts supplied within the order of accuracy of the measurements. The error in these measurements is considerably greater than that of the method adopted in the investigation, on account of the difficulty of determining the correction for the sensitiveness of the Wheatstone's bridge system, which is, of course, different for each current used.

§ 4. *Reduction of the Galvanometer Deflexions.*

It has been pointed out that it was not possible to get the temperature of the grid absolutely steady. As a rule there would be a regular drift corresponding to a gradual rise of temperature; in other, less common, instances the drift would be in the opposite direction. Sometimes, of course, there would be an irregular variation of the zero, but unless this was small the readings then obtained were discarded.

In order to eliminate the effect of the drift arising from changes in the steady temperature of the grid, the method was adopted of taking a large series of readings in succession, for equal periods of time, with the thermionic current alternately on and off. Thus the thermionic current would be allowed to flow into the grid for, say, 30 seconds. This gave rise to a deflexion of the galvanometer indicating a rise of temperature. The thermionic current would then be turned off for an equal period, and the galvanometer spot would be deflected back in the opposite direction. It would not, as a rule, reach the initial zero in this period of time, owing to the occurrence of the gradual drift. Again, on turning on the thermionic current for the same length of time, a deflexion would be obtained in the original direction; but at the end of this period the reading would not be the same as in the first case. The effect of the drift will be eliminated if we subtract the mean of the first and third readings from the second; and if we subtract the mean of the second and fourth readings from the third, we shall get independent values of the effect, from which the drift has been eliminated. Treating the successive readings in this way, it will be seen that we can obtain any desired number of individual determinations of the effect. Moreover, if we take a sufficiently large number, not only will the steady drift be eliminated, but the effects of any chance fluctuation in the temperature of the grid will also be obliterated. As a matter of fact, one could see at a glance whether the chance fluctuations were considerable or not, and only those readings in which they were insignificant were retained.

It will be seen that this method of reducing the readings can be summarized by the following rules, according as the number of readings is odd or even :—

1. Odd number of readings. To half the first and last add twice all the other odd readings. From this subtract 3/2 times the second and last but one, plus twice all the other even readings.

2. Even number of readings. To half the last plus 3/2 times the second add twice all the other even readings. From the sum subtract half the first, plus 3/2 times the last but one, plus twice all the other odd terms.

In each case the value thus obtained will be $n-2$ times the effect of putting on the current, if there are n readings.

§ 5. *Results of the Experiments.*

Experiments were made first with a grid cut out of platinum foil ·0031 cm. thick. The mean width of the strip was ·041 cm. and its length was about 27 cm. Its resistance was 10·04 ohms at 14 C. and varied from about 13 to 15 ohms during the experiments while the measurements were being taken. This increase in the resistance was due to the increase in the temperature of the strip caused by the thermal radiation from the hot osmium filaments. For this reason the effect is measured not at the temperature of the room, but at some higher temperature, which may be calculated from the change in the resistance of the filaments. The resistance of the leads to the grid was ·08 ohm, and this has to be subtracted from the above values in calculating the temperature.

This grid was experimented with under two different sets of conditions. In the first set before each experiment it was placed in a beaker containing nitric acid and made the positive electrode while the acid was electrolysed. In this way nascent electrolytic oxygen was deposited on it for various lengths of time. In the other set of experiments the grid was made the negative electrode in the electrolytic cell, filled with the dilute sulphuric acid, so that nascent electrolytic hydrogen was deposited on it for various lengths of time. It has been shown by H. A. Wilson [*] that when platinum is made the positive electrode in an electrolytic cell containing nitric acid for a considerable length of time, and subsequently heated, it is found to give a relatively small emission of negative electrons, and this corresponds to a large value of w. Saturating the wire with hydrogen, either electrolytically or otherwise, is found to endow it with the

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[*] Phil. Trans. A, vol. ccii. p. 243 (1903).

property of relatively large negative thermionic emission, and corresponds to a diminution in the value of w. It therefore seemed desirable to examine whether this difference in the power of thermionic emission produced by saturating the metal with oxygen and hydrogen respectively had its counterpart in the heating effect under investigation.

Furthermore, in order to examine whether the effect measured depended very much on the geometrical configuration of the platinum forming the grid, experiments were also made with a grid consisting of platinum wire of circular section ·0012 cm. in diameter. The length of the wire in this grid was approximately 36 cm. In this case the filament was not subjected to the electrolytic treatment described above, the effect being measured only for the natural state of the metal.

§ 6. *Typical Experiment.*

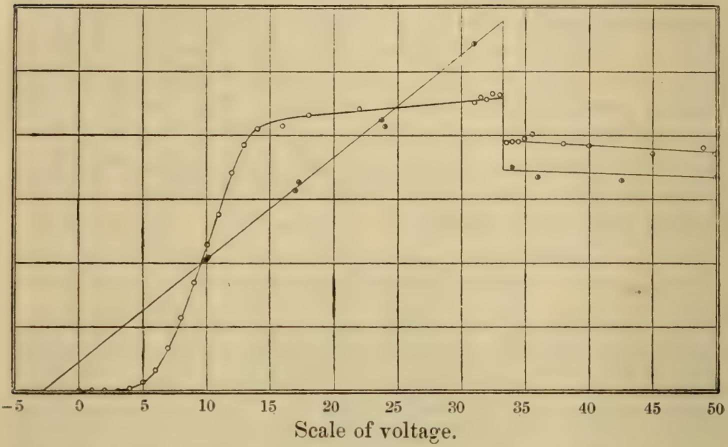
The method of observing can best be made clear by describing a typical set of observations. In every case the current-E.M.F. curve was first determined, and this was usually repeated at the end of the set. Generally speaking the thermionic current rose gradually during the course of the series of observations, so that at the end the saturation current would often be twice as great as at the beginning. It was also, as a rule, somewhat more difficult to saturate, as saturation is reached with a lower voltage the smaller the current. In this experiment the values of the saturation currents are given in the following table. The first horizontal row gives the values of the negative voltage applied to the negative end of the filament. The second row gives the corresponding values of the currents at the beginning, and the third row those at the end. In the second row the unit of current is $5·66 \times 10^{-6}$ ampere, while in the third row it is $10·4 \times 10^{-6}$ ampere. The current-E.M.F. curves always possess the same characteristics.

Current and Electromotive Force.

v …	0	1	2	3	4	5	6	7	8	9	11	15	24·2
i …	·2	·9	3·0	7·2	12·9	19·2	25·1	30·7	33·5	34·9	36·2	38·2	37·7
i …	·4	1·0	2·3	5·4	9·6	14·7	19·9	24·6	28·7	31·0	32·5	34·9	

For very low voltages the current increases very slowly with the applied E.M.F. This is followed by a short range of voltage along which the current increases very rapidly and is very nearly a linear function of the voltage. This stage again ends rather abruptly, and after that the current increases very slowly with the applied voltage, of which, however, it is again an approximately linear function. The character of the curves can be best realized by reference to figure 3, which shows the values of the currents, obtained in another experiment plotted against the corresponding electromotive forces. The values are shown thus o. It will be seen that in this case approximate saturation is attained in the neighbourhood of 14 volts. After that the increase in the current is relatively small. In the experiment to which the numbers in the preceding table refer, the current was approximately saturated at 8 volts.

Fig. 3.



The heating effect was next determined for a series of different voltages, and as a rule these were all chosen so as to exceed the voltage where approximate saturation occurred. In this way it was possible to avoid the difficulty which arises from the fact that when the current is varying rapidly with the voltage the mean potential difference through which the electrons fall does not correspond to that at the middle of the filament.

In order to explain the method of taking the observations, a typical series for one particular voltage will now be given. In this experiment the range of voltage was from 0 to 8. That is to say, when the thermionic current was "on" the potential at the negative end of the filament as measured by the voltmeter, V, was 8 volts. When it was "off" the potential of this end of the filament as measured by the voltmeter was 0 volt. The sliding contact at H was, therefore, set so that when the rocking switch A was turned the reading on the voltmeter V changed from 0 to 8 volts. The balance was then tested by the method previously described, and if it was out by more than two or three per cent. of the expected deflexion it was adjusted so as to be as near right as possible. But if the proportion was not greater than that indicated it was measured and subsequently allowed for. In the present instance the balance test gave 2·4 divisions "with the effect," that is to say, it tended to produce a spurious effect which would increase the true effect by that amount. This was recorded and no further adjustment was made. The thermionic current was next measured and found to be equal to 33·8 divisions, the micro-ammeter being shunted with ten ohms. The potential drop along the filament was then observed on the voltmeter V_2, and found to be equal to 3·62 volts. The resistance of the grid was observed as 15·28 ohms. The deflexions of the galvanometer G were now recorded as the thermionic current was turned on and off consecutively at the end of every 60 seconds. The following readings were taken :—

Off ……	77·5	80·5	80	79	82	82	83	83·5	83
On ……	183	185	182·5	184	188	191	192·5	191·5	

The thermionic current was again read and found to be 34·4 divisions. It had thus increased ·6 of a division during the experiment, so that the mean value 34·1 was taken as the correct one. The balance was again tested and found to be 1·4 division "with," or one division less than at the beginning. The mean correction on account of the lack of balance is, therefore, 1·9 divisions to be subtracted. When the seventeen readings given in the table are treated by the rule described on page 184, the mean heating effect is found to be 105·84 divisions, from which we have to subtract 1·9 on account of the balance not being exact, leaving 103·94. This is then divided by the value of the thermionic current, 34·1 divisions, giving 3·043 as the magnitude of the effect with eight volts. As a rule, and particularly if the thermionic current was increasing at all rapidly with the time, its value was observed after each four successive readings of the galvanometer, and by so doing a more exact estimate of the average value of the thermionic current could be obtained. Experiments in which there was a big jump in the thermionic current or a big change in the balance during the course of an experiment were invariably rejected.

A set of measurements similar to the above was made for each of the voltages tested. In the present experiment the voltages used were 15, 8, 11·1, 5, 24·2, in the order named. The corresponding values of the heating effect per unit thermionic current in scale-divisions are respectively 4·98, 3·04, 3·93, 2·07, and 10·04. If these are plotted against the voltage applied to the negative end of the filament, it will be seen that they are all practically on a straight line with the exception of the one with five volts, and in this case, since the effect to be measured is small on account of the smallness of the thermionic current and the voltage through which the electrons fall, the deviation from the line is probably no greater than the experimental error. It will be seen that the line cuts the voltage axis at a point on the negative side of the origin corresponding to $-3·0$ volts. If we confine ourselves to the points corresponding to the voltage for which the current was practically saturated (which in the present case comprises all the points which fall accurately on the line) it is clear that the mean potential difference through which the electrons fall will correspond to that at the middle point of the filament. Our origin of voltage should, therefore, be taken at a point to the right of that in the diagram by an amount equal to $\frac{1}{2}$ of the drop along the filament, or 1·81 volt. The voltage, therefore, which is equivalent to that through which the electrons would have to fall in order to give rise to a heating effect equal to that part of the effect which is independent of the voltage will be $3·0+\frac{1}{2}\times 3·62=$ 4·81 volts.

Each determination of the value of the constant ϕ involves the determination of a number of points on the diagram in the manner indicated. In most cases measurements were taken for a number of different voltages, and a line drawn through the series of points. In a few cases it was considered sufficient to obtain two concordant readings at each of two points sufficiently far apart, say 8 and 24 volts, and to draw a straight line through them, but generally speaking this was checked up by determining the point midway between them, and if all the points did not lie on a straight line the matter was investigated further.

In figure 3 the results of another series of observations are shown diagrammatically. The abscissæ represent voltages at the negative end of the filament. The thermionic current is shown thus ○, and the heating effect per unit thermionic current thus ⊙. In this case again the points are seen to be on a straight line, which cuts the axis of abscissæ at about -3 volts.

§ 7. *Discontinuity at High Potentials.*

An interesting phenomenon was observed when the investigation was pushed to higher potentials than those so far recorded. It was found, for example, that with the platinum grid which had been exposed to hydrogen, when potentials higher than 33 volts were used to measure the effect a smaller heating effect was obtained for a given thermionic current than at somewhat lower voltages. When the matter was examined in greater detail it was found that at a certain voltage there was a sharp drop in the value of the heating effect per unit current. In the experiment under discussion this took place at 33 volts. From 36 to 50 volts the heating effect per unit current appeared to be almost independent of the voltage. The sudden drop in the heating effect was found to be accompanied by a simultaneous discontinuity in the current-E.M.F. curve. In figure 3 the heating effect and the current-E.M.F. are plotted together. The points on the current-E.M.F. curve are shown thus ○, and the heating effect thus ⊙. We have not yet had time to examine this interesting phenomenon in detail, but two possible explanations suggest themselves. One is that for some reason or another when the voltage exceeds the critical value the discharge, or part of it, takes place to the part of the grid in the immediate neighbourhood of the glass supports, and part of the heating effect is conducted into the glass and does not make itself felt in the grid. The second, which is more interesting, is that the phenomenon is connected with the reflexion of the electrons or the emission of secondary electrons at the surface of the metal. In that case it seems quite conceivable that there may be a sudden increase in the amount of this effect at a certain potential: that the secondary electrons thus emitted escape from the grid with considerable velocities, manage to pass out of its sphere of action, as it were, and drift into the other parts of the field; so that, for example, instead of entering the grid and ultimately passing through the instrument which measures the thermionic current they reach the positive terminal of the osmium filaments. Some such view would account for the simultaneous discontinuity in both the heating effect and the thermionic current. In order to account for the fact that at higher potentials the heating effect is independent of the voltage, we should have to suppose that the kinetic energy of the particles thus lost by the grid increased in a greater ratio than that of the potential driving them. When the investigation was pushed to still higher potentials it was found that an arc or spark discharge took place which melted the grid. The melting took place inside the brass support carrying the filament. This may perhaps be regarded as an argument in favour of the first view. It is, however, impossible to settle the question until further experiments have been made; so far we have contented ourselves with being careful to employ only potentials below the critical point in order to insure the absence of complications arising from this cause.

§ 8. *Grid saturated with Oxygen.*

The results of all the experiments made with the grid of platinum strip after saturation with oxygen by electrolysis in nitric acid are exhibited in the following table:—

Number of Experiment.	Time electrolysed since last experiment.	Interval (seconds).	Pressure (mm.).	P. D. (volts).	Bridge current $\times 10^3$.	Saturation current $\times 10^5$.	Uncorrected value (volts).	Resistance cold (ohms).	Resistance hot (ohms).	Correction for joulage (volts).	Final corrected value (volts).
1.	1⅔ hrs.	60	·02	3·32	17·1	(1) 7·45 (2) 13·3	6·84	8·2	12·4	·21	6·36
2.	20 hrs.	30	(1) ·01 (2) ·002	3·12	17·0	(1) 10·77 (2) 21·24	5·86	10·04 (14°C.)	14·2	·24	5·35
3.	12 hrs.	30	(1) ·013 (2) ·004	3·56	17·1	(1) 8·92	6·13	......	14·3	·24	5·62
4.	not touched since last experiment.	30	(1) ·008	2·90	16·6	(1) 5·1 (2) 12·1	6·07	......	13·2	·22	5·58
5.	7⅓ hrs.	30	......	3·06	16·4	(1) 5·8	5·99	9·67 (22°C.)	13·4	·22	5·50
6.	34 hrs.	30	·006	3·17	16·5	(1) 10·43 (2) 16·85	5·99	......	14·2	·23	5·49

In the second column are given the times during which the oxygen was being deposited by electrolysis. The electrolytic currents used were always of the order of ·1 ampere. The third column gives the interval of time during which the thermionic current was turned on or turned off. In the fourth and subsequent columns, where the numbers are preceded by the figures 1 or 2 respectively in brackets, (1) denotes that the value in question was that at the beginning of the observations, whereas (2) denotes the value at the end of the observations. The fifth column gives the fall of potential along the osmium filament due to the heating current.

The numbers in the eighth column represent the values of the effect in volts obtained by producing the line through the points back to where it cuts the voltage axis, and adding to the negative voltage at this point on the axis half the value of the potential drop in column five. Columns nine and ten enable an approximate estimate to be made of the temperature of the grid, and also the correction in column eleven to be calculated. This correction will be considered more fully below.

It will be seen that the numbers in the last column are in very good agreement. The agreement between the last five is very much better than that of ~~the~~ first with any of the others. We have, however, carefully compared the observations and have not been able to detect anything in the numbers belonging to the first set which would warrant their rejection. The mean of the whole six observations is 5·65 volts. If we reject the first observation the mean is reduced to 5·51 volts.

§9. *Grid saturated with Hydrogen.*

Experiments were made with the grid of platinum strip after it had been saturated with hydrogen by electrolysis of dilute sulphuric acid for varying periods of time. The results are exhibited in the following table :—

Number of Experiment.	Time electrolysed since last experiment.	Interval (seconds).	Pressure (mm.).	P. D. (volts).	Bridge current $\times 10^3$.	Saturation current $\times 10^5$.	Uncorrected value (volts).	Resistance hot (ohms).	Correction for joulage (volts).	Final corrected value (volts).
1.	12 hrs.	30	......	3·88	16·6	(1) 13·55	5·72	15·50	·26	5·19
2.	20 hrs.	30	......	3·62	16·8	(1) 5·67	4·77	14·8	·25	4·25
3.	Running since last experiment.	30	·005	3·62	16·0	(2) 7·08	4·67	15·2	·25	4·50
4.	,,	60	......	3·62	16·0	(1) 15·31	5·15	15·32	·25	4·63
5.	,,	60	......	3·62	16·0	(1) 21·67	5·51	15·28	·25	4·99
6.	Recharged.	60	......	3·42	5·0	(1) 10·4	4·71	15·16	·08	4·36
7.		30	......	3·24	5·0	(1) 26·4	4·23	15·14	·08	3·88
8.	Recharged.	30	......	3·04	5·0	(1) 27·4	5·87	15·47	·07	5·53
9.		30	·012	3·02	5·0	(1) 15·7	6·13	13·9	·07	5·79
10.	Recharged.	30	......	3·02	5·0	(1) 29·9	6·09	14·4	·07	5·75

The numbers in the various columns represent the same quantities as the corresponding columns in the previous table. In the last five sets of experiments the precise treatment of the grid was not recorded, but before the experiments Nos. 6, 8, and 10 the filament was exposed for varying lengths of time to hydrogen by electrolysis of sulphuric acid. A glance at the last column will show that the agreement of the results among one another is not so good as in the case with the experiment when the strip had been exposed to nascent oxygen in nitric acid. We have not yet been able to trace the cause of this disagreement with certainty. The mean of all the ten values gives 4·85 volts for the effect. It will be noticed that the three last voltages are considerably higher than any of the others. If these are rejected, the mean is brought down to 4·49. There does not, however, seem to be any compelling reason for rejecting them, as the individual observations look satisfactory, and so far as we are able to judge, they were made under conditions similar to those which held while the other observations were being made.

Taking a general view of the whole results which have been obtained so far, it would seem that saturation of the filament with hydrogen reduces the magnitude of the effect nearly one volt from the value obtained when it has been saturated with oxygen.

§ 10. *Platinum Wire Grid.*

As has been stated above, experiments were also made with a grid wound with platinum wire of ·012 cm. diameter. The results of these experiments are exhibited in the following table:—

Number of Experiment.	Interval (seconds).	P. D. (volts).	Bridge current $\times 10^3$.	Saturation current $\times 10^5$.	Uncorrected value (volts).	Resistance hot (ohms).	Correction for joulage (volts).	Final corrected value (volts).
1.	30	3·04	5·0	(1) 18·28	6·22	11·8	0·6	5·89
2.	30	3·00	5·0	(1) 18·45	5·95	11·4	0·6	5·62
3.	30	2·98	5·0	(1) 22·57	6·69	11·72	0·6	6·36
4.	120	2·98	5·0	(1) 22·57	5·69	11·72	0·6	5·36

The corresponding columns give the values of the same quantities as in the previous table. The last two experiments were made with different intervals of time. In one set the thermionic current was turned on and off every thirty seconds, and in the other set every two minutes. A marked difference between the two values was obtained, but we are inclined to think that a great deal of this arises from some independent cause, as another experiment, made especially to test this point, and which is not recorded in the table, gave a small difference in the opposite direction. It is difficult to get accurate observations with intervals as long as two minutes, and the fact that the value 6·36 for thirty-second intervals is much greater than the number given by the two previous observations tends to shed doubt on this set of experiments. The mean of all the experiments gives 5·81 volts for the effect. If the third is rejected on account of its deviation from the mean, and the fourth on account of the time not being the same, the mean of the two is 5·75 volts. This is not very different from the values given by the experiments in oxygen. The fact that it is somewhat higher may perhaps be taken to indicate that there is an apparent increase in the magnitude of the effect when the thickness of the metal used is increased.

§ 11. *Graphical Treatment.*

In order to see at a glance the degree of consistency of the results a graphical method of exhibiting them has also been adopted. Owing to the variation of some of the conditions, such as, for example, the sensitiveness of the galvanometer from one set of experiments to another, change of temperature of the grid, etc., the heating effect for a given number of volts per unit thermionic current as measured in scale readings, does not mean the same thing in the different sets of experiments. It is, therefore, necessary in comparing the different experiments to reduce all the measurements to a uniform scale. This has been done by drawing the best line through each individual series and putting the value of the scale deflexion per unit thermionic current at an arbitrary voltage (as a matter of fact, 12 volts was taken) equal to some arbitrary quantity, say 4. The individual readings for different voltages were then reduced to the scale thus obtained and have all been plotted together in the accompanying diagram (Pl. III. fig. 4). In this diagram the voltage is represented horizontally and the effect on the standard scale vertically. The points for the grid saturated with oxygen are marked thus ⊕, the points for the grid saturated with hydrogen thus ⊙; while the points with the platinum wire grid are shown thus ●. As the diagram is constructed, the points appear to fall into two groups, each lying very near a straight line. This is because the hydrogen group has been separated from the oxygen group by shifting its scale of voltage four units to the right so that for the points which fall in the right hand group the voltages are less than the reading on the scale of abscissæ by 4 volts. The points for the platinum wire grid have been plotted twice, once on each of the two voltage scales mentioned. Thus they fall near to the line drawn through the oxygen points as well as to the line drawn through the hydrogen points. It will be seen that the oxygen points fall on the straight line with exceedingly close accuracy, and that the platinum wire points also fall on the same line with about the same accuracy. As has already been observed, the hydrogen points are not so consistent among themselves and the best line through them falls a little off the best line through the platinum wire points. When corrected for the joulage and for the temperature energy of the electrons, the best line through the oxygen points on this diagram gives for the mean value 5·45 volts, while the best line through the hydrogen points gives 5·05 volts. The value obtained in this way for oxygen is somewhat less and for hydrogen somewhat greater than the arithmetical mean of the observations previously obtained. But they agree in indicating that the effect when the filament has been saturated with hydrogen is lower than the value in oxygen.

It is remarkable that *all* the observations on the platinum grid saturated with oxygen and the platinum wire grid, which have been used in deducing the values given in the previous table, should fall so nearly on the straight line as they are seen to do from fig. 5 (Pl. III.). It will be recollected that the individual values for the effect recorded in those tables showed considerable variation. This emphasizes the importance of taking every observation with great care and accuracy since it is clear that a small error in the position of the line makes a very large percentage error in the final value of the effect.

The position of the points in figure 4 is corrected for the difference in the potential drop along the filament in the different experiments, but no correction has been made on account of the difference in the heating effect of the Wheatstone's bridge current in the different cases. It is not believed that the omission of this correction has made any appreciable difference to the accuracy of alignment of the points.

§ 12. *The Potential Driving the Thermionic Current.*

When the applied voltage is such that the current is saturated, the same number of electrons per unit length will be emitted by every portion of the hot wire. In that case the mean value of the potential which drives the current will clearly be the potential of the middle of the wire. In the stage where saturation has not been attained this will no longer be true, as a greater number of electrons will be emitted per unit length from those parts of the filament for which the negative potential is greatest. In that case, however, the true average potential of all the emitted electrons will be obtained if the current-E.M.F. curves are analysed in the following manner:—

The thermionic current per unit length of the wire will be different for different parts of the wire and will be greatest where the negative potential of the filament is greatest. The potential will vary from point to point of the wire on account of the difference of potential required to drive the heating current through it. If the potential at any point is V, we can denote the thermionic current per unit length at that point by $f(\mathrm{V})$. Then the observed current, i, will be the integrated effect of this over the whole length of the wire. Thus if l is the length of the wire, we shall have

$$i = \int_0^l f(\mathrm{V})dx = \frac{1}{\partial\mathrm{V}/\partial x}\int_{\mathrm{V}_0}^{\mathrm{V}_l} f(\mathrm{V})d\mathrm{V},$$

since $\frac{\partial \mathrm{V}}{\partial x}$, the gradient driving the heating current, is constant. Hence

$$\frac{\partial i}{\partial \mathrm{V}} = \frac{1}{\partial\mathrm{V}/\partial x}[f(\mathrm{V}_l) - f(\mathrm{V}_0)]$$

where V_l and V_0 are the potentials at the two ends of the wire. If V is less than $l\frac{\partial \mathrm{V}}{\partial x}$, then $f(\mathrm{V}_0)$ is in general equal to 0 since it corresponds to a positively charged part of the wire, so that $f(\mathrm{V}_l) = \frac{\partial \mathrm{V}}{\partial x} \times \frac{\partial i}{\partial \mathrm{V}}$. We can thus obtain the value of $f(\mathrm{V})$ over this range by simply differentiating the current-E.M.F. curve with respect to V, since this curve expresses i as a function of V.

In some cases it has been observed that for very small values of V the thermionic current had a small value independent of the voltage. In this case we have

$$f(\mathrm{V}) = i/l \quad \text{or} \quad f(\mathrm{V}_0)\Big/\frac{\partial \mathrm{V}}{\partial x} = \frac{i}{\mathrm{V}},$$

where V is the potential fall along the hot wire.

When V is greater than $l\frac{\partial \mathrm{V}}{\partial x}$,

$$\frac{1}{\partial \mathrm{V}/\partial x} f(\mathrm{V}_l) = \frac{\partial i}{\partial \mathrm{V}} + \frac{1}{\partial \mathrm{V}/\partial x} f(\mathrm{V}_0),$$

so that to obtain $f(\mathrm{V})$ as a function of V we proceed as follows:—First take $\mathrm{V}=\mathrm{V}_1$ between 0 and $l\frac{\partial \mathrm{V}}{\partial x}$. Then the value of $f(\mathrm{V}_1)$ is equal, by what has gone before, to $\frac{\partial \mathrm{V}}{\partial x}\frac{\partial i}{\partial \mathrm{V}}$. Next take

$$\mathrm{V}_l = \mathrm{V}_2 = \mathrm{V}_1 + l\frac{\partial \mathrm{V}}{\partial x}.$$

Then

$$\frac{1}{\partial \mathrm{V}/\partial x} f(\mathrm{V}_2) = \frac{\partial i}{\partial \mathrm{V}} + \frac{1}{\partial \mathrm{V}/\partial x} f(\mathrm{V}_1).$$

Since $f(\mathrm{V}_1)$ has already been determined, differentiation of the current-E.M.F. curve enables us to determine $f(\mathrm{V}_2)$. We then take

$$\mathrm{V}_l = \mathrm{V}_3 = \mathrm{V}_2 + l\frac{\partial \mathrm{V}}{\partial x},$$

and thus deduce the value of $f(\mathrm{V}_3)$. Proceeding in this way, we can obtain the values of $f(\mathrm{V})$ corresponding to a series of constantly increasing values of V. We now multiply each value of $f(\mathrm{V})$ by the corresponding value of V. V is the potential difference driving the current $f(\mathrm{V})dx$ which originates from the element dx of the hot wire, so that it is clear that the average potential difference through which the electrons fall, corresponding to any observation where the thermionic current is i, will be equal to

$$\frac{\int_0^l \mathrm{V}f(\mathrm{V})dx}{\int_0^l f(\mathrm{V})dx} = \frac{1}{i}\int_0^l \mathrm{V}f(\mathrm{V})dx = \frac{1}{i\frac{\partial \mathrm{V}}{\partial x}}\int_{\mathrm{V}_0}^{\mathrm{V}_l} \mathrm{V}f(\mathrm{V})d\mathrm{V}.$$

The value of this definite integral can readily be obtained graphically if $Vf(V)$ is plotted as a function of V. An example exhibiting the method of applying this correction for the difference of potential at different points of the wire will now be given.

The only set of observations which has been examined in this way are those obtained with the platinum grid saturated with hydrogen No. 7. In this case the observations for the current-E.M.F. are shown thus ○ in the diagram fig. 5, Pl. III. The best curve possible was drawn through the observational points and the values of the tangents of the angles of inclination, of the tangents to the various points of this curve, with the axis of voltage were measured. The direction of the tangents was determined by placing a mirror at various points on the curve in such a direction that the curve and its reflexion are continuous. The edge of the mirror is then perpendicular to the direction of the tangent. The tangents were measured at points a distance apart equal to the fall of potential (3·267 volts) along the strip as required by the foregoing theory. From these the values of $\frac{1}{\partial V/\partial x}\cdot f(V)$ were determined. The values of this function were then multiplied by V, the voltage at the negative end of the strip, and plotted on the diagram. The values of $\frac{1}{\partial V/\partial x}\,Vf(V)$ are shown thus ⊗. They are seen to lie on a smooth curve passing through the origin. The values of

$$\frac{1}{\partial V/\partial x}\int_{V_0}^{V_l} Vf(V)dV$$

were next found by counting up the number of squares in a portion of the diagram similar to that shaded and bounded on the top by the graph of $\frac{1}{\partial V/\partial x}Vf(V)$, on the bottom by the axis of voltage and on the sides by the two vertical lines a distance ∂V apart, where ∂V denotes the potential drop along the filament. The values of these integrals were then divided by the values of the current i from the strip at the corresponding voltages. The resulting quantities are denoted thus ⊕. They are seen to lie on a curve, the major part of which consists of a straight line pointing to a voltage equal to 1/2 of the drop of the potential along the filament. Since the diagram represents the voltage applied to the negative end of the filament, it follows that this line points, as it should, to the true zero of average voltage. Along the part of the curve which corresponds to approximate saturation the deviation from linearity cannot be detected. But where the current is far from saturation the points on it lie very considerably above the straight line, so that in this region a considerable error would be introduced by supposing that the average energy of the thermions emitted by the filaments corresponded to what they would gain if they all fell through a difference of potential equal to that at the middle of the filament. Practically all the observations which have been made fall within the part of this curve where the deviation from the linear relation is less than the error of observation.

§ 13. CORRECTIONS.

(1) *For the Temperature Energy of the Electrons.*

We have seen that the heating effect for zero applied voltage consists of two parts, (1) the part which we are measuring due to the difference of the potential energy of the electrons inside and outside the metal, and (2) a part which is equal to the difference between the kinetic energy of thermal agitation of the electrons as they are emitted from the hot metal and the value which that quantity would have at the temperature of the grid. Thus, if θ_1 is the temperature of the osmium filament and θ_2 that of the grid, this part of the heating effect will be equal to

$$\frac{\alpha}{e}(\theta_1-\theta_0)=\frac{n\alpha}{ne}(\theta_1-\theta_0),$$

where n is the number of molecules in a cu. cm. of gas under standard conditions of temperature and pressure.

Then $n\alpha \times 273$

$= \text{the translational kinetic energy in 1 cu. cm. of } H_2$ at 0° C. and 760 mm.

$= \frac{3}{2}p = \frac{3}{2} \times 76 \times 13{\cdot}6 \times 981 \times 10^{-7}$ joule.

$ne =$ charge carried by $\frac{1}{2}$ cu. cm. of H_2 in electrolysis

$= 4{\cdot}327$ coulombs.

Let us assume, what is approximately correct, that the temperature of the osmium is 2000° C. above the temperature of the grid. Then substituting the above values, we find

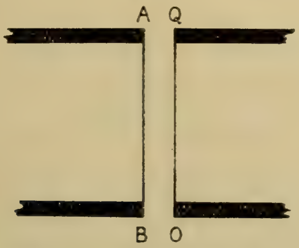
$$\frac{\alpha}{e}(\theta_1-\theta_0)={\cdot}25 \text{ volt}.$$

It is necessary, therefore, to subtract this amount from the observed value of the heating effect in order to deduce the part which depends on the change in the potential energy.

(2) *The Direct Heating Effect of the Thermionic Current.*

In addition to the effects which have been mentioned, the grid will be continuously heated by the current in the Wheatstone's bridge circuit. When the thermionic current is turned on, the conduction current flowing along the grid at any point will be altered, so that there will be a change in the heating effect due to the conduction current. We shall now proceed to show how the rate of heat production due to this cause may be calculated. Suppose AB (fig. 6) represents a length of heated metal emitting electrons, and the material of the grid is represented diagrammatically by the line OQ. Then at any instant a uniform current i arising from the Wheatstone's bridge circuit will be flowing along OQ. In addition to this there will be a thermionic current flowing from AB into various points of OQ. Let the thermionic current into OQ at any point be j per unit length. Then the thermionic current into a length dx of OQ at the point x is equal to $j dx$. The total thermionic current into the grid will thus be $J=\int_0^Q j\,dx$. In the arrangement that we have used part of the thermionic current flows out of one end of the grid and part out of the other (see fig. 1). There will, therefore, be a point M in the grid where the thermionic current contributes nothing to the value of the current along it, so that the current at this point has the same value i_0, whether the thermionic current is on or off. Let us take this point as origin and let x denote distance along the strip, x being positive upwards. Let the co-ordinates of Q and O be x_1 and $-x_0$ respectively. Then the current along the grid at any point $x=i_0+\int_0^x j dx$. Let R be the resistance per unit length of the grid. Then the rate of heat production in the length dx

Fig. 6.



$$=\mathrm{R}dx\left(i_0+\int_0^x jdx\right)=\mathrm{R}\left\{i_0^2+2i_0\int_0^x jdx+\left(\int_0^x jdx\right)^2\right\}dx.$$

When there is no thermionic current, the rate of total heat production

$$= R\int_{-x_0}^{x_1} i_0^2 dx.$$

So that the increase, δQ, due to the thermionic current

$$= R\int_{-x_0}^{x_1} dx \left\{ 2i_0\int_0^x jdx + \left(\int_0^x jdx\right)^2 \right\}.$$

As an illustration, let us suppose that j has the same value at every point. Then

$$\delta Q = R(x_1+x_0)\left\{ij(x_1-x_0)+\tfrac{1}{3}j^2(x_1^2-x_1x_0+x_0^2)\right\}.$$

We can determine the position of the point M from the conditions which have to be satisfied in order that there should be no current through the galvanometer G (fig. 1) when the thermionic current is turned on. For, we shall have that the drop of potential from M along S through the resistance R_1, shunted by the battery circuit and the resistance R_2 to K, is equal to the drop of potential from M along S to L, so far as the thermionic current is concerned. The drop of potential from M to K due to the thermionic current is equal to

$$R\int_0^{x_1} dx\int_0^x jdx + P\int_0^{x_1} jdx, \text{ where } P = \frac{R_1(B+R_2)}{R_1+B+R_2},$$

B being the resistance of the battery circuit. The drop from M to L

$$= R\int_0^{x_0} dx\int_0^x jdx.$$

In addition, the potential drop due to the thermionic current from K to E

$$= R_4\int_0^{x_1} jdx = \text{the drop from L to E} = R_5\int_0^{x_0} jdx.$$

In the particular case when j is constant, these two relations become

$$\frac{R}{2}jx_1^2+jx_1P = \frac{R}{2}jx_0^2, \text{ or } Rx_1^2+2Px_1 = Rx_0^2 \quad . \quad . \quad (1)$$

and

$$jx_1R_4 = jx_0R_5, \text{ or } x_1R_4 = x_0R_5. \quad . \quad . \quad . \quad (2)$$

We see, therefore, that $x_0/x_1 = R_4/R_5$. In the experiments

R_4/R_5 was comparable with 200, so that x_0 is practically equal to the whole length l of the grid. Let us, therefore, put as an approximation $x_0 = l$ and $x_1/x_0 = 0$. So that $\delta Q = Rl(\frac{1}{3}j^2l^2 - ijl)$. In this case we also have $Rl = S$, the resistance of the grid, and $jl = J$. So that

$$\delta Q/J = S(\tfrac{1}{3}J - i).$$

In the experiments the maximum values of these quantities were respectively $S = 15$ ohms, $J = 3 \times 10^{-4}$ amp., and $i = 17 \times 10^{-3}$ amp. So that the maximum value of this correction $\delta Q/J = {\cdot}25$ volt.

Although the above calculation of the correction has only been carried out for the case where j is constant, it can readily be seen that a similar result will follow for any distribution of j which is symmetrical about the central point of the grid. As this condition was very nearly fulfilled in practice, the above method of calculation has been used in estimating the magnitude of the correction for the direct heating effect of the thermionic current. The relation between the direction of the thermionic current and the direction of the bridge current was such that this correction involved a deduction from the observed value in all cases. The actual values of the amounts which have to be subtracted on this account are given in the last column but one of the various tables above.

§ 14. *Possible Sources of Error.*

It will readily be conceded that the foregoing results leave no doubt as to the existence of the effect under investigation or of its order of magnitude ; but, at the same time, it is very difficult to obtain results of a high order of accuracy. We are unable at present to locate the source of such inconsistencies as have been experienced. A glance at the tables would seem to indicate that there is a correlation between the magnitude of the observed effect and the pressure of the gas in the apparatus. If it is desired to carry out experiments of this nature with reasonable rapidity it is difficult to reduce the pressure of a gas below ·005 mm. owing to the fact that the development of heat in the osmium filament raises the temperature of the whole apparatus very considerably and causes an inconvenient amount of gas to be evolved. We have made direct experiments in order to see if an increase of gas pressure gave rise to an increase in the apparent value of the effect. These experiments show that if there is any effect due to pressure it is probably too small to account for the observed differences.

Another difficulty that we have to contend with arises from the fact that the hot filaments continually sputter particles on to surrounding objects, so that the grid very rapidly becomes covered with a layer of material deposited on it from the osmium filaments. We are not sure, however, that this alters the magnitude of the observed effect, as in some cases, for example oxygen No. 4, the value 5·58 was obtained after a continuous heating of some twenty hours; whereas the preceding experiment gave a value of 5·62. In other experiments a change seemed to be observed after continued heating, but there is no conclusive evidence that the change was due to the sputtered material. The possibility of an alteration both from the pressure of the gas and from sputtering lands us in a dilemma, because to get the apparatus down to a really low pressure it is necessary to heat the filaments continually for a long time, whereas to avoid the accumulation of the sputtered material it would be advisable to take the observations as quickly as possible after the apparatus had been set up.

We have already pointed out that the rate at which the grid heats up depends not only on the total rate of heat production within it, but also on its mode of distribution. For instance, for a given rate of heat production the increase of temperature in a given interval is not the same when the heat is produced throughout the volume of the grid by increasing the current in the Wheatstone's bridge circuit as it is when it is produced by the impact of the electrons. A source of error of somewhat similar character may possibly arise when the heating effects at different voltages are compared with one another by comparing the rise in temperature in equal times; since it is probable that the distribution of the current into the grid will be different at different voltages. We should expect that the electrons would be more likely to be collected into a small region in the centre of the grid when the difference of potential between the filaments and the grid is relatively large. This might introduce a difference in the rate of rise of temperature of the grid as between high and low voltages, even if the actual total rate of heat production were the same. It is difficult either to test for this effect or to eliminate it if it occurs, but it seems fairly certain that it cannot lead to very big errors. It is to be borne in mind that since the resistance of the grid is proportional to the absolute temperature at every point, the increase in the total resistance will be independent of the distribution of the heat communicated to it, provided that the total amount of heat communicated is identical in the cases compared. It is also necessary that the heat communicated should be similarly distributed about the cross section of the grid and that the latter should be uniform.

One possible source of error that we considered arises from the cooling effect produced by the escape of the thermions from the osmium filament. This will make the temperature of the filament lower when the thermionic current is on than when it is off, and hence the thermal energy radiated to the grid will be less when the thermionic current is on. We should therefore expect a change of temperature of the grid independently of any of the causes discussed hitherto. This effect was tested for in the following manner.

The grid and its connexions, which were otherwise insulated, were connected by a wire with the negative end of the filament. A suitably high potential difference, which could be reversed, was applied between the filament and the surrounding brass box, so that the thermionic saturation current could be made to flow at will from the filament to the box when desired. With this arrangement there is no thermionic current from the filament to the grid, so that any change produced in the temperature of the latter will arise from changes in the thermal radiation it received from the filaments. Under these circumstances it was found that no change was produced in the resistance of the grid when the thermionic current from the filaments to the case was turned on or off. This shows that under the conditions of the experiments the cooling effect arising from the emission of the electrons by the filaments is too small to exert any appreciable influence on the temperature of the grid through the change in thermal radiation which it causes. This possibility can therefore be entirely left out of consideration as a disturbing factor.

§ 15. *Comparison with the Work done during the emission of Electrons from Hot Metals.*

Without being able to assign any very satisfactory reason, we are inclined to think that the most probable values of the effect are those which are obtained after the high values in the tables are omitted. Thus for platinum saturated with oxygen by electrolysis in nitric acid the value of ϕ probably corresponds very closely with the work done in falling through a potential difference of 5·5 volts, whereas for platinum saturated with hydrogen by electrolysis of dilute sulphuric acid the mean value obtained, when the last three series of observations are neglected, is 4·5 volts.

On account of the greater consistency of the measurements the value for oxygen is probably considerably more reliable than that for hydrogen. With the exception of the single high value, which has been omitted, the five remaining determinations for oxygen agree with one another within the limits of observational error.

It is interesting to compare these values of ϕ with the values of the corresponding quantity deduced from experiments on the variation with temperature of the negative thermionic emission from hot platinum. This method of deducing the value of ϕ has already been explained by O. W. Richardson. A little further explanation will perhaps not be superfluous. The coefficient b in the formula $A\theta^{1/2}e^{-b/\theta}$, which represents the variation of the thermionic emission from a hot metal with the temperature, is $\frac{\phi e}{R}$, where e is the charge on an electron and R is the gas constant reckoned for a single molecule. Hence if n is the number of molecules in 1 c.c. of a gas under standard conditions of temperature and pressure,

$$b=\frac{\phi e}{R}=\frac{\phi ne}{R_1},$$

where R_1 is the constant in the equation $pv=R_1\theta$ reckoned for 1 c.c. of gas at 0° C. and 760 mm. pressure. ne is clearly the quantity of electricity required to liberate half a cubic centimetre of H_2 at 0° C. and 760 mm. pressure in a water voltameter, and is $=\cdot 4327$ electromagnetic units. The value of R_1 is $3\cdot 72\times 10^3$erg/°C. Substituting these values, we find that

$$\phi=8\cdot 59\times 10^{-5}\times b \text{ volts.}$$

The value of ϕ given by Richardson[*] in his first series of measurements is 4·1 volts. This is a little lower than what the value of b from which it is calculated requires, on account of approximate values of R and e having been used. Recalculating from the experimental value of b, using the relation given in the last paragraph, we find $\phi=4\cdot 26$ volts.

More recent work has shown that this value is smaller than that from pure platinum, as the results there given indicate that the metal used in these experiments was probably not free from traces of hydrogen. The best value hitherto obtained is probably one given by H. A. Wilson[†] for a wire carefully freed from hydrogen by treatment with nitric acid.

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[*] Phil. Trans. A, vol cci. p. 497 (1903).

[†] Phil. Trans. A, vol. ccii. p. 243 (1903).

His value of b, when reduced in the manner described above, gives $\phi = 5{\cdot}63$ volts. Another satisfactory set of measurements is given by Deininger[*], who finds $\phi = 5{\cdot}1$ volts. Deininger, however, seems to have used the same approximate values of R and e as were used by Richardson in his first paper. Using the better values of the constant e/R given above, we find from Deininger's value of b that $\phi = 5{\cdot}26$ volts. Another determination to which some weight should be attached is a more recent one by Richardson[†]. The individual observations in this set are not so good as in the two others, but they have the merit of comprising concordant values for two different specimens of platinum.

If we take the mean of the values given in the last paragraph, assigning different weights to the different determinations, namely 3 to Wilson's, 2 to Deininger's, and 1 to Richardson's, we find $\phi = 5{\cdot}54$ volts. This may be taken to be coincident with the value 5·5 volts found for the corresponding quantity in the present investigation, within the limits of the errors of observation.

Values of b for the electronic emission from hot platinum in an atmosphere of hydrogen have been given by Wilson[‡] and Richardson[§]. These depend not only on the pressure of the hydrogen, but on the previous history of the platinum as well. The values given by Wilson are for a new wire and are as follows:—

Pressure of H...	·0013 mm.	·112 mm.	133 mm.
Value of b	$6{\cdot}0 \times 10^4$	$4{\cdot}30 \times 10^4$	$1{\cdot}80 \times 10^4$
Value of ϕ	5·16 volts	3·70 volts	1·546 volts.

Richardson's values, which are for an old wire in hydrogen, are as follows:—

Pressure of H...	1·9 mm.	226 mm.
Value of b	$6{\cdot}0 \times 10^4$	$2{\cdot}78 \times 10^4$
Value of ϕ	5·16 volts	2·39 volts.

The platinum in our experiments was saturated with hydrogen by electrolysis of dilute sulphuric acid and it is impossible to say which of the above values our results should be compared with. All the results in hydrogen have one feature in common, namely that they give a smaller value of ϕ than that given by a platinum wire which is free from hydrogen.

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[*] *Ann. der Phys.* iv. vol. xxv. p. 304 (1908).

[†] Phil. Trans. A, vol. ccvii. p. 1 (1906).

[‡] *Loc. cit.*

[§] *Loc. cit.*

§ 16. *The Concentration of the Free Electrons in Platinum.*

The fact that the values of ϕ, given by measurements of the thermionic emission and by the heating effect, are so nearly identical would seem to indicate that it does not depend very much on the temperature of the metal. It has been pointed out by Richardson* that the temperature variation of ϕ is of importance in connexion with the determination of the concentration of the free electrons in a metal. The coincidence of the two values of ϕ would indicate that the value of the concentration deduced from experiments on the thermionic emission is not far from the truth.

§ 17. *Conclusion.*

Further measurements on a series of metals are in progress and the results will be published shortly. It seems desirable to postpone further discussion of the results of the present paper until the whole can be considered together.

In concluding we wish to express our thanks to Messrs. Baldwin, Carter, Critchlow, Ferger, Frederick, and Gibbs, Honours Students in Physics, who have assisted us in taking a number of the observations.

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XV. *The Limitations of the Weston Cell as a Standard of Electromotive Force.* *By* S. W. J. Smith, *M.A.*, *D.Sc.*, *Lecturer on Physics, Imperial College of Science and Technology*†.

§1. THIS paper contains an attempt to explain Mr. F. E. Smith's recent experiments on the cadmium amalgams of the Weston cells ‡ in terms of the theory of solutions.

The manner in which, according to this theory, the amalgams crystallize is indicated, and it is shown why, with this mode of crystallization, the effect of the slowness of diffusion is so pronounced, and also why sudden cooling to a temperature below the freezing point of mercury must produce a comparatively uniform alloy.

The cause of the most obvious differences between the behaviour of the "chilled" and of the "slowly cooled" amalgams is then at once apparent.

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* Phil. Trans. A, vol. ccii. p. 543 (1903); Phys. Rev. vol. xxvii, p. 528 (1908).

† Communicated by the Physical Society: read May 27, 1910.

‡ Phil. Mag. Feb. 1910, pp. 250–276.

But there are certain much less obvious differences of which, in view of the importance of the Weston cell as a standard (if for no other reason), it is desirable to know the cause.

An all-fluid amalgam, of course, yields the same E.M.F. whether previously chilled or cooled slowly. An all-solid alloy, on the other hand, always gives a higher E.M.F. when solidified by chilling.

The E.M.F. of the chilled amalgam thus in general equals or exceeds that of the slowly cooled amalgam.

But in the range of the two-phase alloys, over which the E.M.F. varies comparatively little with the total percentage of Cd, the opposite is true. The E.M.F. of the slowly-cooled amalgam now either equals or exceeds that of the chilled amalgam.

The excess never amounts to more than a few hundred-thousandths of a volt; but is important in measurements of the highest precision and requires explanation.

It is shown that this phenomenon may be due to electrolytic surface effects arising from the lightness and want of uniformity of composition of the solid grains in the slowly cooled amalgams.

Instances of similar effects, liable to escape notice, are to be found amongst the data for the all-solid alloys.

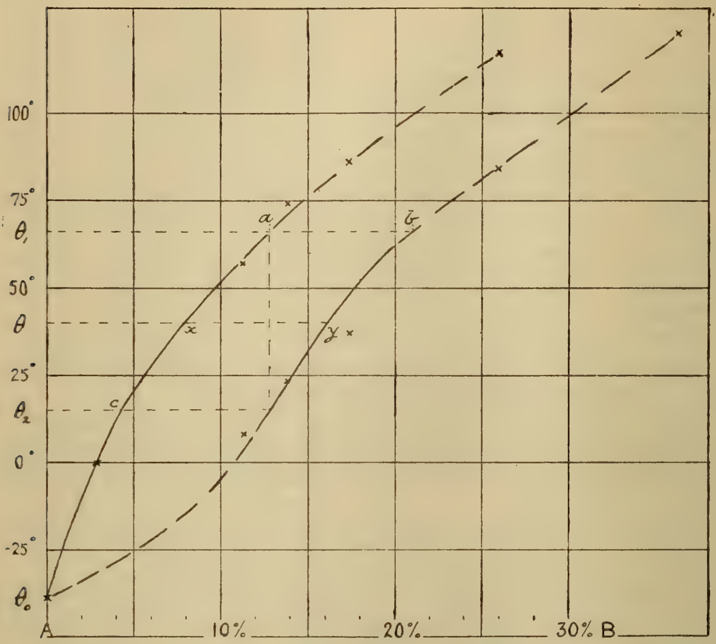
Finally, the question as to whether there is any range over which the E.M.F. is absolutely independent of the percentage of cadmium is discussed.

Theory and experiment alike suggest that the E.M.F. must rise as the percentage increases; but the variation frequently does not amount to more than a few millionths of a volt for one per cent. variation of the cadmium content.

§ 2. *A mode of crystallization of binary alloys.*—The various ways in which fluid mixtures of two metals can freeze have been carefully studied within recent years. One of these is shown in fig. 1. The abscissæ represent percentages of one metal (B) in the mixture, reckoned from a zero at which the other metal (A) alone is present. The ordinates represent temperatures. The melting point of A is θ_0. The "freezing point curve" $\theta_0 xa$ gives the temperatures at which different alloys begin to solidify, and shows that the freezing point rises continuously as the percentage of B in the mixture increases. The "melting point curve" $\theta_0 yb$ gives the composition of the solid which deposits from any particular liquid when it begins to freeze. Thus a cooling fluid containing x per cent. of B begins to freeze at θ and y

is the percentage of B which the solid first deposited contains. At any given temperature (θ), liquid and solid alloys can exist in equilibrium only when their percentage compositions have definite values (represented by x and y respectively). The thermodynamical method of accounting for this condition of equilibrium is referred to later (§§ 12 and 14).

Fig. 1.

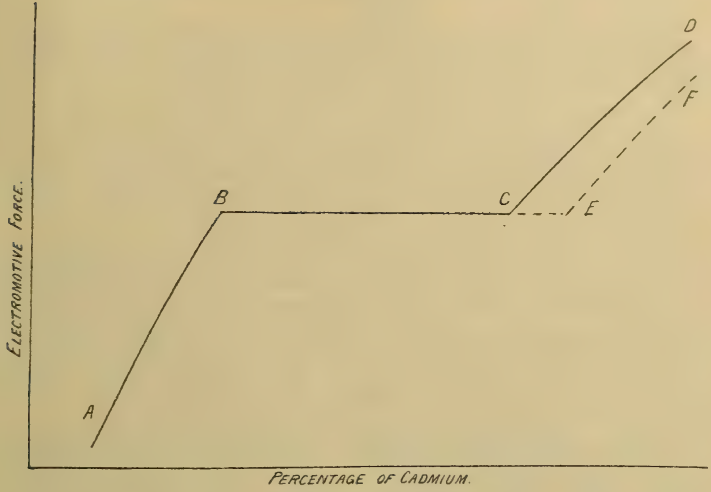


Roozeboom was the first to suggest that the thermal variation of the constitution of cadmium amalgams may be determined by curves like those of fig. 1, so long as the percentage of cadmium does not pass a certain limit (not exceeded in the experiments discussed below), and this suggestion was found to accord with various experimental data obtained by Bijl.

§ 3. *Recent experiments on cadmium amalgams.*—Mr. F. E. Smith has thrown fresh light upon the problem and provided new material for investigation by examining the effect of "chilling," *i. e.* of cooling the amalgams suddenly from temperatures at which they are wholly fluid to a temperature below the freezing point of mercury.

The most striking result of his experiments is shown in fig. 2, which exhibits (diagrammatically) how, at a constant temperature, the E.M.F. of a Weston cell alters with the percentage of Cd in the amalgam. In one set of experiments, represented by the curve ABCD, the amalgam was cooled suddenly (as above) to $-50°$ C. and then allowed to rise in temperature to 0° C. before the cell of which it formed part was constructed. In the other set, represented by ABEF, the amalgam was cooled "slowly" (*i. e.* from the liquid state to 0° C. in several hours) before being used.

Fig. 2.



On the scale of representation, the curves are identical from A to C, and BCE is a horizontal straight line. The observed time effects and variations in the horizontal parts of the curves are discussed later.

It is easy to anticipate from fig. 1 that the curve for measurements like those of fig. 2 will consist of two branches joined by an intermediate horizontal portion. For at a given temperature θ, any amalgam containing less than x per cent. Cd would be all-liquid, and any amalgam containing more than y per cent. Cd might be all-solid; while intermediate amalgams could consist of mixtures in different proportions of x per cent. liquid and y per cent. solid respectively.

In all-liquid and all-solid amalgams the electromotive force would, it is natural to suppose, vary continuously with the percentage of Cd. In mixtures consisting of the same two constituents (in different proportions) it might similarly be expected that the electromotive effect would remain constant.

In this way the general form, either of ABCD or of ACEF, could be accounted for; but the cause of the difference between the two curves is not immediately obvious.

§ 4. *The freezing of slowly-cooled amalgams.*—To understand the exact significance of fig. 2, it is necessary to consider how a mixture, to which fig. 1 applies, freezes.

According to this figure, an alloy containing a per cent. Cd should begin to freeze at θ_1 and should apparently become solid at θ_2. But, because of the extreme slowness of diffusion in solids, this will happen only when the rate of cooling is so slow that it cannot be dealt with in practice.

At the temperature θ_1 a fluid amalgam containing a per cent. Cd and a solid amalgam containing b per cent. Cd are in equilibrium. When the temperature is lowered slightly a fluid amalgam containing slightly less than a per cent. Cd will be in equilibrium with a solid amalgam containing slightly less than b per cent. A small quantity of the a per cent. amalgam may therefore solidify.

As the temperature falls the percentages of Cd contained by fluid and solid amalgams in equilibrium become continuously lower. The amount of solid material will therefore increase; but the percentage of Cd in the newest crystals will always be less than in those previously formed.

The fluid existing at any given stage of the cooling will be in equilibrium with the solid with which it is in direct contact, but, since most of the successive growths will take place around earlier crystals, this solid will in general enclose older solid, richer in Cd.

There must thus be a continuous diffusion of Cd in the crystallized part of the material from within towards the surface.

In any practical case, where the rate of cooling is not infinitely slow, the diffusion outwards will be very gradual and will not keep pace with the lowering of temperature.

Thus, although (for true equilibrium) an amalgam containing a per cent. Cd should be all-solid just below θ_2, a considerable quantity of liquid, containing c per cent. Cd, will remain. The solid in contact with this liquid will contain a per cent. Cd, but will envelop a considerable quantity of solid richer in Cd than itself, and there will be, in consequence, neither so little c per cent. liquid nor so much a per cent. solid as true equilibrium would imply.

A superior estimate of the amount of liquid remaining at θ_2 can, however, be found. Thus we may imagine that the cooling from θ_1 to θ_2, of an amalgam containing a per cent.

Cd, takes place by steps of $d\theta$, and that no diffusion takes place from the solid formed in one step to that formed in the next. Also that the solid formed in any step is of uniform composition and in complete equilibrium with the liquid which remains. Under such conditions, it can be estimated that (in some of the amalgams) about one third of the material might still be fluid at θ_2 although, according to fig. 1, the whole should be solid *.

§ 5. *The effect of sudden cooling.*—From the above sketch of the process of crystallization we see that the surface of a "slowly" cooled amalgam will generally contain a lower percentage of cadmium than the material as a whole, and may even be fluid, although the temperature and percentage composition of the material are such that it should (in true equilibrium) be a uniform solid.

We see also that the relation between the curves ABCD and ABEF of fig. 2 is immediately explicable if, for any reason, the amalgams of the branch CD are of more uniform composition than those of EF.

The former amalgams were cooled suddenly from the fluid state to a temperature much below that at which they would have become completely solid if the rate of cooling had been infinitely slow. Each alloy would therefore pass rapidly through the range of temperature in which equilibrium between two phases is possible, and although, in each element of the material, there might be incipient crystallization with accompanying redistribution of the Cd, as the temperature fell, this process being slow could not proceed very far.

The greater part of the solidification would thus take

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* Thus at the end of the first step the temperature is $\theta_1-\delta\theta$, the liquid phase contains $(a-\delta a)$ per cent. Cd and the solid phase $(b-\delta b)$ per cent. And, of m grams of a per cent. alloy, the quantity

$$\delta m_1=\frac{\delta a}{(b-a)-\delta(b-a)}m$$

will have frozen. It happens that for a considerable range of temperatures and concentrations in the present case, the liquidus and solidus curves of fig. 1 are sufficiently nearly parallel straight lines to permit the assumption, $\delta(b-a)=0$, between θ_1 and θ_2. From this also, if we assume that there are n equal steps of $\delta\theta$ in the cooling process, we get $n\delta a=b-a$, and hence $\delta m_1=m/n$. The quantity of liquid remaining at the end of the first step is thus $m\left(1-\frac{1}{n}\right)$. Continuing the process it will be found that the quantity of liquid remaining at the end of the nth step is $m\left(1-\frac{1}{n}\right)^n$ which, if we assume n to be very large, has the value $m/2{\cdot}72$ very nearly.

place at a temperature at which Cd and Hg can exist together in equilibrium only as a homogeneous mixture *. It would therefore occur without redistribution of the Cd with respect to the Hg. What "differential" crystallization there was would be on a scale relatively so minute that the process of equalization by diffusion and the approach to true equilibrium would take place comparatively rapidly as the temperature rose.

There is, therefore, no difficulty in finding a satisfactory general interpretation of fig. 2, as a consequence of fig. 1.

We may now proceed to examine the data more minutely.

§ 6. *Quantitative comparison of the "chilled" and "slowly cooled" amalgams.*—It is reasonable to suppose that two amalgams have the same surface composition when they give the same steady E.M.F. at the same temperature, even although their average compositions may be different.

Hence, if we assume as a first approximation that the values of x and y at any temperature θ (when fig. 1 is taken to represent cadmium amalgams) can be deduced from the thermo-electromotive properties of the series of chilled amalgams of Table VIII. (*l. c.* p. 268), we can determine the state of the surface of any slowly cooled amalgam when the E.M.F. which it gives is known.

For this purpose, some of the data for the slowly-cooled amalgams (Tables I. and II., *l. c.* pp. 256, 257) were plotted, as in fig. 3, along with the data for the chilled amalgams. The dotted curves refer to the former.

Table A, below (p. 214), summarizes the inferences which can be drawn from the figure when the data are interpreted in the way above described.

Each row of numbers gives, for a particular temperature, the surface constituent or constituents of the slowly cooled amalgams (11 to 20 per cent. Cd) deduced by interpolation from the curve, at that temperature, for the chilled amalgams. The table begins with the results at 15° C. after the amalgams had stood for three months at this temperature.

(i.) At 15° C. (according to Table VIII.) any amalgam containing less than about 4·3 per cent. Cd should be all liquid, and any containing more than about 12·85 per cent. Cd should be all solid (if in equilibrium). According to Table A, the surface of the 11 per cent. slowly cooled amalgam is a mixture of these alloys. The surfaces of the 12 per cent. and 13 per cent. amalgams appear to be solid alloys containing slightly above 12·85 per cent. Cd. Each of

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* See § 14 below.

Fig. 3.

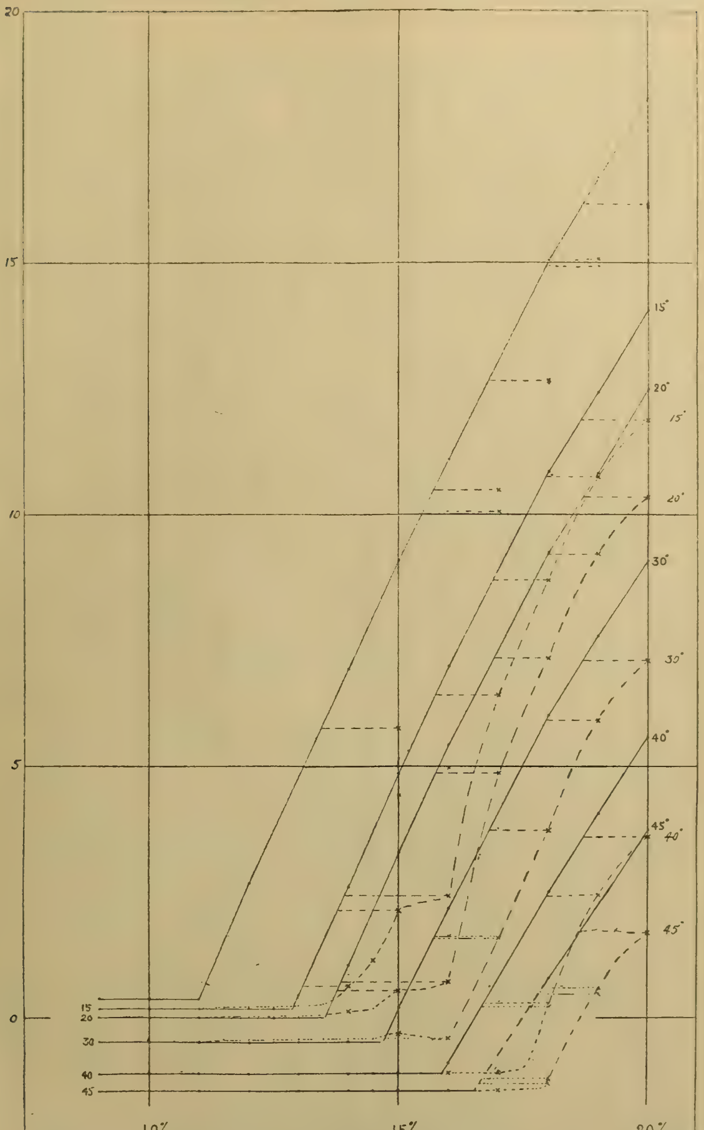

TABLE A.

Mean Percentage of Cd in Amalgam. →	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	Temperature. ↓	Time. ↓
Surface Percentages of Cd in Amalgams at different Temperatures deduced from Tables I., II., and VIII. **i.**	12·85 4·3	12·88 (approx.)	12·9 (approx.)	13·1 (approx.)	13·78	13·92	15·75	16·88	17·95	18·65	15°	after about 3 months at 15° C.
ii.	13·5 4·9	13·52 (approx.)	13·52 (approx.)	13·6 (approx.)	13·77	13·86	15·75	16·9	17·98	18·68	20°	
iii. →	14·7 6·4	14·72 (approx.)	14·73 (approx.)	14·74 (approx.)	14·78 (approx.)	14·75 (approx.)	$15{\cdot}^{73}_{7}$	$16{\cdot}^{83}_{79}$	17·95	18·68	30°	
iv.	15·9 7·9	15·9 7·9	15·9 7·9	15·9 7·9	15·9 7·9 (approx.)	15·9 7·9 (approx.)	15·9 7·9 (approx.)	$16{\cdot}^{7}_{68}$	17·95	18·68	40°	
v.	16·5? 8·8	16·5? 8·8	16·5? 8·8	16·5? 8·8	16·5? 8·8 (approx.)	16·5? 8·8 (approx.)	16·5? 8·8 (approx.)	$16{\cdot}^{67?}_{62?}$	$17{\cdot}^{9}_{83}$	18·65	45°	
deduced from Tables III. & VIII. **vi.**	11·0 2·7	11·0 2·7	11·02 (approx.)	11·02 (approx.)	12·83	11·55	15·48	16·77	17·95	18·65	0°	about 2 days after cooling from 45° C.
	11·0 2·7	11·01 (approx.)	11·02 (approx.)	11·22 (approx.)	13·45?	13·2	15·7	16·8	18·01	18·68	0°	about 6 weeks later.

the succeeding amalgams (with the exception of the 16 per cent. amalgam which for some accidental [*] reason behaves irregularly) is superficially weaker in Cd, in nearly the same proportion (0·92 to 0·94) in each case, than the amalgam as a whole.

(ii.) At 20° C. (to which the cells were next heated) any amalgam containing less than about 4·9 per cent. Cd should be all-liquid, and any containing more than about 13·5 per cent. Cd should be all-solid. The surface of the 11 per cent. amalgam is a mixture of these alloys, and as before the surfaces of the 12 per cent. and 13 per cent. amalgams appear to be solid and to contain slightly more than the percentage of Cd (13·5 per cent.) in the richer constituent of the two-phase amalgam. The surface of the 14 per cent. amalgam contains about 13·6 per cent. Cd.

It will be noticed that the surface concentrations of the richer alloys (15 to 20 per cent.) as deduced by this method are, as nearly as can be measured, the same at 20° as at 15°.

(iii.) At 30° C., the equilibrium amalgams should (according to Table VIII.) contain approximately 6·4 per cent. and 14·7 per cent. Cd. With certain limitations, discussed later in § 9, (which apply equally to similar cases at the other temperatures), the surface of the 11 per cent. amalgam is now a mixture of these alloys. And we might expect that the surfaces of the 12 to 16 per cent. amalgams would be similarly constituted. But, as in (i.) and (ii.), the surface film in these amalgams seems to be solid, since it contains a slightly higher percentage of Cd than the solid component of the two-phase system.

From the results in column (ii.) we might expect the surfaces of the 17 to 20 per cent. alloys to remain unchanged. It will be seen that this is true of the 19 and 20 per cent. amalgams; but the percentages of Cd in the surfaces of the 17 and 18 per cent. amalgams are beginning to diminish slightly and are exhibiting a time effect.

The significance of these unlooked-for differences is discussed in § 10 below.

(iv.) At 40° C. the limiting alloys contain about 7·9 per cent. and 15·9 per cent. Cd. As we might expect, the surfaces of the 19 and 20 per cent. amalgams remain unchanged. On the other hand, the percentage of Cd in the

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[*] It is obvious that irregularities of cooling and distribution must sometimes occur. That sudden changes of the slopes of the curves, between 15 and 20 per cent. Cd, are due to accidental irregularities is shown by comparison of the present data with those for another series (Table VI. *l. c.*), in which similar changes of slope occur at other percentages.

surface of the 18 per cent. amalgam is continuing to fall. The surface of the 17 per cent. amalgam has become practically a two-phase system.

(v.) At 45° C., the limiting percentages are about 8·8 and 16 5. The surface of the 20 per cent. amalgam remains practically unchanged; but, unexpectedly as before, the surface percentage in the 19 per cent. amalgam is now slowly falling. The decrease at the surface of the 18 per cent. amalgam continues.

(vi.) The amalgams were now cooled to 0° C. After six weeks at this temperature (last row of Table A) the surfaces of all the amalgams containing more than 14 per cent. Cd (excluding the irregular 16 per cent. amalgam) had returned practically to the state in which they were when the measurements at 15°, as in (i.), were made.

Table IX. (*l. c.* p. 269), described as typical, can be analysed (by comparison with Table VIII.) in exactly the same way as Tables I. and II. In connexion with this Table the author writes:—"At temperatures near to but below the first transition temperature the diffusive processes in an unstable amalgam are no doubt accelerated, and the outer shell becomes richer in cadmium with a corresponding increase in the E.M.F. of the cell. . . . ." No doubt rise of temperature will accelerate the diffusion; but it is to be remarked that, as shown in Table A, an "unstable" amalgam which has stood for some time at the ordinary temperature can be raised through 20° or 30° C. without measurable increase in the surface percentage of cadmium, and that the first noticeable effect of temperature rise is a surface decrease of an unexpected kind. The same effect is shown in Table IX.

Sometimes (*e. g.*, *l. c.* pp. 260, 261, and Conclusion 1, p. 274) Mr. F. E. Smith writes as if an unstable amalgam may consist of one central solid mass surrounded by a shell of lower concentration. It seems to me, however, that this state of affairs must be very exceptional.

§ 7. *The probable structure of frozen amalgams.*—It is a well-established characteristic of crystallization in general, that it proceeds around nuclei distributed more or less uniformly throughout the cooling material. The uniformity of distribution of the nuclear growths will be affected in the present case by the fact that the solid grains are of less density than the fluid out of which they separate. The first grains to form must tend to rise. On account of their smallness they will not rise rapidly. As crystallization proceeds a solid net-work will develop within the material. The later crystallization will take place from fluid entangled within the meshes of this net-work. Consequently the material need not in general separate into upper, all-solid, and lower, all-fluid, parts.

In an amalgam which is still partially fluid, but would be all-solid in true equilibrium, at the temperature of observation, the mean concentration of a layer near the surface will no doubt be greater than that of a layer near the bottom. But the difference need not be very marked, and there may be an appreciable quantity of fluid in the spaces between individual grains near the surface, which will take a long time to disappear. If the density effects are appreciable, a greater proportion of the earliest formed crystals will be present in the upper layers. The centres of the grains nearest the surface may then be richer in Cd than the centres of those lower down; but even when the amalgam has stood long enough for the upper portion to become solid throughout, there will be graduations in the percentage of Cd, from point to point in that portion, of which the existence will become obvious (as described below) when the temperature is raised.

§ 8. *An effect of the presence of the electrolyte at the surface of the amalgam.*—The surface layer of a partially crystallized amalgam will consist of a number of grains between which are spaces filled with liquid amalgam. Some of the solid grains will in general project slightly above the mean surface level. The layer of fluid amalgam covering these will be, at most, very thin.

Under the ordinary process of diffusion from the grains the liquid surrounding them will gradually diminish in amount, more or less uniformly in all directions. But it is important to notice that the process of equalization of distribution of Cd will be accelerated, in the surface, when (as in the case of the Weston cell) the amalgam is covered by a solution of cadmium sulphate.

The very thin layers of x per cent. fluid in immediate contact with the surface grains * will soon receive enough Cd by diffusion to convert them into solid containing more than y per cent. Cd (fig. 1). In consequence they will no longer be in electromotive equilibrium with the neighbouring, relatively thick, layers of surface fluid which still contain

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* When a saturated solution of $CdSO_4$ is poured over the fresh surface of a partially fluid amalgam, the positions of these surface grains can easily be seen.

only x per cent. Cd. Electrolytic action will ensue. Cadmium will enter solution round the surface grains and will be deposited upon the adjacent fluid.

The electrolyte will thus act as a distributor, over the whole surface, of the cadmium diffusing from the surface grains. The surface will thus tend to acquire a thin and probably solid skin which, on account of its lesser density, will have no tendency to sink below the underlying fluid.

In the presence of $CdSO_4$ solution, the whole of the surface film may therefore become solid and of uniform composition, although, on account of the extreme slowness of ordinary intermolecular diffusion, there may still be an appreciable quantity of fluid alloy underneath.

§ 9. "*Minor irregularities*" *of Weston cells.*—Regarding the surface behaviour of partially fluid amalgams in the above way, it is possible to account for peculiarities, at first sight perplexing, of the horizontal branches of the curves for the chilled and the slowly cooled amalgams. The vertical scale of fig. 3 is not sufficiently open to show these peculiarities clearly. They are exhibited in fig. 4 which represents the behaviour of the amalgams, at various temperatures, over the range represented by the branch BC of fig. 2.

The data for the chilled amalgams are marked by dots and for the slowly cooled amalgams by crosses.

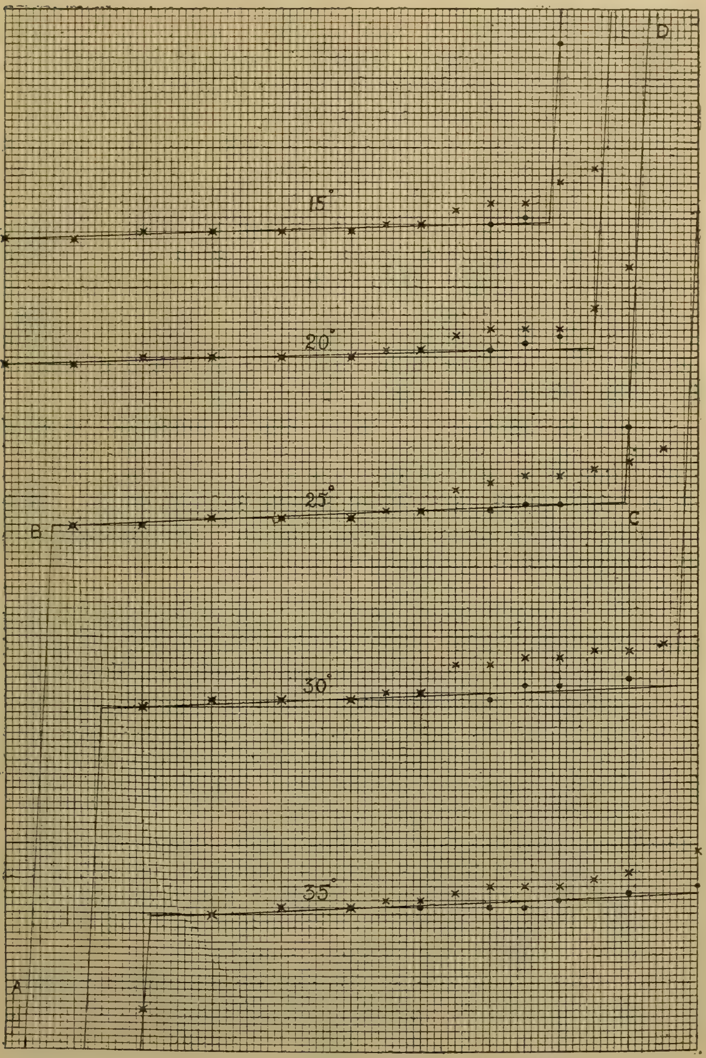
In the slowly cooled amalgams, as in the chilled, the rise of E.M.F. near B is at most very gradual. But, towards C, the former amalgams behave differently. The rise is much greater than in the chilled amalgams, and the E.M.F. of a slowly cooled amalgam is now considerably greater than that of the corresponding chilled amalgam.

This effect is exhibited numerically in Table A, and has already been alluded to in § 6. It may be explained as follows :—

We assume, for reasons given in § 5, that the solid grains in partially fluid chilled amalgams are of more uniform composition than those in similar slowly cooled amalgams. A chilled amalgam which is nearly all solid at any temperature θ will consist mainly of solid y per cent Cd amalgam, together with a small amount of fluid containing x per cent. Cd.

A slowly cooled amalgam, of the same average composition, will contain a smaller proportion of solid grains ; but these will be richer in Cd. Their surfaces will contain y per cent. Cd ; but their interiors will contain more. If a sufficient number of these grains be present in the surface originally, or rise thereto after detachment by heat, they may produce a thin surface skin containing more than y per cent., as

Fig. 4.



described in § 8 above. The slowly cooled amalgam will then give a greater E.M.F. than the corresponding chilled amalgam.

The excess over y per cent. Cd in the surface will only be appreciable when the surface skin is relatively thick, *i. e.* when the surface grains are relatively numerous. For much of the under surface of the skin will be in contact with liquid x per cent. alloy, and cannot therefore contain more than y per cent. Cd.

Thus it is only in the stronger slowly cooled amalgams that the E.M.F. can be much greater than that of the two-phase alloy—in agreement with fig. 4.

In keeping with this view of the behaviour of the stronger slowly cooled amalgams, the percentage of Cd in the surface skin of any of them may increase within certain limits as the temperature rises. Thus when the temperature of one of these amalgams is raised from θ to θ', the solid grains must partially liquefy. By this means the percentage of Cd in the fluid alloy is raised from x to x', and the percentage of Cd in the new surfaces of the solid grains is y', greater than y. Electrolytic effects may ensue as before and cause the surface skin percentage to rise above y'.

As the temperature is raised the surface grains may become relatively more numerous at first, since additional grains may float up to the surface; but in the end the surface skin will grow thinner and the E.M.F. will approach nearer to that of the two-phase amalgam corresponding with the temperature of observation.

§ 10. *Skin effects in all-solid amalgams.*—It will be obvious that electrolytic skin effects of the kind described in § 8 may occur in amalgams which are already all-solid, but in which ordinary diffusion effects are still proceeding with appreciable velocity. In such cases the surface film may acquire a larger share of the effects of diffusion than areas just below the surface, with the result that these may be less rich in Cd than the surface layer itself.

Evidence of this condition of affairs is revealed when the data of Tables II. and VIII. are compared as in Table A above (see § 6), where it is shown that the surface begins to change at a temperature lower than that at which it would if no weaker amalgam were present near it.

Similar considerations might explain otherwise puzzling time effects exhibited by the chilled amalgams of Table VI. (*l. c.* p. 266). In these, practically without exception, the marked increase of E.M.F. which occurs in the first few days is succeeded by a small but unmistakeable decline. An effect so general cannot be due to accidental irregularities in the process of crystallization.

The statement that "it may be due to the chilling producing a too highly concentrated amalgam in the outer shell" scarcely removes the need for further explanation. Effects of this kind are not confined to the chilled amalgams. The 15, 17, and 19 per cent. amalgams of Table II. show appreciable decline in the surface percentage of Cd during the three months at 15° C.

Another possible cause * of a slow decrease of E.M.F., which should be mentioned, depends upon the deduction (from § 12 below) that the equilibrium concentration of Hg salt in solution round an amalgam must be less than that round pure mercury. In cells of the Weston type, Hg salt must thus be diffusing continuously from cathode to anode and the amount of Hg in the latter must be slowly increasing by precipitation. Fortunately, the diffusion will generally be so slow that its effect upon the E.M.F. of a two-phase amalgam will remain unnoticeable for a very long time. But if the anode surface consists of a thin single-phase skin the percentage of Hg within it may increase perceptibly in a comparatively short period.

§ 11. *The question of the horizontality of BC in fig. 2.*—The skin effects described in § 9 arise primarily from the lightness of the solid grains and from their want of uniformity of composition. As soon as such effects become appreciable, departure from horizontality must ensue. A measure of the importance of these effects is given by the difference between the E.M.F.s of the richer amalgams, chilled and slowly cooled, of fig. 4.

But another question remains. If the amalgams (chilled or otherwise) were of quite uniform composition between B and C, differing only in the relative amounts of x per cent. and of y per cent. amalgams present, would BC be absolutely horizontal, *i. e.*, would the E.M.F.s of all the amalgams within this region be found to be identical, however refined the means of comparison might be?

The data of fig. 4 seem to establish the fact that there is always a slight rise from B towards C. In the region near B the amount of solid amalgam is so small that there is little room for appreciable variation in the percentage of Cd between the centres and surfaces of individual grains. Hence, as the electromotive data show, chilled and slowly cooled amalgams containing the same percentage of Cd must

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* Possible effects at the cathode are outside the range of the present paper.

here be of practically identical composition. But even in this region the E.M.F. curve slopes upwards.

It is thus impossible to say beforehand that the E.M.F. does not rise as the percentage of Cd in the amalgam increases, even when the crystals are as uniform as they can possibly be.

§ 12. *The possibility of equilibrium between two amalgams and the same electrolyte.*—The question raised in the preceding section cannot be answered satisfactorily without more careful consideration of the conditions of equilibrium between each amalgam and the electrolyte than has been so far necessary.

It will perhaps be useful to indicate first how, neglecting surface energy, the conditions of equilibrium between the two homogeneous amalgams can be represented thermodynamically *.

The total energy ϵ of a homogeneous substance containing masses m_1 and m_2 of its two components can change by acquisition of heat (alteration of the entropy η), performance of external work (alteration of the volume v) and change of composition (alteration of the mass of either constituent).

For a reversible change we may write

$$d\epsilon = \left(\frac{\partial\epsilon}{\partial\eta}\right)_{vm_1m_2} d\eta + \left(\frac{\partial\epsilon}{\partial v}\right)_{\eta m_1m_2} dv + \left(\frac{\partial\epsilon}{\partial m_1}\right)_{\eta vm_2} dm_1 + \left(\frac{\partial\epsilon}{\partial m_2}\right)_{\eta vm_1} dm_2.$$

The values of the first and second partial differential coefficients are obviously θ and $-p$. The terms containing them represent the energy variation due to change in the heat content and volume of the working substance; the remaining terms indicate how the energy variation depends upon the composition. The partial differential coefficients which they contain are functions of the composition of the working substance and we may write

$$d\epsilon = \theta\, d\eta - p\, dv + \mu_1\, dm_1 + \mu_2\, dm_2.$$

For any other homogeneous mixture of the same substances, also capable of reversible variation, we may write

$$d\epsilon' = \theta\, d\eta' - p\, dv' + \mu_1'\, dm_1' + \mu_2'\, dm_2'.$$

Now suppose that these two mixtures can coexist in equilibrium.

By hypothesis the components are independent variables. We may imagine that a small quantity *dm* of the m_1 component leaves the second phase and enters the first in such a

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* *Cf.* Gibbs, Trans. Conn. Acad. vol. iii. pt. 1, p. 115.

way that the transference takes place without change in the entropy or volume of either phase. The energy variation of the system would then be

$$\left(\frac{\partial\epsilon}{\partial m_1}\right)_{\eta v m_2} dm_1 + \left(\frac{\partial\epsilon'}{\partial m_1'}\right)_{\eta' v' m'_2} dm_1' = (\mu_1 - \mu_1')dm.$$

But since neither the entropies nor the volumes change, the system neither does external work nor acquires heat. Consequently we must have

$$\mu_1 - \mu_1' = 0,$$

and, by a similar argument,

$$\mu_2 - \mu_2' = 0.$$

These and two other equations, derived one from each phase at given θ and p, suffice to define the conditions of equilibrium completely—the essential variables being

$$m_1/v,\ m_2/v \quad \text{and} \quad m_1'/v',\ m_2'/v' \text{ respectively}^*.$$

In assuming, as above, that the total energy of a known mass of each phase, at given θ and p, is dependent only on its composition, we neglect the possible influence of surface energy.

We may continue to suppose that, to a first degree of approximation, the surface tension and electrostatic potential difference between the x per cent. and y per cent. amalgams are negligible and proceed to examine the conditions under which the two amalgams could coexist in presence of the same electrolyte.

Considering first the equilibrium of fluid amalgam and electrolyte, reversible exchange of Cd or Hg between electrode and electrolyte will be possible since the latter is a solution of sulphates of Hg and Cd. But while the masses dm_1 and dm_2 of the metals may be considered neutral in the amalgam, they are associated with definite positive charges, which we may write $k_1\,dm_1$ and $k_2\,dm_2$, when in solution.

In order that (as in the equations already given) we may still regard m_1 and m_2 as independent variables, we assume that when a quantity dm_1 of mercury leaves the solution, a quantity dm_3 of anions (SO_4) carrying the charge

$$k_3\,dm_3 = -k_1\,dm_1$$

also leaves the solution and accumulates at the surface separating electrode and electrolyte. We assume also that

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[*] *Cf.* § 14, below.

a similar effect accompanies the transference of dm_2 of cadmium.

In consequence, if we suppose the electric potential of the amalgam to be V and of the electrolyte to be V$''$, it will be seen that the reversible energy variation may now be written

$$\begin{aligned} d\epsilon + d\epsilon'' = {} & \theta(d\eta + d\eta'') - p(dv + dv'') + (\mu_1 - \mu_1'')dm_1 \\ & + (\mu_2 - \mu_2'')dm_2 + (\mathrm{V} - \mathrm{V}'')(k_1\,dm_1 + k_2\,dm_2) \\ & + (\bar{\mu}_3 - \mu_3'')\left(\frac{k_1}{k_3}dm_1 + \frac{k_2}{k_3}dm_2\right), \end{aligned}$$

in which
$$\left(\frac{\partial\epsilon}{\partial m_1}\right)_{\eta v m_2} = \mu_1 + k_1\mathrm{V} + \frac{k_1}{k_3}\mu_3,$$

with similar expressions for the other quantities, μ_3 referring to the surface layer and μ_3'' to the interior of the electrolyte.

For equilibrium, as before,

$$\left.\begin{aligned} & (\mu_1 - \mu_1'') + k_1(\mathrm{V} - \mathrm{V}'') + \frac{k_1}{k_3}(\bar{\mu}_3 - \mu_3'') = 0, \\ \text{and} \quad & (\mu_2 - \mu_2'') + k_2(\mathrm{V} - \mathrm{V}'') + \frac{k_2}{k_3}(\bar{\mu}_3 - \mu_3'') = 0. \end{aligned}\right\}$$

In the same way, considering the solid amalgam and the electrolyte, we must have

$$\left.\begin{aligned} & (\mu_1' - \mu_1'') + k_1(\mathrm{V}' - \mathrm{V}'') + \frac{k_1}{k_3}(\bar{\mu}_3' - \mu_3'') = 0 \\ \text{and} \quad & \\ & (\mu_2' - \mu_2'') + k_2(\mathrm{V}' - \mathrm{V}'') + \frac{k_2}{k_3}(\bar{\mu}_3' - \mu_3'') = 0. \end{aligned}\right\}$$

Considering the equilibrium of the amalgams with each other we assume

$$\mu_1 = \mu_1', \quad \mu_2 = \mu_2'. \quad \text{and} \quad \mathrm{V} = \mathrm{V}'.$$

Suppose now that we ignore possible differences at the surfaces separating the electrolyte and the fluid and solid amalgams respectively and put $\bar{\mu}_3 = \bar{\mu}_3'$ (see also § 13, below).

Then it will be possible to find values of μ_1'', μ_2'' and μ_3'', which will be related in such a way as to satisfy the above equations simultaneously and make

$$\mathrm{V} - \mathrm{V}'' = \mathrm{V}' - \mathrm{V}''.$$

In other words it will be possible to find electrolytes within which the two amalgams can exist side by side in complete equilibrium. With any one of these electrolytes the E.M.F. would be independent of the relative amounts of the two phases present.

§ 13. *The effect of surface energy.*—If, as above, the surface energy variations of the liquid and solid amalgams are regarded as identical, the conditions of equilibrium assume a simplicity which there is no doubt they do not possess.

We do not know the relative importance of the energy per unit area of the surface separating the amalgams; but the difference between the energies of the surfaces separating the respective amalgams and the electrolyte is perceptible. The liquid amalgam appears always to spread over the surface of the solid amalgam in the presence of the electrolyte. We may therefore assume that the surface energy between solid amalgam and electrolyte is greater than that between liquid amalgam and electrolyte.

There are phenomena which show that the relation between surface energy and potential difference is often very complex and § 12 is put forward merely as a method of representing the general nature of what occurs. It can be seen, however, that even if the conditions of equilibrium were as simple as those already given, the difference of surface energy would cause μ_3' to exceed $\bar{\mu}_3$. The two amalgams could not then, subject to the condition $V-V''=V'-V''$, be in equilibrium with the same electrolyte.

The value of $V''-V'$ satisfying the second pair of equations would be greater than that of $V''-V$ satisfying the first two, *i. e.*, the potential of a given electrolyte with respect to the solid amalgam would exceed that of the same electrolyte with respect to the fluid amalgam. Hence, supposing $V=V'$, the amalgams could not coexist in contact with the same electrolyte.

Such considerations are enough to show that there is no theoretical necessity for horizontality of BC. It is much more likely that the equilibrium at the anode is between a variable phase and the electrolyte, and that the E.M.F. electrolyte/electrode is distinctly greater when the amalgam is one which is just on the point of partial liquefaction at θ than when it is one in which the last traces of solid have just disappeared.

There is therefore every probability [*] that the E.M.F. of a cell of the Weston type must always be to some extent dependent upon the percentage of Cd in the amalgam.

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[*] Mr. F. E. Smith has kindly supplied me with further details of some of the measurements recorded in his Table VIII. which confirm this view.

§ 14. *The application of the phase rule to cadmium amalgams.*—The considerations given at the beginning of § 12 were introduced in order to explain a method of regarding the effects of surface energy. They also supply a means of interpreting the "equilibrium curves" of fig. 1. As in § 12, if two homogeneous phases containing components A and B can coexist in equilibrium we must have not only equality of temperature and pressure, but also two other equalities which we may write $\mu_a = \mu_a'$ and $\mu_b = \mu_b'$.

To determine completely, at given θ and p, the state of any mixture of A and B, we require to know how these "potentials" vary with c, the percentage of B in the mixture.

It is conceivable that the substances can form a series of mixtures in all proportions and that any one of these can be entirely fluid or entirely solid at the temperature θ. For a homogeneous mixture, at constant temperature and pressure, we must have

$$m_a d\mu_a + m_b d\mu_b = 0.$$

Considering all-fluid mixtures first we may suppose, following Gibbs*, that, when c approximates to zero, μ_b must have a very large negative value, whilst μ_a is finite and $d\mu_a/dc$ has a finite negative value. Similarly, when c approximates to 100, μ_a must have a very large negative value, while μ_b is finite and $d\mu_b/dc$ has a finite positive value.

The curves connecting the variations of μ_a and μ_b with c may no doubt be complicated; but, in the simplest cases, they may (from what precedes) take forms like AM and BN of fig. 5.

We may assume that analogous relations, represented by the curves A′M′ and B′N′, hold for the all-solid mixtures.

If, as in fig. 5, a temperature is chosen which is below the freezing point of B, but above the freezing point of A, we shall have $\mu_b > \mu_b'$ for the phases of pure B, and hence B will lie above B′; but $\mu_a' > \mu_a$ for the phases containing pure A, so that A′ will be above A.

The conditions for coexistence of a fluid phase containing x per cent. B and a solid phase containing y per cent. B are

$$[\mu_a]_{c=x} = [\mu_a']_{c=y}$$

and

$$[\mu_b]_{c=x} = [\mu_b']_{c=y}.$$

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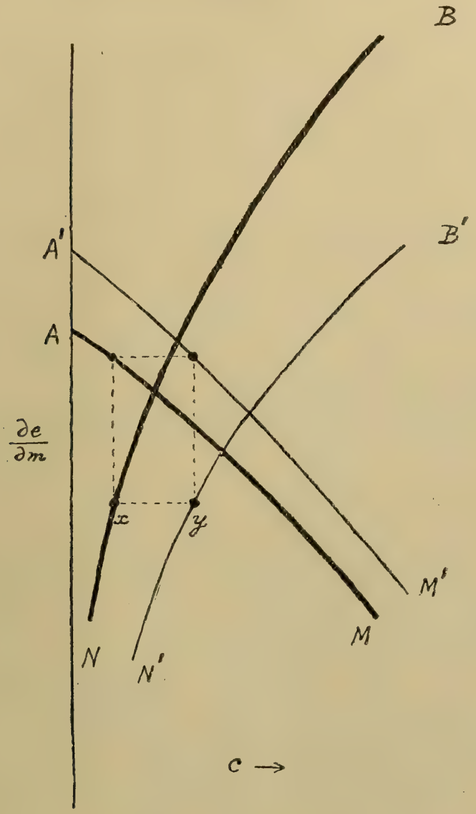
[*] *L. c.* p. 194.

Inspection of fig. 5 will suffice to show the possibility of finding values of x and y which satisfy these conditions.

Fig. 5.



The same conclusion can be reached, less directly, by considering the variations with c of the total thermodynamical potentials ζ and ζ' per 100 grams of all-fluid and all-solid mixtures, remembering the relations

$$d\zeta/dc = \mu_b - \mu_a \quad \text{and} \quad d\zeta'/dc = \mu_b' - \mu_a'.$$

In the system of fig. 5, therefore, coexistence of two phases is possible when the liquid phase contains x per cent. B and the solid phase y per cent. B. All mixtures containing between x per cent. and y per cent. of B, and only those, can split into two phases.

If, however, the temperature is below the freezing point of A, as well as below that of B, the relative positions of AM and A′M′ will be reversed and it will now be impossible to find values of x and y for which μ_a, μ_a' and μ_b, μ_b' respectively, are equal. In other words, one-phase solid mixtures only will be stable *.

If it is assumed that the μc variations for the mixtures of Hg and Cd used in Weston cells are of the form represented (diagrammatically) in fig. 5, it can at once be seen why the amalgams exhibit the properties which have been discussed.

§ 15. *The temperature coefficients of cadmium-mercury cells.*—The efficiency of the Weston cell as a standard does not depend only on the fact that the chemical composition of the amalgam can vary within considerable limits without producing more than a few millionths of a volt difference in the electromotive force ; but also upon the extreme smallness of the effect of temperature change near 0° C.

It is instructive to consider how the existence of the two-phase amalgams happens to be the cause of the second phenomenon.

The data of Table XI. (*l. c.* p. 273) show that the smallness of the temperature coefficient is not due to absence of heat exchanges with the surroundings during isothermal working of a two-phase cell, but to the fact that these nearly balance each other. Somewhere near 5° C. there is an exact balance and the temperature coefficient vanishes.

Above 5° C., the temperature coefficient has a small negative value. This means that slightly more heat escapes from the cell (during action) than it absorbs from the outside. The presence of the two-phase amalgam reduces the net loss of heat. For, during the working of the cell, the average percentage of Cd in the anode must diminish and the equilibrium compositions of the coexisting phases can only be maintained by reduction in the amount of the richer (solid) phase. This will occasion absorption of heat and so reduce the net amount evolved.

Below 5° C., the absorption just mentioned slightly overbalances the remaining effects and the temperature coefficient is positive.

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* *Cf.* § 5 above.

XVI. *On the Shape of the Atom.* *By* R. D. KLEEMAN, *D.Sc., B.A., Mackinnon Student of the Royal Society; Emmanuel College, Cambridge*[*].

AT the absolute zero of temperature the molecules of a substance would probably be in contact with one another. From a knowledge of the density of different substances at the absolute zero we could therefore determine the real relative volumes of different atoms and molecules. The density of a substance at the absolute zero cannot be found directly, but it can be calculated with probably fair accuracy. Such a calculation has been carried out by Guldberg[†] for a number of substances. And Traube[‡] has shown, using these determinations, that the volume of an atom is proportional to the square root of its atomic weight, and the volume of a molecule therefore proportional to the sum of the square roots of the atomic weights of the atoms composing the molecule. A knowledge of the connexion between the volume of an atom and its atomic weight does not by itself furnish any information as to its shape, but this relation in conjunction with the cross-section of the atom, which can be obtained from the kinetic theory of gases, gives us some information on this point, as will be shown in this paper.

The shape of the atom which suggests itself as the most probable, and which is the one usually assumed, is that of the sphere. Assuming then that the atom is spherical in shape, we have that its volume is proportional to r^3 and its cross-section proportional to r^2, where r is the radius of the atom. Since its volume is also proportional to $m^{1/2}$, where m is its atomic weight, its cross-section is proportional to $m^{1/3}$.

In Tables I., II., and III. values of Q, the sum of the diametrical sections of the spheres of action of the molecules contained in unit volume of a gas at atmospheric pressure, are given for a number of vapours. The values contained in Tables I. and II. were taken from Meyer's 'Kinetic Theory of Gases,' pages 303, 307, and 308, and those in Table III. were obtained from Landolt and Börnstein's Tables, 5th edition. They correspond to a temperature of 0° C. The sum of the sections Q is obtained from the equation

$$Q=\tfrac{1}{4}\pi s^2 N=\frac{1}{4\sqrt{2}\,L},$$

where s is the mean radius of the sphere of action of a

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[*] Communicated by the Author.

[†] *Zeit. für Phys. Chemie*, xxxii. p. 122 (1900).

[‡] *Phys. Zeit.* p. 667, Oct. 1909.

molecule, N is the number of molecules in unit volume at atmospheric pressure, and L is the mean free path of a molecule. Since N has the same value per unit volume for all gases at the same temperature and pressure, the diametrical sections of any two molecules are to one another as the corresponding values of Q. The tables contain also the values of $\Sigma m^{1/3}$, the values of $m^{1/3}$ used for their calculation being given at the head of Table I. The last column of each table gives the ratio of Q to $\Sigma m^{1/3}$.

Table I.

Cube roots of the atomic weights of a number of atoms: $H=1$, $C=2{\cdot}29$, $N=2{\cdot}41$, $O=2{\cdot}52$, $Fl=2{\cdot}67$, $S=3{\cdot}18$, $Cl=3{\cdot}29$, $Br=4{\cdot}31$, $I=5{\cdot}03$, $Hg=5{\cdot}85$.

Gas.	Q.	$\Sigma m^{1/3}$.	$\frac{Q}{\Sigma m^{1/3}}$.
CO	18,700	4·81	3,888
CO_2.................	27,000	7·33	3,684
N_2	18,600	4·82	3,859
N_2O	27,100	7·34	3,693
NO	19,200	4·93	3,895
O_2	17,400	5·04	3,452
CH_4	22,200	6·29	3,530
C_2H_6O	43,500	13·10	3,321
C_2H_5Cl	49,300	12·87	3,830
H_2	9,900	2·00	4,950
NH_3	24,900	5·41	4,603
C_2H_4	42,500	8·58	4,953
CH_3Cl	40,100	8·58	4,673
C_2N_2	43,900	9·42	4,660
SO_2.................	37,900	8·22	4,610
HCl	25,100	4·29	5,851
Cl_2	38,800	6·58	5,896
H_2O	24,900	4·52	5,509
H_2S	29,300	5·18	5,657

If the atoms of a molecule all lie in a plane, then, as Meyer has shown in his 'Kinetic Theory of Gases,' pp. 304–309, the cross-section of a molecule ought to be approximately equal to the sum of the cross-sections of the component atoms. The cross-section of a molecule should therefore be an additive quantity relating to its atoms, and this Meyer finds to be approximately the case. If, further, the shape of the atom is spherical and its volume proportional to $m^{1/2}$, the cross-section of a molecule will be proportional to $\Sigma m^{1/3}$, and the ratio $\frac{Q}{\Sigma m^{1/3}}$ will be constant. This, as will be seen from the tables, is to a certain extent realized.

TABLE II.

	Q.	$\Sigma m^{1/3}$.	$\frac{Q}{\Sigma m^{1/3}}$.
Alcohols.			
Methyl Alcohol ... CH_4O	49,000	8·81	4,418
Ethyl ,, ... C_2H_6O	64,700	13·10	4.939
Propyl ,, ... C_3H_8O	87,100	17·39	5,009
Butyl ,, ... $C_4H_{10}O$	107,800	21·68	4,973
Isobutyl ,, ... $C_4H_{10}O$	105.200	......	4,852
Amyl ,, ... $C_5H_{12}O$	127,000	25·97	4,890
Hexyl ,, ... $C_6H_{14}O$	159,300	30·26	5,144
Acids.			
Formic acid ...... CH_2O_2	43,900	9·33	4,706
Acetic ,, ... $C_2H_4O_2$	59,500	13·62	4,359
Propionic acid ... $C_3H_6O_2$	77,900	17·91	4,349
Butyric ,, ... $C_4H_8O_2$	106,500	22·20	4,797
Isovalerianic acid. $C_5H_{10}O_2$	142,600	26·49	5,395
Ethers.			
Ether .... $C_4H_{10}O$	89,700 80,380	21·62	4,149 3,716
Methyl ether ...... C_2H_6O	43,500	13·10	3,321
Esters.			
Methyl formate... $C_2H_4O_2$	56,700	13·62	4,164
Methyl acetate ... $C_3H_6O_2$	78,900	17·91	4,406
Ethyl formate ... ,,	83,500	,,	4,662
Ethyl acetate ... $C_4H_8O_2$	102,000	22·20	4,594
Methyl propionate ,,	92,600	,,	4,171
Propyl formate ,,	98,900	,,	4,454
Ethyl propionate $C_5H_{10}O_2$	116,300 87,500	26·49	4,390 3,303
Isobutyl formate ,,	86,700	,,	3,273
Methyl butyrate ,,	115,500	,,	4,360
Methyl isobutyrate ,,	111,200 88,400	,,	4,198 3,337
Propyl acetate ... ,,	90,700	,,	3,424
Ethyl butyrate... $C_6H_{12}O_2$	129,300	30·78	4,200
Ethyl isobutyrate ,,	123,000	,,	3,996
Isobutyl acetate ,,	133,600	,,	4,341
Propyl propionate ,,	136,300	,,	4,429
Ethyl valerianate $C_7H_{14}O_2$	149,000	35·07	4,248
Isobutyl propionate ,,	152,400	,,	4,344
Propyl butyrate ,,	145,600	,,	4,142
Propyl isobutyrate ,,	137,700	,,	3,926
Isobutyl butyrate $C_8H_{16}O_2$	165.700	39·36	4,209
Isobutyl isobutyrate ,,	165,200	,,	4,197
Propyl valerianate ,,	163,700	,,	4,159
Amyl propionate ,,	177,100	,,	4,499
Amyl isobutyrate $C_9H_{18}O_2$	185,600	43·65	4.246
Isobutyl valerianate ,,	186,500	,,	4,273

The deviations from constancy are more likely due to the values of Q not giving the true relative values of the sections of the molecules, than to the atoms not being spherical in shape, or their volumes not being proportional to $m^{1/2}$. The value of Q must obviously include a certain amount of space not occupied by the atoms, especially that situated near the centre of the molecules. The amount of included space in a molecule will depend on the arrangement of its atoms. Probably the variation of Q with temperature is largely due to a variation of the amount of unoccupied space included in Q.

The values of $\frac{Q}{\Sigma m^{1/3}}$ in Table I. show a distinct tendency to fall into three groups, the values of each group being approximately constant. Each group probably corresponds to a certain arrangement of the atoms corresponding to which a certain proportion of external space is included in Q.

The same tendency is exhibited by the values in Table II. The values belonging to the same chemical group are approximately constant. This is best shown by the alcohols and esters. In a few cases two values of Q for the same vapour are given in the table corresponding to different observers. The large differences that sometimes exist between the results of different observers, which are probably due both to errors of experiment and different methods of measurement, suggests that the deviations from constancy of the ratio $\frac{Q}{\Sigma m^{1/3}}$ are to a certain extent due to erroneous values of Q.

TABLE III.

	Q.	$\Sigma m^{1/3}$.	$\frac{Q}{\Sigma m^{1/3}}$.
$C_2H_4Br_2$	68,000	17·20	3,954
C_2H_4ClBr	63,000	16·18	3,894
$CHBr_3$	74,000	16·22	4,562
C_2H_5I	49,900	14·61	3,415
C_4H_9I	74,600	23·19	3,224
CH_3I	42,300	10·32	4,100
{ Hg	51,400	5·85	8,788
{ Hg_2	......	11·70	4,394

Table III. contains the ratio of $\frac{Q}{\Sigma m^{1/3}}$ for a few molecules which contain heavy atoms. It will be seen from the table that if the mercury molecule is taken as monatomic the value of the ratio is much larger than it should be on that assumption, but if it is taken as diatomic the ratio fits in well with the others. This suggests that a molecule of mercury in the gaseous state at zero temperature is probably diatomic.

We have compared the values of Q for different gases at zero temperature. It is probable, however, that the proper temperatures for comparison are corresponding temperatures. The range of the data is, however, not sufficiently extensive to allow a comparison to be made for corresponding states.

The coefficient of viscosity η of a gas is given by the equation $\eta=\frac{mv}{4\pi s^2}$, where v is the velocity of translation of a molecule. The equations for η and Q thus both contain the square of s, and the relative values of each of these two quantities for the substances belonging to one of the groups given in Tables I. and II., can therefore be obtained with the same degree of accuracy from these equations on $m^{1/3}$ being substituted for s^2. This applies also to the coefficient of diffusion δ of a molecule in a gas composed of molecules of the same kind, which is given by $\delta=\frac{mv^3}{12p\pi s^2}$, where p denotes the pressure of the gas.

The coefficient of diffusion δ_{12} of a gas 1 into a gas 2 is given by the equation

$$\delta_{12}=\frac{\mathrm{K}}{m_2^{1/2}(s_1+s_2)^2},$$

where K is constant at constant pressure and temperature, and s_1, s_2 are respectively the radii of the spheres of action of the molecules 1 and 2. Now s_1 and s_2 are, according to the results obtained in this paper, proportional to $(\Sigma m_1^{1/3})^{1/2}$ and $(\Sigma m_2^{1/3})^{1/2}$ respectively, and the above equation may therefore be written

$$\delta_{12}=\frac{\mathrm{K}_1}{m_2^{1/2}\{(\Sigma m_1^{1/3})^{1/2}+(\Sigma m_2^{1/3})^{1/2}\}^2},$$

where K_1 is a constant. This equation may be used to calculate relative values of δ_{12}.

Table IV. contains the coefficients of diffusion of a number of gases into each other, they were taken from Meyer's 'Kinetic Theory of Gases,' p. 275. The values in the table labelled "calculated" were obtained by means of the above formula. The value for N_2O-CO_2 was put equal to the observed and the other values reduced correspondingly. The calculated values, it will be seen, are approximately equal to the observed; the agreement, however, is not very good. The equation may thus be used to obtain a rough idea of the value of the coefficient of diffusion of two gases into one another.

TABLE IV.

Diffusion of gas takes place from right to left.	Coefficients of diffusion.		
	Observed.	Calculated.	Calculated by another formula.
H_2 —O_2	·722	·948	·871
H_2 —CO	·642	·940	·904
H_2 —CO_2	·556	·724	·723
H_2 —SO_2	·480	·668	·655
CO —O_2	·180	·166	·116
O_2 —CO_2	·161	·125	·160
CO —CO_2	·160	·136	·125
CH_4—CO_2	·159	·159	·151
Air —CO_2	·142	·136	·125
N_2O—CO_2	·089	·089	·089

The formula for the coefficient of diffusion used in this paper is the one usually given in treatises on the kinetic theory of gases. Maxwell has given another formula for the coefficient of diffusion based on the assumption that the force of attraction or repulsion between two molecules varies inversely as the fifth power of their distances of separation. This law, the writer* has shown, holds approximately for distances of the order of the distances of separation of the molecules in a liquid, and the attraction is further proportional to the product $(\Sigma m_1^{1/2})(\Sigma m_2^{1/2})$. Maxwell's equation accordingly becomes

$$\delta_{12}=K_1\left\{\frac{m_1+m_2}{m_1m_2(\Sigma m_1^{1/2})\,(\Sigma m_2^{1/2})}\right\}^{1/2},$$

where K_1 is constant at constant temperature and pressure. The values of δ_{12} obtained by this equation are given in the fourth column of Table IV. The values of δ_{12} calculated by these two different formulæ agree better with one another than with the observed values. On the whole both agree equally well with the facts.

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[*] Phil. Mag. May 1910, p. 783.

Some further deductions of interest can be made relating to the properties of the atom. If the mass of an atom is denoted by m, its volume, we have seen, is proportional to $m^{1/2}$, and its density therefore proportional to $\frac{m}{m^{1/2}}$ or $m^{1/2}$. Thus the density of atoms increases with increase of atomic weight. The density of a lead atom is thus about 14 times that of a hydrogen atom, and the density of a hydrogen atom about 30 times that of an electron. That the density of an atom should increase with the atomic weight we should expect since there would be a tendency of the atom to contract under the mutual attraction of its parts, and this would increase with the mass of the atom.

The writer* has shown that the attraction other than gravitational between two molecules a given distance apart is proportional to the product $(\Sigma m_1^{1/2})(\Sigma m_2^{1/2})$. This attraction gives rise to the surface-tension of liquids, chemical combination, &c. This fact may now be stated in a different form, namely, that the attraction is proportional to the product of the volumes of the molecules. It was also shown in the paper mentioned that the attraction of several atoms close together, as they occur in a molecule, is not exactly additive. We see now how this may be caused. When a number of atoms concentrate to form a molecule each atom must contract slightly owing to the attraction of the different parts of the molecule on one another. The attractive force of each atom at an external point is therefore less than it would be if the other atoms were absent. The contraction of the atoms would be greatest at their surfaces of contact, which would have the effect of increasing the extent of the total surface of contact. The stability of the structure of the molecule would thereby be increased.

An electron in the neighbourhood of an atom will be attracted by it due to electrostatic induction. If the atom is considered a perfect conductor of electricity the attraction is given† by

$$\frac{e^2a^3(2f^2-a^2)}{f^3(f^2-a^2)^2},$$

where a is the radius of the atom, and f the distance of the electron from the centre of the atom. When f is large in

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* *Loc. cit.*

† Maxwell's 'Electricity and Magnetism,' vol. i. 3rd edition, p. 251.

comparison with a the expression becomes $\frac{e^2a^3}{f^5}$. Now a^3 is proportional to the volume of the atom, and this, we have seen, is proportional to $m^{1/2}$, and the attraction is thus proportional to the square root of the atomic weight of the atom and inversely proportional to the fifth power of the distance of separation of the electron from the centre of the atom. It is of interest that the "chemical" attraction between two atoms follows a similar law. Thus the writer has shown in the paper mentioned above that the "chemical" attraction between two atoms is proportional to the product of the square roots of their atomic weights, or, if one atom is always the same, proportional to the square root of the other atom, and inversely proportional to the fifth power of their distance of separation. The above result is of interest and importance in connexion with the passage of α or β particles through matter.

It is also interesting to note that the forces are of the same order of magnitude. Thus if we substitute $3{\cdot}4\times10^{-10}$ for e and 10^{-8} for a, the expression for the electric attraction becomes $\frac{11{\cdot}56\times10^{-44}}{f^5}$. The constant K relating to the chemical attraction between two atoms—say of lead, corresponding to the above constant (e^2a^3), was calculated to be equal to $4{\cdot}14\times10^{-44}$, which is of the same order of magnitude as the above value.

When a β particle in passing through matter encounters an atom it gets deflected from its course and also produces secondary β rays from the atom. The amount of secondary radiation, and its direction of propagation and that of the primary β ray after an encounter, will depend on the nature of the encounter. Let us suppose the secondary radiations from a large number of atoms taken at random are made from the same atom with the paths of the primary rays parallel to one another, the deflected primary rays being included in the secondary radiation. The relative distribution of the secondary radiation round the atom in direction of motion with respect to the direction of motion of the primary electrons, and the distribution of velocity among the electrons moving in any given direction, will be independent of the number of atoms considered if a sufficiently large number is taken. The various angles made by the secondary rays with the direction of propagation of the primary β rays will be grouped about a mean somewhat like the molecular velocities according to Maxwell's law. The value of this mean angle, or the distribution of the radiation, must depend to a certain extent on the nature of the atom. The distribution of the secondary radiation outside an atom produced by a β ray must obviously depend largely on the amount of matter of the atom traversed by the β ray. Therefore, if the atom is spherical in shape a given increase in the atomic weight would produce less change in the magnitude of the mean angle of distribution when the atom is large than when it is small, since the change in the diameter of the atom will be smaller in the former case than in the latter. We should therefore expect the limiting distribution of the secondary radiation to depend less on the nature of the atom the greater its atomic weight.

This could be tested by means of the following arrangement. Suppose we have a number of slabs of different kinds of matter of infinite thickness, and some of the atoms in each slab eject electrons at right angles to one of the faces of the slab with the same velocity, which is also independent of the nature of the matter. The radiation from both of the faces of a slab would consist of real secondary radiation and deflected primary rays. Now when we are dealing with slabs of infinite thickness the ratio of the two radiations from the opposite sides of a slab is independent of the density of the slab ; it is also independent of the proportion of the atoms which eject β rays. These ratios for slabs of different substances would therefore afford some information on the relative limiting distribution of the secondary radiation round the atom.

Now the experiments of Prof. Bragg and Dr. Madsen [*] on the secondary cathode rays ejected by γ rays satisfy the above conditions. They showed that the electrons ejected by γ rays move in the direction of propagation of the rays, and if the rays are hardened by being first passed through a thick screen of lead, the velocity of these electrons is practically independent of the nature of the matter in which they are produced. They next carried out a set of measurements of the amounts of secondary cathode radiation from the two sides of plates of different materials sufficiently thick to give the maximum amount of radiation—which is equivalent to dealing with plates of infinite thickness, the γ rays passing through each plate at right angles to one of the surfaces. The ratios of the radiations from the two opposite sides of each plate for hard γ rays have been calculated from a table given

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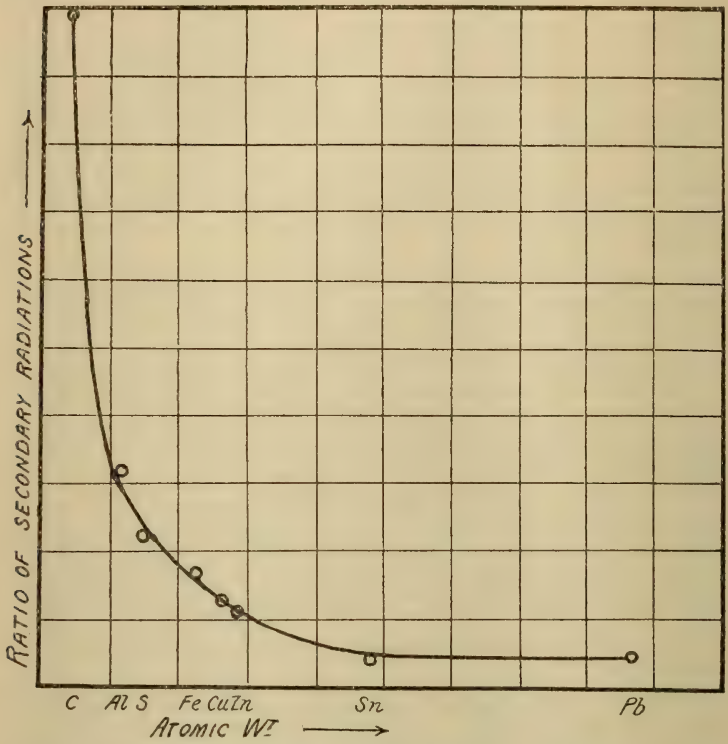
[*] Phil. Mag. xvi. pp. 918-939, Dec. 1908.

in the paper mentioned above, and are plotted in the diagram. It will be seen that the ratio changes very rapidly with the atomic weight when it is small, but it gradually becomes constant for atoms of high atomic weight. The relative distribution of the secondary radiation round an atom thus gradually becomes constant as its atomic weight increases, and this we have seen is most likely to be the case if the atom is spherical or approximately spherical in shape.



Cambridge, April 23, 1910.

XVII. *On the Theory of Radiation.* *By* Sir J. J. Thomson, *M.A., F.R.S., Cavendish Professor of Experimental Physics, Cambridge*[*].

In the Philosophical Magazine for August 1907, I discussed a theory of radiation from hot bodies which regarded the radiation as arising from the impact of negatively charged corpuscles with the molecules of the body; the impact starting

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[*] Communicated by the Author.

electric pulses which collectively constitute the radiation from the body. When we resolve, by Fourier's theorem, this radiation into its constituent harmonic vibrations, we find that the amount of light of any given period depends upon the ratio of that period to the time occupied by a collision. It was shown, moreover, that this radiation would not conform to the Second Law of Thermodynamics unless the time occupied by a collision varied inversely as the kinetic energy of the corpuscle before it came into collision, and in addition, that the time of collision of a corpuscle moving with a given speed must be constant and independent of the nature of the molecule against which the corpuscle collides. I showed that the first of these conditions would be satisfied if the forces exerted during the collision between a corpuscle and a molecule varied inversely as the cube of the distance between them ; the second condition will be satisfied if the collision is regarded as taking place, not between the corpuscle and the molecule as a whole, but as between the corpuscle and systems dispersed through the molecules, these systems being of the same character in whatever molecules they may be found, and repelling the corpuscle with forces varying inversely as the cube of the distance between them. Forces of this type would be exerted by electric-doublets of constant moment with their negative ends pointing to the corpuscles.

In this paper I shall consider more in detail the collision theory of radiation when the forces exerted during collision vary inversely as the cube of the distance between the colliding bodies. In the paper already quoted it is shown (see Phil. Mag. xiv. p. 225) that if $\mathrm{E}q$ be the energy per unit volume of the radiant energy with frequencies between q and $q+dq$,

$$\mathrm{E}q=\frac{1}{3}\,\frac{m\mathrm{K}}{\pi^2\mathrm{V}^3}\phi_1{}^2q^2dq,$$

where m is the mass of a corpuscle, V the velocity of light *in vacuo,* K the specific inductive capacity of the luminous body, and

$$\phi_1=\int_{-\infty}^{+\infty}f(\lambda)\cos q\lambda\,.\,d\lambda,$$

where $f(\lambda)$ is the acceleration of the corpuscle at the time λ.

We shall first find $f(\lambda)$ when the repulsion varies inversely as the cube of the distance. If x be the distance of the corpuscle from the system with which it collides,

$$m\frac{d^2x}{dt^2}=\frac{\mu}{x^3},$$

$$\frac{1}{2}m\left(\frac{dx^2}{dt}\right)=-\frac{1}{2}\frac{\mu}{x^2}+\frac{1}{2}mv^2,$$

where v is the velocity of the corpuscle before the collision. If we take $t=0$ when the corpuscle is closest to the molecule, we get by integrating this equation

$$x^2=v^2\left(t^2+\frac{\mu}{mv^4}\right),$$

$f(t)$ the acceleration of the corpuscle is equal to μ/mx^3, and thus

$$=\frac{\mu}{mv^3\left(t^2+\frac{\mu}{mv^4}\right)^{\frac{3}{2}}}.$$

And
$$\phi_1=\frac{\mu}{mv^3}\int_{-\infty}^{+\infty}\frac{\cos qt\,dt}{\left(t^2+\frac{\mu}{mv^4}\right)^{\frac{3}{2}}}.$$

To calculate the integral, let

$$u=\int_{-\infty}^{+\infty}\frac{\cos qt\,dt}{(t^2+c^2)^{\frac{3}{2}}}.$$

By differentiation, and integration by parts, we easily find

$$\frac{1}{q}\frac{du}{dq}=\frac{d^2u}{dq^2}-c^2u,$$

or if $cq=x$,

$$\frac{1}{x}\frac{du}{dx}=\frac{d^2u}{dx^2}-u.$$

If $u=xw$, this equation becomes

$$\frac{d^2w}{dx^2}+\frac{1}{x}\frac{dw}{dx}-w\left(1+\frac{1}{x^2}\right)=0 \quad . \quad . \quad . \quad . \quad (1)$$

Now the solution of the equation

$$\frac{d^2y}{dx^2}+\frac{1}{x}\frac{dy}{dx}-y\left(1+\frac{n^2}{x^2}\right)=0$$

is (since this is Bessel's equation with ιx for the independent variable)

$$\mathrm{AI}_n(x)+\mathrm{BK}_n(x),$$

where A and B are arbitrary constants, and

$$I_n = J_n(\iota x),$$

$$K_n = (-1)^n 1 \,.\, 3 \,.\, 5 \,.\, (2n-1) x^{-n} \int_0^\infty \frac{\cos (x \sinh \phi)}{\cosh^{2n} \phi} d\phi^*.$$

Tables for K_0 and K_1, and I_0 and I_1 are given by Mr. W. S. Aldis, Proceedings of the Royal Society, vol. lxiv. p. 203.

$I_n(x)$ becomes infinite when x is infinite, while $K_n(x)$ vanishes in that case.

We see that the solution of (1) is

$$w = AI_1(x) + BK_1(x).$$

Since u and therefore w vanish when x is infinite, $A=0$, and we have

$$u = xw = BxK_1(x),$$

where
$$K_1 = -\frac{1}{x} \int_0^\infty \frac{\cos (x \sinh \phi)}{\cosh^2 \phi} d\phi.$$

Since when $x=0$,

$$u = \int_{-\infty}^{+\infty} \frac{1}{(t^2+c^2)^{\frac{3}{2}}} dt = \frac{2}{c^2},$$

and
$$xK_1 = -\int_0^\infty \frac{d\phi}{\cosh^2 \phi} = -1,$$

we see that
$$B = -\frac{2}{c^2};$$

hence
$$\phi_1 = \frac{\mu}{mv^3} \int_{-\infty}^{+\infty} \frac{\cos qt\, dt}{\left(t^2 + \frac{\mu}{mv^4}\right)^{\frac{3}{2}}},$$

$$= -2v\sqrt{\frac{\mu}{mv^4}}\, qK_1\left(q\sqrt{\frac{\mu}{mv^4}}\right).$$

As $\frac{1}{2}mv^2$ is the kinetic energy of a corpuscle, we have if the corpuscles are in thermal equilibrium with the body

$$\tfrac{1}{2}mv^2 = \alpha\theta,$$

where θ is the absolute temperature of the body, and

$$\alpha = 1{\cdot}42 \times 10^{-16},$$

hence, if $h = \frac{1}{2}\sqrt{\mu m}$, we have

$$\phi_1 = -2v\left(\frac{hq}{\alpha\theta}\right) K_1\left(\frac{hq}{\alpha\theta}\right),$$

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* See Gray and Matthews, Bessel's Functions, p. 67.

and E_q the energy of the radiation with frequencies between q and $q+dq$ is

$$\frac{8}{3}\frac{\alpha\theta}{\pi^2V^3}\left\{\frac{hq}{\alpha\theta}K_1\left(\frac{hq}{\alpha\theta}\right)\right\}^2 q^2dq.$$

Denoting for brevity the function $xK_1(x)$ by $T(x)$ we may write this as

$$\frac{8}{3}\frac{\alpha\theta}{\pi^2V^3}T^2(hq/\alpha\theta)q^2dq.$$

If λ is the wave-length corresponding to the frequency q,

$$q=\frac{2\pi}{\lambda}V,$$

and E_λ the energy in the radiation with wave-lengths between λ and $\lambda+d\lambda$ will be

$$\frac{8}{3}\frac{\alpha\theta}{\pi^2V^3}T^2(hq/\alpha\theta)\,q^4\frac{d\lambda}{2\pi V}.$$

The value of q which makes the coefficient of $d\lambda$ in this expression a maximum is evidently such that if $\frac{hq}{\alpha\theta}=x$, then x is determined by the condition that $x^3K_1(x)$ should be a maximum; from the values of $K_1(x)$ given by Mr. Aldis in the Tables already referred to I find that $x=2{\cdot}4$; hence if λ_m is the value of λ which makes the energy between λ and $\lambda+d\lambda$ a maximum at the temperature θ when $d\lambda$ is given, we have

$$\frac{h2\pi}{\lambda_m\alpha\theta}=\frac{2{\cdot}4}{V},$$

or

$$\lambda_m\theta=\frac{2\pi}{h\alpha}\frac{V}{2{\cdot}4}.$$

Thus $\lambda_m\theta$ is a constant, and this constant is known with considerable accuracy from the experiments which have been made on the radiation from a black body. The value of this constant found by Lummer and Pringsheim * is 2940×10^{-4}. If we call this quantity ϕ, we have

$$E_\lambda=\frac{8}{3}\frac{\alpha\theta}{\lambda^4}8\pi T^2(2{\cdot}4\phi/\lambda\theta)d\lambda. \quad . \quad . \quad . \quad . \quad (2)$$

Since $T(x)=xK_1(x)=-1$ when x is very small, we see that for long waves

$$E_\lambda \text{ varies as } \frac{\theta}{\lambda^4}d\lambda.$$

The same law is given by both Rayleigh's and Planck's values for E_λ.

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* *Verh. deutsch. phys. Ges.* i. p. 230.

When x is very large, then (Gray and Matthews, Bessel's Functions, p. 68)

$$K_1(x) = -\sqrt{\frac{\pi}{2x}}\,\epsilon^{-x}\left\{1 + \frac{(4-1)}{8x} + \frac{(4-1)(4-3^2)}{2\,!\,(8x)^2} + \dots\right\},$$

and we see that for short wave-lengths

$$E_\lambda \text{ varies as } \frac{1}{\lambda^5}\,\epsilon^{-\frac{4\cdot 8\,\Phi}{\lambda\theta}}\,.\,d\lambda.$$

For these wave-lengths Lord Rayleigh's formula makes

$$E_\lambda \text{ vary as } \frac{\theta}{\lambda^4}\,\epsilon^{-\frac{4\Phi}{\lambda\theta}}\,.\,d\lambda,$$

and Planck's

$$E_\lambda \text{ vary as } \frac{1}{\lambda^5}\,\epsilon^{-\frac{4\cdot 95\,\Phi}{\lambda\theta}}\,.\,d\lambda.$$

Thus for both long and short waves the variation of E_λ with temperature and wave-length indicated by the preceding theory is very much the same as that given by Planck's theory; from Aldis's Tables the values of E_λ given by equation (2) can easily be calculated when λ and θ are given.

From the equation

$$2\pi h = \frac{2\cdot 4\,.\,\alpha}{V}\,.\,\lambda_m\theta$$

we find, putting $\alpha = 1\cdot 42 \times 10^{-16}$; $\lambda_m\,.\,\theta = 2940 \times 10^{-4}$, that

$$h = 5\cdot 3 \times 10^{-28}.$$

But $h = \frac{1}{2}\sqrt{\mu m}$. If we suppose the repulsive force due to an electric doublet of moment M, $\mu = 2Me$, and we have approximately

$$2Mem = 10^{-54},$$

or $$Me^2 = 2\cdot 5 \times 10^{-37} ;$$

taking $e = 4 \times 10^{-10}$, then $M = 1\cdot 5 \times 10^{-18}$.

The distance between the charges in the doublet would thus be 4×10^{-9} cm.

The existence of these doublets has a very important bearing on the theory of the distribution of energy in light-waves. There are many phenomena which can be interpreted as indicating that the energy in radiation is made up of definite units, and that these units are indivisible, the energy in each unit of light of frequency n being $h'n/2\pi$ where h' is a constant introduced by Planck, having the value $6\cdot 55 \times 10^{-27}$ erg. sec. As an example of a phenomenon which suggests this division of the energy of light into definite units, we may quote the very interesting experiments made by Ladenburg on the energy possessed by the corpuscles which are emitted by bodies when exposed to ultra-violet light. Ladenburg found that the maximum energy of these corpuscles was independent of the intensity of the light, that it varied but little with the nature of the body from which they were emitted, and was proportional to n the frequency of the light, being of the order $h'n/2\pi$ where h' is Planck's constant. These results admit of very straightforward interpretation on the unitary view of the structure of light, each corpuscle being regarded as taking up one unit of energy from the light which caused its ejection. There seems to me, however, to be grave objections to the assumption that units of light are incapable of alteration; for example, why should a unit of light when passing over a corpuscle be obliged to communicate to it either the whole of its energy or none at all?

If we suppose that doublets exist in the atom, then experiments such as Ladenburg's admit of a different interpretation from that just given. If AB is a doublet with the positive end at B, and P a corpuscle, then it is possible to have a state of steady motion when P describes a circle round AB as axis, the plane of the orbit being at right angles to AB and the centre of the orbit on the prolongation of AB.

The equations of motion of a particle moving under the influence of the doublet are easily found. Let $r=\mathrm{OP}$ the distance of the corpuscle from O the centre of the doublet, θ the angle which OP makes with AB the axis of the doublet, and ϕ the angle which the plane POB makes with a fixed plane. Then m being the mass and e the charge on a corpuscle, M the moment of the doublet, we have

$$m\left(\frac{d^2r}{dt^2}-r\sin^2\theta\dot{\phi}^2-r\dot{\theta}^2\right)=-\frac{2\mathrm{M}e}{r^3}\cos\theta,$$

$$m\left(\frac{d}{dt}(r^2\dot{\theta})-r^2\sin\theta\cos\theta\dot{\phi}^2\right)=-\frac{\mathrm{M}e\sin\theta}{r^2},$$

$$m\frac{d}{dt}(r^2\sin^2\theta\dot{\phi})=0.$$

In the state of steady motion both r and θ are constant and v the velocity of the particle $=r\sin\theta\dot{\phi}$, hence we have

$$\left.\begin{aligned}\frac{mv^2}{r}&=\frac{2\mathrm{M}e\cos\theta}{r^3}\\ \cot\theta\, mv^2&=\frac{\mathrm{M}e\sin\theta}{r^2}\end{aligned}\right\}\quad\ldots\ldots\ldots\quad(3)$$

Hence $$\tan^2\theta=2\,;$$

$$\tfrac{1}{2}mv^2=\sqrt{\mathrm{M}me}\cos^{\frac{3}{2}}\theta\,.\,\dot{\phi}$$

$$=\sqrt{\mathrm{M}me}\,.\,\frac{1}{3^{\frac{3}{4}}}\dot{\phi},$$

or since $h=\dfrac{1}{\sqrt{2}}\sqrt{\mathrm{M}me}$,

$$\tfrac{1}{2}mv^2=h\frac{\sqrt{2}}{3^{\frac{3}{4}}}\dot{\phi}.$$

Thus since $\frac{1}{2}mv^2$ is the kinetic energy and $\dot{\phi}$ the frequency of the steady motion, we see that the steady motion of the corpuscle is such that the kinetic energy is proportional to the frequency.

We can easily show that if the corpuscle is disturbed from the state of steady motion, and if $r+\rho$, $\tan^{-1}\sqrt{2}+\vartheta$, where ρ and ϑ are small, are the values of ρ and ϑ in the disturbed motion, then

$$m\frac{d^2\rho}{dt^2}=0,$$

$$\vartheta''+2\dot{\phi}^2\vartheta=0,$$

or the frequency of the vibration about the steady motion is $\sqrt{2}$ times the frequency of the steady motion, and both are proportional to the kinetic energy of the corpuscle in its steady motion.

By altering the distance of the corpuscle from the centre of the doublet always keeping $\tan\theta=2$, we can make the frequency for steady motion any thing we please, the kinetic energy will always be proportional to the frequency.

Hence, if the atoms contain doublets, it is probable that in a certain number of cases these doublets will have corpuscles circulating round them, in some atoms the distance of the corpuscles from the doublet will have one value, in others another, and these differences in the distances will give rise to steady motions with different periods. Thus in a body made up of an enormous number of atoms, there are systems consisting of a doublet and a corpuscle in steady motion, the frequency of the motion having all values, the kinetic energy of this motion bears a constant ratio to the frequency, the frequency being independent of the kind of atom in which the steady motion takes place. What will be the behaviour of such a body when an electric wave of definite frequency passes through it? The electric forces in the wave might do work upon the doublet, twisting its axis so as to alter the angle it makes with the radius to the corpuscle. From the principle of resonance the alteration in the angle will be far greater when the frequency of the steady motion of the corpuscle coincides with that of the incident electric wave than in any other case. A large alteration in the angle will, however, result in the corpuscle getting free from the doublet and going off with much the same kinetic energy as it had in the steady motion; this, as we have seen, is equal to the frequency multiplied by Planck's constant. On this view then a light-wave would liberate corpuscles whose frequency when in a state of steady motion is the same as that of the light, and the kinetic energy of these corpuscles would be proportional to the frequency. Thus the energy of the corpuscles ejected by the light would on this view be proportional to the frequency of the light, whether the energy of the light-wave was made up of different units or not; so that we cannot regard Ladenburg's experiments as a proof of the unitary structure of light. Again, the number of atoms in which there is steady motion of the kind we are considering having a frequency nearly equal to some particular value, is probably a very small fraction of the whole number of molecules, so that the number of particles emitted would on any view as to the constitution of a light-wave be small compared with the number of molecules passed over by the light. This theory enables us to explain the electrical effects produced by light, without assuming that light is made up of unalterable units, each containing a definite and, on Planck's hypothesis, a comparatively large amount of energy, a view which it is exceedingly difficult to reconcile with well-known optical phenomena. The existence of the doublets produces throughout the body systems (the corpuscles in steady motion) which act like resonators, having frequencies of all values, and possessing an amount of energy proportional to the frequency.

The magnetic properties of bodies show, I think, that the whole number of these systems in steady motion for the whole range of frequencies cannot be large compared with the number of atoms. For the corpuscle moving round the circle with radius $r \sin\theta$ and velocity v is equivalent to a magnet whose moment is $\frac{1}{2}evr\sin\theta$.

We see, however, from equations (3) that $vr\sin\theta$ is constant for all the systems and equal to

$$\frac{2}{3^{\frac{3}{4}}}\sqrt{\frac{\mathrm{M}e}{m}};$$

so that

$$\frac{1}{2}ev\sin\theta = \frac{1}{3^{\frac{3}{4}}}\frac{e}{m}\sqrt{\mathrm{M}me}$$
$$= 5 \times 10^{-21}, \text{ approximately.}$$

Thus, if there were but one system per atom, the sum of the moments of the magnets in a cubic centimetre of gas at standard temperature and pressure would, taking the number of molecules in the cubic centimetre as equal to 3×10^{19}, be ·30, which is about half the value of the same quantity for oxygen, the most magnetic gas known.

XVIII. *Notices respecting New Books.*

Les Oscillations électriques : Principes de la Télégraphie sans fil. By C. Tissot. Paris : Octave Doin et fils.—*Théorie des Moteurs Thermiques.* By E. Jouguet. Paris : Octave Doin et fils.

BOTH of these small books belong to the useful series published under the name of *Encyclopédie Scientifique.* The former consists of a very clear summary of the principles underlying the modern theory of electric waves and their applications. Although it is mainly mathematical yet the author is fully abreast of recent experimental work, and his mathematics is selected so as to elucidate phenomena and not to display merely abstract properties of equations. It can be recommended as giving a thoroughly satisfactory presentation of the subject.

The same attention to the practical side is paid in M. Jouguet's volume on Heat Engines. Nevertheless it is only to the engineer who wishes to discuss scientifically the principles of his practice that the work will prove attractive. To such, however, the book will be found to contain a very thorough elementary treatment of the energy and heat relations of thermal transformations including a complete discussion of the sources of loss of efficiency. Like many others amongst the French School of Physicists, M. Jouguet is specially good on the subject of irreversible transformations. Concerning his numerical data, perhaps it may be pointed out that the retention of the old formula for the connexion of latent heat of steam with temperature, is liable to criticism in the light of more recent determinations.

XIX. *Intelligence and Miscellaneous Articles.*

To the Editors of the Philosophical Magazine.

The University, Glasgow,
June 17th, 1910.

Gentlemen,—

REFERRING to Mr. W. J, Harrison's further statement in the Phil. Mag. for June regarding my paper "On the Damping of Long Waves in a Rectangular Trough," Phil. Mag. [6] vol. xvii. pp. 154–164, I do not admit the legitimacy of his criticism but am undesirous of pursuing the matter further.

R. A. Houstoun.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

In a paper published in the Phil. Mag. for May 1910, p. 725, Mr. and Mrs. Soddy and Mr. Russell describe some highly interesting experiments on the absorption of the γ rays of radium by different materials. Since these experiments bear on some of my work on γ rays, I would like to make a few remarks upon them.

According to a formula which they use, the γ rays of radium appear to be homogeneous. I would like to point out that the formula used, like all the other absorption formulæ, can only approximately represent the facts. Besides the absorption of the rays secondary radiation of a more absorbable type than the primary is produced, and some primary rays probably get scattered without any change in their nature. The formula used does not take any account of this, and in fact it is impossible at present to formulate one that does. I therefore venture to think that the primary γ rays are not homogeneous. The experiments that have been carried out on the change in penetrating power of the cathode rays ejected from substances exposed to the γ rays of radium by previous screening of the rays, cannot be brought into harmony with the idea that they are homogeneous. Thus I[*] have shown by means of a magnetic deflexion method that the proportion of slow cathode radiation to the more penetrating from lead exposed to γ rays becomes less when the rays are previously passed through a metal screen. This was also shown by Prof. Bragg and Dr. Madsen[†] using a method of scattering. Mr. and Mrs. Soddy and Mr. Russell think that the soft cathode radiation is solely due to the soft secondary γ rays generated in the substance by the primary rays. If that were so, the proportion between the cathode radiation of different penetrating powers would be independent of screening, but according to the experiments quoted it is not.

I have carried out some experiments on the "scattering" of γ rays of different penetrating powers. These experiments are too lengthy to be discussed in this connexion in this letter. I may mention only that the scattering of "hard" rays, obtained by previously passing the γ rays through a lead screen, is less than that of the "softer" unscreened rays. However, the experiments of Mr. and Mrs. Soddy and Mr. Russell should throw some additional light on the intricate mechanism of the absorption of γ rays.

Yours faithfully,

Cambridge, May 19.

R. D. KLEEMAN.

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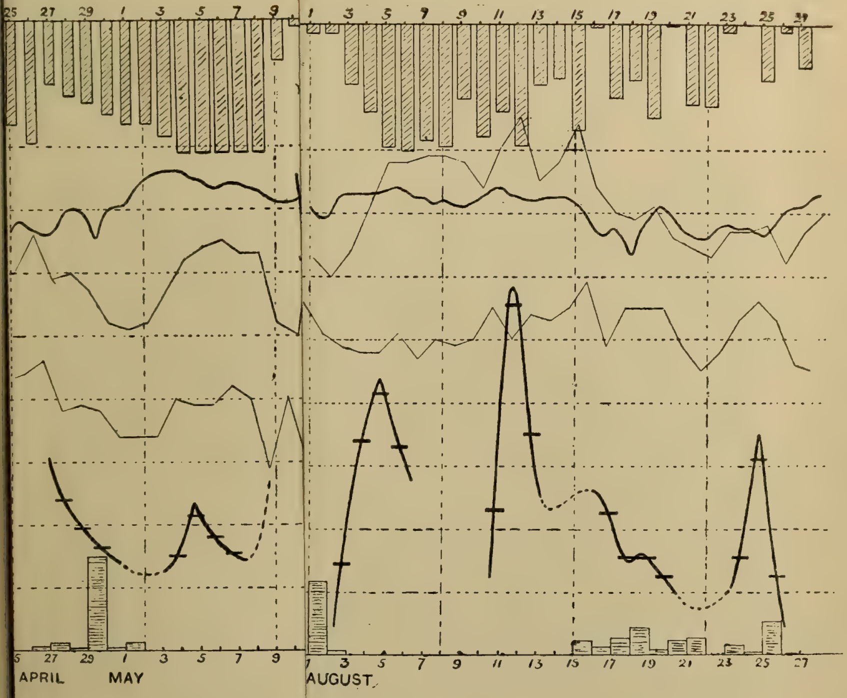
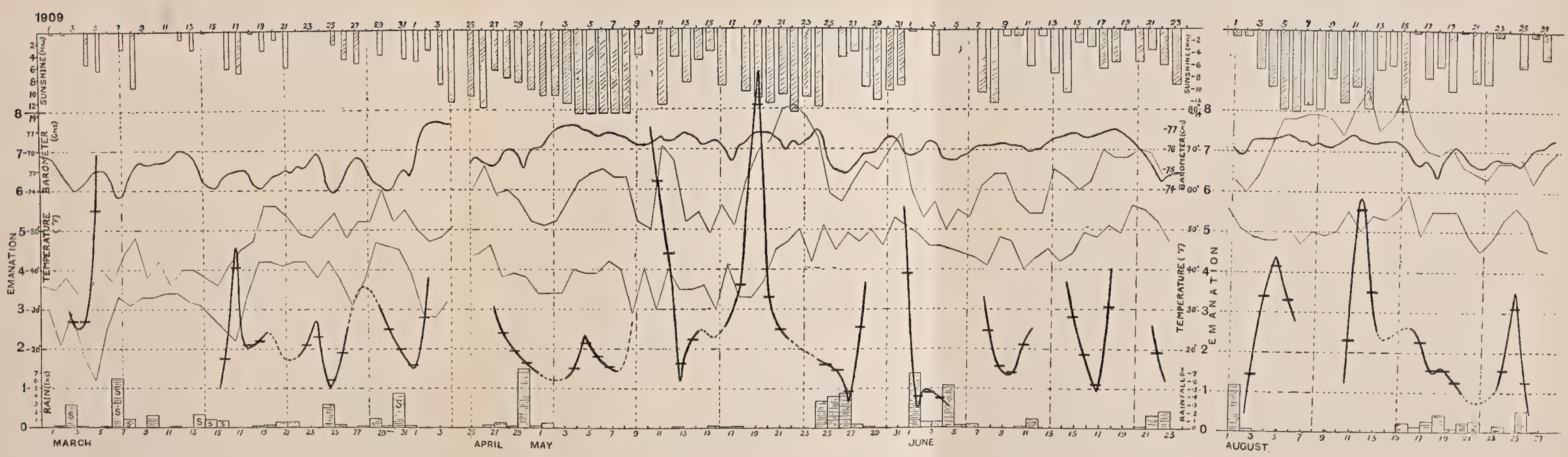
[*] Proc. Roy. Soc. A. vol. lxxxii. p. 128 (1909).

[†] Phil. Mag. xv. pp. 663–675, May 1908.

Phil. Mag. Ser. 6, Vol. 20, Pl. I.

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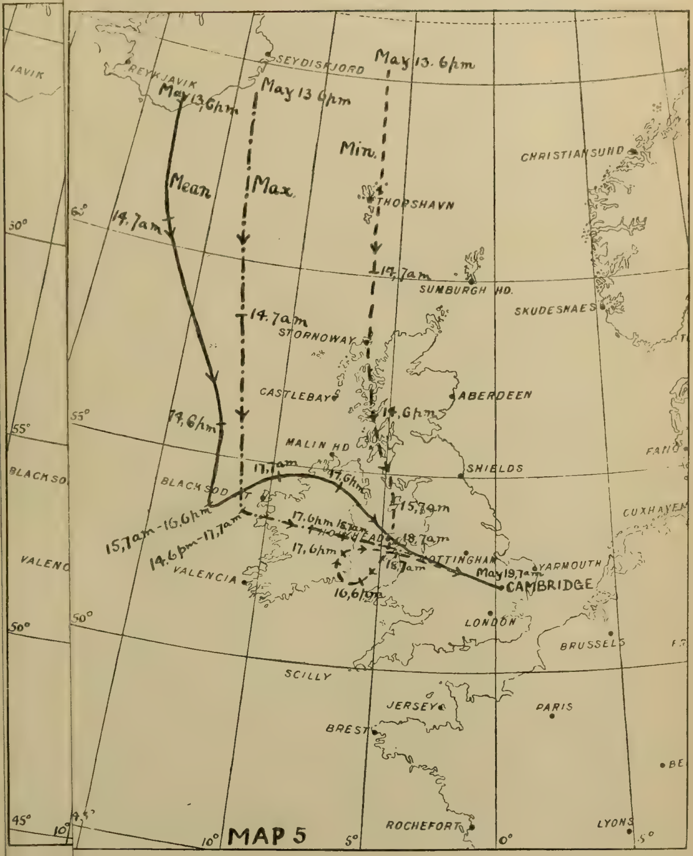
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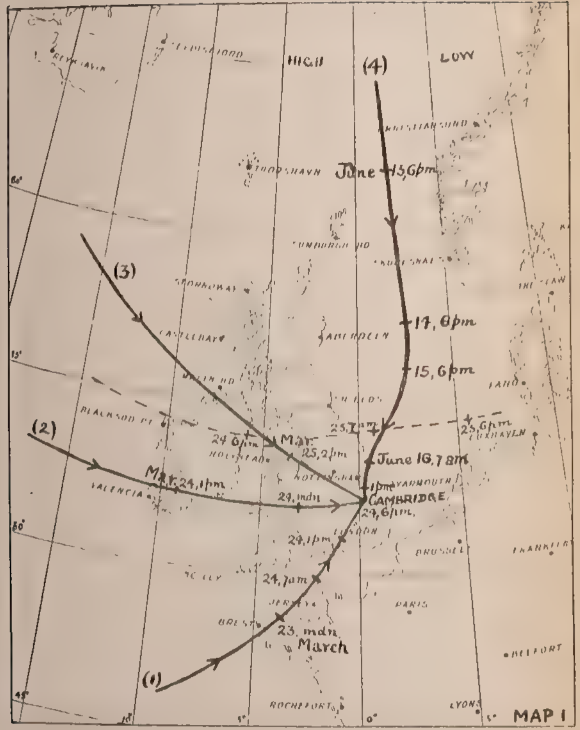
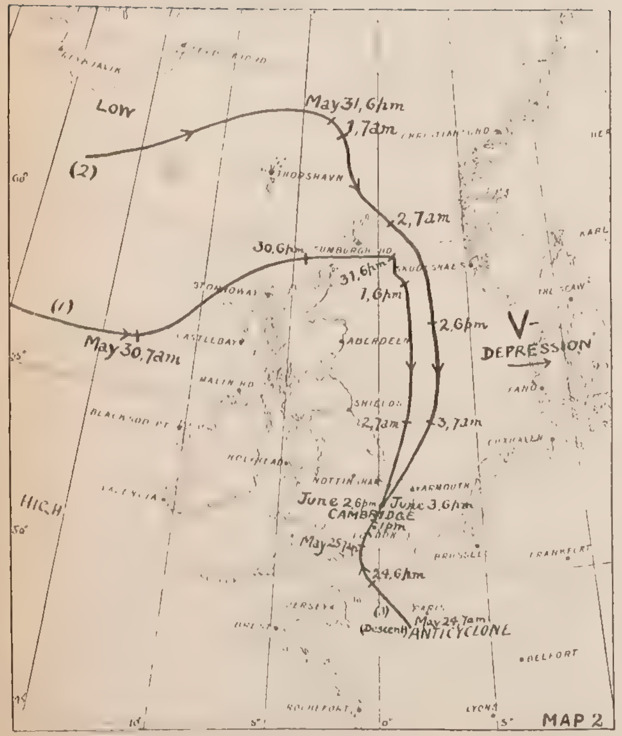
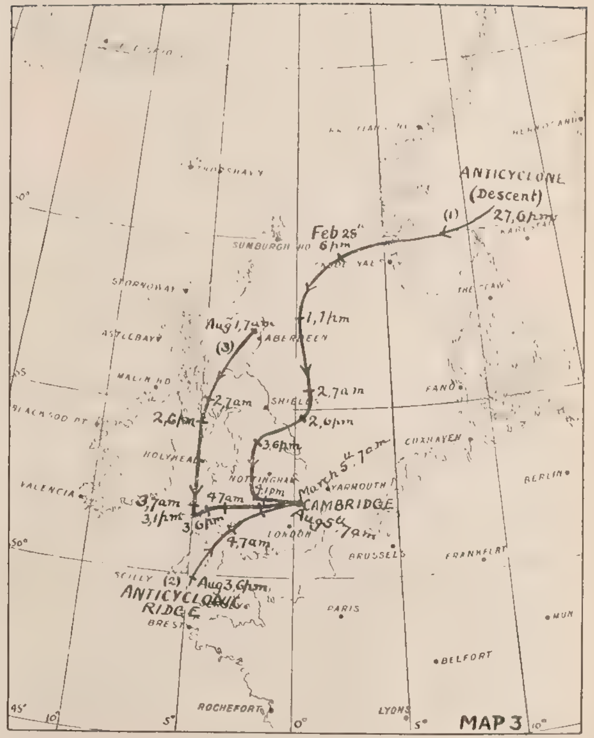
MAP 5



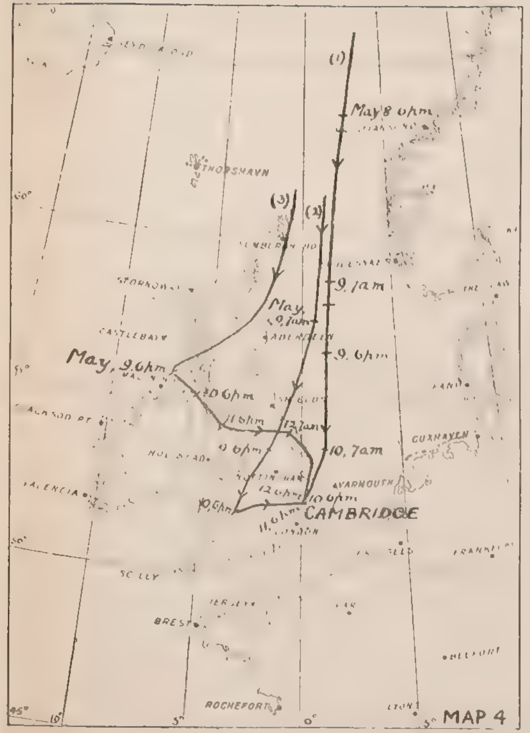
MAP 1



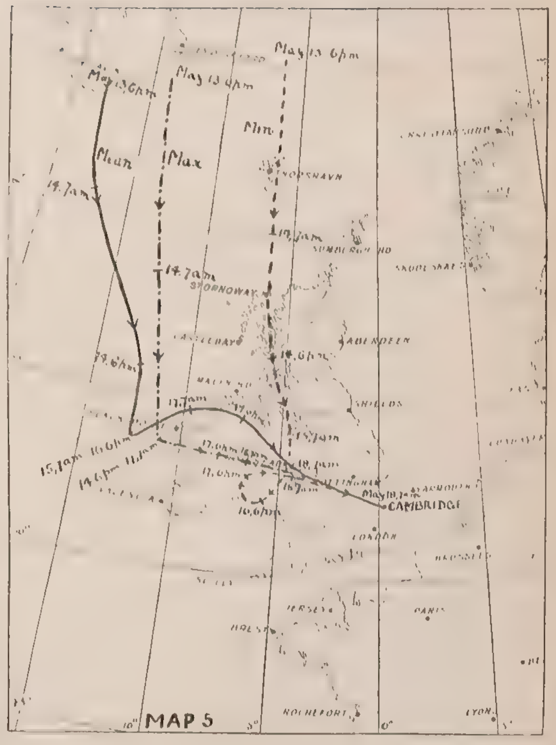
MAP 2



MAP 3

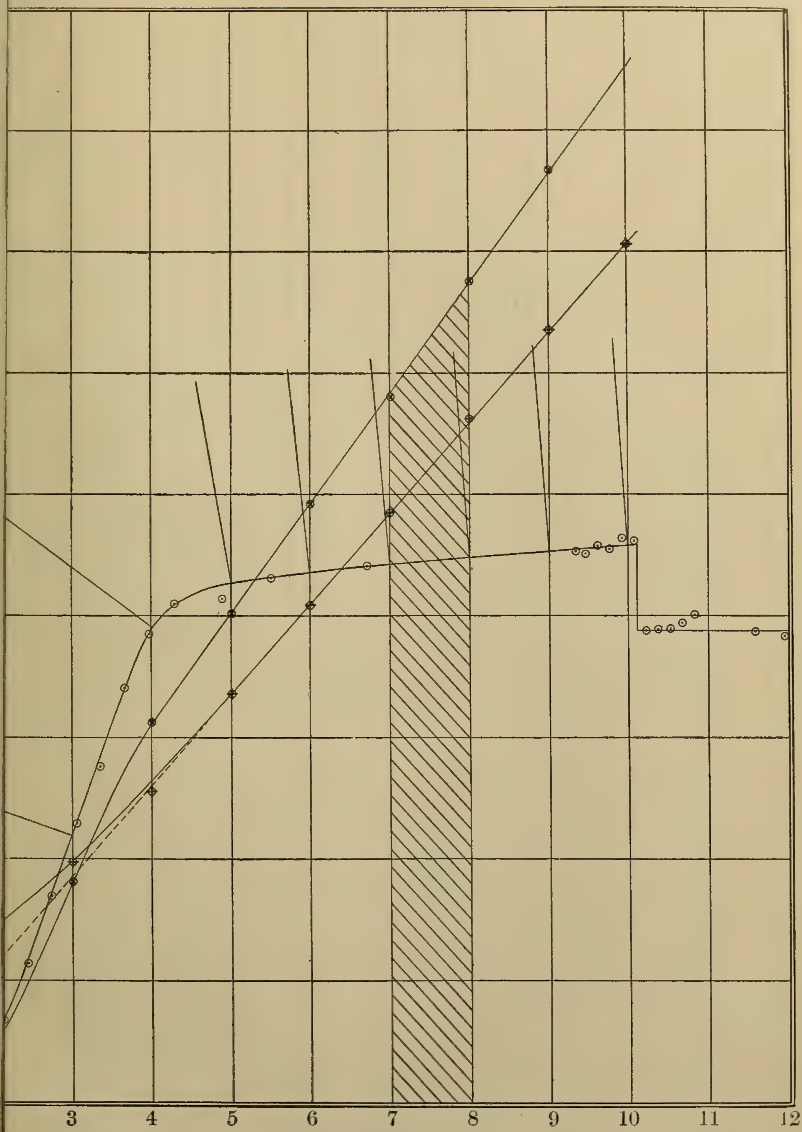


MAP 4



MAP 5

FIG. 5.



(1 div. = 3·267 volts.)

Fig. 4.

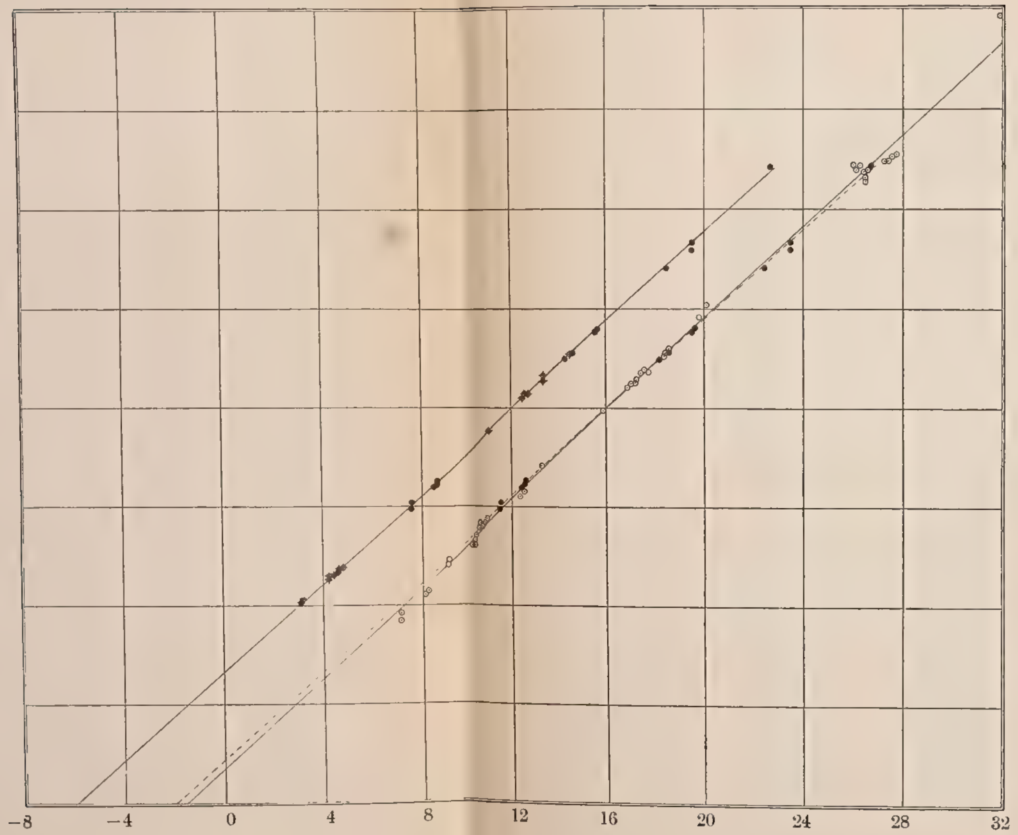
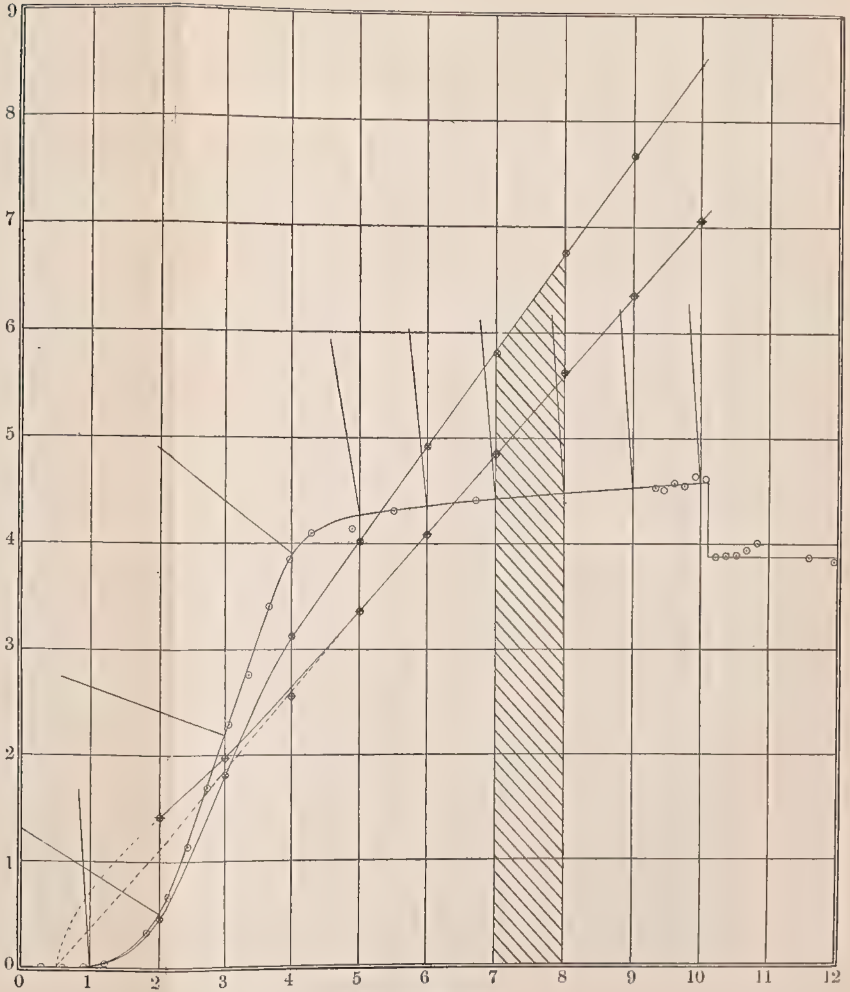


Fig. 5.



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XX. *Molecular and Electronic Potential Energy.*

By WILLIAM SUTHERLAND*.

IN previous communications it has been shown that cohesion can be explained by the attractions between each molecule and its immediate neighbours. For the general case of a homogeneous isotropic substance the most convenient average arrangement of the molecules to be taken as mathematically representative of that of Nature is the cubical one, in which case each molecule has six nearest neighbours. Each molecule may be regarded as an electrized sphere analogous to the Earth as a magnetized sphere. It has an electric moment, which in several of my papers is denoted by es, originally used to indicate the simplest electric moment, that of two opposite electron charges e at distance s apart. But es may be regarded as the symbol for the electric moment of the molecule, however produced. Outside of the molecule the electrization acts like an electric doublet of infinitely small axis but of finite moment es placed at the centre of the molecule. For the sake of simplicity and without any real loss of generality we may imagine the electric axis of a molecule parallel to one set of the edges in our assumed cubical arrangement. Then in order that a molecule may attract its six immediate neighbours it must have its electric axis similarly directed to those of its two axial neighbours, and oppositely directed to those of its four lateral neighbours.

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* Communicated by the Author.

The diagram represents these relations in perspective for a central molecule and its six neighbours. Let R be its distance from its neighbours. Then it attracts the two axial

Fig. 1.

neighbours with a force $6e^2s^2/R^4$ and its four lateral with a force $3e^2s^2/R^4$. The mean attraction is $4e^2s^2/R^4$. Concerning the forces between the central molecule and the more remote ones we see that they are either repulsions or attractions whose average effect can be calculated. I propose to treat it as negligible in comparison with the attractions of the six immediate neighbours. The reason for doing so is this. The molecules of Nature are in motion, the directions of their axes are changing. Our cubical arrangement of the molecules and the assumed directions of the axes becomes a closer representation of the facts of Nature, the smaller the multiple of R to which it is extended from a central molecule. Even for a molecule and its six nearest neighbours at any instant the cubical arrangement is not a true picture. The real state of affairs is a succession of distorted cubical arrangements with a strictly cubical arrangement for a mean. We deprive our schematic representation of plasticity if we make the one set of dividing planes apply to a large number of molecules. The best way of stating the position is to say that near a molecule the arrangement of other molecules is approximately cubical at any instant, but that the accumulated effects of small departure from the strict cubical arrangement make the relations between any molecule and those which are not its immediate neighbours not expressible by means of a single cubical arrangement. For these reasons then I propose to investigate molecular potential energy on the following simple principle, that a molecule attracts its six nearest neighbours with a force $4e^2s^2/\mathrm{R}^4$, and that its effects on all other molecules may be neglected.

1. *The so-called internal molecular pressure, the* $\mathrm{K}\rho^2$ *of Laplace and the* a/v^2 *of van der Waals.*

The attraction of a molecule for one neighbour having the average value $4e^2s^2/\mathrm{R}^4$, the attraction per unit area of matter lying on one side of a plane exerted on that lying on the other is $4e^2s^2/\mathrm{R}^6$. If m is the mass of a molecule and $\rho(=1/v)$ is the density of the substance, $\mathrm{R}^3=m/\rho$, so we may write

$$\mathrm{K}\rho^2=a/v^2=4e^2s^2/\mathrm{R}^6=4e^2s^2\rho^2/m^2=4e^2s^2/m^2v^2. \quad . \quad (1)$$

2. *The internal virial* $\frac{1}{2}\,.\,\frac{1}{2}\Sigma\Sigma\, rf(r)$.

With $f(r)$ to denote the attraction between two molecules at distance r apart, this evaluation becomes easy. Let us make it for unit mass of the substance consisting of n molecules in volume v. For a molecule and each of its six immediate neighbours $rf(r)$ becomes $4e^2s^2/\mathrm{R}^3$. The first Σ extends only to the six nearest neighbours, so

$$\Sigma\, rf(r)=24e^2s^2/\mathrm{R}^3.$$

Then $$\Sigma\Sigma\, rf(r)=24ne^2s^2/\mathrm{R}^3,$$

and $$\tfrac{1}{2}\,.\,\tfrac{1}{2}\Sigma\Sigma\, rf(r)=6ne^2s^2/\mathrm{R}^3=6n\rho e^2s^2/m=6n^2\rho e^2s^2$$
$$=6\rho e^2s^2/m^2=3\mathrm{K}\rho/2. \quad . \quad . \quad (2)$$

3. *Molecular potential energy.*

The potential energy of a molecule and one nearest neighbour for an attraction $4e^2s^2/\mathrm{R}^4$ is $4e^2s^2/3\mathrm{R}^3$. For the six nearest neighbours it is $8e^2s^2/\mathrm{R}^3$, and for the n molecules in volume v it is $n/2$ times this, the factor $\frac{1}{2}$ being introduced to avoid counting the mutual energy of two molecules twice in the summation. So for the potential energy of unit mass we have

$$4ne^2s^2/\mathrm{R}^3=4n^2e^2s^2\rho=4\rho e^2s^2/m^2=\mathrm{K}\rho. \quad . \quad . \quad (3)$$

4. *Surface energy.*

First let us take the imaginary case of a substance whose surface is common with that of a vacuous space. A molecule on the surface has now only five nearest neighbours, if we carry our cubical scheme right up to the surface. The attraction of one nearest neighbour would be unbalanced by an equal opposite force. So a process of adjustment takes place in the surface layer of molecules. Part of the adjustment consists of evaporation into the vacuum, but for the moment we may neglect the effects of this. The main part of the adjustment consists in a changed arrangement of the molecules in the surface layer, involving a change of density which is often small compared with the density because of the small compressibility of liquids and solids. To a first approximation we may say that a molecule in the surface layer has only 5/6 of the potential energy of a molecule in the body. If then we regard the potential energy of the whole mass as being due to compression brought about by the attractive forces between neighbours, then we must say that each molecule on the surface has superposed on this compressional energy a tensional supply which is 1/6 of the potential energy of a molecule in the body. So the surface energy per molecule is $4e^2s^2/3R^3=4ne^2s^2/3$, and the surface energy per unit surface often denoted by α is $4e^2s^2/3R^5$. This will apply to a liquid in contact with its vapour whose density is small enough to be neglected. The case in which the effect of the vapour becomes appreciable can be treated as a special one of the following.

5. *Surface energy at the contact of two substances.*

Here the attraction between unlike molecules enters. Let the one substance be called 1, and have quantities assigned to it by the subscript 1, the other substance being 2. Then the average attraction between a molecule of 1 and a neighbouring molecule of 2 is $4e_1s_1e_2s_2/{}_1R_2{}^4$, where ${}_1R_2$ has still to be defined. It is the average distance between the surface layer of molecules of 1 and the surface layer of molecules of 2. Thus the representative cubical arrangement of six molecules of 1 round a central molecule in the body of 1 is to be replaced for a central molecule in the surface layer by five molecules of 1 in cubical order round it, and one molecule of 2 at distance ${}_1R_2$ in the sixth direction. So the surface energy of a molecule in the surface of 1 is $4(e_1{}^2s_1{}^2/R_1{}^3-e_1s_1e_2s_2/{}_1R_2{}^3)/3$, and for a molecule in the surface of 2 it is $4(e_2{}^2s_2{}^2/R_2{}^3-e_1s_1e_2s_2/{}_1R_2{}^3$. Per unit surface the energies are $4(e_1{}^2s_1{}^2/R_1{}^3-e_1s_1e_2s_2/{}_1R_2{}^3)/3R_1{}^2$ and $4(e_2{}^2s_2{}^2/R_2{}^3-e_1s_1e_2s_2/{}_1R_2{}^3)/3R_2{}^2$, so for the total surface energy or tension α we have

$$3\alpha/4=e_1{}^2s_1{}^2/R_1{}^5-e_1s_1e_2s_2(1/R_1{}^2+1/R_2{}^2)/{}_1R_2{}^3+e_2{}^2s_2{}^2/R_2{}^5. \quad (4)$$

The conditions of statical equilibrium are not provided by our definition of ${}_1R_2$ and placing of molecules in the sixth direction. An adjustment takes place, whose effects are neglected.

6. *Surface energy of a liquid in contact with its vapour.*

Here there is more difficulty in specifying an artificial arrangement which will represent the average case of Nature. A molecule of the surface layer of the vapour in a cubical scheme has five nearest neighbours amongst the vapour molecules and one nearest amongst the surface molecules of liquid, but there are many surface molecules of the liquid which are almost as near as the nearest, half of these repelling and half attracting. But it seems to me that it is right to assume that the electrical adjustments to minimum potential energy which cause a molecule of vapour not at a surface to attract its six immediate neighbours, will likewise cause it, when it is in a surface layer, to determine in all the near molecules of the liquid surface such a total electric moment as attracts it as if the sixth vapour molecule were present alone in the place of the nearest liquid molecule. In Nature the surface molecule of vapour is not stationary in the average position, but it moves right up to the liquid surface, establishing for itself there liquid conditions, it may retreat, or its place may be taken by a molecule leaving the liquid. Our assumption averages the values of the force experienced during this motion, and supposes it to be equal to the force between two vapour molecules whose distance apart is the average distance of a surface molecule of vapour from the liquid surface. On this supposition there is no reason to expect any appreciable perturbation of the vapour density except in the layer quite close to the liquid. It leads to somewhat different results from those obtained in my paper "The Principle of Dynamical Similarity in Molecular Physics" (*Boltzmann Festschrift*, 1904, A. Barth, Leipzig) from similar considerations. By suitably changing the symbols in the last section with subscript 2 for vapour we get for the tensional surface energy of a molecule in the liquid $4e^2s^2(1/R_1{}^3-1/{}_1R_2{}^3)/3$, and for the compressional surface energy of a molecule in the vapour $4e^2s^2(1/R_2{}^3-1/{}_1R_2{}^3)/3$, the total per unit surface being

$$\alpha=4e^2s^2\{1/R_1{}^5-(1/R_1{}^2+1/R_2{}^2)/{}_1R_2{}^3+1/R_2{}^5\}/3. \quad . \quad (5)$$

It has been assumed here that *es* remains constant during the change from liquid to vapour. It is possible that two molecules approaching one another might alter one another's electric moments by a process of induction or otherwise. This is a very important matter in connexion with the electrization of molecules. In section 10 we shall be investigating a change of equal importance within each molecule due to variation of its distance from its neighbours. Evidence bearing upon a real or apparent change of *es* with R will be discussed in the next section, the subject of the present section being resumed in 8.

7. *The virial of molecular attraction expressed empirically.*

In "The Laws of Molecular Force" (Phil. Mag. [5] xxxv. 1893, p. 211) it was shown from the extensive experiments of Amagat that the equation of van der Waals applies to the whole gaseous region of the element gases H_2, O_2, N_2, and to CH_4, down to and a little beyond the critical volume. Let us write that equation in its properly extended dynamical form for comparison with the equation of the virial of Clausius. It is

$$\frac{3}{2}pv=\frac{3}{2}\mathrm{RT}+\frac{3}{2}\mathrm{RT}\frac{v}{v-b}-\frac{3}{2}\frac{a}{v}. \quad . \quad . \quad . \quad (6)$$

The term on the left is the virial of the external pressure, the first term on the right is the translatory kinetic energy of the molecules, the second is the virial of the repulsive forces which act during molecular collisions, and the third is the virial of molecular attraction. The form of this third term when compared with (2) with $\rho=1/v$, shows that for the element gases and CH_4 the electric moment *es* does not vary with the distance between neighbour molecules either in reality or in effect. But in the same paper it was shown from Amagat's experiments on CO_2 and from those of Ramsay and Young on $(C_2H_5)_2O$ that for typical compounds the equation takes empirically not the form of that of van der Waals, but this

$$\frac{3}{2}pv=\frac{3}{2}\mathrm{RT}+\frac{3}{2}\mathrm{RT}\frac{2k}{v+k}-\frac{3}{2}\frac{l}{v+k}. \quad . \quad . \quad (7)$$

This applies from $v=\infty$ to the critical volume which is nearly $7k/6$, and it holds approximately down to $v=k$. Here we have two remarkable differences from the equation of the van der Waals type. Originally I supposed these to be due to a pairing of the compound molecules, but in later papers attributed them to molecular entanglements during collision. We have now again to consider them more closely. In the first place the virial of the repulsive forces during collision takes the form $2k/(v+k)$ times, instead of $b/(v-b)$ times $3\mathrm{RT}/2$. Now in the kinetic theory of gases $v-b$ enters because under given conditions the mean free path of a molecule diminishes with increasing size of the molecule, the effect of this in the dynamical calculation of the virial of the collisional forces is to subtract b from v, the molecules being assumed to act during collision like perfectly resilient spheres. So the form $v+k$, in which k is added to v, indicates that during the collision of compound molecules, there is some cause which lengthens the mean free path, or in other words, reduces the frequency of collisions. A temporary entanglement during collision is the probable cause of this effect. It must be remembered that though we assign a certain electric moment to the whole molecule, the atoms contribute to this electric moments of their own according to laws investigated in my papers on molecular attraction. The great distinction between the molecules of element gases and those of compound gases is this, that in the diatomic element gases the two atoms are identical. Although consisting of two atoms the molecule of an element gas, while not homogeneous, is more nearly homogeneous than that of a compound. When two compound molecules are colliding, the permanent electrical differences amongst the atoms may prevent the electric fields of the whole molecules from adjusting themselves as they do when the molecules are far apart. It may be more an affair of the atoms in contact than of the whole molecule. Thus the effective moments of the molecules in contact may be different from what they are when the molecules are separate. We can account for the virial of the attractions taking the form $3l/2(v+k)$ instead of $3l/2v$, if we write that form $(3l/2v)\{v/(v+k)\}$ and interpret the factor $v/(v+k)$ as expressing the change which takes place in the e^2s^2 of $6pe^2s^2/m^2$ in (2) with changing distance between neighbour molecules, that is, with changing v. This change in es may sometimes be partly of the nature of an effect of mutual induction, but it seems to me that in the collisional virial the change of form from $v-b$ to $v+k$ is suggestive rather of entanglement during molecular encounter, the atomic electric fields being thrown into a confusion which on the averages causes the colliding molecules to have smaller total electric moments effective than when they are free. The equation for ethylene shows the transition from the type for elements to that for compounds. As CH_4 ranges itself with the element gases, we infer that the electric fields of C and of 4H are united up into one simple field like that of the element gases. In the paper cited it is shown that down to $v=k$ the virial of molecular attractions has the form $l/(v+k)$ when the factor 3/2 is omitted. When $v=k$ it is $l/2k$, and for values of v less than k it is $l/2v$. Thus in typical compounds l in the virial of the attractions and in the attractional potential energy has for the liquid state half the value for the gaseous. These points and many others will be cleared up only by a kinetic theory of liquids worked out as completely as the kinetic theory of gases. It is because of this form $l/(v+k)$ involving change of l from l to $l/2$ that I retain l as the symbol for a quantity standing for the K of Laplace who puts $\rho=1$, and the a of van der Waals.

8. *Surface energy of a liquid and its vapour* (*continued from* 6).

Having satisfied ourselves that for the element gases and CH_4 the value of e^2s^2 may be taken to be the same in the states of liquid and vapour, we can write for them the equation for surface tension α

$$3\alpha/4=e^2s^2\{1/\mathrm{R}_1{}^5-(1/\mathrm{R}_1{}^2+1/\mathrm{R}_2{}^2)/{}_1\mathrm{R}_2{}^3+1/\mathrm{R}_2{}^5\}. \quad . \qquad (8)$$

For a typical compound, if we express the various effective values of es in terms of that for the vapour when $v=\infty$ or $\rho=0$ denoted by e_gs_g, then for the liquid $e^2s^2=e_g^2s_g^2/2$, and for the vapour $e^2s^2=e_g^2s_g^2v/(v+k)=e_g^2s_g^2/(1+k\rho)$, so

$$3\alpha/4=e_g^2s_g^2\{1/2\mathrm{R}_1{}^5-(1/\mathrm{R}_1{}^2+1/\mathrm{R}_2{}^2)/{}_1\mathrm{R}_2{}^3 2^{\frac{1}{2}}(1+k\rho)^{\frac{1}{2}}$$
$$+1/\mathrm{R}_2{}^5(1+k\rho)\}. \quad . \quad . \qquad (9)$$

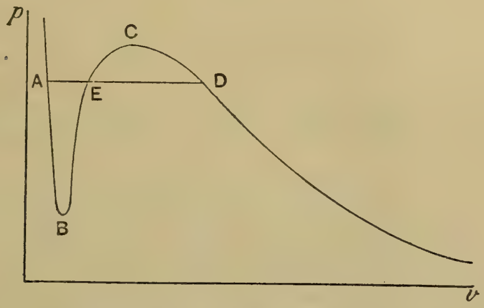
Though empirically $k=6v_c/7=6/7\rho_c$, where ρ_c is the critical density, it simplifies matters to assume that in this connexion k can be replaced by $1/\rho_c$, and then

$$3\alpha/4=e_g^2s_g^2\{1/2\mathrm{R}_1{}^5-(1/\mathrm{R}_1{}^2+1/\mathrm{R}_2{}^2)/{}_1\mathrm{R}_2{}^3 2^{\frac{1}{2}}(1+\rho/\rho_c)^{\frac{1}{2}}$$
$$+1/\mathrm{R}_2{}^5(1+\rho/\rho_c)\}. \quad . \qquad (10)$$

This vanishes at the critical point, as it ought.

For the further development of this equation we can proceed as in the *Boltzmann Festschrift*, but more definitely and rigorously. Let us consider two typical neighbour molecules as regards the relative motion of approach and departure. Suppose one fixed while the other performs the relative motion. Its kinetic energy may be such as will just carry it to rest at infinity, or it may be more or less than that amount. The relative orbit may be one of infinite range with finite or zero velocity at infinity, or one of finite range. The most beautiful and familiar instances of these three classes of relative orbits are those described under a force varying inversely as the square of the distance, as in the case of comets under the influence of the sun. The hyperbola is the orbit open at infinity on account of there being more kinetic energy at any point than just suffices to carry the comet to infinity, the parabola is the orbit of infinite range with zero velocity at infinity, the ellipse the orbit of finite range because nowhere is the kinetic energy equal to that acquired by falling from rest at infinity. By this consideration of orbits we can give a dynamical definition of the states of vapour and liquid. In a vapour the relative orbit of two neighbour molecules is an arc of a curve of infinite range open at infinity, in a liquid the relative orbit is one of finite range. At the critical point the orbit is a transitional form, like the parabola, between these two, being of infinite range but closed at infinity. Liquefaction is the gathering together of neighbours of relative orbits of finite range, evaporation is the segregation of neighbours whose relative orbit is of infinite range. When a liquid is in contact with its vapour we have just seen from statical considerations that the surface layer of molecules in the liquid is in tension, as if at less pressure, while the surface layer of molecules of vapour is in compression, as if at higher pressure than prevails away from the surface. Let us state the facts with the aid of the James Thomson ABCD curve, which replaces the straight line AD of condensation at constant saturation pressure. The state of the surface layer of the liquid is expressed by a point between A and B, let us say at B. The state of the surface layer of vapour is represented by a point between D and C, let us say at C. The states represented by points between B and C are unstable. The two surface layers of molecules consist of subsaturated liquid and supersaturated vapour. The two layers might be replaced by a single homogeneous medium occupying the same space in a state represented by the point E, the instability being interpreted as a continual change of state, both condensation and evaporation, occurring at the transition from liquid to vapour.

Fig. 2.



Dynamically we may regard this medium as consisting of molecules so moving that the relative orbit of two neighbours is a closed orbit of infinite range similar to the parabolic orbit of comets. Let the liquid and vapour be at absolute temperature T, then the difference between this fictitious medium of transition and the substance at the critical temperature T_c is that at kinetic energy corresponding with T, and at density associated with ${}_1R_2$ two neighbour molecules in the medium could just separate to an infinite distance apart and come to rest. Let ρ_s be the density associated with ${}_1R_2$, then ρ_s corresponds with that distance between neighbours which allows their kinetic energy proportional to T just to give them a relative orbit of infinite range, while ρ_c corresponds with that distance between neighbours at the critical point which allows their kinetic energy proportional to T_c just to give them a relative orbit of infinite range. Thus the difference of the potential energy of a molecule in our fictitious medium of density ρ_s, and that of a molecule in the critical state is equal to that of their kinetic energies. Let us now return to equations (8) and (10) and derive from them the average potential energy of a molecule amongst those in the surface layer of liquid and the surface layer of vapour, namely

$$4e^2s^2(1/R_1{}^3-2/{}_1R_2{}^3+1/R_2{}^3)/6, \quad . \quad . \quad (11)$$

and

$$4e_g^2s_g^2\{1/2R_1{}^3-2/{}_1R_2{}^3 2^{\frac{1}{2}}(1+\rho/\rho_c)^{\frac{1}{3}}+1/R_2{}^3(1+\rho/\rho_c)\}/6. \quad (12)$$

The first and the last terms taken together are the mean energy of a molecule in the liquid and a molecule in the vapour, which we may identify with the potential energy of a molecule in our fictitious medium of density ρ_s. Again the middle term becomes the potential energy of a molecule at density ρ_c, if we identify ${}_1R_2{}^3$ with m/ρ_c in elements, and with $m/2^{\frac{1}{2}}(1+\rho/\rho_c)^{\frac{1}{2}}\rho_c$ in compounds. To this definition of ${}_1R_2$ I have been led by the consideration that it is the simplest one which will give the relation discovered by Eötvös, which we shall obtain at once, for the last expression is now equal to the difference between the kinetic energy of a molecule at T_c and at T. So, passing from molecules to gram-molecules, we have the result that the surface energy or tension per gram-molecule $\alpha(M/\rho)^{2/3}$ is equal to the difference between the translatory kinetic energy of $N^{2/3}$ molecules (N being the number of molecules in a gram-molecule) at T_c and at T, namely $3R(T_c-T)/2N^{1/3}$ where R is the gas constant when the energy is expressed in ergs for a gram-molecule, having the value

$$1{,}014{,}000 \times 22430/273 = 83 \times 10^6,$$

and $$N = 2{\cdot}77 \times 10^{19} \times 22430.$$

Thus $$\alpha(M/\rho)^{2/3} = 1{\cdot}46(T_c - T). \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

This is the relation discovered by Eötvös (Wied. *Ann.* xxvii. 1886, p. 448) by means of the principle of corresponding states enunciated by van der Waals. In his experiments Eötvös found 2·23 to be the numerical coefficient in place of the 1·46 just found. For 36 normal compounds Ramsay and Shields found 2·121 to be the mean value of this constant of Eötvös. For Cl_2 it is 1·91, O_2 1·66, and N_2 1·53 (*Boltzmann Festschrift*, p. 384). The agreement between the theoretical coefficient and these experimental values is sufficiently close to justify the reasoning of this section and the assumption ${}_1R_2{}^3 = m/\rho_c$ in elements, and $= m/2^{\frac{1}{2}}\rho_c(1+\rho/\rho_c)^{\frac{1}{2}}$ in compounds, or in other words that at the passage from the surface layer of the liquid to the surface layer of the vapour the critical density prevails in elements, and a closely related density in compounds. The chief reason for the difference between 1·46 and 2·12 is that in our reasoning, by confining our attention to the kinetic energy and the attractional potential energy, we have neglected the energies associated with the external pressure and with the collisional forces, that is, the energies corresponding with the virials $3pv/2$ and $3RTv/2(v-b)$ or $3RT2k/2(v+k)$. These approximately neutralize one another so long as we can use the equation $pv = RT$ approximately, and that is why we have been able to reason successfully as if the molecules were planets and comets free from external force and free from collisions. At the critical point and near it the approximation $pv = RT$ is too rough, whence the discrepancy between 1·46 and 2·12. It would lead us too far from the present subject to discuss the inclusion of these two neglected terms. The chief object of the present section is to show how the classical statical theory of surface tension, developed by Laplace, Young, and Gauss, in the days before the kinetic theory of matter, is connected with the more recent discoveries made in the light of that theory. Closely connected with the discovery of Eötvös is that made by Cailletet and Mathias (*Comptes Rendus*, cii. 1886, p. 1202) which I have discussed in the *Boltzmann Festschrift.* With temperature as abscissa and density as ordinate they plotted the densities of liquid and saturated vapour right up to the critical point, forming two branches of a curve which merged into one another at the critical point. When the points of mean density are marked they yield a straight line inclined to the axes. The mean density is a linear function of the temperature. That is the discovery made by Cailletet and Mathias. S. Young (Phil. Mag. [5] l. 1900, p. 291) has shown that there is a small departure from linearity. The relation of Cailletet and Mathias is expressed completely by the equation

$$\rho_1+\rho_2-2\rho_c=2c(\mathrm{T}_c-\mathrm{T}), \quad . \quad . \quad . \quad . \quad (14)$$

to which S. Young adds on the right a small term in $\mathrm{T}_c^2-\mathrm{T}^2$.

By the principle of corresponding states c is a parameter such that $c\mathrm{T}_c/\rho_c=1$, the actual values calculated by S. Young ranging from 0·932 for fluorbenzene to 1·061 for ethyl formate. For C_2H_4 the value rises to 1·30, and for N_2O to 1·49. For Cl_2 it falls to 0·7675. If we return to equation (10) with our interpretation of it, we can write it

$$l\alpha(\mathrm{M}/\rho)^{2/3}=4(\rho_s-\rho_c)e_g^2s_g^2\mathrm{N}^{2/3}/3=2(\rho_1+\rho_2-2\rho_c)e_g^2s_g^2\mathrm{N}^{2/3}/3 \quad (15)$$
$$=1{\cdot}46 \text{ (or } 2{\cdot}12)(\mathrm{T}_c-\mathrm{T}).$$

Since by the principle of corresponding states we derive from this $(\rho_1+\rho_2-2\rho_c)/2\rho_c=(\mathrm{T}_c-\mathrm{T})/\mathrm{T}_c$ which is the law of Cailletet and Mathias, it follows that

$$e_g^2s_g^2=3\times1{\cdot}46 \text{ (or } 2{\cdot}12) \ \mathrm{T}_c/8\rho_c\mathrm{N}^{2/3}. \quad . \quad . \quad . \quad (16)$$

The law of Cailletet and Mathias is identical with that of Eötvös by virtue of the relations which we have adopted between R_1, ${}_1\mathrm{R}_2$, R_2 on the one hand and densities on the other. The equations just given contain the fourth and fifth methods of calculating the attractional virial parameter l as developed in "The Laws of Molecular Force" (Phil. Mag. [5] xxxv. 1893, p. 211), namely, from the data of the critical point and from surface tension.

9. *The surface energy of mixed liquids.*

Here an interesting kinetic point is raised in connexion with our principle that molecules can be treated as though each attracted only its six immediate neighbours. Consider a mixture of liquids 1 and 2 containing 100 molecules of 1 to 1 of 2. Then in a permanent uniform distribution of the molecules, no molecule of 2 has another molecule of 2 amongst its six immediate neighbours, for it is surrounded by more than 100 molecules of 1. In a purely statical theory with the assumption of permanent uniform distribution the mutual energy of two molecules of 2 would not enter into the expression for the potential energy of any molecule or of an average molecule.

Then again the cubical arrangement seems an unsuitable one to assume for a mixture of unlike molecules unless the volume occupied by a molecule of each is the same. Nevertheless, by the application of kinetic principles we get over these two difficulties in the following way. If ρ is the density of a mixture containing n_1 molecules of 1 per unit mass, it will contain $n_1\rho$ per unit volume. It contains n_2 of 2 per unit mass and $n_2\rho$ per unit volume. Let n_{01} denote the number of molecules of 1 per unit mass in the pure liquid, n_{02} being the number for 2. Then according to the statistical principles used in the kinetic theory we state that the time for which a molecule of 1 in the mixture is one of the immediate neighbours of a molecule of 1 is the fraction $n_1\rho/n_{01}\rho_1$ of the corresponding time for the pure liquid 1. Now from (3) we know that the average potential energy of a molecule of 1 having molecules of 1 for its neighbours all the time is $4e_1{}^2s_1{}^2/\mathrm{R}_1{}^3$. Hence the potential energy of a molecule of 1 and the other molecules of 1 in the mixture is $4n_1\rho e_1{}^2s_1{}^2/\mathrm{R}_1{}^3n_{01}\rho$: so the mutual potential energy of the n_1 molecules is $4n_1{}^2e_1{}^2s_1{}^2\rho$. In this way by making our cubical arrangement the standard of reference where it was geometrically possible we have been able to pass to the case of mixtures where it is impossible.

As to the mutual potential energy of the n_1 and the n_2 molecules we can find it most simply by considerations of symmetry from the result just obtained. When n_1 and n_2 are large, the number of pairs of a molecule of 1 with a molecule of 1 is $n_1{}^2/2$ nearly, while the number of possible pairs of a molecule of 1 with a molecule of 2 is n_1n_2. Hence for the desired result there needs only to replace in $4n_1{}^2e_1{}^2s_1{}^2\rho$ the $n_1{}^2$ by $2n_1n_2$ and $e_1{}^2s_1{}^2$ by $e_1s_1e_2s_2$, obtaining $8n_1n_2e_1s_1e_2s_2\rho$. If we desire to get this from first principles we may return and analyse the product $4n_1(e_1{}^2s_1{}^2/\mathrm{R}_1{}^3)(n_1\rho/n_{01}\rho_1)$ in the following manner. As $\mathrm{R}_1{}^3n_{01}\rho_1=1$, we have $n_1\rho/n_{01}\rho_1$ equal to the total volume of the molecules of liquid 1 in unit volume of the mixture or to $n_1\rho/2$ times the volume of a pair of molecules of 1 when they are neighbours. Thus the mutual potential energy of the n_1 molecules is equal to three times the energy of a pair of them as neighbours $4e_1{}^2s_1{}^2/\mathrm{R}_1{}^3$ multiplied by $n_1\rho/2$ times the volume of a pair as neighbours, multiplied by n_1. Let ${}_1\mathrm{R}_2$ be the distance between a molecule of 1 and of 2 in their average positions as neighbours, then the mutual potential energy of one molecule of 1 and all the molecules of 2 is $4e_1s_1e_2s_2/{}_1R_2^3$ multiplied by $n_2\rho/2$ times $2{}_1R_2^3$, so for the n_1 molecules the factor n_1 is introduced and a factor 2 introduced because of the contrast pointed out above between $n_1^2/2$ and n_1n_2. Thus we arrive at the same result as before. For the total potential energy of the n_1+n_2 molecules in unit mass of mixture we have

$$4\rho(n_1e_1s_1+n_2e_2s_2)^2=4\rho(p_1e_1s_1/m_1+p_2e_2s_2/m_2)^2, \qquad (17)$$

where p_1 and $p_2=1-p_1$ are the masses of liquids 1 and 2 in unit mass of the mixture.

The attractional virial for such a mixture is 3/2 times the potential energy. As to the surface energy we shall consider only the case where the effect of the vapour is negligible. Then by similar reasoning to that just used in calculating the potential energy of unit mass we find that liquid 1 in the mixture contributes the fraction $(n_1\rho/n_{01}\rho_1)^2$ of its surface energy per unit area as a pure liquid to the surface energy of the mixture, and so

$$\alpha=(n_1\rho/n_{01}\rho_1)^2\alpha_1+2(n_1n_2\rho^2/n_{01}n_{02}\rho_1\rho_2)\alpha_1^{\frac{1}{2}}\alpha_2^{\frac{1}{2}}+(n_2\rho/n_{02}\rho_2)^2\alpha_2$$

$$\therefore\ \alpha/\rho^2=(p_1\alpha_1^{\frac{1}{2}}/\rho_1+p_2\alpha_2^{\frac{1}{2}}/\rho_2)^2. \quad . \quad . \quad . \quad (18)$$

This equation was verified (Phil. Mag. [5] xxxviii. 1894, p. 188 ; xl. 1895, p. 1) by the same experiments as proved the formula corresponding with $4e_1s_1e_2s_2/{}_1R_2^4$ for the force of attraction between two unlike molecules. If this formula were to hold in a purely statical theory of surface energy it would imply that the distribution of the mixed sets of molecules was a purely random one. Any regular distribution favouring the existence of a minimum potential energy would be excluded. Such a result is highly improbable, and therefore the formula just established may be regarded as evidence in favour of the active motion of the molecules in a liquid. This kinetic method of investigating mixed liquids has been neglected in the past, but it has many useful applications.

By means of the results of this section we can explain the remarkable fact that so many ordinary liquids mix with so little contraction or expansion and so small an evolution of heat. Such cases as the rise of temperature on mixing water with sulphuric acid or with ethyl alcohol are marked exceptions. For the change of potential energy on mixing a mass p_1 of liquid 1 with $p_2=1-p_1$ of liquid 2 we have

$$4\rho(p_1e_1s_1/m_1+p_2e_2s_2/m_2)^2-4p_1\rho_1e_1^2s_1^2/m_1^2-4p_2\rho_2e_2^2s_2^2/m_2^2.$$

In "Further Studies on Molecular Force" (Phil. Mag. [5] xxxix. 1895, p. 1) it was shown that for most elements in their compounds, except the metals, *es* for the atom is nearly proportional to the volume of the atom, so for the molecules of most ordinary liquids *es* is proportional to the volume m/ρ. So the change of energy on mixing is proportional to

$$4\rho(p_1/\rho_1+p_2/\rho_2)^2-4p_1/\rho_1-4p_2/\rho_2.$$

If this is 0, then $$1/\rho=p_1/\rho_1+p_2/\rho_2,$$

which states that mixture occurs without change of volume. Thus the absence of change of volume and of thermal effect connected with potential energy are related. As the limiting volume of the molecule is proportional to its electric moment, and as the molecules of ordinary liquids at ordinary temperatures occupy nearly their limiting volumes, we may conclude that constancy of volume on mixing and constancy of electric moment are connected.

10. *The relation of Mills.*

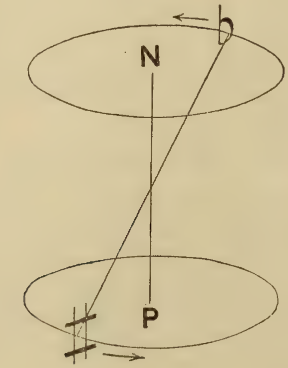
This has been discussed recently in "The Electric Origin of Molecular Attraction" (Phil. Mag. [6] xvii. 1909, p. 657), but requires to be considered further in the present connexion. In the simplest case the change of attractional potential energy for an element gas when unit mass is changed from liquid to saturated vapour is $4e^2s^2(\rho_1-\rho_2)/m^2$. For a typical compound the change is

$$4e_g^2s_g^2\{\rho_1/2-\rho_2/(1+k\rho_2)\}/m^2,$$

or nearly $$4e_g^2s_g^2\{\rho_1/2-\rho_2/(1+\rho_2/\rho_c)\}/m^2.$$

The simplest hypothesis that we could make concerning the internal latent heat of vaporization would be to equate it to these changes of potential energy. For an element gas at different temperatures we should have the internal latent heats proportional to the difference of the densities of liquid and saturated vapour, and for a typical compound proportional to $\rho_1/2-\rho_2/(1+k\rho_2)$, or nearly to $\rho_1/2-\rho_2/(1+\rho_2/\rho_c)$. But the relation of Mills makes latent heat proportional to $\rho_1{}^{\frac{1}{3}}-\rho_2{}^{\frac{1}{3}}$. The interpretation of these results leads to an important principle concerning the motion of the electrons which form a molecule. In an investigation of the nature of dielectric capacity (Phil. Mag. [6] xix. 1910, p. 1) the molecule was treated as made of pairs of opposite electrons, each pair having an electric moment $e\sigma$. The sum of the components of $e\sigma$ parallel to the axis of electrization of the whole atom or molecule forms *es*. For the maintenance of this state of affairs we must imagine each pair of electrons in motion round the axis of electrization. If we imagine the axes of magnetization and of rotation in the Earth to coincide, it will furnish a large mechanical model of the pair of electrons, magnetization replacing electrization. The pair of electrons is a gyrostat electrized parallel to the axis of rotation. The electrons of a pair do not move round one another in a plane, but each may be treated on the averageas moving in a plane at right angles to the axis of electrization. The figure illustrates the conception. PN is the axis of electrization, the positive

Fig. 3.



electron moving in a circle round P as centre in the direction shown by an arrow, and the negative electron round N. The components of the attraction between ♯ and ♭ along P♯ and N♭ keep ♯ and ♭ in their circular orbits, while the components of the attraction along NP equilibrate the forces acting on ♯ and ♭ on account of the electric field of the whole molecule parallel to NP. The length of NP is σ. Other rotational motions of these electric gyrostats may have to be considered in other connexions, but at present the motion postulated suffices. The independence of electric moment in the molecules of the element gases both of temperature and density indicates that P♯ and N♭ are small compared with NP, and that the rotatory energy of a pair of electrons is a constant like its electric moment. Probably the same statements apply to compounds, the change associated with the replacing of v in the attractional virial by $v+k$ being probably apparent rather than real. Imagine an element gas so compressed that there is no gap between molecule and molecule, the whole mass being a uniform collection of pairs of electrons at distance r_1 apart, each pair having an electric moment $e\sigma_1$ proportional to r_1. Imagine the whole expanded till it fills the volume which it would have as saturated vapour. Let the distance between neighbour pairs be r_2, and suppose the electric moment $e\sigma_2$ now proportional to r_2, so that the medium in its second state is geometrically similar to what it was in the first, then on account of $e\sigma$, and therefore es changing in the proportion of r_1 to r_2, and therefore of R_1 to R_2 the corresponding molecular distances, the change of attractional potential energy is not proportional to $\rho_1 - \rho_2$ but to $\rho_1^{1/3} - \rho_2^{1/3}$. Now in the second state suppose that the electrons fall together in groups so as to form the actual molecules of the saturated vapour. The potential energy lost in this collapse will be converted into translatory kinetic energy of the electron pairs, for we have seen that their rotational energy seems to be constant. The relation of Mills shows that none of this kinetic energy appears as heat, for our imaginary operations have simply converted the liquid into vapour at the same temperature. The loss of potential energy during the imagined collapse has become kinetic energy required by the pairs of electrons to maintain dynamical equilibrium in the non-uniform state when they are collected in groups to form molecules. This kinetic energy may be regarded as internal molecular potential energy. When there is a change of molecular state the total change of potential energy is equal to the difference of the changes occurring when all the electrons forming the molecules fall from one and the same imaginary uniform distribution to each of the non-uniform distributions forming a molecular state. The total energy required to change one heterogeneous distribution of pairs of electrons into another is equal to the differences between the changes required to transform the heterogeneous states into the same homogeneous one, it is equal to the work required to change the distance apart of the molecules from the one heterogeneous state to the other against the attraction of neighbours according to the inverse fourth power law, together with the supply of internal energy required to maintain dynamical equilibrium under the changed conditions of heterogeneity. The sum of these two quantities of energy forming the total internal latent heat is subject to the law discovered by Mills. This law could be explained by itself by supposing that each molecule attracts its six immediate neighbours with a force varying inversely as the square of the distance between them, and that no internal change takes place in molecules when their distance apart is changed. But the large mass of evidence gathered in my papers on molecular attraction is quite against this simple hypothesis, while it all supports the law of force expressed by $4e_1s_1e_2s_2/{}_1R_2^4$. The true significance of the relation of Mills seems to me to be the indication of broad simple dynamical law in the kinetics of electrons forming atoms. These ideas lead at once to the following speculation.

11. *The nature of chemical potential energy.*

If the view proposed in the last section is correct, namely, that a part of the latent heat of vaporization of a liquid is kinetic energy supplied to the electrons of atoms to establish dynamical equilibrium under changed conditions of heterogeneity, it follows that the heat of chemical reactions is energy given out because of changed heterogeneity of the electrons in the reacting atoms. Is it possible that the pairs of electrons of two chemically combined atoms mingle like the molecules of two mixed liquids? Even if such mixture does not take place, the close approach of two different swarms of pairs of electrons may produce instability in the dynamical equilibrium of each and a fall into a new position of equilibrium with evolution of heat in the process. The internal energy of the radium atom is of the type here supposed to reside in all atoms as kinetic energy of the constitutive pairs of electrons.

Melbourne, April 1910.

XXI. *On the Forces at the Surface of a Needle-Point discharging in Air.* By A. P. Chattock, *Professor of Physics in the University of Bristol* [*].

C D.F

THE strength of the field at a spherically ended electrified needle-point may be measured in terms of the pull of the lines of force upon its surface [†], if the pull is due to the lines of force alone; a condition which is only strictly fulfilled when the point is not discharging.

In 1897, while attempting to extend this method to a discharging point, I tried the effect of supplying the latter with ions of opposite sign to itself obtained from a second point in its neighbourhood. Some rather interesting effects were observed in air at atmospheric pressure; but as at the time no explanation of them was forthcoming their discussion was postponed, and they remained unpublished.

Recently while looking over the record of the experiments

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[*] Communicated by the Author.

[†] Chattock, Phil. Mag. [5] xxxii. p. 285. Young, Phil. Mag. [6] xiii. p. 542.

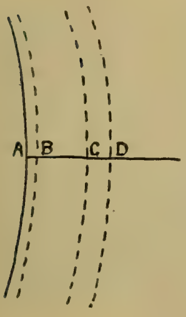
it occurred to Mr. Tyndall that an explanation of some of the results had become possible in the light of modern theories of discharge. We therefore repeated and extended the old work, and an account of what has been done follows the present paper. This has rendered necessary a discussion of the question how far the pull at a discharging point is due to the field at its surface, and how far to purely mechanical forces brought about by the discharge; and an attempt is here made to estimate the magnitude of these forces, and to show that they may be neglected in the case of our experiments.

Positive Discharge from a Single Point.

When a sharp point discharges positive electricity in air at atmospheric pressure it usually becomes capped with a luminous velvety layer, probably not more than one or two hundredths of a millimetre in thickness. This layer and the air near it is presumably the region in which ionization occurs, and from it therefore ions of opposite signs travel towards and away from the point respectively.

In fig. 1 A represents the surface of the discharging point, much magnified, A and D the limits of the ionizing layer, and A D the axis of the point.

Fig. 1.



Before discharge sets in the field at points along A D will fall off for some distance in nearly inverse proportion to the squares of the distances of these points from the centre of curvature of A; but on the occurrence of discharge some of the lines of force from A will end on ions between A and D, say at B, and others beginning on ions of opposite sign, say at C, will continue on towards the right, with the result that the field is weakened between B and C.

At the same time changes of pressure are set up in the gas by the moving ions; those at C reducing the pressure between A and C, and those at B raising it upon A, so that B C is a region of low pressure as well as of low field intensity.

Take first these mechanical effects of the discharge. To simplify the argument, suppose that there is a single layer of negative ions at B and another of positive ions at C; and let the charge per square centimetre on B be $-\rho$ and that on A $+\sigma$. The pull per square centimetre on A due to the lines of force ending upon its surface is $2\pi\sigma^2$; and if p_1 be the pressure excess upon A above the atmosphere due to the B ions, and p_2 the corresponding reduction of pressure in AC due to the C ions, the resultant pull per square centimetre on A will be

$$p = 2\pi\sigma^2 - p_1 + p_2,$$

$-p_1 + p_2$ thus representing the change in the pull per square centimetre on the point due to the current discharged from it if the above is a complete account of the pressure-producing part of the process.

The object of what follows is to compare the magnitude of this change with $2\pi\sigma^2$.

Suppose first that the C ions are absent, and consider the effect of p_1 by itself.

The ions in the B layer are attracted by A, and the force of this attraction imparts momentum to them, some of which remains in the ions while the rest is transmitted to the gas through which they move.

Now in the case of ordinary positive point discharge the B ions start very close to A, and it is safe to assume that both parts of the momentum end by being given up to the point in the form of the steady pressure p_1. p_1 is thus equal to the force per square centimetre to which the B layer is subjected, viz. $4\pi\sigma\rho - 2\pi\rho^2$, and we therefore have

$$\begin{aligned} p &= 2\pi\sigma^2 - 4\pi\sigma\rho + 2\pi\rho^2 \\ &= 2\pi(\sigma - \rho)^2. \end{aligned}$$

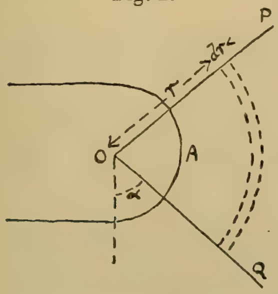
This means that as far as their mechanical effect on the pull is concerned the B ions might just as well have been rigidly attached to A. In other words, if we attempt to calculate the field at the point from the observed pull upon it we shall obtain a value which is less than that of the field at A by the number of lines of force attached to the B ions, and which is therefore due to those lines alone which cross the ionizing region unbroken.

Next consider the suction effect, p_2, of the C ions.

In ordinary positive point discharge these ions also start very close to the surface of the metal, but they move off to distances which are usually large compared with the size of the point. Except in the region near the point, therefore, the momentum they give to the gas is felt as a pressure on any fixed plate or other bodies there may be opposite the point, and does not sensibly affect p.

Let A in fig. 2 represent the section of a hemispherical point. Near its surface, discharge, when it occurs, will be approximately radial, and may be thought of as filling the cone POQ which has its apex at the centre of curvature of the point.

Fig. 2.



If f is the field in any spherical layer centred at O and of radius r and thickness dr, the momentum given to this layer per square centimetre per second will be

$$d\mu = f\rho' dr,$$

assuming that ions of one sign only are present, and that ρ' is the *volume* density of the electricity they carry.

Also, if V is the specific velocity of these ions, C the current from the point, and Ω the solid angle of the discharge cone

$$C = \rho' f V \Omega r^2.$$

Hence

$$d\mu = \frac{C}{V\Omega} \cdot \frac{dr}{r^2}.$$

Suppose now that the sides of the cone are impermeable to gas. $d\mu$ will result in a difference of pressure dp between the two surfaces of the spherical layer such that

$$dp = d\mu\,;$$

and if r_0 is the radius of the point and the ions are all supposed to start from there, the pressure within the cone at the metal surface will be less than that at a distance r from O by the amount

$$\int_{r_0}^{r} dp = \frac{C}{V\Omega}\left(\frac{1}{r_0} - \frac{1}{r}\right).$$

With sharp points for which r_0 is a small fraction of a millimetre we may put $r = \infty$, and obtain a value for the integral which is not much greater than if r is a millimetre or so, the result being an upper limit to the value of p_2 for the conditions assumed, viz.

$$p_2 = C/V\Omega r_0.$$

For positive discharge in air at atmospheric pressure I find that the field f_0 at the centre of a hemispherical point when discharge is just ceasing is given by the empirical formula

$$f_0 r_0^{0\cdot 45} = \text{constant},$$

where the constant as corrected by Young (*loc. cit.*) is 85 if r_0 is in centimetres and f_0 in E.S. units *.

Hence

$$\sigma = 18/4\pi r_0^{0\cdot 45},$$

and

$$\frac{p_2}{2\pi\sigma^2} = \frac{\mathrm{C}\,0\cdot 0035}{\mathrm{V}\Omega r_0^{0\cdot 1}} = k.$$

The largest current used in the experiments referred to was about 15 microamperes, and the largest value of r_0 was 0·062 cm. V for positive discharge in unit E.S. field is 400 cm. sec.$^{-1}$, and Ω was roughly 2π judging by the area of the glow.

k for these data is 0·12; and, for the smallest point of radius 0·004 cm., $k=0\cdot 14$.

As the area of the point surface at which discharge occurred happened to coincide with that upon which effective pull (*i. e.* pull with a component parallel to the axis of the point) was exerted by the field, these values of k give the ratio of the total axial suction effect of the C ions to the total axial pull of the field on the assumption that both σ^2 and p_2 were similarly distributed over the discharge area.

σ^2 was probably uniform (see below), but as the current density must have varied from zero at the edge to a maximum at the centre of the discharge area, p_2 must have varied in a corresponding manner. The exact law of this variation we have no means of knowing, but we may obtain an idea of the sort of error introduced by assuming p_2 uniform, if we adopt some arbitrary law: say p_2 proportional to sin α (fig. 2).

Remembering that the total suction normal to the surface of the point will be the same whatever the law, this particular law leads to an axially resolved suction equal to four-thirds that for uniform distribution of p_2. In other words, if we take

$$k = 0\cdot 14 \times 4/3 = 0\cdot 19,$$

we shall correct for the want of uniformity in the distribution for this particular case.

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* This power of r_0 and the value of the constant were obtained recently, and differ considerably from those given in my original paper (*loc. cit.*). The difference is due to the tapering of the sewing-needles used in the earlier measurements, the effect of which upon the pull was unwarrantably neglected. The later measurements were made upon platinum wires with their ends rounded to hemispheres in the blowpipe.

This means that if we calculate f_0 from P, the total resolved pull on the point, and assume p_2 uniform, f_0 will be 7 per cent. too high; whereas if we assume the sine law it will be 9 per cent. too high; always supposing of course that the values of k obtained above are correct.

Actually, however, they are too high for the following two reasons :—

1. The 400 cm. sec.$^{-1}$ taken for V represents the specific velocity of fully formed ions. If the C ions do not at once reach their full size, V will be greater than 400 and k proportionately less.

2. A still stronger reason for reducing k is the fact that in actual discharge the surrounding gas is not kept out of the discharge cone as has hitherto been assumed. It is of course really quite free to flow in laterally, and so to prevent the pressure from falling in the region of the point to anything like the extent the above values of k suggest. Instead of producing a slope of pressure, the drag of the ions must be mainly converted into motion of the gas, and the resulting momentum thus transmitted to the plate rather than to the point.

It seems clear, therefore, that as the error in f_0 due to the suction of the C ions is probably not much more than 9 per cent. without either of these reductions, it will be safe to neglect it altogether when they are taken into account.

Consider now the electrical effect of the discharge.

The ionizing layer is traversed by both B and C ions. The B ions are densest at the side of the layer next the point, and the C ions at its other side. The ionizing field will therefore contain lines of force due to both B and C ions, none of which are measured by the pull; and the field calculated in terms of the pull is consequently too small.

It is probable, however, that the ions are swept away so quickly that their lines of force form a negligibly small part of the field at the point. Let t be the thickness of the ionizing layer and τ the average density of the charge on the B ions, close to the metal :

$$\tau = \frac{C}{\Omega r_0^2} \cdot \frac{1}{f_0 V},$$

and $4\pi\bar{\tau}t$ is that part of the field at the metal which is due to the B ions if $\bar{\tau}$ is the average value of τ through the distance t.

The distribution of τ through t is of course unknown, but as the effect of the B ions will be shown to be small, we may obtain an idea of its magnitude if we assume τ to vary uniformly from its maximum value to zero in passing through the ionizing layer, put $4\pi\tau t = 2\pi\tau t$, and take for f_0 in the expression for τ the value obtained from the pull, viz. $85/r_0^{0 \cdot 45}$.

Estimating the thickness of the glow as 0·005 cm., a number which is certainly too high, *and assuming that this represents t,* $2\pi\tau t$ is about 1 per cent. of f_0 for the sharpest point used and much less for all the others, when the current is 15 microamperes.

Whether the glow and the ionizing region are exactly equal in extent is, however, doubtful. As already mentioned, f_0 for discharge is proportional to $r^{0 \cdot 45}$; the value of f_0 therefore increases rapidly with the curvature of the point, and it is difficult to see why this should be, unless the only effect of the curvature upon the field (viz. the divergence of the lines of force) is able to influence the ionizing process.

But for this to be, the ionizing region must reach far enough beyond the point to feel the divergence of the lines; in other words, it seems as though t should be comparable with the radius of the point in spite of the fact that the luminous region is practically confined to the surface of the metal.

Yet even if t is equal to r_0, the field of the B ions is less than 3 per cent. of f_0 for the sharpest point and still less for the others; hence when account is taken of the fact that the ions are newly formed and probably travel much faster than we have supposed, there is not likely to be any serious error introduced if f_0 calculated from the pull be taken as the true field at the point.

One other effect of the discharge should be mentioned. The field in the discharge area is presumably constant, so that where discharge occurs σ will also be constant, and Young's correction (*loc. cit.*) for the distribution of σ will be reduced.

When the discharge area is confined to the centre of the point his constant must be used, and

$$f_0 = 1 \cdot 085\sqrt{8P}/r_0\,;$$

but for the point under discussion glow was visible over the whole hemispherical end of the point from 15 down to 1 microampere, and possibly lower. In all cases of positive discharge from this point the values of f_0 have been calculated from the formula

$$f_0 = \sqrt{8P}/r_0.$$

It appears from the foregoing arguments that the only force of any importance at the surface of a positive discharging point is the pull of the field upon the metal. This field we should expect to be independent of the current from the point, at any rate for a considerable range of current; and the fact that, as the following table shows, the values of f_0 calculated from the pull are nearly constant thus gives considerable support to those arguments.

In the table are given the values of $\sqrt{8P}$ for various currents from a positive point of radius 0·018 cm. discharging against a flat metal plate 2·2 cm. distant.

$\sqrt{8P}$.	C in microamperes.
7·46	0·19
7·42	1·84
7·41	3·09
7·39	5·45
7·39	6·90
7·39	8·01
7·39	9·39
7·38	10·90
7·37	13·38
7·38	9·39
7·38	7·21
7·41	4·20
7·41	1·64
7·43	0·79
7·46	0·52
7·93	0·0

Negative Discharge from a Single Point.

Ω for negative discharge is usually much less than for positive—several hundred times less in the case of the large point; and the glow projects into the gas to a distance comparable with the diameter of the point instead of being confined to the surface of the latter, its form varying from radial to trumpet-shaped.

That Ω is small means that p_2 is large; but as the area affected by p_2 will be small in the same proportion, these two effects will roughly cancel, and the only important change in the suction of the C ions will be due to the easier access of the outside gas to the cone of discharge, which implies a greater reduction of p_2 for a negative than for a positive point.

As the glow projects into the gas the C ions start, on the average, further from the point, and this also implies a reduction in p_2.

The B ions, so far as their mechanical effect is concerned, may be expected to behave much as they did for positive discharge, except that their momentum will not now be given up to the point quite so completely.

For these reasons the pull on a negative discharging point is probably quite as little affected by the mechanical forces of the current as that on a positive point.

There is, however, an electrical effect of the negative discharge which requires consideration.

The bounding surface of the discharge cone separates two fields—an outer one composed of lines which pass unbroken from the point into the gas, and an inner one composed partly of unbroken and partly of broken lines.

Suppose that in fig. 2 we pass from A outwards along the discharge cone. The number of lines of force contained by the cone decreases to a minimum near the centre of the ionizing region, and then increases until this region is passed. It follows that if we draw side by side with the discharge cone a second similar cone in the outer field, this second cone must contain, on the average, a number of lines which lies between the maximum and minimum numbers in the discharge cone if the outer and inner fields are to be in equilibrium with one another.

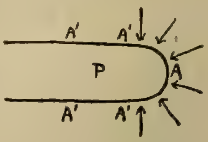
Owing to the narrowing of the discharge area, and the increased thickness, t, of the ionizing region, the field in the latter, unlike that for a positive point, is chiefly composed of broken lines. This would result in P being far too small to give a correct value of f_0 if the discharge area covered the end of the point; but as it is, P is almost wholly due to the lines of the outer field. If therefore we write

$$f_0 = 1{\cdot}085 \sqrt{8P}/r_0,$$

we shall obtain a number which is less, but perhaps not much less than the value of the field at the bottom of the discharge cone. Except when the current is small, the measurement of f_0 for negative discharge is thus somewhat indefinite.

Discharge between two Points.

Fig. 3.



Suppose that to a positive point P (fig. 3) negative ions are sent from a second point N in its neighbourhood, and that the average field in the ionizing layer remains unaltered. The momentum effect of the N ions on P may be conveniently discussed under two heads.

1. That of N ions which will ultimately reach the hemispherical end of P by the arrow-marked paths.

These will behave like C ions reversed, with this difference —the momentum they impart to the gas keeps to the cones of discharge down which they pass to A much more than with C ions because the sides of the point as well as its ends are receiving ions whereby the pressure of the gas is raised at A′A′ as well as at A, and the lateral escape of gas from A is consequently hindered.

The proportionate change (reduction) in p will thus be not much less than that calculated above for C ions travelling in gas-proof cones, viz.

$$k = \frac{C\,0{\cdot}0035}{V\Omega r_0^{0{\cdot}1}},$$

where Ω is 2π and C is that part of the current carried by N ions which reaches the hemispherical end of P. C is thus several times less than the whole current carried to the point by N ions.

The N ions are fully formed when they reach P, so that 400 cm. sec.$^{-1}$ is now the correct value for V.

In the experiments with two points, both of which were discharging, a current of 15 microamperes meant of course a smaller current carried by N ions, and of this a fraction only arrived at the end of P. If we estimate this fraction at one-fifth and calculate an upper limit for k by assuming that the whole 15 microamperes were carried by N ions, the result is 0·016 for the largest and 0·021 for the smallest point.

The error introduced into f_0 by neglecting this part of the momentum of the N ions is thus of the order of 1 per cent.

2. The remainder of the momentum received by P from the N ions. This is due to the wind set up by the whole of the N ions in passing from N to the conductors connected with P, instead of, as in 1, to the much smaller number which reach the end of P.

It is impossible to calculate the effect of this momentum on P, but an upper limit was obtained by surrounding P with a small cage of which the wires were close enough to shield P electrically, but open enough to allow the wind to pass freely through, the wimshurst being turned at the same rate as in the actual experiments, and the pressure on P measured by tilting the apparatus. Under these circumstances P would be more blown against than without the cage, partly because the cage would attract to itself more of the N ions by reason of its size, and partly because the current from the cage would be less than from P uncovered, and so the wind from N would be less reduced by ions travelling against it.

In no case was the observed force of the wind on P greater than 2 per cent. of the pull when the cage was removed, and the error in f_0 due to this cause must therefore have been less than 1 per cent.

As to the electrical effect of the N ions, it may be sufficiently described by saying that when they enter the ionizing layer they behave like B ions, and before entering it they play the part of the fixed plate.

And since their mechanical effect on the pull is so small it follows that under the conditions of current and size of point considered above the conclusions already arrived at as to the connexion between f_0 and P for single discharging points of either sign will still hold when N ions are supplied.

Reaction of the Electric Wind.

It may not be out of place here to refer to the assumption sometimes met with in text-books and elsewhere, that the reaction of the electric wind is to be found at the discharging point.

Reaction there must of course be—somewhere—when the wind is started, and its amount must be that of the momentum given per second to the ions; but only an extremely small part of it is to be found at the point itself.

It is true that if a needle with a sharp point and its other end blunt be electrified until the point discharges, it will tend to recede from its discharging end. The electric windmill is a well-known instance of this. But the needle moves because it it pulled more strongly at the blunt than at the sharp end, not because it is pushed back at the latter. If the blunt end be electrically shielded the needle tends to come forward, and to about the same extent that it did before discharge set in; it is the shield which now exhibits reaction by its increased tendency to move backwards.

But the effect on the shield is only part of the wind reaction. When discharge starts the distribution of electricity on all the surrounding conductors changes, and the electrical forces on them alter in such a way that the resultant of these alterations acts in the opposite direction to the wind, and is equal to its reaction.

The wind reaction is thus to be found upon the electrified portions of both electrodes; but the portion which probably feels it as little as any is that part of the point surface at which the discharge actually occurs.

Conclusions.

When discharge occurs at a sharp point in air at atmospheric pressure, the current, dimensions, and other conditions being those considered in this paper, it is possible to calculate the strength of the field in the ionizing region at the surface of the point to within one or two per cent. for a positive and less accurately for a negative point in terms of the mechanical pull upon its surface; and this conclusion holds if the point be supplied with ions of opposite sign to itself from a second point in its neighbourhood.

XXII. *On the Ionizing Processes at a Point discharging in Air. By* A. P. CHATTOCK, *Professor of Physics, and* A. M. TYNDALL, *B.Sc., Lecturer in Physics, in the University of Bristol**.

[Plate IV.]

IN explaining the phenomena of discharge at sharp points in gases under normal conditions, Sir J. J. Thomson postulates an initial ionization of a few isolated molecules in the gas as a preliminary to the process of discharge.

Suppose a point to be gradually charged with positive electricity in the presence of these isolated ions. The field near its surface is at first unable to do more than clear them away as fast as they are formed; but as soon as it is strong enough to impart to the positives among them sufficient energy to enable these to ionize fresh molecules in their turn, ordinary positive discharge sets in, and a large current may result, accompanied by glow at the point and wind.

In the case of a negative point the field has also to reach a high enough value to enable the initially formed positive ions to form fresh ions; but they now have the alternative of doing this where they bombard the surface of the metal instead of in the gas, and the field required is not necessarily so high as when gaseous molecules are to be ionized.

For both kinds of discharge the supply of positive ions is pictured as kept up by ionization due to negative ions, these having been produced by previously formed positive ions and so on. Both signs of ion have therefore to be able to ionize as each produces the other; and since positive ions require a stronger field for this than negative it is always the field required by the positive ions which has to occur at the point.

* Communicated by the Authors.

In what follows $f+$ stands for the field at an electrified point in which positive ions are able to ionize, and $f-$ for the corresponding field for negative ions; $f+$ having different values according as the positive ions produce others in the gas or at the metal surface.

Suppose now that to a charged point ions of opposite sign to itself are supplied in considerable quantities from some source in its neighbourhood. We may call such ions *external ions.*

With a positively charged point there are three distinct cases that may occur :—

(*a*) If the external ions find a field at the point which is less than $f-$ they will simply pass to the point and give rise to a current from it equal to that which they themselves carry.
(*b*) If the field lies between $f-$ and $f+$, each external ion will produce several more before reaching the point, and the current resulting may be a considerable multiple of that carried by the external ions.
(*c*) If the field exceeds $f+$ the double ionization by both positive and negative ions will accompany the ionization by the external ions, and a current due to ordinary positive point discharge will be added to that of the external ions.

With a negatively charged point these cases reduce themselves to *a* and *c*, the signs + and − being interchanged: *b* does not occur because $f+$ is greater than $f-$ and the external ions are positively charged.

If the appearance of light at the point is to be taken as indicating ionization there, it will follow that for *a* the point will be dark, while for *b* and *c* it will glow.

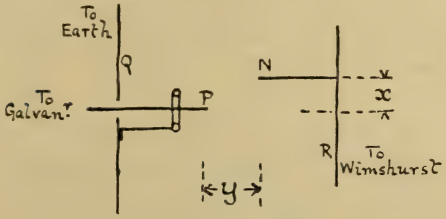
It is to be understood in the above, that the initially ionized molecules are too few in number to be taken account of in comparison with the external ions supplied.

These principles are illustrated in a general way by experiments on discharge between two points, made some years ago, which we have lately repeated and extended, and of which the following is an account :—

A horizontal platinum wire P (fig. 1) with its end rounded to a hemisphere in the blowpipe was suspended so that it protruded through a hole in a vertical metal plate Q.

P and Q were both earthed, Q directly and P through a galvanometer. Opposite P and in the same vertical plane was a sharp sewing-needle N connected to a wimshurst,

Fig. 1.



and so arranged that the vertical component x and the horizontal component y of its distance from P could be varied. The radius of P (0·031 cm.) was about 7 or 8 times greater than that of N, so that N discharged more readily than P; and the tendency of N to start first was further increased by surrounding P with a wire ring about 11 mm. in diameter, with its plane about 7 mm. behind the point P. By varying x and y it was thus possible to supply P with varying numbers of ions from N both before and after P itself began to discharge on its own account.

The end of P was viewed through a reading microscope, and the resultant pull, P, upon its surface was measured by tilting the whole apparatus so as to keep P always upon the cross-wire.

It has been shown[*] that under these conditions, if the current from the point is not greater than 15 microamperes, the disturbing effect of the discharge upon the pull of the field on the point is probably negligible compared with the pull itself, and that if r is the radius of the point, and f_0 the field at the centre of its surface due to the lines of force in the ionizing layer,

$$f_0 = \frac{\sqrt{P}}{r} \times \text{constant},$$

where the constant is 2·83 for positive, and approximately 3·07 for negative discharge.

In most of the earlier observations N was about 2 cm. long and projected from a flat plate R parallel to Q; y was kept at 1·6 cm. and x was varied. In the second set which was made with entirely new apparatus, y was varied, and

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[*] Chattock, Phil. Mag. pp. 272–274 of present number.

the two points were kept in line with one another, the radius of the point being the same as before (0·031 cm.).

In a third set points with radii lying between 0·062 and 0·004 cm. were used.

The results of the second set for positive and negative are plotted in Curves I. and II. respectively, as they were obtained for the widest range of conditions; but all three sets agree closely in their main features.

Positive Discharge from P.

Curves I. (Pl. IV.) apparently exhibit all the three cases, *a*, *b*, *c*, described on p. 278. Each curve is made up of a steep part S, and a nearly horizontal part H, joined by a curve. Somewhere in this curve or below it P began to glow, so that along S the discharge was dark and along H luminous. The exact position of the beginning of the glow was not easy to determine, as the light nearly always grew gradually from small beginnings, and though the observations were made in the dark it was extremely difficult to tell when it first became visible. In this respect the glow differed markedly from that at a negative point which started suddenly.

S and H correspond closely with cases *a* and *b* respectively. For besides the fact that the discharge in S is dark and in H luminous, the values of f_0 for H rise as they should do when the number of external ions is reduced by increasing y; and f_0 reaches its maximum value when N is removed altogether ($y=\infty$), H then corresponding with case *c*.

When $y=0·2$ cm. f_0 has been reduced about 2·3 times, the discharge being still apparently ordinary point discharge; but if the points are put 0·15 cm. apart streams of small sparks result *.

Provided the frequency of these sparks is not too great we may write

$$f_0=\mathrm{K}t,$$

where t is the time counted from the last spark and K is a constant. If P is the average pull on the point, we have

$$\frac{3·07}{r}\sqrt{P} = \text{apparent value of } f_0$$
$$=\frac{\text{maximum value of } f_0}{\sqrt{3}}.$$

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* It is possible by getting the discharge to start with y greater than 0·15, and then decreasing it to get point discharge at this distance also. This was done in the case of the readings discussed below.

The maximum value of f_0 just before each spark passed is given by the dotted line in Curves I. for $y=0{\cdot}15$ cm.

An interesting detail was noticed in connexion with the position of the glow on P in the first set of experiments. Here N was on one side of P and the glow always appeared on the side facing N, but became symmetrical when N was removed. This is consistent with what was said above, as ionization in the reduced fields of case *b* can only occur when the external ions approach the point. A negative point, on the other hand, only glows in case *c*, and it can then discharge whether external ions are arriving or not; this agrees with the fact that the position of the negative glow was far less dependent upon the position of N than that of the positive.

Negative Discharge from P.

Here, as with positive discharge, the curves consist of two distinct portions, S and H, corresponding respectively to dark and luminous discharge. Of these S, as before, represents case *a*, and if for a moment we neglect the curve for $y=1{\cdot}0$, H in every case appears to correspond with case *c*, as it should, the ordinates of the various H curves down to $y=1{\cdot}5$ being roughly the same as those for no discharge from N ($y=\infty$).

For $y=0{\cdot}5$ and $0{\cdot}3$ the curves were cut off short by the passage of sparks between N and P, but there seems no reason to suppose that if their H portions had been obtainable they would have differed in position from the others for normal point discharge.

In the case of $y=0{\cdot}3$ the curve is shown forking. The reading at the top of the lower branch was taken just before a single spark passed, while that for the upper branch corresponded with a stream of sparks. The ordinate of the latter was therefore multiplied by $\sqrt{3}$, as explained above, and this has brought it well among the rest of the H curves. The dotted lines correspond with the discharge of streams of sparks as before.

Between $y=0{\cdot}3$ and $y=0{\cdot}15$ there appears to be a fundamental change in the character of the discharge. The ordinates of $y=0{\cdot}15$ have been multiplied by $\sqrt{3}$, but this has not brought them anywhere near the top of $y=0{\cdot}3$.

It is possible that in the curve for $y=1{\cdot}0$ we have the transition stage connecting $y=0{\cdot}3$ and $y=0{\cdot}15$. In normal point discharge the glow is confined to the region near the point, but in this case ($y=1{\cdot}0$) it reached right across from N to P in the form of faintly luminous streamers, which occasionally passed into sparks for currents above about 12 microamperes. It is true that 1·0 does not lie between 0·3 and 0·15, but the current was evidently on the verge of sparking all along $y=1{\cdot}0$, and a very small change in the conditions was probably enough to cause streamers to pass into sparks or sparks into streamers for $y=1{\cdot}0$, 0·5, and 0·3. Streamers were, in fact, once or twice obtained for $y=0{\cdot}3$.

Values of Ionizing Fields.

There is no indication in Curves I., as the supply of external ions increases, of any limit to the lowering of the H portions beyond the accidental one of sparking.

This was at first sight disappointing ; for according to the theory when the field at the point is below $f-$, it ought not to be possible to obtain luminous discharge, and it seemed unlikely that the positive and negative ions should require such very different fields to ionize in as corresponded with the highest and lowest H curves obtained.

Now, provided there are enough external ions present to produce a detectable amount of light, the beginnings of glow should occur when, and not before, the field reaches the value $f-$.

To test this we measured f_0 at the moment the glow first became visible for a wide range of distances between P and N. Under these conditions it was to be expected that the field in which the glow was first seen would be constant and equal to $f-$ so long as the supply of external ions was sufficient ; but that when the supply fell short the glow produced in this field, though still present, would not be detectable, and the field corresponding to the first *visible* glow would therefore be higher than $f-$.

Further, the field would continue to rise as the external ions became fewer until it reached the value at which ordinary positive point discharge sets in.

The supply of external ions may be reduced by increasing either x or y. As, however, a sufficient increase of y made it impossible for our wimshurst to produce the highest field at P, we kept y constant at 1·5 cm. and varied x.

To limit the spreading of the ions from N this needle was made to project from the flat plate R (fig. 1) and x was altered by moving N and R together. In this way we were able to reach values of f_0 which were practically identical with those obtained when N was removed from R.

The resulting values of f_0 are given by the line marked Field in Curves III. (Pl. IV.), and are in good accord with this theory—rather surprisingly good accord considering the great difficulty of determining exactly when the glow started in the case of the observations at the lower fields. (In the high fields it began more suddenly and was brighter.) There is an obvious halting place at a field of 250 E.S. units in the falling of f_0 as x decreases.

The fact of the field being thus constant over a certain range of x values does not, however, prove that there is no glow below this particular field. The amount of light in the glow depends on the current arriving at the point and on the field there ; and if the current happened to be constant for this range of x, a constant field might merely mean that until this field was reached the glow was too weak to be seen, and not that it was absent altogether.

To meet this objection we have plotted in Curves III. the current received by P at the moment the glow became visible. Starting with $x=0$ (N and P opposite one another), it will be seen how very far from constant this current is. It falls rapidly as x increases until the value of f_0 begins to change.

The subsequent rise and fall of the current curve at higher values of x is attributable to the fact that, when x is comparable with y, P receives most of the current on its sides. For as soon as the N ions are too few to give a detectable glow without a higher field f_0 and therefore the current from N increases, the result being that P receives a larger total current than before, though its end of course does not. At still higher values of x, f_0 becomes constant, and the same as for R without N ; the current now falls off once more as it should, and the end of P presumably receives no ions at all.

Although, as already explained, if we alter y instead of x, we cannot trace the field curve up to the top, it is possible to obtain the horizontal part at $f-$.

In Curves IV. are plotted the results of experimenting in this way with the same two points. The field curve becomes horizontal at about 240, which agrees with the 250 just obtained for $f-$, and the current curve also shows the same sort of behaviour as the one in Curves III.

But the most interesting feature of Curves IV. is the way in which the field drops below the horizontal when N is brought nearer to P than about a centimetre. At this point the rise of the current, when y is decreased, becomes less marked, and when N is 0·7 cm. from P the rise changes to a fall. This also implies a falling field; and it thus appears that at a distance from their origin of less than a centimetre the N ions possess the power of ionizing air in fields which steadily decrease as this distance decreases.

This is precisely what we should expect if the N ions take time to grow to their full size, and it is interesting to consider it in connexion with other facts bearing on the growth of ions.

Franck * has shown that when discharge occurs in air from the sides of a fine wire in a strong field, it is extremely probable that the ions, whether positive or negative, do not reach their full size while travelling a distance of 7 mm. We † have shown, by a different method of experimenting, that when discharge occurs from a fine point, both the positive and the negative ions probably travel about 3 mm. before they are fully formed—a result which is consistent with Franck's, when it is remembered that the average field in the 3 mm. was probably lower than in Franck's 7 mm., and the ions consequently travelled slower. With the relatively blunt point of the present experiments the distance should be greater, and we now find that the distance of growth in the case of the negative ions seems to have increased to a centimetre or so.

All these facts thus hang well together, as far as they go, and so afford support to the view that the negative ions do really take time to grow after leaving N.

The lower limit to the size of a negative ion is the corpuscle. If the second drop in the field curve is really due to a growth of the ions, the curve ought either to become horizontal again when the still lower field is reached in which corpuscles can ionize the air, or else to cut the vertical axis at this field. We have made a number of experiments on the starting of the glow in this critical region, the mean of the results being given in Curve V. It was found impossible to bring N nearer to P than 0·14 cm. on account of sparking, but down to this distance P could be made to glow in what seemed to be the normal manner. The numbers obtained were rather irregular, and it was only by making many observations that we were able to obtain so smooth a curve. We do not therefore wish to press conclusions drawn from them until we have studied this part of the field more carefully. As the curve stands, however, it certainly does show a tendency to cut the vertical axis at a field of about 75 E.S. units.

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* Franck, *Ann. der Physik,* Vierte Folge, Bd. xxi. p. 984.

† Chattock & Tyndall, Phil. Mag. [6] vol. xix. p. 449 (1910).

Reference was made in the preceding paper to the fact that the field in which ordinary positive point discharge occurs depends upon the curvature of the point; and that in consequence of this dependence the ionizing region probably extends a sufficient distance from the metal to feel, as it were, the divergence of the lines of force.

It is interesting to find that the fields in which the glow first appears in the presence of N ions are similarly dependent upon the point. This is shown by the following Table, in which are given the results of experiments upon four points of different sizes.

r.	f_1.	$f_1 r^{0{\cdot}45}$.	f_2.	f_1/f_2.	f_3.	f_1/f_3.
0·0619	293	84	157	1·9	30 ?	10
0·0310	410	86	245	1·7	70 ?	6
0·0105	662	85	325	2·0	130 ?	5
0·0043	975	84	433	2·2	120 ?	8

r is the radius of the point in centimetres; f_1 the field in which ordinary positive point discharge is on the verge of stopping; f_2 the lowest field in which glow is caused by fully formed N ions; and f_3 the field in which corpuscles give rise to glow, if the views expressed above are correct. The values of f_3 are queried on account of the great uncertainty attending their determination.

The third column illustrates the exactness of the empirical relation between f_1 and r, and the rough constancy of the fifth and seventh columns shows that f_2 and f_3 also depend on r in a more or less similar manner.

It must be remembered that all these fields are rapidly divergent, and that their values are given at the surface of the metal. We do not yet know the values of the *weakest* fields in which the corresponding ionizing processes can occur because we do not know how far the ionizing regions extend from the point.

We found that there was a certain hysteresis in the appearance and disappearance of the glow, especially for small values of y, the current having to be raised considerably before the glow would start, after which it slowly worked back to a minimum. At this minimum the glow could be made to appear and disappear by slightly increasing or diminishing the current strength, and it was there that the field was measured in each case.

The hysteresis is perhaps connected with the fact that when P begins to discharge it sends + ions to N. These, by rendering the escape of corpuscles easier (see below), may increase the average ionizing power of the negative ions sent to P and so diminish the field necessary for glow, and therefore indirectly the current.

Ageing of the Point.

While external ions appear to exercise little influence upon negative discharge from a new point the case is different for an old one. It is well known that when a point has been used a good deal it "ages" for negative discharge by requiring, not only a higher field to keep a given current flowing from it, but a field which fluctuates widely; the ageing having apparently no effect upon positive discharge from the same point.

In the first set of experiments thirty curves were obtained altogether for positive and negative discharge with and without N, and by the end of the nineteenth the point showed signs of ageing. This appears from Curves VI. (Pl. IV.), where the unconnected dots and circles represent discharges from a negative point against a plate without N.

Those observations made before the nineteenth curve are marked by the dots, and if joined up by lines give curves that are more or less smooth; but the circles which mark the later observations give curves which zigzag up and down in the most irregular way if treated similarly. Instances of this irregularity are shown in Curves VII., where are plotted the twenty-first and twenty-eighth curves taken for negative discharge without N.

If, however, external ions are supplied to the point the irregularity vanishes. This is illustrated by the twenty-fourth curve, also plotted in Curves VII., which was taken with N at distances $x=1{\cdot}5$, $y=1{\cdot}6$ cm.

In these earlier observations, as in the later ones of Curves II., those for which external ions were supplied give curves which are in close agreement with one another. The mean position of the earlier of these curves is shown by the line A A in Curves VI., and may be said to follow approximately the line of dots. It is true that at small currents A A is appreciably above the dots, as it is above the lowest dots throughout its length, but if we allow for the fact that the abscissæ of A A are all too large by the currents carried on the N ions and shift A A to the left the discrepancy becomes less marked.

Roughly, then, it may be said that the effect of external ions upon negative discharge is to remove temporarily the two signs of ageing—high field and fluctuating field at the point; in other words, to render the old point new for the time being.

Ageing has been attributed to some change in the surface of the point, which makes it difficult for positive ions to knock corpuscles out of the metal.

Considering that a point discharging negative electricity produces quantities of positive ions in its neighbourhood, it is not easy at first sight to see why the arrival of a relatively small number of external positives should facilitate the escape of the corpuscles so much. For the only obvious difference between these two sets of ions is that those produced at the point are newly formed, while the externals are old —and this ought to render the externals less able to set free corpuscles instead of more.

An explanation is perhaps to be found in the following theory.

The negative discharge starts in a very small spot upon the point surface, the glow standing out in the form of a luminous trumpet to a distance comparable with the diameter of the point, in a manner suggestive of a rush of corpuscles escaping through some weak spot in the surface of the metal.

When the point ages a very characteristic feature of the discharge is observable. It is often impossible to get small currents to flow steadily. With a new point the current can be made to sink gradually to nothing as the wimshurst is slowed down; but with an aged point it sinks gradually to some low finite value and then stops dead, just as if it had been suddenly switched off.

In the light of this fact let us test the following hypothesis; whatever the nature of the ageing change may be, let its effect be such that the metal refuses to yield up corpuscles under bombardment by positive ions *unless the number of these ions is considerable.*

The hypothesis is consistent with the switching off effect just referred to.

It explains, what appears to be the case from Curves VI. and VII., that ageing has less effect on the field at large currents than at small ones.

It explains the fact that discharge will not start as a rule from an aged point until its electrification is far in excess of what is required when the point is new. For this starting of discharge depends on the presence of initially formed positive ions; and if, as these are very few in number, they fail to obtain corpuscles from the metal, their only alternative will be to ionize the gas, which of course means a higher field.

Lastly it explains the effect of external ions on an aged point. When discharge starts in the manner just described by ionizing the gas, the region on the point at which it takes place will be determined by geometrical conditions alone, and will therefore have no particular connexion with the place where corpuscles come out most easily. It will, in fact, tend to be the place where the point has been most used, and therefore where they come out with greatest difficulty, so that even when the current is well started and the supply of positive ions sufficient to obtain corpuscles from the point we may still expect an abnormally high field there.

Now allow the initially formed ions to be reinforced by supplies of external ions sufficiently large to knock out the corpuscles freely. It will no longer be necessary to raise the field to that required for ionizing the gas before discharge will start, as the conditions for ordinary negative discharge will obtain. But whereas when discharge was started by initially formed ions alone it tended to occur at an aged place on the point, it now starts at the place where corpuscles come out easiest, since a large area of the point surface is bombarded by the external ions, and the unaged spots upon it are therefore sure to be discovered. The point should consequently behave like a new one, and this, as the experiments show, is precisely what happens.

Our somewhat arbitrary assumption, that a small supply of positive ions is prevented by the ageing change at a point from bombarding corpuscles out of it, while a large supply is not, thus seems to fit the facts fairly well.

In time of course a point ought to become aged all over if persistently supplied with external ions. We do not know whether this happens or not, but it is possible that the beginnings of the process are to be seen in those curves of the first set which were taken for negative discharge with

N present. Nos. 9, 10, 13 and 14 agree with one another to within about 0·5 per cent., and nos. 24 and 25, the only others available, are practically coincident with one another, but 24 and 25 are about 3 per cent. higher than the four earlier ones.

Relation between the Fields for Positive and Negative Discharge.

The field at the outer surface of the ionizing layer at a positive point is the minimum in which positive ions can ionize. At a negative point the field at the surface of the metal is that required by positive ions to knock out corpuscles ; and if from any cause they are unable to do this there is still the ionizing of the gas itself open to them. It follows that the ionizing field at the surface of a negative point can never be quite as great as that at the surface of a positive point if the positive ions produced at each are the same.

In Curves VI., the line B B represents the field-current curve for positive discharge against a plate only, and it will be seen that the majority of the negative points are well above it.

As explained in the preceding paper, the absolute values of the negative fields are not so accurately known as those of the positives, but it is unlikely that this will account for so large a discrepancy as the one in question.

We are inclined to explain it as follows :—The negative glow stands out a long way from the point. A considerable proportion of the positive ions formed in it have consequently some distance to travel before reaching the point, and will have grown beyond their initial size when they arrive. We shall thus probably be dealing with older positive ions on the average in negative than in positive point discharge, and the occurrence of the stronger fields at the negative than at the positive point is thus reasonable.

It is consistent with this that the field at a negative point becomes less, relatively to that at the same point positive, as the sharpness of the point increases [*] ; for at sharp points the glow does not stand out so far, and as the ions thus have a shorter distance to go, and also move faster in approaching the point, they will be newer when they get there.

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[*] Chattock, Phil. Mag. [5] vol. xxxii. p. 285 (1891).

Summary.

1. A supply of negative ions from without to a positively electrified point lowers the ionizing field at its surface.

2. Positive ions supplied to a negative point are without effect when the point is new.

These two facts are shown to be consistent with accepted theory.

3. A negative point may become aged with use, but temporarily acquires the properties of a new one when bombarded with positive ions.

4. The minimum ionizing field for fully formed negative ions is about half, and that for corpuscles about one-seventh of the field in which ordinary positive point discharge takes place. In each case the field is measured at the surface of the metal.

XXIII. *The Flow of Energy in an Interference Field.* By MAX MASON, *Ph.D., Professor of Mathematical Physics, University of Wisconsin**.

THE following investigation may answer some of the questions recently raised by Professor R. W. Wood †, regarding the lines of energy flow in a field produced by two similar light sources.

The discussion will be limited, for simplicity, to the following case: Two points A_1, A_2 are centres of electromagnetic radiation, produced by the isochronous vibration of equal point charges. The direction of vibration will be taken at right angles to the line A_1A_2. Those lines of energy flow will be studied which lie in the plane containing the line A_1A_2 and perpendicular to the direction of vibration

§ 1. *The differential equation of the lines of mean energy flow.*

Let r_1 and r_2 be the distances from A_1 and A_2 to the point P (fig. 1). The electric and magnetic vectors at P due to the radiation from A_1 and from A_2 will be denoted by $\mathbf{E}_1$, $\mathbf{H}_1$; $\mathbf{E}_2$, $\mathbf{H}_2$. The vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are of unit length and have the directions from A_1 to P and from A_2 to P respectively; $\mathbf{j}$ is a unit vector in the direction of vibration.

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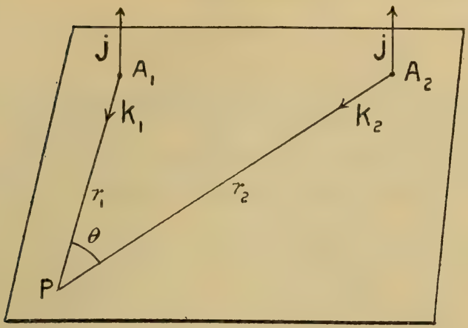
* Communicated by the Author.

† Phil. Mag. 1909, xviii. p. 250.

Fig. 1.



Since **j** is perpendicular to $\mathbf{k}_1$ and to $\mathbf{k}_2$ the electric and magnetic vectors at P have the following values*:

$$\mathbf{E}_1 = \frac{-a\cos n\left(t-\frac{r_1}{c}\right)}{r_1}\mathbf{j}, \quad \mathbf{H}_1 = \frac{-a\cos n\left(t-\frac{r_1}{c}\right)}{r_1}[\mathbf{k}_1\,\mathbf{j}],$$

$$\mathbf{E}_2 = \frac{-a\cos n\left(t-\frac{r_2}{c}\right)}{r_2}\mathbf{j}, \quad \mathbf{H}_2 = \frac{-a\cos n\left(t-\frac{r_2}{c}\right)}{r_2}[\mathbf{k}_2\,\mathbf{j}],$$

where c is the velocity of light and a is a constant depending on the charge of the vibrators and the amplitude of the vibration.

The flow of energy is determined by the Poynting vector

$$\mathbf{S} = \frac{c}{4\pi}[\mathbf{E}\,\mathbf{H}] = \frac{c}{4\pi}[\mathbf{E}_1+\mathbf{E}_2, \quad \mathbf{H}_1+\mathbf{H}_2].$$

On writing

$$a\cos n\left(t-\frac{r_1}{c}\right) = \mathrm{C}_1, \quad a\cos n\left(t-\frac{r_2}{c}\right) = \mathrm{C}_2,$$

the equation

$$\frac{4\pi\mathbf{S}}{c} = \left[\left(\frac{\mathrm{C}_1}{r_1}+\frac{\mathrm{C}_2}{r_2}\right)\mathbf{j}, \quad \frac{\mathrm{C}_1}{r_1}[\mathbf{k}_1\mathbf{j}] + \frac{\mathrm{C}_2}{r_2}[\mathbf{k}_2\mathbf{j}]\right]$$

is obtained. Now

$$[\mathbf{j}, [\mathbf{k}_1\mathbf{j}]] = \mathbf{k}_1, \quad [\mathbf{j}, [\mathbf{k}_2\mathbf{j}]] = \mathbf{k}_2,$$

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* Terms containing higher powers of r_1 and r_2 in the denominators are disregarded. The formulas are in agreement with H. Hertz, *Ann. Phys. Chem.* xxxvi. p. 1 (1888). See, *e. g.*, Abraham, *Theorie der Elektrizität,* vol. ii. p. 62, or Lorentz, 'The Theory of Electrons,' p. 56.

and therefore

$$\frac{4\pi\mathbf{S}}{c}=\mathbf{k}_1\left\{\frac{C_1^2}{r_1^2}+\frac{C_1C_2}{r_1r_2}\right\}+\mathbf{k}_2\left\{\frac{C_2^2}{r_2^2}+\frac{C_1C_2}{r_1r_2}\right\}.$$

We are principally interested in the *time mean* $\bar{\mathbf{S}}$ of the vector $\mathbf{S}$, which determines a field of steady flow. By integrating over a period and dividing by the period, the following values for the time means of C_1^2, C_1C_2, C_2^2 are obtained:

$$\overline{C_1^2}=\overline{C_2^2}=\frac{a^2}{2},$$

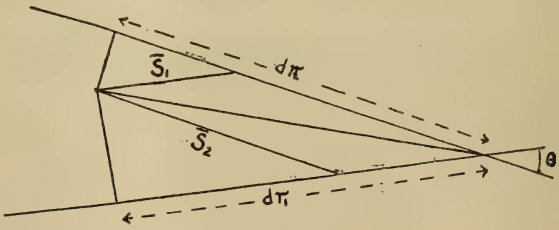
$$\overline{C_1C_2}=\frac{a^2}{2}\cos\frac{n}{c}(r_2-r_1)=\frac{a^2}{2}\cos\frac{2\pi}{\lambda}(r_2-r_1),$$

where λ is the wave-length. Therefore

$$\frac{8\pi\bar{\mathbf{S}}}{a^2c}=\mathbf{k}_1\left\{\frac{1}{r_1^2}+\frac{\cos\frac{2\pi}{\lambda}(r_2-r_1)}{r_1r_2}\right\}+\mathbf{k}_2\left\{\frac{1}{r_2^2}+\frac{\cos\frac{2\pi}{\lambda}(r_2-r_1)}{r_1r_2}\right\}.$$

By the aid of this expression the differential equation of the lines of mean energy flow may be found, *i. e.* the differential equation of the curves which have the direction of $\bar{\mathbf{S}}$ at each point. Along such a curve r_2 may be considered as a function of r_1. If $\bar{S}_1$ and $\bar{S}_2$ denote the coefficients of $\mathbf{k}_1$ and $\mathbf{k}_2$ in the above equation, it may readily be seen (fig. 2)

Fig. 2.



that along the curve in question

$$dr_2:dr_1=\bar{S}_2+\bar{S}_1\cos\theta:\bar{S}_1+\bar{S}_2\cos\theta,$$

where θ is the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$. *The differential equation of the lines of mean energy flow is therefore*

$$\frac{dr_2}{dr_1}=\frac{r_2^2\cos\theta+r_1^2+r_1r_2(1+\cos\theta)\cos\frac{2\pi}{\lambda}(r_2-r_1)}{r_2^2+r_1^2\cos\theta+r_1r_2(1+\cos\theta)\cos\frac{2\pi}{\lambda}(r_2-r_1)}.$$

§ 2. *The form of the mean energy curves in the neighbourhood of a point.*

We shall first investigate the curves "microscopically," examining them in a region whose dimensions are of the order of magnitude of the wave-length. On account of the great value of $\frac{2\pi}{\lambda}$ all terms in the differential equation except $\cos\frac{2\pi}{\lambda}(r_2-r_1)$ may be regarded as constant for this investigation. Let $r_1=\rho_1$, $r_2=\rho_2$ be the point in whose neighbourhood the curves are to be studied. The differential equation is then

$$(\rho_2^2+\rho_1^2\cos\theta)dr_2+\rho_1\rho_2(1+\cos\theta)\cos\frac{2\pi}{\lambda}(r_2-r_1)(dr_2-dr_1)$$
$$=(\rho_1^2+\rho_2^2\cos\theta)dr_1,$$

and its solution is

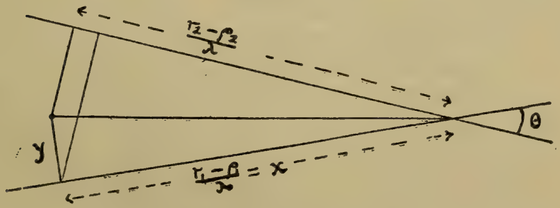
$$r_2(\rho_2^2+\rho_1^2\cos\theta)+\rho_1\rho_2(1+\cos\theta)\frac{\lambda}{2\pi}\sin\frac{2\pi}{\lambda}(r_2-r_1)$$
$$=r_1(\rho_1^2+\rho_2^2\cos\theta)+\text{const.}$$

It may be assumed without loss of generality that $\rho_2-\rho_1=m\lambda$, where m is some integer. Then the equation of the curve which passes through the point $r_1=\rho_1$, $r_2=\rho_2$ is

$$(\rho_2^2+\rho_1^2\cos\theta)\frac{r_2-\rho_2}{\lambda}-(\rho_1^2+\rho_2^2\cos\theta)\frac{r_1-\rho_1}{\lambda}$$
$$=-\frac{\rho_1\rho_2}{2\pi}(1+\cos\theta)\sin\frac{2\pi(r_2-r_1)}{\lambda}.$$

It will be convenient to introduce rectangular coordinates

Fig. 3.



x, y as new variables in this equation, such that (fig. 3)

$$\frac{r_1-\rho_1}{\lambda}=x,\quad \frac{r_2-\rho_2}{\lambda}=y\sin\theta+x\cos\theta.$$

The equation then takes the form

$$y \sin \theta(\rho_2^2 + \rho_1^2 \cos \theta) + x\rho_1^2(\cos^2 \theta - 1)$$
$$= -\frac{\rho_1\rho_2}{2\pi}(1 + \cos \theta) \sin 2\pi[y \sin \theta - x(1 - \cos \theta)].$$

On introducing the parameter

$$\alpha = y \sin \theta - x(1 - \cos \theta),$$

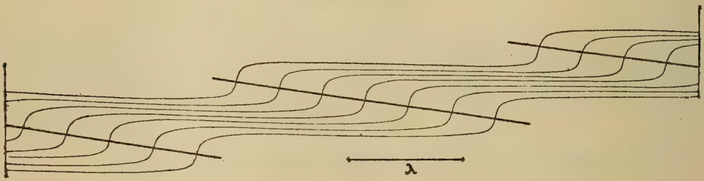
the following parametric equations of the curve are obtained:

$$x = \frac{\rho_1\rho_2(1 + \cos \theta) \sin 2\pi\alpha}{2\pi(1 - \cos \theta)(\rho_2^2 - \rho_1^2)} + \frac{(\rho_2^2 + \rho_1^2 \cos \theta)\alpha}{(1 - \cos \theta)(\rho_2^2 - \rho_1^2)},$$

$$y = \frac{\rho_1\rho_2(1 + \cos \theta) \sin 2\pi\alpha}{2\pi \sin \theta(\rho_2^2 - \rho_1^2)} + \frac{\rho_1^2(1 + \cos \theta)\alpha}{\sin \theta(\rho_2^2 - \rho_1^2)}.$$

The curves may be readily plotted from these equations. The figure (fig. 4) shows a set of curves of mean energy flow in the neighbourhood of the point for which $\rho_2/\rho_1 = 4/3$, $\theta = \pi/2$. (The orientation of the set with respect to the centres of radiation is shown in fig. 5, below.) The heavier straight lines give the position of the interference minima, lines given by $r_2 - r_1 = \text{const.}$, or "microscopically," by $y \cos \theta + x(\cos \theta - 1) = \text{const.}$ The energy thus "crinkles" through the field, tending to flow along the bright interference bands, and to cut across the dark bands.

Fig. 4.



It may be noted that the variation of the energy in passing from a bright interference band to a dark band decreases as we approach the line A_1A_2 between A_1 and A_2, and *there are no interference maxima or minima on the line* A_1A_2 *between the sources of radiation.* In fact, the energy is proportional to

$$\mathbf{E}_1^2 + 2(\mathbf{E}_1\mathbf{E}_2) + \mathbf{E}_2^2 + \mathbf{H}_1^2 + 2(\mathbf{H}_1\mathbf{H}_2) + \mathbf{H}_2^2;$$

the vectors have the values given in § 1, and the angle between $\mathbf{H}_1$ and $\mathbf{H}_2$ is θ; so that the above quantity is (using the abbreviations C_1, C_2 of § 1)

$$\frac{C_1^2}{r_1^2}+\frac{2C_1C_2}{r_1r_2}+\frac{C_2^2}{r_2^2}+\frac{C_1^2}{r_1^2}+\frac{2C_1C_2}{r_1r_2}\cos\theta+\frac{C_2^2}{r_2^2}$$

$$=2\left\{\frac{C_1^2}{r_1^2}+\frac{C_2^2}{r_2^2}+\frac{C_1C_2}{r_1r_2}(1+\cos\theta)\right\}.$$

The time mean of this quantity is, by § 1, proportional to

$$\frac{1}{r_1^2}+\frac{1}{r_2^2}+\frac{1}{r_1r_2}\cos\frac{2\pi}{\lambda}(r_2-r_1)(1+\cos\theta).$$

The truth of the above statements is seen at once from this expression.

§ 3. *The general course of the mean energy curves (course of the beam).*

It is seen from the "microscopical" equation of the energy curves that the points on an energy curve for which $r_2-r_1=m\pi$ all lie on the straight line

$$r_2(\rho_2^2+\rho_1^2\cos\theta)=r_1(\rho_1^2+\rho_2^2\cos\theta)+\text{const.},$$

and the energy curve winds back and forth across this line. The "general direction" of the energy flow in the neighbourhood of the point r_1, r_2 is therefore given by

$$\frac{dr_2}{dr_1}=\frac{r_1^2+r_2^2\cos\theta}{r_2^2+r_1^2\cos\theta}.$$

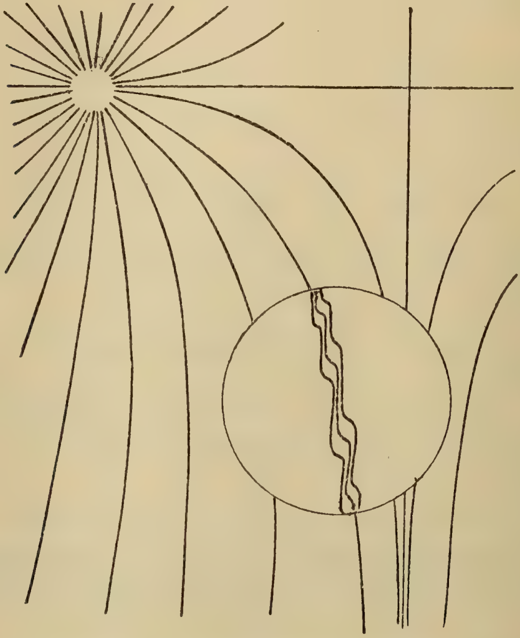
This is also the general direction of the set of curves of fig. 4, as a whole, *i. e.* the direction of the "beam." Now this is exactly the differential equation that would be derived from the expression for $\bar{\mathbf{S}}$ in § 1 if the terms involving $\cos\frac{2\pi}{\lambda}(r_2-r_1)$ were not present, *i. e.* it is a curve which is tangent at each point to the vector

$$\bar{\mathbf{S}}=\mathbf{k}_1\frac{1}{r_1^2}+\mathbf{k}_2\frac{1}{r_2^2}.$$

But this vector represents the velocity produced in an infinite liquid by two equal sources at A_1 and A_2. *The "general course" of a curve of mean energy flow (course of a "beam") is therefore that of a line of flow of an incompressible fluid, produced by two equal sources at* A_1 *and* A_2.

In fig. 5 the curves giving the course of the beam are shown, with an enlargement which indicates the "microscopic" form of the rays in the neighbourhood of the point $r_2/r_1=4/3$, $\theta=\pi/2$.

Fig. 5.



XXIV. *A Constant Pressure Gas Thermometer.* By William Miller, *M.A., D.Sc., Ph.D., Senior Science Master, Dollar Institution*[*].

THE difficulties of construction of a satisfactory gas thermometer, either for laboratory practice or for refined measurements, are well known. A correction is always necessary for that part of the gas which occupies the stem of the instrument, unless the bulb and all that part of the stem occupied by the gas are immersed in the same bath. The importance of this correction increases as the temperature rises, and as more and more gas is expelled from the bulb into the stem, so that the mass of gas contained in the stem becomes comparable with that enclosed by the bulb.

In colleges and schools the direct verification of Charles's

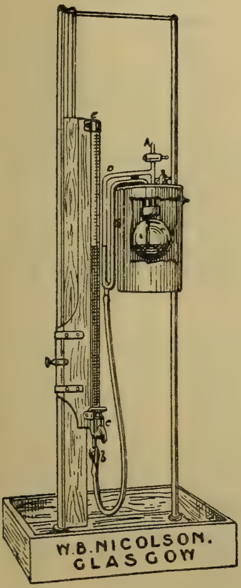
[*] Communicated by the Author.

constant pressure law is often evaded by a combination of the constant volume law with Boyle's law. Apart altogether from the advisability of a direct verification, more particularly as this is the form in which the law is most frequently applied, the latter method is quite unsuitable for pupils at the age when this is generally taken up in schools.

The instrument described below has surmounted those difficulties, so far as ordinary laboratory work is concerned, and may also be used where even a very considerable degree of accuracy is required.

The gas thermometer consists of a glass bulb of about 150 c.c. capacity connected by a siphon S to a graduated tube. During an experiment there is always in the bulb from 10 to 50 c.c. of mercury which siphons over into the measuring tube. In this way the expansion of the gas is made to take place wholly within the bulb, and therefore within the heater. As the gas expands more mercury is expelled and its volume measured.

Fig. 1.



A capillary tube D leaves the top of the bulb and joins the siphon-tube lower down, forming a level indicator outside the heater and enabling the pressure to be accurately adjusted. There is never more than one thousandth of the whole volume of the gas outside the heater.

By first filling the bulb completely with mercury from the top of the measuring tube and packing the heater with ice, 100 c.c. of any gas may be allowed to enter the bulb at a temperature of 0° C. The volume may be measured at any temperature between 0° and 100° C. The calculation of the coefficient of expansion of the gas is greatly simplified by taking 100 c.c. at 0° C. and heating through a range of 100 degrees. The expansion of the flask is to a large extent compensated by the expansion of the mercury, and the error particularly at 100° C. is almost negligible.

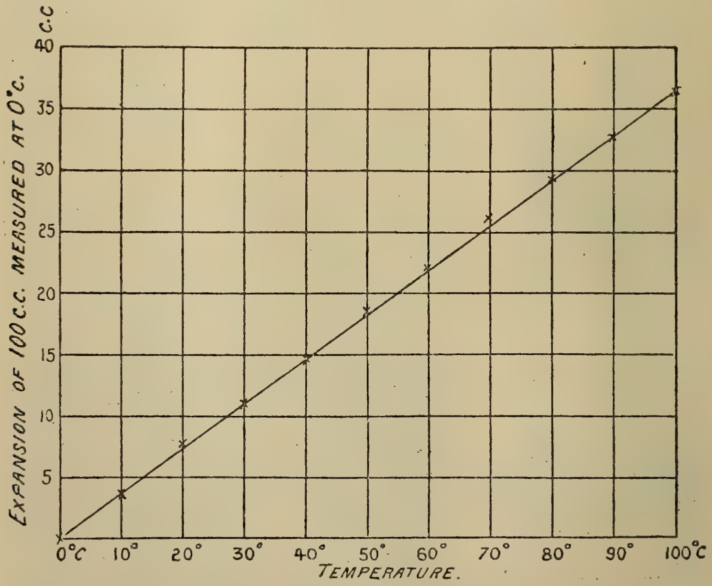
The following are the results for dry air obtained in an ordinary laboratory experiment without any corrections being applied, either for the expansion of the flask or for the error of the thermometer due to the part of the mercury thread projecting out of the heater.

Temperature.	Expansion.	Differences.
0° C.	0 c.c.	......
10° C.	3·6 c.c.	3·6 c.c.
20° C.	7·55 c.c.	3·95 c.c.
30° C.	11·0 c·c.	3·45 c.c.
40° C.	14·8 c.c.	3·8 c.c.
50° C.	18·7 c.c.	3·9 c.c.
60° C.	22·1 c·c.	3·4 c.c.
70° C.	26·1 c.c.	4·0 c.c.
80° C.	29·4 c.c.	3·3 c.c.
90° C.	32·7 c.c.	3·3 c.c.
100° C.	36·5 c.c.	3·8 c.c.

$$\text{Coefficient of expansion} = \frac{36{\cdot}5}{100 \times 100} = {\cdot}00365.$$

The results are shown graphically below.

Fig. 2.—Expansion of Dry Air (uncorrected).



Further observations were undertaken to investigate the degree of accuracy attainable by the instrument. A standardized thermometer was used and a correction applied for that part of the mercury thread which projected outside the heater. Also when the stop-cock on the top of the bulb is left open so that the pressure inside the bulb is exactly equal to that outside, it is found that the mercury in the level indicator suffers a small capillary depression as compared with that in the measuring tube; this amounted to exactly one of the smallest divisions on the graduated tube. By bringing the level indicator in front of the graduated tube an allowance is made for this in each reading.

By means of a preliminary experiment the errors of volume due to the expansion of the flask, of the mercury, and to the unequal heating of the mercury outside the heater, etc. were determined as follows :—

The bulb was completely filled with clean dry mercury at 0° C. and heated to a temperature of 100° C. The readings on the graduated tube at the intermediate temperatures give the expansion of the mercury in addition to the other errors mentioned above. To obtain the error in a gas-expansion experiment at any temperature t, let v be the total volume of gas within the bulb (obtained by adding the expansion found at temperature t to the initial volume at 0° C.) then the expansion at temperature t of this volume of *mercury* can be accurately determined by calculation from the known expansion of mercury. If we subtract this calculated expansion of a volume v of mercury from the reading in the preliminary experiment at temperature t, then the difference gives us the error of the instrument at that temperature. By a preliminary experiment of this kind the instrument can be standardized. The following are the errors thus obtained for the apparatus used in the succeeding investigations :—

Temperature.	Final correction (to be subtracted).
0° C.	0 c.c.
10° C.	·14 c.c.
20° C.	·18 c.c.
30° C.	·23 c.c.
40° C.	·21 c.c.
50° C.	·20 c.c.
60° C.	·18 c.c.
70° C.	·18 c.c.
80° C.	·16 c.c.
90° C.	·12 c.c.
100° C.	·07 c.c.

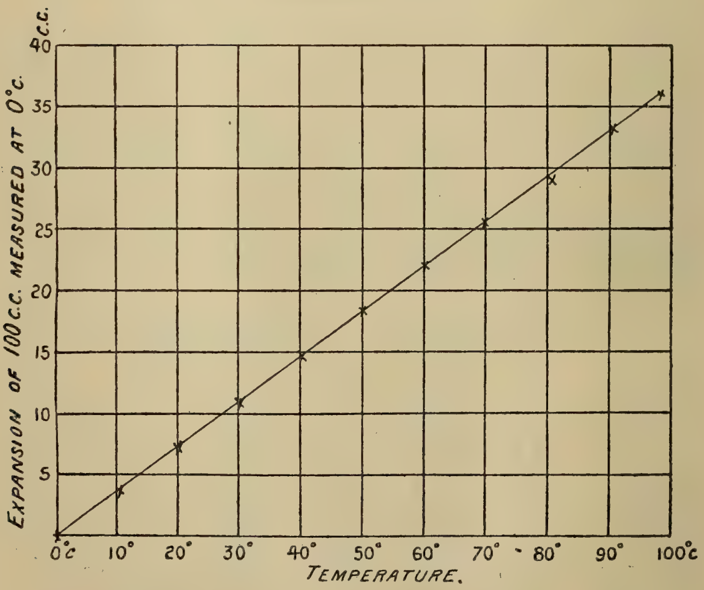
It will be seen that in every case the error is very small, tending to vanish near 100° C., and for ordinary laboratory work quite negligible.

Expansion of dry air.

Temperature.	Expansion.
0° C.	0 c.c.
10°·5 C.	3·8 c.c.
20° C.	7·32 c.c.
30° C.	10·97 c.c.
40° C.	14·79 c.c.
50° C.	18·5 c.c.
60° C.	22·17 c.c.
70°·1 C.	25·82 c.c.
80°·2 C.	29·24 c.c.
90°·4 C.	33·36 c.c.
98°·4 C.	36·03 c.c.

Coefficient of expansion =·003669.

Fig. 3.—Expansion of Dry Air.



Expansion of sulphur dioxide.

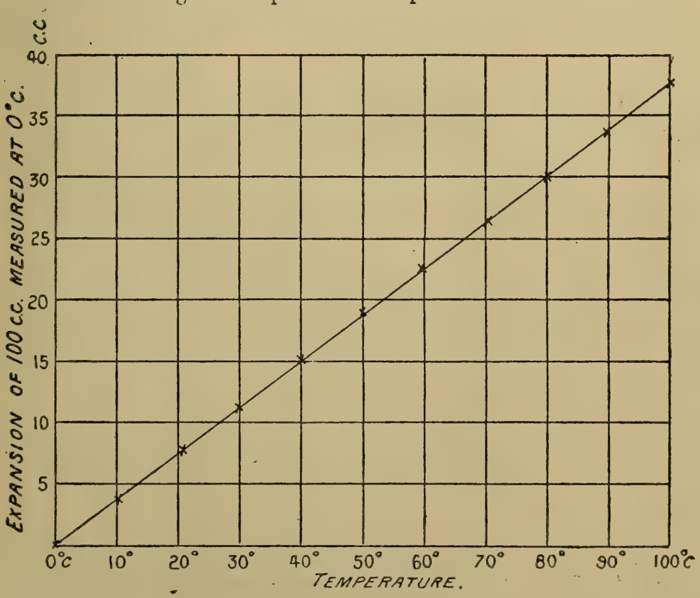
The gas was prepared by means of sulphur and strong sulphuric acid, and passed through a sulphuric acid drier.

During the experiment the barometric pressure remained constant at 77·00 cm.

Temperature.		Expansion.
0° C.	....	0 c.c.
10°·1 C.	....	3·76 c.c.
20°·9 C.	....	7·8 c.c.
30° C.	....	11·32 c.c.
40° C.	....	15·06 c.c.
50°·2 C.	....	19·0 c.c.
59°·8 C.	....	22·6 c.c.
70°·3 C.	....	26·52 c.c.
80°·2 C.	....	30·14 c.c.
89°·7 C.	....	33·86 c.c.
100°·4 C.	....	37·74 c.c.

Coefficient of expansion = ·003760.

Fig. 4.—Expansion of Sulphur Dioxide.



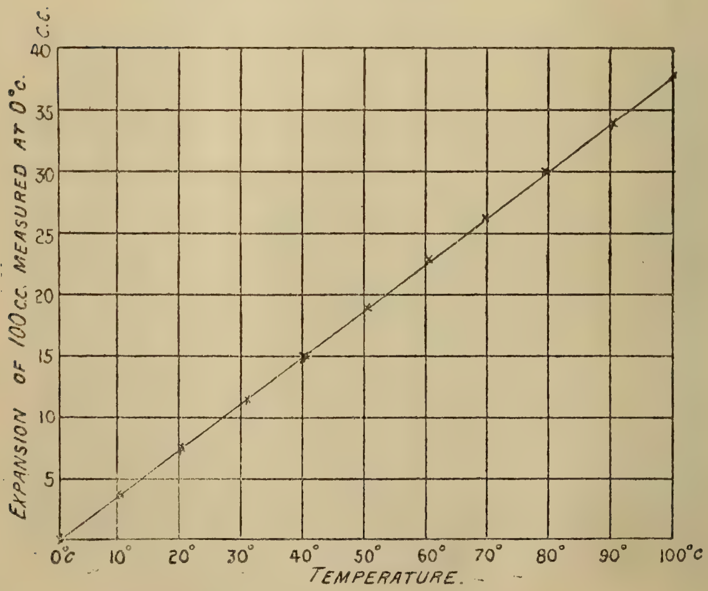
Expansion of hydrochloric acid gas.

The gas was prepared by means of an aqueous solution of hydrochloric acid and strong sulphuric acid. It was dried by means of strong sulphuric acid. The barometric height remained constant at 76·96 cm.

Temperature.	Expansion.
0° C.	0 c.c.
10°·7 C.	3·83 c.c.
20°·4 C.	7·5 c.c.
30°·5 C.	11·37 c.c.
40° C.	14·92 c.c.
50° C.	18·82 c.c.
60°·1 C.	22·6 c.c.
69°·5 C.	26·06 c.c.
79°·35 C.	29·94 c.c.
90°·2 C.	33·66 c.c.
100°·4 C.	37·56 c.c.

Coefficient of expansion = ·003741.

Fig. 5.—Expansion of Hydrochloric Acid Gas.



A graph on a small scale conveys no correct idea of the regularity of the results. To test the results properly they should be graphed on as large a scale as possible.

XXV. *A Hydrodynamical Illustration of the Theory of the Transmission of Aerial and Electrical Waves by a Grating.* *By* HORACE LAMB, *F.R.S.*, *and* GILBERT COOK, *M.Sc.*[*]

THE theory of the scattering of aerial and electrical waves by isolated obstacles whose breadth is small compared with the wave-length has been discussed in a series of papers by Lord Rayleigh[†]. A direct verification of the results is hardly to be looked for, but the case of a grating, which has been investigated by one of the present writers[‡], would appear to be more promising in this respect; and in fact the transmission of Hertzian waves by a metallic grating has been studied experimentally, and compared with the theory by Schaefer and Langwitz[§], and by G. H. Thomson[‖], and a satisfactory agreement has been found.

A confirmation of the mathematical formulæ may, however, be sought in another direction. It is known[¶] that in the case of a cylindrical obstacle, or system of obstacles, the problem is identical with that of waves on a sheet of water of uniform depth, as modified by cylindrical obstacles whose generating lines are vertical. In particular, in the longitudinal oscillations of water in a long and narrow rectangular tank, having one or more such obstacles near its centre, we have an exact analogue of aerial waves incident on a grating, provided the obstacles be disposed with the proper degree of symmetry. The effect of the obstacles in altering the period of the gravest mode of oscillation can in certain cases be calculated, and the comparison with experiment is of course a very simple matter.

The mathematical theory[**] may, for the purpose in hand, be briefly recapitulated. The origin being taken in the undisturbed level of the water-surface, and the axis of z being directed vertically upwards, we have to satisfy the equation

$$\nabla^2\phi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

subject to the condition that the normal derivative $\partial\phi/\partial n$ shall vanish at the rigid boundaries, and that

$$\sigma^2\phi = g\frac{\partial\phi}{\partial z} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[*] Communicated by the Authors.

[†] Phil. Mag. [5] vol. xlii. p. 259 (1897), and vol. xliv. p. 28 (1897); Sc. Papers, vol. iv. pp. 283, 305.

[‡] H. Lamb, Proc. Lond. Math. Soc. vol. xxix. p. 523 (1898); Hydrodynamics, 3rd ed., §§ 300, 301.

[§] *Ann. d. Phys.* vol. xxi. p. 587 (1906).

[‖] *Ann. d. Phys.* vol. xxii. p. 365 (1907).

[¶] Rayleigh, Phil. Mag. [5] vol. i. p. 257 (1876); Sc. Papers, vol. i. p. 265.

[**] Hydrodynamics, §§ 226, 251.

at the free surface ($z=0$), the time-factor for the simple-harmonic vibration being assumed to be $e^{i\sigma t}$. If the depth be h, the condition of zero vertical velocity at the bottom ($z=-h$) is satisfied if we assume that ϕ involves z only through a factor of the form $\cosh k(z+h)$; and the condition (2) then gives

$$\sigma^2=gk\tanh kh. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

It remains to satisfy (1), which now takes the form

$$\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}+k^2\phi=0, \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

and the condition that $\partial\phi/\partial n=0$ at the vertical boundaries. The analysis is now identical with that which applies to the two-dimensional form of the problem of aerial waves, or of electrical waves when the *magnetic* force is everywhere parallel to z. The conditions stated determine the admissible values of k, and the corresponding frequencies are then given by (3).

Proceeding to the case of the rectangular tank, we take the origin at the centre of the free surface, and the axis of x parallel to the length (l). If there were no obstacles, then in the case of the longitudinal oscillations the second term in (4) would disappear, and we should have, in the anti-symmetrical modes,

$$\phi=\mathrm{A}\sin kx, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

the factors which involve z and t being omitted. The condition that $\partial\phi/\partial x=0$ for $x=\pm\frac{1}{2}l$ then gives $\cos\frac{1}{2}kl=0$, the lowest root of which is $kl=\pi$. The period is accordingly that of water-waves of length $2l$, viz.*:

$$\frac{2\pi}{\sigma}=2\sqrt{\left(\frac{\pi l}{y}\cdot\coth\frac{\pi h}{l}\right)}. \quad . \quad . \quad . \quad . \qquad (6)$$

The horizontal dimensions of the obstacles being supposed small compared with l, the transverse component (v) of the velocity will be sensible only in their immediate neighbourhood. We may imagine two planes $x=\pm x'$ to be drawn,

such that x' is moderately large compared with the dimensions in question, whilst still small in comparison with l. Outside

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* The verification of this formula was at one time a favourite lecture experiment of the late Sir George Stokes.

these, we shall have

$$\frac{\partial^2\phi}{\partial x^2}+k^2\phi=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

approximately, and therefore, for $x>x'$,

$$\phi=\text{A}\sin kx+\text{B}\cos kx, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

whilst, for $x<-x'$,

$$\phi=\text{A}\sin kx-\text{B}\cos kx, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

ϕ being, in the gravest mode, an odd function of x.

In the region *between* the planes $x=\pm x'$ the configuration of the lines $\phi=$const. is, on the principles explained by Helmholtz and Lord Rayleigh *, sensibly the same as if in (4) we were to put $k=0$. So far as this region is concerned, the problem is in fact the same as that of the conduction of electricity in a bar of metal which has the same form as the actual mass of water, and has accordingly one or more perforations occupying the place of the obstacles. The electrical resistance between the two planes is then equivalent to that of a certain length $2x'+\alpha$ of an unperforated bar of the same section. The difference of potential between the two planes may be taken to be $2(k\text{A}x'+\text{B})$, by (8), since kx' is small; and the current per unit sectional area is $k\text{A}$, approximately. Thus

$$2(k\text{A}x'+\text{B})=(2x'+\alpha)k\text{A}, \quad . \quad . \quad . \quad (10)$$

whence

$$\text{B}/\text{A}=\tfrac{1}{2}k\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and

$$\phi=\text{A}(\sin kx+\tfrac{1}{2}k\alpha\cos kx), \quad . \quad . \quad . \quad . \quad . \quad (12)$$

for $x>x'$.

The condition to be satisfied at the end $x=\frac{1}{2}l$ gives

$$\cos\tfrac{1}{2}kl-\tfrac{1}{2}k\alpha\sin\tfrac{1}{2}kl=0, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which determines k. When, as in the experiments to be described, $k\alpha$ is a small quantity, this is equivalent to

$$\cos\tfrac{1}{2}k(l+\alpha)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

so that the introduction of the obstacles has the effect of virtually increasing the length of the tank by α.

The value of α is known in two cases. When the plane $x=0$ is occupied by a thin rigid diaphragm of breadth a, having a central vertical slit of breadth c, we have †

$$\alpha=\frac{2a}{\pi}\log\sec\frac{\pi(a-c)}{2a}. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

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[*] Theory of Sound, § 313.

[†] Hydrodynamics, p. 512. The notation is slightly altered.

The experiment was tried in this form, and the results were satisfactory so far as they went; but the motion was so rapidly damped that it was difficult to determine the period with any great accuracy. When the oscillations were started it was necessary to wait for some time until the turbulent motion of the water swirling round the sharp edges of the slit had subsided.

The remaining case is covered by the formulæ *

$$\left.\begin{aligned}\phi&=x+\tfrac{1}{2}\alpha\frac{\sinh\dfrac{2\pi x}{a}}{\cosh\dfrac{2\pi x}{a}-\cos\dfrac{2\pi y}{a}},\\ \psi&=y-\tfrac{1}{2}a\frac{\sin\dfrac{2\pi y}{a}}{\cosh\dfrac{2\pi x}{a}-\cos\dfrac{2\pi y}{a}},\end{aligned}\right\}\quad .\ .\ .\ (16)$$

where ψ is the stream-function in the electrical (conduction problem, a denoting as before the breadth of the tank. The stream-lines $\psi=\pm\frac{1}{2}a$ correspond to the sides; for $x=0$ we have $\phi=0$, and for $x=\infty$, $\phi=x+\frac{1}{2}a$. The stream-line $\psi=0$ consists partly of an oval curve

$$\cosh\frac{2\pi x}{a}-\cos\frac{2\pi y}{a}=\alpha\frac{\sin\dfrac{2\pi y}{a}}{2y}, \quad .\ .\ .\ (17)$$

which may be taken to represent the section of the obstacle, and partly of the portions of the axis of x which lie outside this oval. By assigning different values to α we obtain a series of possible forms.

When the ratio α/a is small, the oval reduces to a circle

$$x^2+y^2=b^2, \quad .\ .\ .\ .\ .\ .\ .\ (18)$$

approximately, provided

$$\alpha=2\pi b^2/a. \quad .\ .\ .\ .\ .\ .\ .\ (19)$$

This implies that the ratio b/a must be small; but it appears on examination that the circular form is not seriously departed from even when α/a is a considerable fraction. Suppose, for example, that the transverse diameter is one-half the breadth, a ratio not exceeded in the actual experiments. If in (17) we put $x=0$, $y/a=\frac{1}{4}$, we find $\alpha/a=\frac{1}{2}$.

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* Hydrodynamics, p. 514.

The half-breadth of the oval in the direction of x is found by putting $y=0$; thus

$$\cosh\frac{2\pi x}{a}=1+\frac{1}{2}\pi, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

whence $x/a=\cdot 2537$. The two diameters therefore agree within $1\frac{1}{2}$ per cent.

The cylinders used were of circular section, and the value of α was calculated from the formula

$$\alpha=2b\tan\frac{\pi b}{a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where b denotes the radius; this is obtained by putting $x=0$, $y=b$ in (17). The theoretical period was then obtained from (6), with $l+\alpha$ written for l.

The tank used in the experiments was 5 feet long, 8·95 in. wide, and about 12 in. deep. A series of observations was made with different depths of water, in the case of each cylinder, and the period compared with that obtained when the cylinder was removed. In order to ensure an exact comparison a hook gauge was used, and the level of the water adjusted so as just to reach the sharp point.

The oscillations were started by alternately raising and lowering one end of the tank, in an approximately simple-harmonic manner, by means of a lever, the period corresponding as nearly as might be to that of the free oscillations. In this way the production of minor surface waves was discouraged; but it was found impossible, when the obstacle was present, to avoid altogether the simultaneous generation of the second normal mode of oscillation, whose period is (very nearly) half that of the fundamental mode which was the object of study. The effect of this was, however, completely eliminated by the method used for counting the oscillations. This consisted in observing, by means of a telescope with cross-wires set up at one end of the tank, the reflexion of a sharply defined object on a distant building, the axis of the telescope being directed to a point on the central transverse line of the water surface. The second mode of oscillation referred to affects the level, but not the inclination, of this part of the surface; and the modes of still higher frequency subsided too rapidly to affect the observations, which were of course only begun after a short interval.

It was found possible in this way to observe as many as 200 oscillations with an initial vertical amplitude of about $\frac{1}{2}$ in. at the end of the tank; but it was found that greater accuracy was secured by counting only about half this number, owing to the occurrence of ripples due to accidental tremors, which interfered sensibly when the amplitude had become very small. The intervals of time measured in successive experiments under the same conditions were found to agree within 0·2 sec., so that the period of oscillation could be inferred with an error of not more than 0·002 sec.

The results are shown in the annexed table. The first column gives the depth of the water beneath the point of the hook gauge. The second column shows the period as observed when there is no obstacle, and the third as calculated from the formula (6). The fifth and sixth columns show the observed and calculated periods when a cylindrical obstacle of the diameter indicated is introduced, the theoretical period being based on the formula (21), as explained. The last two columns show the observed and calculated increase in the period, due to the obstacle, in the various cases.

Depth of water.	Period when no cylinder present.		Diameter of Cylinder.	Period.		Increase in period.	
	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.
ins.			ins.				
7·3	2·324	2·313	4·5	2·489	2·479	·165	·166
,,	2·324	2·313	3·45	2·413	2·401	·089	·088
,,	2·324	2·313	2·21	2·358	2·346	·034	·033
,,	2·324	2·313	1·59	2·338	2·329	·014	·016
8	2·210	2·221	4·5	2·364	2·380	·154	·159
,,	2·224	2·221	3·45	2·304	2·304	·080	·083
,,	2·215	2·221	2·21	2·245	2·252	·030	·031
,,	2·212	2·221	1·59	2·226	2·237	·014	·016
8·4	2·167	2·173	4·5	2·322	2·328	·155	·155
,,	2·167	2·173	3·45	2·249	2·254	·082	·081
,,	2·167	2·173	2·21	2·198	2·204	·031	·031
,,	2·168	2·173	1·59	2·182	2·189	·014	·016
9	2·112	2·108	4·5	2·258	2·257	·146	·149
,,	2·112	2·108	3·45	2·192	2·187	·080	·079
,,	2·112	2·108	2·21	2·142	2·138	·030	·030
,,	2·101	2·108	1·59	2·115	2·123	·014	·015
9·4	2·062	2·070	4·5	2·211	2·215	·149	·145
,,	2·063	2·070	3·45	2·138	2·146	·075	·076
,,	2·062	2·070	2·21	2·088	2·099	·026	·029
,,	2·062	2·070	1·59	2·075	2·084	·013	·014

A slight and variable error in level in the bed of the tank could not be avoided, and the depth measured at the position of the hook-gauge does not therefore represent quite accurately the *mean* depth. This circumstance accounts for the discrepancies between the numbers in the second and third columns, but would hardly affect at all the comparison in the last two columns.

The experiments could no doubt be improved upon in various ways, but the agreement, as they stand, between theory and observation seems satisfactory. It may be worth while to remark that a slight inclination of the bed of the tank, or a slight want of symmetry, or even of verticality, in the position of the cylindrical obstacle, would only affect the period by a small quantity of the *second* order.

XXVI. *A Galvanometer for Alternate Current Circuits.* *By* W. E. Sumpner, *D.Sc., and* W. C. S. Phillips, *B.Sc.*[*]

THE steady electromotive forces and highly sensitive galvanometers available for use with direct current tests render such tests excellent whether deflexional or balance methods are in question. Tests involving change of current, such as induction measurements, are not so satisfactory. In ballistic tests the best galvanometers are in many cases not sensitive enough, and though balance methods are available they are usually not so simple in working as those in which steady currents are employed. Alternate current tests are still less satisfactory. It is impossible to generate an electromotive force whose constancy is comparable with that of a battery or accumulator. Special difficulties arise owing to effects of frequency, wave-form and phase. Balance methods can be devised, but they are rarely of much use, owing to the above difficulties and to the absence of sensitive instruments. A distinct advance has been made during the last few years by the construction of improved forms of vibration galvanometer. But this instrument overcomes only some of the difficulties. It is a sensitive indicator rather than a measuring instrument. It must be adjusted to resonance for the best effects, and its sensitiveness is necessarily affected by slight changes in current frequency.

The sensitiveness of ballistic galvanometer tests can be greatly increased by the use of mechanical commutators such as the secohmmeter of Ayrton and Perry, or subsequent modifications of this by Fleming and Lyle. But such methods only make use of a crude form of alternate current, and it appears that the simplest and most effective cumulative method for testing effects due to changes of current, must in the end prove to be one involving the use of alternate

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[*] Communicated by the Physical Society: read June 10, 1910.

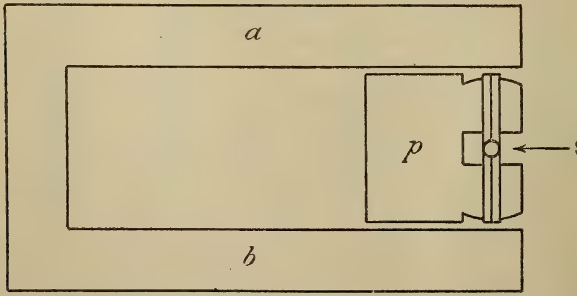
currents generated in the ordinary way. The construction of the indicating instrument constitutes the real obstacle. The reflecting instrument for alternate current circuits described in this paper is the result of an attempt to overcome this difficulty. The instrument is like a moving coil galvanometer in almost every respect, except that its field is due to an electromagnet excited by an alternating voltage. The theory of non-reflecting instruments of the same type has already been fully explained *, but it may be convenient to briefly refer to it.

If an alternating voltage V be applied to an electromagnet whose winding consists of m turns, the core flux N will be such that

$$V = rA + m\dot{N}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where r is the resistance of the coil and A the current traversing it. If the coil and electromagnet be so designed that for currents of the frequencies used the resistance is negligible in comparison with the impedance, we can neglect the term rA. It follows that the rate of change of N will be at each instant a measure of V, and this will be true whatever the permeability or hysteresis of the core. We thus have a magnet whose strength is accurately determined by the applied voltage whatever the physical properties of the core. Such an electromagnet can easily be made very strong. Moreover, the shorter the air-gap between the poles is made, the denser is the magnetic flux due to a given current, and the greater is the ratio of impedance to resistance for a given winding. Thus the stronger the electromagnet is made by improving its magnetic circuit, the more accurate it becomes, provided this electromagnet is excited by the voltage of the circuit.

Fig. 1.



The instrument here described has a laminated electromagnet formed of stampings shaped like figure 1. These

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* Proc. Roy. Soc. vol. lxxx. (1908), "Alternate Current Measurement."

stampings are of two kinds—a rectangular portion with two straight limbs, *a*, *b*, forming the core of the electromagnet, and a specially shaped stamping, *p*, between the poles. The stamping, *p*, is separated from the magnet limbs on each side by an air-gap. Each gap consists of two portions, a narrow part about 1 mm. across bounded by the straight edges of *p*, and a wider portion in which one of the vertical sides of the moving coil can turn round the curved edges of *p*. The moving coil, of 50 turns, is similar in shape, suspension, and mode of control to that of an ordinary permanent magnet instrument. It has a central spindle indicated at *s* and working in a recess suitably stamped in *p*. The pile of stampings is about 4 cm. deep and 9 cm. long, the limbs being 1 cm. wide. Each of the limbs, *a*, *b*, is wound with a coil of 2000 turns of fine wire, and also with a coil of 100 turns of thicker wire. The two fine wire coils are put in series and connected to three terminals; the two thicker coils are also put in series and joined up to two additional terminals. Thus the instrument can be excited by a winding consisting of either 200, 2000, or 4000 turns, according to the voltage used. The iron is not too strongly magnetized if the winding used contains 20 turns per volt on 50 cycle circuits. Thus 200 volts may be applied to the 4000 turn coil, or 10 volts to the 200 turn coil. But the instrument is so sensitive that such excitation will only be needed for exceptional tests. The moving coil may be used with a condenser or other apparatus, either on some special circuit, or in conjunction with one or other of the field coil windings. The instrument has been constructed by Robt. W. Paul, to whom several of the working details are due. The following are some of the uses:—

Use as a Voltmeter.

If a voltage V be applied to a field coil of *m* turns and if another voltage V_1 be applied through a condenser of K microfarads to the moving coil, it can be shown that the torque acting on the moving coil is a measure of

$$\frac{1}{m}\mathrm{K}\,\overline{\mathrm{V}\mathrm{V}_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or of the mean product of the two voltages. If the condenser voltage is obtained from one of the field coils of *n* turns the torque is measured by

$$\mathrm{K}n\left(\frac{\mathrm{V}}{m}\right)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

There is really another factor the value of which would not be quite constant if the induction density in the gap varied with the position of the moving coil. But in the present instrument this factor is essentially constant owing partly to the shape of gap adopted, and partly to the fact that for a reflecting instrument the movement of the coil is very slight. Numerous tests have shown that for any given choice of coils and condenser, the scale deflexion is strictly proportional to the square of the applied voltage quite up to the limits of the scale used (300 mm. each side of zero for a scale distance of 1 metre).

The numbers denoted by m and n may each be chosen either 200, 2000, or 4000, while the capacity K may be given widely different values. It is thus clear that the instrument can be used as a voltmeter for a large number of ranges. It will be sufficient to indicate two of these. From a number of tests made under various conditions, the value of expression (3) when V is measured in volts and K in microfarads is found to be $1{\cdot}6 \times 10^{-4}$ for a scale deflexion of 200 millimetres. It follows that this deflexion can be obtained

for 200 volts if $m=4000$, $n=200$, and $\mathrm{K}=3{\cdot}2\times10^{-4}$ m.f.,

or for 20 millivolts if $m=200$, $n=4000$, and $\mathrm{K}=4{\cdot}0$ m.f.

The deflexion is independent of frequency and wave-form if the field winding to which the voltage is applied has a resistance negligible in comparison with its impedance. This will always be the case if the frequencies used are high. But if the frequency is low and the mass of copper used in the magnetizing coil is small, the resistance of this coil will become comparable with its impedance. The deflexion will then be dependent on frequency, though for a given frequency it will still be a measure of the product $\mathrm{K}\,\mathrm{V}^2$. Thus if a coil of two turns be wound round the core of the magnet and be used as the exciting winding ($m=2$), and if the moving coil be used with the same condenser and field winding as in the second case above ($n=4000$, $\mathrm{K}=4$), a deflexion of 200 mm. will correspond with a reactive voltage in the two-turn coil of only 0·2 of a millivolt. But it will be necessary to apply a much greater voltage than this to cause the magnetizing current to flow through the resistance of the winding. The instrument will still act as a voltmeter for constant frequency circuits, but its indications will be sensitive to change of frequency.

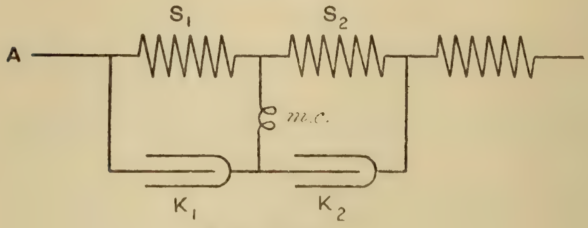
With the instrument as actually wound, the effect of frequency can be represented by the measured values of the quantity (3) for a deflexion of 200 mm. If this quantity when multiplied by 10,000 be called Q, then for the arrangement $m=4000$, $n=200$, the value of Q is 1·62 for 50 cycle circuits, 1·61 for 100 cycle circuits, and 1·73 for 25 cycle circuits. That is, the deflexion for a given value of V^2 is essentially the same for all frequencies above 50 cycles per second, but is $6\frac{1}{2}$ per cent. less if the frequency is dropped to 25 cycles per second. For the arrangement $m=200$, $n=4000$, a change of frequency produces greater effect. The deflexion for a given value of V^2 is 5·2 per cent. greater for 100 cycles, and 18·6 per cent. less for 25 cycles, than it is for 50 cycles. When the main coil is used for both voltage and condenser ($m=n=4000$) there is no appreciable change of constant for frequencies between these limits.

The effect of frequency on the value of Q is mainly due to the phase error represented approximately by the ratio of resistance to impedance of the coil to which the voltage is applied. This ratio on 50 cycle circuits is 2·6 per cent. for the 4000 turn coil, and 10·6 per cent. for the 200 turn coil. But Q is also affected by slight amounts of magnetic leakage (between the windings) dependent on the arrangement of coils used. Other properties of the magnet are deducible from the data that on 50 cycle circuits the power factor of the magnetizing coil is 0·14; the ampere turns needed for the magnet are $6u$; and the flux density in the iron is $80u$; where u is the number representing the voltage applied per 1000 turns, or the millivolts per turn. For special uses of the instrument the phase error of the magnet can be reduced by applying a suitable condenser direct to one of the field windings. Thus the power factor of the 200 turn coil can be raised to unity on 50 cycle circuits by applying a condenser of 1·1 m.f. to the 4000 turn coil, the ratio of resistance to impedance is reduced from 10·6 per cent. to 1·5 per cent., and the phase error is reduced to zero.

Use with Null Methods.

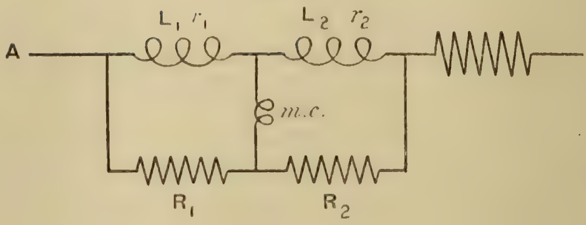
Figs. 2–7 illustrate the ordinary bridge methods for comparing inductances and capacities. In these methods a ballistic galvanometer is used as an indicator, and to test the balance the current A through the arms of the bridge is made or broken by a key. The equation representing the condition for inductive balance is indicated in each case beside the figure. The zero deflexion condition for steady currents holds necessarily in the three cases of figs. 2, 4 and 6; but a troublesome special adjustment is needed in the case of fig 3; while in the cases of figs. 5 and 7 the adjustment for steady currents is impossible. In these figures capacities, self-inductances, and mutual inductances are respectively denoted by the letters K, L, M; resistances are indicated by the letters R, r, and S; while the indicator is denoted by *m.c.*

Fig. 2.



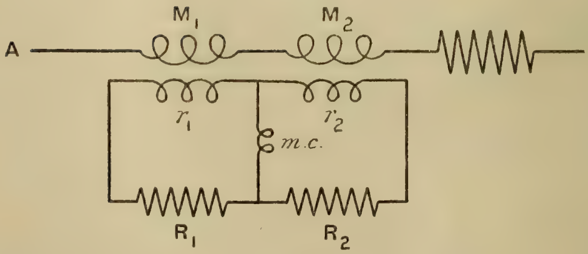
$$K_1S_1 = K_2S_2.$$

Fig. 3.



$$\frac{L_1}{R_1+r_1} = \frac{L_2}{R_2+r_2}.$$

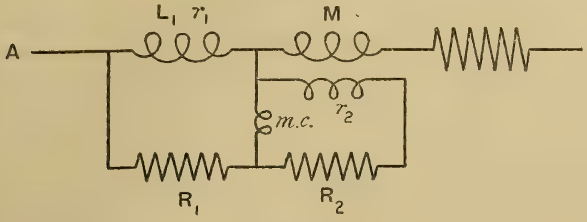
Fig. 4.



$$\frac{M_1}{R_1+r_1} = \frac{M_2}{R_2+r_2}.$$

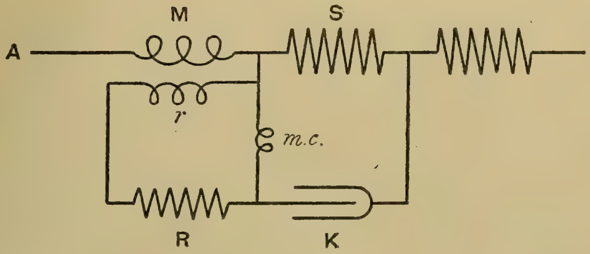
All these methods may be used with the present instrument for steady inductive balances on alternate current circuits, and the same formulæ apply to the zero deflexion

Fig. 5.



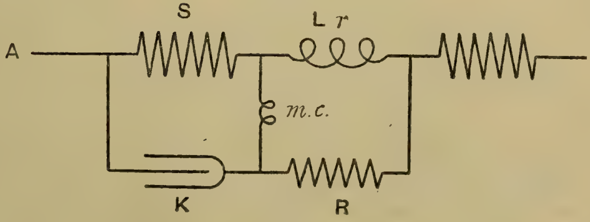
$$\frac{L}{R_1+r_1}=\frac{M}{R_2+r_2}.$$

Fig. 6.



$$\frac{M}{R+r}=KS.$$

Fig. 7.



$$KS=\frac{L}{R+r}.$$

condition, provided (i.) the alternate voltage V applied to the field-coil of the instrument also causes the current A through the bridge conductors, (ii.) the alternate current A is made essentially cophasal with V by the use of suitable non-inductive resistances as indicated by the zigzag lines in the figures, (iii.) the moving coil *m.c.* of the instrument is placed directly across the bridge (using a reversing key when desirable).

It results from the special properties of the instrument that the flux in the gap of the electromagnet is in quadrature with the applied voltage (and thus in quadrature with A). The inductances or capacities produce voltages or currents also in quadrature with A, and thus in phase with the flux, so that their phase is such that they produce the maximum torque on the moving system.

These methods have all been thoroughly tested on alternate current circuits with the present instrument, and with most satisfactory results. The balance can be adjusted with ease to one part in 10,000, when the voltages set up on the coils or condensers are merely of the order of one volt, and thus suitable for use with the resistance boxes ordinarily found in laboratories.

Certain special points call for notice. When a balance of great precision is needed, the minute electromotive force *e*, induced in the moving coil by the alternating field of the magnet, tends to cause a small deflexion disturbing the balance. When the moving coil circuit is essentially non-inductive, as for the cases of figs. 3, 4 and 5, the current due to *e* will be in phase with *e*, and in quadrature with the flux, and in such cases the corresponding deflexion will in general be negligible. For the inductive circuits represented in figs. 2, 6 and 7, this will not be the case, and a small deflexion due to *e* will occur. But in all cases any effect due to *e* can be accurately eliminated by using a false zero method, that is, by adjusting the balance till the reading on the scale is unaltered by switching the bridge current A on or off. The induced voltage *e* is due to the voltage applied to the field coil, and is unaffected by changes in A. In most cases it will be found sufficiently accurate to take the mean of the two conditions of balance obtained by using a reversing key with the moving coil. The false zero method is simpler and is mathematically accurate, though in practice, as with all false zero methods, there is a liability to a small error due to the variations of the false zero deflexion in sympathy with fluctuations in the main current or voltage.

The formula given for balance expresses the necessary and sufficient condition that the two electromotive forces set up in the coils, or on the condensers, of the bridge, send, through the moving coil, currents which are equal in magnitude and exactly opposite in phase*. But if this condition is not quite fulfilled, the unbalanced current will not necessarily be in the best phase to influence the deflexion unless certain limitations are borne in mind. The resistances R must not be made too small, and the resistances S must not be made too large. Otherwise the sensitiveness of the instrument to indicate want of balance is adversely affected, although the condition of balance remains as stated, except for minute correction terms, due to secondary effects of self-induction, &c., which have been neglected.

We have found on investigation that the only cases which need be considered are those in which condensers are used (figs. 2, 6 and 7). The value of KSp (where p is 2π times the frequency) represents the tangent of the angle by which the phase of the moving coil current differs from that of the magnet field. It may easily become comparable with unity, as will be apparent from the fact that on 50 cycle circuits with K equal to 1 microfarad, and S equal to 1000 ohms, the value of KSp is 0·314. But it will be found easy to adjust the conditions of the bridge in all the cases considered so as to render these tests quite satisfactory in practice.

One or two examples of these bridge methods may be given to illustrate the conditions of working.

The method of fig. 6 was used to test the values of M for a primary coil of 500 turns in conjunction with two secondary coils. The three coils were wound on a wooden bobbin and the primary wire was suitable for a current of 2 amperes. A current of 1·1 ampere was passed through the bridge, and 28 volts were applied to the 4000 turn coil, the frequency being 50 cycles per second. A standard resistance of 0·9995 ohms was used for S, and a standard mica condenser of 1·0155 m.f. was used for K. An ordinary resistance-box was used for R. Using the first secondary coil the value of $R+r$ was adjusted to 4225·1 ohms. The corresponding value of M works out to be 4·2885 millihenries. A similar test with the other secondary yielded 3·8499 m.h., and one with the two secondaries in series yielded 8·1398 m.h. The sum of the values of M for the two secondaries is 8·1384 m.h. The small inconsistency is easily attributable to errors in the resistance-box, to small capacity effects in these resistances,

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* This is strictly true for the cases of figs. 2, 4, and 6. In the cases of figs. 3, 5, and 7 an additional current through the moving coil is caused by the resistance of the inductance coils. This current is in quadrature with the field, and does not cause any deflexion. There is thus no need for a troublesome double adjustment as in corresponding tests in which other instruments are used.

or to similar causes of no present interest, the point being that it was possible to adjust R to one part in 40,000, under conditions of test which could easily have been rendered more sensitive. The current used with the bridge could have been quadrupled, and the strength of the field could have been increased ten times, without injuring the apparatus, and without altering the quantities under test.

The method of fig. 2 was used to compare the capacity of a paraffin paper condenser (about 0·9 m.f.) with the standard mica condenser just referred to. The 4000 turn field-coil was subjected to 20 volts on a 50 cycle circuit. From this voltage was obtained, by means of a small transformer, a cophase voltage of 2·5 volts suitable for the bridge conductors. The resistances S were kept below 2000, and various tests were made. It was always possible to adjust the balance to 1 part in 10,000, but the inconsistencies in the various tests amounted to 2 parts in 1000 and are attributable to phenomena (such as a partial conduction in the paper condenser) affecting the exact formula for balance.

An adjustable air-condenser, formed of a fixed and moving set of plates like a multicellular voltmeter, was tested for capacity against the standard mica condenser above referred to. The maximum capacity was measured as 0·0023 m.f., or only 0·2 per cent. of that of the standard. It was always possible to measure the capacity in any position far more accurately than the condenser could be adjusted to this position. The method of fig. 2 was used, but higher voltages were applied to the bridge than in the previous test. The 4000 turn field-coil was subjected to 30 volts, and this voltage was also used for the condenser bridge, a resistance of 9000 ohms, made for the pressure circuit of a wattmeter and suitable for high voltages, being used in association with the air-condenser. The standard mica condenser was used as K_1. The associated resistance S_1 was taken from an ordinary resistance-box. It was set at various values up to 22 ohms as a maximum. The 9000 ohm resistance was used for S_2, and the air-condenser K_2 was adjusted for each value of S_1 till balance was obtained. The maximum voltage to which S_1 was subjected in these tests was less than 0·1 volt. The false zero method was employed for balance, the moving coil voltage causing a deflexion of about 10 centimetres.

It is to be noted that in all these bridge tests the phase error of the electromagnet due to the resistance of the field winding does not lead to any error, but merely causes a negligible change of sensitiveness due to a shift of phase of the moving coil current as compared with that of the field.

Other Uses of the Instrument.

The voltmeter tests previously described show that the instrument can be used to measure very small capacities, especially in cases where it is possible to apply high voltages to the condenser. It will be apparent from expression (2) that if the voltage V_1 applied to the condenser is in phase with the voltage V applied to the field, and a known multiple of it, the sensitiveness can be indefinitely increased by making V_1 large.

Thus two circular brass plates of 7·3 cm. diameter and about 6 mm. apart were tested as a condenser, and found to have a capacity of 6×10^{-6} microfarad. This capacity caused a deflexion of 180 mm. when 102·4 volts were applied to the 4000 turn coil, and, by means of a transformer, 890 volts were applied to the condenser plates through the moving coil. The capacity tested being so small it was found necessary to eliminate capacity effects associated with the wires used for the connexions. This was done by taking the difference of two deflexions obtained with the connexion to one of the plates alternately made and broken. Earthing conditions had to be carefully attended to. Good values have been obtained for the specific inductive capacities of plates of various dielectrics, but we have as yet not had time to properly carry out such tests, which for accurate results require balance methods with guard-ring condensers.

The instrument has not yet been tested with alternate currents of higher frequencies than 100 cycles per second, but there appears no reason to suppose there will be any difficulty in the way of its use for high frequency work.

Added July, 1910.—Mr. A. Campbell has drawn our attention to a paper, previously unknown to us, in which Stroud and Oates (Phil. Mag. 1903) describe an instrument resembling in some respects the galvanoneter here referred to. The paper gives data of the electromagmet showing that it contained a greater volume of iron than that of the instrument here described. But no details are given of the air-gap between the poles, and it does not appear that any attempt was made to produce a magnetic field whose phase is essentially in quadrature with that of the applied voltage. The characteristics of the present instrument are the result of such a relationship. In the Stroud galvanometer the field in the gap is probably stronger and less uniform than that of the instrument here described ; since the disturbing influence of this field on the moving system seems much more serious.

XXVII. *The Production of Cathode Particles by Homogeneous Röntgen Radiations, and their Absorption by Hydrogen and Air.* *By* R. T. Beatty, *M.A*, *B.E.*, 1851 *Exhibition Scholar, Emmanuel College, Cambridge* *.

[Plate V.]

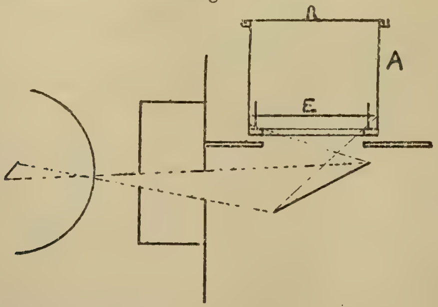
THE properties of the cathode particles produced when Röntgen radiations fall upon various substances have been investigated by several physicists. The work of Cooksey † and Innes ‡ has shown that the velocities of these cathode particles are independent of variations in the intensity of the Röntgen radiations used, and also independent of the nature of the substance struck by these radiations, but that the velocities increase with an increase in the penetrating power of the exciting Röntgen radiations.

The work of Barkla and Sadler upon homogeneous radiations enables one to use beams of definite quality and differing widely in penetrating power, and it seemed that by using such beams more precise information might be gained about the cathode particles emitted from metals placed in the path of such beams.

In view of the anomalous behaviour of hydrogen with regard to ionization phenomena, it was determined to investigate the coefficients of absorption by hydrogen and air of the cathode particles emitted from a sheet of silver leaf which was placed in the path of the homogeneous radiations described above.

The homogeneous radiations from the metals Fe, Ni, Cu, Zn, As, Sn, were excited by suitable radiations from a Röntgen bulb.

Fig. 1.



A homogeneous radiation so produced entered the cylindrical ionization chamber A (fig. 1) through a thin parchment window. It then passed through a silver leaf, and

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* Communicated by Prof. Sir J. J. Thomson.

† C. D. Cooksey, Amer. Jour. Sci. [4] xxiv. 1907, p. 285.

‡ P. D. Innes, Roy. Soc. Proc., ser. A. lxxix. pp. 442–462, Aug. 2, 1907.

was finally absorbed completely in a thick brass disk E which served as electrode. The cathode particles which emerged from E were absorbed by a layer of paper gummed on the surface of E, and so contributed nothing to the ionization in the region ER.

Another portion of the radiation, travelling at right angles to the plane of the paper, entered an electroscope (to be referred to as the primary electroscope) which served to standardize the amount of homogeneous radiation emitted by the radiator.

As the quality of the homogeneous radiation is unaffected by small variations in the bulb, and as the quantity of radiation entering the chamber A is always the same fraction of that entering the primary electroscope, no discordance in the results can arise from slight variations in the bulb.

Apparatus.

A cylindrical brass ionization vessel was constructed with an internal diameter of 11 cms. (fig. 2). A circular opening, 7 cms. in diameter, was made in the bottom, and a piece of copper gauze was fitted into this opening and carefully soldered round the edges so as to be quite flush with the bottom of the vessel. The details of this arrangement are shown in fig. 3. A cap CC was then cast in brass and turned down to fit tightly over the bottom BB. The cap was made with a circular opening of the same size as that in BB. A sheet of thin parchment was used to cover the Cu gauze: its weight was equivalent to that of ·005 mm. of Al.

Fig. 2.

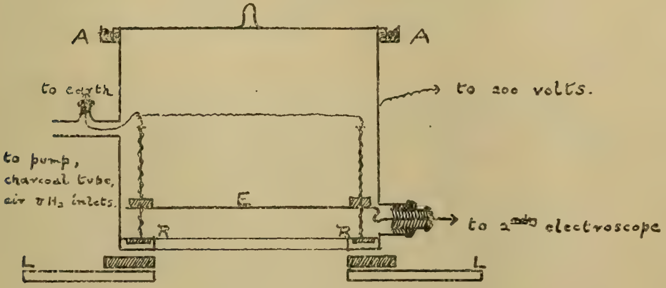
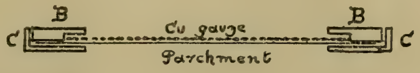


Fig. 3.



Parchment was found not to be air-tight, and after some trials the method of treating it which gave most satisfaction was to plunge it in boiling paraffin wax, and then remove the excess of wax between filter-papers. This treatment increased the weight of the paper to that of ·01 mm. of Al, but still its absorption of even the Fe radiation was quite small. The parts shown in fig. 3 were assembled by heating BB and CC, covering them with a layer of beeswax and resin, placing the parchment in position and pressing CC tightly on BB. When the joint was made in this manner no trouble with leakages of air ever arose in this part of the apparatus.

A brass ring RR was placed above the gauze, as shown in fig. 2, and the opening in it was covered with a parchment sheet tightly gummed on. Above this came the electrode E, a thick brass disk which could be raised or lowered by three vertical screws passing through ebonite plugs in the disk. The points of these screws rested on three small ebonite blocks which fitted in recesses in RR (see fig. 2) and a conical depression at the centre of each block ensured that E could always be replaced in exactly the same position. A wire was led from E to the secondary electroscope, and as the vessel was put at a high potential a guard ring was used.

As the vessel had to be opened many times during the course of the experiment, it was necessary to have a lid which could be rapidly and efficiently sealed on or removed. The usual method of soldering seemed unattractive, and, instead, a brass casting AA was screwed on the outside of the vessel, forming a deep channel into which melted wax could be poured. The lid was then placed in position so that the rim fitted into this channel, and a blowpipe flame raised the lid to such a temperature (about 100° C.) that the wax became fluid. On cooling, the joint became quite air-tight.

The whole vessel was placed above a circular opening in a thick lead plate LL, and insulated from the lead by ebonite blocks.

The internal arrangements of the vessel were adjusted as follows. A silver leaf was attached to the upper surface of RR while the parchment covering of the latter was moist. The parchment on drying shrank and formed a perfectly plane surface with the leaf adhering to it everywhere. E was then placed on RR and the screws adjusted till the two were parallel. A microscope was used to determine the distance between these surfaces with a possible error of ·02 mm.

This distance was 5 mm. when soft radiations were used. RR was then placed in position in the vessel, E was placed on top of it and connected to the secondary electroscope.

The lid was heated and put in position after the screws had been connected to earth.

Method of Experimenting.

When the bulb was in action the air between E and R was ionized and a charge communicated to E. The pressure of the air inside the vessel was varied, and the ionization in the space ER was measured at different pressures (the primary electroscope being always used to standardize the ionization).

The sources of this ionization are twofold :—

(1) Ionization due to Röntgen radiations alone. This has been shown by Crowther [*] to vary directly as the pressure of the air.

(2) Ionization due to cathode particles emerging from the silver leaf. The amount of ionization due to this source will remain constant as long as the pressure is great enough to absorb all the particles. When the pressure is lower some of the particles will reach E before being absorbed, and the ionization will decrease.

Hence, given the actual curve, we can find the part due to cathode ionization by drawing through the origin a line parallel to the straight portion of the curve, and drawing the curve whose ordinates are got by subtracting the ordinates of this line from those of the actual curve.

Fig. 6 (Pl. V.) shows how the ionization due to the cathode particles is deduced from the actual curve.

The pressure at which the ordinate of the cathode curve is half the maximum ordinate gives the pressure at which half the energy of the cathode particles which start from R reaches E.

Knowing the distance between R and E, the temperature of the room, and the critical pressure, we can now calculate the thickness of the layer of air at 760 mm. pressure and 15° C., which would absorb one half of the energy of the cathode particles starting from R.

Further, we can easily determine from the curves the ratio of total ionization due to the cathode particles which emerge to the ionization due to Röntgen radiations in the layer of air between R and E (*e. g.* PN/QN, fig. 6), and also how the total number of ions made by the cathode particles

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[*] J. A. Crowther, Roy. Soc. Proc. A. lxxxii. 1909, p. 103.

changes when these particles are absorbed completely by air and hydrogen respectively.

For each radiation a complete curve was first obtained with air: then the air was completely pumped out, the final exhaustion being effected by means of a charcoal tube surrounded by liquid air. Hydrogen was then admitted and another curve obtained. The results for Fe, Zn, Sn are shown in figs. 4, 5, 6 (Pl. V.).

Preparation of the Hydrogen.

Special care was taken to obtain pure hydrogen, as a very small percentage of impurity will increase the ionization in it perceptibly. Pure zinc and sulphuric acid (Kahlbaum) were used, the acid being diluted with ten times its volume of distilled water, the mixture being then boiled to expel dissolved air: a little copper sulphate was also added. The reaction took place in a special form of kipp of small volume, the greater part of which was kindly constructed for me by Mr. A. Ll. Hughes. The gas was passed through KHO, and stored over pure H_2SO_4: it was then admitted to the ionization vessel through phosphorus pentoxide and through a spiral glass tube immersed in liquid air.

Tables I. and II. show the results obtained with air and hydrogen.

TABLE I.—Air.

Radiator.	*t*.	λ.	C.	T.
Fe	·00804	87·2	·149	13·0
Cu	·0135	51·9	·239	12·4
Zn	·0164	42·7	·268	11·4
As	·0255	27·43	·522	14·3
Sn	·1762	3·97	3·50	13·9

TABLE II.—Hydrogen.

Radiator.	*t*.	λ.	R.	N.
Fe	·0410	17·05	5·12	1·01
Cu	·0733	9·55	5·44	1·00
Zn	·0909	7·71	5·54	·98
Sn	1·37	·51	7·79	1·00

In both tables:

t = thickness of gas in cms. at normal pressure and temperature required to absorb one half of the energy of the cathode particles.

λ = coefficient of absorption of the cathode particles by the gas, assuming that they are absorbed exponentially.

As a matter of fact, reference to the curves shows that the exponential law is departed from, but it is convenient to calculate λ from t for comparison with other values.

In Table I., C = amount of cathode energy emerging from the leaf divided by the ionization in a layer of air 1 cm. thick just above the leaf (the air being at normal pressure and temperature) due to Röntgen radiation. In the preliminary account [*] of this research the numbers in this column were not reduced to these standard conditions. Also it was found that the silver leaf was so thin that with the Sn radiation some of the cathode particles produced at the back of the leaf were able to penetrate through to the front. Obviously as the thickness of the leaf is increased the number of cathode particles emerging will increase until all particles starting from the back of the leaf are unable to penetrate to the front. A thicker leaf was accordingly used, and the number 3·50 in column C was found.

Now if N particles emerge per second from a metallic surface, and if λ be their coefficient of absorption in the metal, the number of particles produced per second in unit thickness of the plate will be $N\lambda$, if we assume an exponential law of absorption.

λ for silver is unknown, but we may assume it to be proportional to that for air in each case [†]. Accordingly the numbers in column 4 have been multiplied by those in column 3: the numbers in column 5, Table I., have been thus obtained. Here T on this reasoning means the total cathode energy set free by each homogeneous radiation in unit thickness of silver, divided by the ionization in one cm. of air just above the silver (and multiplied by an unknown constant: the ratio of λ by air to λ by silver in each case).

If now we assume that ionization in air is proportional to absorption of the radiations by air, and further that the absorption in air is proportional to that in silver, then T will measure simply the cathode energy set free in silver divided by the absorption by silver of the homogeneous radiation.

The numbers in column 5, Table I., show that the order of

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[*] Proc. Camb. Phil. Soc. vol. xv. pt. v. p. 416.

[†] Lenard, *Wied. Ann.* lvi. p. 255 (1895).

magnitude is the same in each case. Hence we may assume that in the case investigated *a constant fraction of the homogeneous radiation is spent in producing cathode particles.*

Further, if the absorption by air of these radiations were known, we could find this fraction numerically.

In Table II., R is the distance which the cathode particles travel in hydrogen at normal pressure and temperature before becoming half absorbed, divided by the corresponding distance in air.

The ratios increase as the particles become more penetrating. A similar change in R has been observed by Lenard[*] over a much wider range of speeds of cathode particles.

N is the total number of ions produced by a given set of cathode particles when totally absorbed in hydrogen, relative to the number produced in air under the same conditions. *The ratio approaches very closely to unity.*

In Table III. are added some data previously found for cathode particles by Lenard[†] and Seitz[‡].

TABLE III.

Energy of corpuscles in volts.	λ for air.	λ for H_2.	$\frac{\text{Range in } H_2}{\text{Range in air}}$.	Authority.
4,000	645	144	4·48	Lenard
20,000	31	...	...	Seitz
30,000	3·8	·47	8·05	Lenard

It will be seen that the constants relating to the cathode particles due to the Sn radiations are very close to those found by Lenard for corpuscles possessing a velocity due to a drop of potential of 30,000 volts.

In fig. 8 (Pl. V) the coefficients of absorption of the cathode particles are plotted against the absorption by Al of the exciting homogeneous radiations. The curves approach a linear form.

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[*] Lenard, *Ann. der Phys.* xii. p. 732 (1903).

[†] Lenard, *ibid.*

[‡] Seitz, *Ann. der Phys.* xii. p. 860 (1903).

Relative ionization in air and hydrogen due to homogeneous radiations.

The ionization in hydrogen due to soft radiations is so small that the straight portions of the hydrogen curves in figs. 4 and 5 are almost horizontal. A separate set of experiments was made to determine this ionization accurately. The silver leaf was removed from the ionization vessel and the disk electrode replaced by an aluminium wire bent into the form of a ring. A paper strip was wound round the wire to stop cathode radiation from it. The whole volume of the vessel was thus utilized. It is not sufficient to fill the vessel with air and hydrogen alternately, as the small amount of cathode ionization from the paper and cardboard lining would introduce an effect which would increase the value obtained for the direct ionization of the gas. Accordingly the ionization was measured at different pressures, as in the former experiments, and the ratio of the slopes of the linear parts of the curves obtained when the vessel contained air and hydrogen successively gave the ratios of the ionization in these two gases for each radiation, the gases being supposed to be at the same temperature and pressure.

Table IV.

Radiator.	Fe.	Cu.	Zn.	As.	Sn.
$\frac{\text{Ionization in Air}}{\text{Ionization in H}_2}$	175·2	174·5	175·4	174·6	25·0

The relative ionizations of air and hydrogen by primary radiations have been measured by Crowther *. His results are given in the following table.

Table V. (after Crowther).

Equivalent spark-gap of bulb.	8	12	14	16	18	20	24	28
$\frac{\text{Ionization in Air}}{\text{Ionization in H}_2}$ ...	100	77	47·6	14·7	9·35	7·41	6·58	5·56

It will be seen that in Table IV. softer radiations were used than could have emerged from the bulb in Crowther's

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* J. A. Crowther, Roy. Soc. Proc. ser. A. lxxxii. March 10, 1909.

experiments. Also the ratios of the ionizations becomes constant for such radiations. The value for Sn lies where one might expect it considering the penetrating power of the Sn radiation compared to that of the radiation from a Röntgen bulb with the alternative spark-gaps mentioned.

Remarks on figs. 4, 5, 6, 7 (Pl. V.).

In each figure the curves described as "ionization in air" and "ionization in H_2" are those found directly. The curves described as "cathode ionization in air" are obtained by subtracting the part due to direct ionization by the exciting radiation, leaving only that due to cathode particles. The pressure at which this curve rises to half its final value is indicated by a short horizontal line.

In the H_2 curves for Fe and Zn radiations practically all the ionization is due to the cathode particles, so that the curve found directly also represents the ionization due to cathode particles only.

If we take that portion of the ordinate which is intercepted between the "cathode ionization in air" curve and the horizontal straight line which that curve ultimately becomes, and if we plot the logarithms of these intercepts against the corresponding pressures, we get the curves in the figures which are described as log curves. The deviation of these curves from linearity indicates the departure from the exponential law of absorption of the cathode particles.

However, as the particles are already scattered to a great extent before emerging from the silver leaf, an exponential absorption is hardly to be expected. Such an absorption would require certain relations between the numbers and velocities of particles leaving the leaf at different inclinations to the normal.

In determining the cathode ionization in H_2 due to Sn radiation a special method had to be adopted, as owing to the high penetrating power of these particles in H_2 complete absorption of them only took place at pressures nearly atmospheric. A series of readings was taken at different pressures with and without the silver leaf in the path of the radiation. On subtracting corresponding ordinates of these curves we obtain curve III. fig. 7 (Pl. V.) (marked with crosses). The curves referred to as "ionization in air" and "cathode ionization in air" were obtained in the usual way, and the abscissæ of the latter were multiplied by such a number as to make the curve coincide most nearly with the H_2 curve. This number, 7·79, was then taken as the ratio of the penetrating power of the particles in H_2 to that in air.

Discussion of Results.

Shortly after the preliminary account of this paper had been read [*], a research was published by C. A. Sadler [†] in which he studied the emission of cathode particles from various metals under the influence of homogeneous radiations. His numbers, which agree remarkably well, considering the difficulties of the investigation, show that the penetrating power of the cathode particle is independent of the metal in which it originates, and only depends upon the nature of the exciting radiation. The numbers which he obtains for the coefficients of absorption by air of these cathode particles, while trending in the same way as those given in this paper, show numerical differences, particularly in the case of the Sn radiation.

Since the particles in Sadler's experiments emerged from the incidence side of the metal, while those treated of in this paper came from the emergence side, it seemed possible that the cathode particles emerging from opposite sides of the plate might show a want of symmetry in penetrating power. Accordingly the silver leaf was removed from RR (fig. 2) and affixed to the lower side of E, so that cathode particles could only emerge from its incidence side. The coefficients of absorption by air were then determined for the particles excited by the Sn, As, and Fe radiations in exactly the same way as before, and the important discovery was made that the coefficients of absorption of these particles are the same whether they come from the incidence or emergence side of the silver leaf.

TABLE VI.

Radiator.	λ on emergence side.	λ on incidence side.
Sn	3·97	3·91
As	27·43	28·1
Fe	87·2	85·0

This point being settled, various alterations were made in the experimental arrangements in order to test the effect of altering the geometrical conditions. It was thought that the obliquity of incidence of the radiations (see fig. 1) might account for the differences in the values obtained, so the

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[*] Beatty, Proc. Camb. Phil. Soc. vol. xv. pt. v. pp. 416–422, February 21, 1910.

[†] Sadler, Phil. Mag. March 1910, pp. 337–356.

distance between radiator and ionization vessel was increased by six cms., but only a change of one per cent. was obtained in λ when Sn was used as radiator. An attempt was made to use a parallel beam of radiation by causing it to pass along the axes of a bundle of lead tubes placed between radiator and vessel, but the effect then became too small to measure.

It should be mentioned that the portions of the screws between R and E (fig. 2) were covered with paper sheaths to prevent the emission of any particles from them.

An experiment was also made in which a circular disk of lead was placed immediately under the parchment window (fig. 2) with a central hole, 2 centimetres in diameter, cut out of the lead.

The Sn radiation was limited by this hole so that none of it fell on the screws or on the cylindrical portions of the vessel. The value thus found for λ was 3·89, nearly the same as before.

Experiments are at present being made to find directly the amount of corpuscular energy produced in a substance when a definite quantity of Röntgen radiation is absorbed by it. The results of these experiments can be applied to the redetermination of most of the numbers given in this paper by an entirely different method. The author hopes to clear up in this way the differences already mentioned.

Summary.

(1) The absorptions by hydrogen and air of cathode particles excited by homogeneous Röntgen radiations have been measured.

(2) It has been deduced from the numbers obtained that the amount of corpuscular energy set free in silver is roughly proportional to the energy of the exciting radiation absorbed by the silver.

(3) The relation between the absorption of the cathode particles by air and the absorption of the exciting homogeneous radiations by aluminium is nearly linear.

(4) The direct ionization in hydrogen relative to that in air has been measured when homogeneous radiations of different penetrating powers were used to cause the ionization.

(5) When a given set of cathode particles spends all its energy in producing ions in air or in hydrogen the total number of ions produced is the same in each gas.

(6) The penetrating power of the cathode particles has been found to be the same whether emitted from the emergent or incident side of the leaf.

I wish to thank Professor Sir J. J. Thomson for his interest in these experiments.

XXVIII. *A Difference in the Photoelectric Effect caused by Incident and Emergent Light.* *By* OTTO STUHLMANN, Jr., *A.B., Experimental Science Fellow, Princeton University*[*].

Introduction.

RECENT investigations have shown that the ionization produced by the secondary rays arising from a thin metal plate traversed normally by a primary beam of γ, Röntgen, or β rays, is greater on the emergent than on the incident side.

W. H. Bragg[†], in his work on the nature of the γ-rays and Röntgen rays, showed that if γ-rays pass through a thin plate so that the absorption is negligible, the amount of emergent radiation is greater than the incident. This remarkable want of symmetry he points to as appearing fatal to the æther pulse theory of γ-rays and, from their many points of similarity, of the Röntgen rays also. In a later paper on the nature of γ-rays W. H. Bragg and J. P. V. Madsen[‡] also show that this want of symmetry holds for both γ and β-rays. This lack of symmetry for secondary Röntgen rays was also discovered by W. H. Bragg and J. L. Glasson[§]. They showed that this want of symmetry was in general more pronounced for the softer rays than for hard rays. That the proportion of emergent to incident radiation differed considerably for the different radiators, but was much the same for different thicknesses of screen, except that the proportion tended to increase slightly as the screen was made thicker ; and the tendency was most pronounced in the case of those metals which gave out a quantity of soft secondary radiation, the emergent secondary rays being generally in excess of the incident.

The present experiments were made to see if there was any difference in the photoelectric effect caused by the incident light and the light which emerged after passage through a thin metal film.

Apparatus.

Thin films of platinum were prepared by sputtering *in vacuo* from a platinum cathode on to quartz plates 1 mm. thick. Two plates were sputtered simultaneously so as to insure the same thickness for both films. These were now mounted in the centre of two similar brass cylinders A and B

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[*] Communicated by Prof. O. W. Richardson.

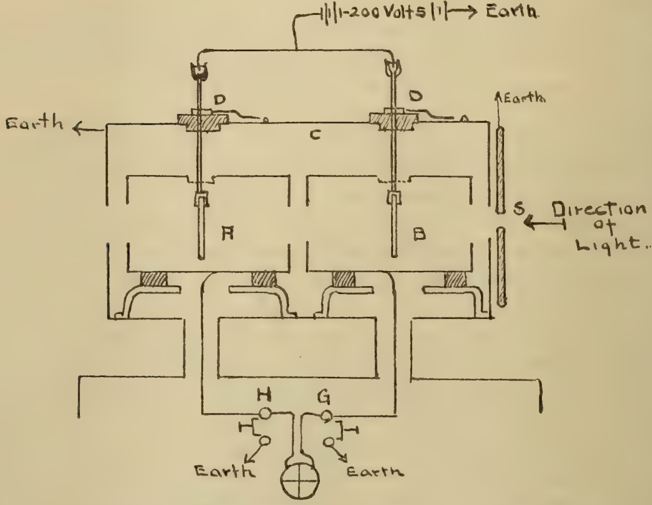
[†] Bragg, 'Nature,' lxxvii. pp. 270–271, Jan. 23, 1908.

[‡] Bragg and Madsen, Phil. Mag. xvi. pp. 918–939, Dec. 1908.

[§] Bragg and Glasson, Phil. Mag. xvii. pp. 855–864, June 1909.

(fig. 1), so that their planes were perpendicular to the axes of the cylinders. The plates had an area of one square centimetre, with parallel faces, although not ground optically accurate. The corners were ground round to prevent leakage to the cylinders. They were mounted in brass clamps supported through the top of an earthed metal chamber, C, by means of hard rubber bushings. A pointer, D, attached to the supports, with suitably arranged stops allowed them to be turned around their axes. The plates were connected to the negative terminal of a 200 volt battery, the other terminal of which was grounded. Experiments showed that this was sufficient to produce saturation.

Fig. 1.



The brass cylinders, 5 cm. long and 2·5 cm. in diameter, were provided with caps the opening through which was 1·5 cm. in diameter. This insured against the possibility of having photoelectric ions drawn over into the adjoining cylinder. The cylinders, resting upon sealing-wax supports, were connected with a Dolezalek electrometer, giving about 900 divisions deflexion per volt, which was placed in an adjoining metal case connected to earth. A narrow beam of ultra-violet light, stopped down to 2 mm. by the opening at S, was allowed to pass down the axes of the two cylinders normally to the plates. An arc, with both rods made of soft iron, running on 4 amp. direct current, was used as the source of ultra-violet light. It was enclosed in a light-tight box provided with a shutter, by which the beam of light passing through the apparatus was controlled. The distance of the arc from the plate B was 55 cm., and from the plate A 60·5 cm.

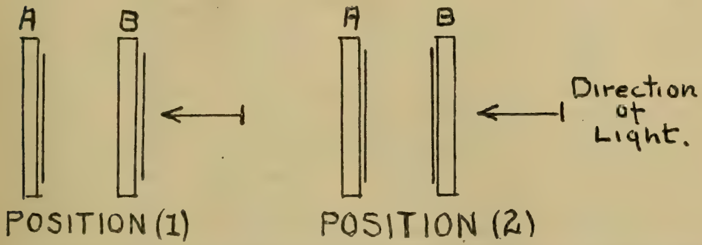
Method of Experimenting.

The saturation current from the illuminated plates to the cylinders could be measured by the following differential method. The keys G, H were opened simultaneously. A beam of light was then thrown on the plates until a measurable deflexion of the electrometer was attained. This deflexion was equal to the difference in the saturation currents from A and B. A was then grounded by connecting G to earth ; the resulting deflexion giving the saturation current from B. The difference between these two readings gave the corresponding reading for A.

The experiment consisted in measuring for various thicknesses of metal films, the saturation current for two successive positions of the plates (fig. 2).

Position (1), A and B so placed that their film side faced the light.

Fig. 2.



Position (2), A with the film side towards the light, and B with the film side away from the light.

Readings were taken alternately for Positions (1) and (2). Thus in every experiment two similar plates with equal thickness of metal films were used, and the ratios of the saturation currents A/B for Positions (1) and (2) successively determined. Hence it is seen that the plate B is always compared for each of the two Positions with plate A. Thus by always referring the measurements to A, the standard plate, the otherwise troublesome variations of intensity of the arc were rendered harmless. Unless the films were very thick it was always found that A/B for Position (1) gave rise to a relatively greater photoelectric effect than the ratio A/B in Position (2), although in the latter case the emergent beam of light was obliged to pass through the quartz plate before affecting the film.

The object of the investigation is the comparison of the ionization due to incident and emergent beams of light of the same intensity. A legitimate way of measuring this intensity is by means of the photoelectric effect such beams produce. Different observers have shown that beams of similar composition under similar conditions produce a photoelectric effect proportional to the intensity of the light, unless the intensity is very small.

If there were no difference in the photoelectric effect produced by incident and emergent beams of the same intensity, the value of the ratio A/B for Position (1) should always be less than that of A/B in Position (2), on account of the absorption by the quartz plate and by the film. As a matter of fact the reverse was always found to be the case with thin films, showing that the ionization is greater for an emergent than an incident beam of the same intensity. It is not difficult to allow for the absorption by the quartz plate, as will be shown below, but the absorption by the film is a more serious matter. This arises from the fact that these films are so thin that the electrons must be regarded as produced throughout the volume of the film. The method was therefore adopted of seeing if the value of the ratio of the fractions A/B in the two positions did not approach a limiting value, as the thickness of both films was indefinitely diminished. This was found to be the case, as will be seen in the sequel. Under these circumstances one could be certain that the limiting value corresponded to the case in which the absorption of the light by the film was negligible; so that, after allowing for the absorption by the quartz plate, the only difference between the ratio A/B in the two positions in the limiting case will arise from a difference in the ionization produced by incident and emergent beams of equal intensity.

The following table gives a set of readings characteristic

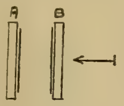
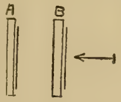
Platinum Set 20.

Position (1).				Position (2).			
B−A.	B.	A.	A/B.	B−A.	B.	A.	A/B.
20·0	76·0	56·0	·736	...	...	...	...
27·0	99·3	72·3	·726	39·0	115·0	76·0	·661
25·0	95·0	70·0	·737	25·0	70·5	45·5	·647
31·0	115·0	84·0	·731	31·0	88·5	57·5	·649
35·0	140·0	105·0	·750	35·2	102·8	67·6	·657
27·0	99·0	72·0	·729	26·0	74·0	48·0	·649
42·0	178·0	136·0	·763	42·0	118·0	76·0	·644
30·0	117·5	87·5	·744	38·0	108·0	70·0	·649
		Average	·739			Average	·651
			Ratio $\frac{(1)}{(2)}$	=1·13			

of the experiments on very thin films of platinum. The maximum deviation from the mean is about 1·5 per cent.

By changing the thickness of the films the following values were obtained:—

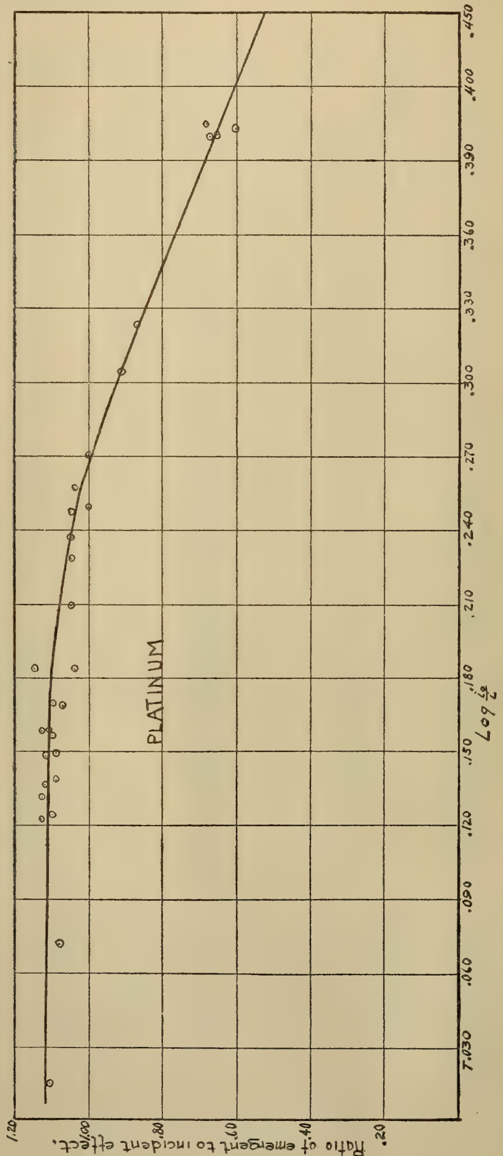
Platinum.

No.			Ratio $\frac{(1)}{(2)}$.	Log $\frac{B}{A}$ Position (1).
	$(2)=\frac{A}{B}$.	$(1)=\frac{A}{B}$.		Equal to log $\frac{i_0}{i}$.
a	·590	·398	·674	$\bar{1}$·399
b	·652	·726	1·09	·138
c	·651	·739	1·13	·131
d	·587	·617	1·05	·209
e	·647	·708	1·09	·149
f	·573	·656	1·14	·183
g	·531	·552	1·04	·257
h	·534	·536	1·00	·270
i	·624	·694	1·11	·158
j	·632	·657	1·04	·182
k	·632	·708	1·12	·148
l	·644	·730	1·12	·136
1	·534	·536	1·00	·271
2	·628	·696	1·10	·156
3	·635	·679	1·07	·168
4	·639	·719	1·12	·143
5	·622	·677	1·10	·169
6	·549	·578	1·05	·237
7	·550	·475	·863	·323
8	·536	·566	1·05	·247
9	·545	·496	·910	·304
10	·611	·397	·649	·400
11	·660	·394	·600	·404
13	·561	·590	1·05	·228
16	·582	·685	1·17	·164
20	·615	·694	1·13	·158
22	·866	·966	1·11	·015
24	·666	·754	1·13	·122

From the above data we see that the effect is a function of the thickness. It was found impossible to determine the thickness of these very thin films directly. From the ratio of A/B in Position (1) it is possible, however, to compare their relative thicknesses with accuracy. For it is known that when light traverses an absorbing medium the logarithm of the intensity varies as the thickness of the medium traversed. Hence from the preceding arguments it will be seen that values of log B/A Position (1) (equal to log i_0/i) will be proportional to the thickness of the film plus that of the quartz plate used.

Hence a curve (see fig. 3) between the ratio of emergent to incident effect plotted against log i_0/i will be identical in form with that plotted against thickness.

Fig. 3.



It is seen from the curve (fig. 3) that as the metal decreases in thickness the emergent beam gradually becomes more predominant in its effect, until a certain thickness is reached where the ratio of emergent to incident light attains a constant value 1·12 to 1·0. The ratio remaining constant over so large a range of thicknesses for the thin films of metal, shows conclusively that the absorption of light and electrons by these films as the beam of energy passes through them is negligible, and falls within the experimental error. So that the intensity of the incident and emergent beams must be sensibly equal, and hence the value arrived at above must be a true difference between the incident and emergent light.

Relative Absorption of Quartz Plate.

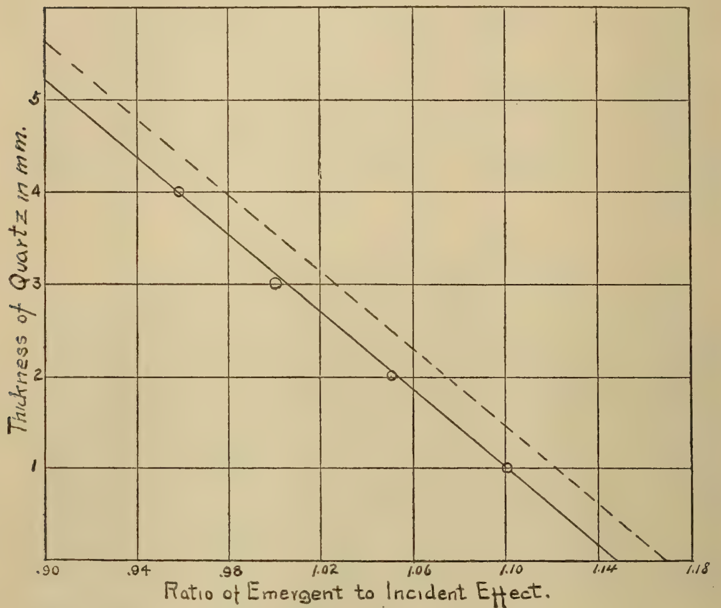
In order to determine how much of the emergent beam was absorbed by the 1 mm. quartz plates, upon which the films were mounted, the following method was resorted to. A relatively thick film was sputtered on a 1 mm. quartz plate. A thick film was preferably used because less error was involved in the measurement of its photoelectric effect, since for equal intensities of light relatively thicker films gave a larger photoelectric effect per unit time of exposure to the light. With this film the experiments for Position (1) and Position (2) in fig. 2 were repeated, and its ratio of emergent to incident effect noted.

A second blank quartz plate 1 mm. thick was now rigidly fastened to the blank side of the sputtered plate B. So that now the light had to pass through 2 mm. of quartz when the above readings were repeated. This was repeated for 3 and 4 mm. quartz plates by addition of a 2 and 3 mm. plate to the original 1 mm. sputtered plate B.

The results were then plotted as shown in fig. 4 (p. 338). It is seen that for a value of emergent to incident effect for the 1 mm. plate equal to 1·10, a value 1·15 should have been attained if no quartz had been present. So that plotting the curve for 1 mm. quartz equal to 1·12 for very thin films, parallel to the original curve, we get a value for the ratio of the emergent to the incident beam equal to the ratio 1·17 to 1·0, or an increase of 17 per cent.

The above results have been confirmed by reversing the direction of the light. For this purpose a speculum metal mirror was placed so that the reflected beam of light could be alternately sent through the cylinders in opposite directions without changing the position of the plates. Experiments were also made to determine whether a slight deviation from the normal, on the part of the plates, would affect the results. A change of five degrees in the position of the plates showed no measurable effect. Blank quartz plates placed in the cylinders gave negative results. A test for photoelectric effects arising from scattered light gave no measurable effects, since the aim in the design of the apparatus was to use so small a beam that it cleared all openings in the apparatus and the reflected beams passed out, back through the openings, through which the incident beam entered.

Fig. 4.



An attempt was made to estimate the absolute value of the thickness of the thin films used, by measuring their resistance. For this purpose "Set 2" of the above data was used. In order to get proper electrical connexions the two opposite edges of the film were silvered by means of the Rochelle Salt Method. Thus a strip of metal film ·78 cm. long and 1 cm. wide was left exposed. Fine copper wire was wound around these edges and electroplated, by means of a copper deposit, to the silver below—thus furnishing a good connexion between the copper wire and the film of platinum. This was now placed in one arm of a Wheatstone's bridge and its resistance measured. Using a value of the specific resistance for thin platinum films equal to 5×10^{-5} ohm as found by Patterson[*], a value for the thickness was found comparable to $\cdot 3 \times 10^{-6}$ cm. Hence the thinnest films used were evidently of order 10^{-7} cm. in thickness. Similar values were found by Patterson for the thinnest films measured by him.

Experiments on other metals are now in progress which will determine the variation of this forward effect with the atomic weight of the element.

Conclusion.

The above experiments show that when beams of ultra-violet light of equal intensity are compared, the ionization they produce is greater on the emergent than on the incident side of a thin platinum film. For a film so thin that the absorption of the light in it is negligible, the ratio of the ionization on the emergent to that on the incident side is as 1·17 is to unity. There is thus an increase of 17 per cent. in favour of the emergent side of the film.

An effect of this kind would obviously be expected on any corpuscular theory of light. It can also be explained on an undulatory theory by a process of the nature of light-pressure, which tends to push the electrons forward in the direction in which the light is propagated. In its ordinary electromagnetic form, however, the undulatory theory does not appear to give rise to effects large enough to explain the phenomena observed. The difficulty appears to be similar to that which arises when the ordinary theory attempts to explain why the ultra-violet light is capable of causing the expulsion of the electrons, with their observed properties, under any circumstances.

This investigation was suggested by Professor O. W. Richardson, and I wish to thank him here for valuable suggestions and advice throughout the course of the work.

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Princeton University.

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[*] J. Patterson, Phil. Mag. iv. p. 663 (1902).

XXIX. *The Relation between Uranium and Radium.*—V.

By FREDERICK SODDY, *M.A.*, *F.R.S.*

IN the last paper on this subject (IV., Phil. Mag. Dec. 1909, p. 846) details were given of the measurements of the quantities of radium in the three uranium solutions, purified by Mr. T. D. Mackenzie some years ago. It was shown that, within the supposed error of measurement, the growth of radium was proceeding at a rate proportional to the square of the time, and the period of the long-lived intermediate parent of radium (ionium) was deduced from this to be 18,500 years in the case of one solution and 26,000 years in that of another. Subsequent measurements have not confirmed these conclusions, and the former apparent rate of growth of radium according to the square of the time has not been maintained in any of the three solutions. A recent redetermination of the constant of the instrument with two of the former standards has shown that it has changed appreciably, the electroscope having become apparently *more sensitive.* The "constant" † is now 5·2, whereas the last calibration tests, carried out over a period between 350 and 250 days previously, had given the mean value of 5·78. Such a change was not anticipated, as neither the electroscope nor its reading microscope has been in any way moved or altered in adjustment since first set up, and both have been kept exclusively for these measurements.

It is very difficult to get a method of checking the sensitiveness of an instrument of this character accurately, which shall be quite free from uncertainty. It is necessary to use a standard solution containing a minute amount of radium, and, as is well known (Mme. Curie, *Le Radium*, 1910, vii. p. 65), these tend to change with time, the amount of radium apparently diminishing, very possibly through the solution of a precipitating constituent from the glass. For fear of this I made some of my standards with very minute quantities of radium (as low as 5×10^{-11} gram). It is unlikely, however, that the quantity of radium could *increase*, as it would have to do in this case to explain the change of the constant of the instrument. In the same paper, however, Mme. Curie called attention to variations amounting to 5 per cent. or more in the estimation of radium by means of the emanation when periods of accumulation longer than 48 hours are employed. Some other indications of a possible "radium X"

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* Communicated by the Author.

† The constant is the number of units of radium (10^{-12} gram) required to produce unit leak, *i. e.* one division a minute.

intermediate between radium and its emanation were also obtained. A freshly crystallized radium chloride appears to suffer a slow augmentation in the rate of production of the radium emanation, whereas a solution from which the radium had been precipitated by sulphuric acid gave a progressively diminishing rate. Still more recently Hahn and Meitner (*Phys. Zeit.* 1910, xi. p. 493) have observed a continuous increase in the activity of a radium salt for many weeks after the emanation has reached equilibrium, to a value more than twice as great as the original equilibrium value, which they regard as indicative of the existence of a radium X. So that it is possible that the apparent variation of the sensitiveness of the electroscope may admit of another explanation.

However this may be, in view of the results obtained during the past year with the uranium solutions, it is necessary to withdraw the estimates of the period of the intermediate parent of radium given in the last paper, and to treat the results as affording data for the calculations of the minimum period, but not as furnishing satistactory evidence so far of the production of radium *from uranium.* I do not think there is any doubt that a steady increase in the amount of radium in all three solutions is taking place, but, as pointed out in a previous paper, this may be explained by the possible presence from the start of a minute quantity of the long-lived parent of radium which I have shown is present in commercial uranium salts in quite easily detectable amount.

With regard to the minimum period the solution containing 408 grams of uranium purified on 13/12/06 gives the most definite results on this point. When last tested, three and a half years from purification, it contained between 8 and 9 units of radium. Seven good measurements have been made on this solution in the last two years, some of which were detailed in the last paper. Even if it be assumed that initially both radium and its parent were completely absent, which is an unlikely supposition, and that the radium present now has all actually been formed from the uranium in the three and a half years, the period of the long-lived intermediate body, supposing there is but one, must be between 37,500 and 33,300 years. There is thus little doubt that the estimates in the last paper were too low, and that there are not as yet sufficient data from which to set an upper limit to this period. There are many reasons for thinking it may even be many times the minimum period assigned, and some of these reasons are discussed in the next two papers.

It thus becomes a matter of considerable importance in the present state of radioactivity to fix at least an upper limit for the period. This could readily be done with the preparation of thorium oxide described by Stefan Meyer and Egon v. Schweidler (*Wiener Anzeiger*, Sitzung. 11/6/09) which has been separated by Auer v. Welsbach from the products obtained by Haidinger and Ulrich (*Wiener Ber.* 1908, cxvii. p. 621) from the radium residues of 30 tons of Joachimsthal pitchblende, and which is stated to contain about 0·25 per cent. of ionium. This, however, appears to have been obtained from measurements of the α-ray activity, by assuming for the substance a period the same as for radium, whereas the period and also the percentage of ionium is at least fifteen times greater. A maximum limit to the amount of ionium present could be fixed by subtracting from its total mass the mass of thorium oxide present. The latter could be determined by comparing the amount of thorium emanation generated in a solution, preferably boiling, of the substance with that from a standard thorium solution of the same age since preparation under the same conditions (Rutherford and Soddy, Phil. Mag. 1902, iv. p. 378). The maximum period of ionium required is simply given by dividing the maximum limit that can be assigned to the mass of the ionium by the mass of radium generated by the preparation in one year. This would fix the period between two limits, and however wide apart they proved at first to be, a very valuable step would have been made.

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XXX. *The Rays and Product of Uranium X.*—II.

By Frederick Soddy, *M.A., F.R.S.*[*]

THE conclusions in the preceding paper as to the minimum period of ionium modify essentially the deductions previously drawn from the behaviour of the uranium X preparations separated from 50 kilograms of uranium nitrate (Phil. Mag. 1909, xviii. p. 858), and it is desirable to give some account of the further progress of this work. It was pointed out that the failure to observe the growth of an α-radiation during the decay of these preparations was inconsistent with the measurements of the rate of production of radium from uranium if uranium X were really in the uranium–radium series. As, however, it has just been shown that the period of ionium was probably greatly underestimated, this failure rather affords additional evidence confirming the extremely long period of this body. Using

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[*] Communicated by the Author.

the new minimum value of 35,000 years instead of the old value of 18,000 years for the period, it follows that the maximum growth of α-rays to be expected from the uranium X preparations corresponds to only 5 divisions a minute, and the detection of this would have been doubtful. Whereas, if, as is not improbable, the real period is much longer than this, the theoretical growth of α-rays becomes certainly too small to be detectable.

In all the preparations the β-rays have decayed normally, so far as can be seen, and in the older preparations are now scarcely detectable. For all the preparations, measurements of the α-radiation by the method and apparatus previously described can now be done without exciting the magnet, and practically the same results are now obtained for the α-radiation, whether the magnet is excited or not. This shows that the method is trustworthy, and that the small proportion of β-rays escaping deviation did not interfere with the initial measurements of the feeble α-radiation, when the preparations were intensely active. This proportion can now be accurately calculated from the known constant of decay, 0·0282 $(\text{day})^{-1}$ (Soddy and Russell, Phil. Mag. 1910, xix. p. 847). About $\frac{1}{750}$ part of the β-rays escape deviation, and therefore it would appear must possess a value for $H\rho$ above 8640.

Most of the preparations have now decayed sufficiently far for the α-radiation to be accurately measured in an ordinary electroscope. There certainly has been no increase in the α-rays. Indeed, the results rather indicate a very slow decay; but more time must elapse before this can be verified.

With regard to the α-ray measurements in hydrogen with the magnet, the results with all the preparations show practical constancy from the start, and the small variations are doubtless due to unavoidable changes in the atmospheric conditions at the time of measurement. The following table refers to the observations with the preparation of the fourth separation. The first 10 observations previously given (*ibid.* p. 863) varied between 37·1 and 40·5, with 38·9 as the mean.

Time (days) ...	0–33 (Mean of 10)	61	75	198	284
α-rays	38·9	39·9	39·5	36·9	38·0

The preparations of the second and third series have behaved quite similarly. The oldest of these was prepared nearly 18 months ago. Any change has been in the nature of a slight decay rather than an increase.

Measured in an ordinary cylindrical electroscope (13 cm. high by 10·5 cm. diameter), the α-activity of the more active of the preparations, namely, those first prepared and therefore containing most of the initial impurities in the uranium, are comparable with that of a similar surface (10 sq. cm.) of uranium oxide. The least active preparations (those of the third separation) possess only about a third of this activity. For the latter it can easily be calculated that the permanent α-radiation produces only about $\frac{1}{4000}$ part of the leak which would have been produced in the same electroscope initially by the β-radiation. The calculated initial β-activity of each of the more active preparations corresponds to about half a million scale-divisions per minute. That produced by the α-rays per sq. cm. of uranium oxide surface is about 44.

Other tests have been done to detect a possible growth of actinium in the preparations. The method employed consists in placing closely over the (positively charged) platinum tray containing the preparation a negatively charged brass plate, removing the latter after a definite period, and measuring its α-activity and its rate of decay. Evidence of actinium was first found when the first preparation had decayed far enough to allow of measurements in an ordinary electroscope. The readings steadily increased after inserting the preparation due to an emanation being generated. The active deposit test showed that actinium was undoubtedly present. The activity of the active deposit decayed to half-value in 37·5 minutes, with an initial delay characteristic of actinium A. After two hours exposure the activity obtained initially increased the natural leak of the electroscope about 10 times, and corresponded to the specific α-activity of 0·65 sq. cm. of uranium oxide. The second preparation gave a detectable active deposit, but it was only one-fifteenth as much as the first. In the single preparations of the third and fourth separations, no actinium whatever could be detected. Quite recently, a combined test with all four preparations of the third and fourth separations showed a just detectable active deposit. Naturally these observations will be continued. Some of them have been in progress seven months, and have shown that if a growth of actinium occurs at all it must be very slow. Its presence in the first preparations may therefore be ascribed to initial impurities in the uranium, which are rapidly separated by the successive crystallizations.

The general result of this investigation is to show that uranium X loses its activity completely without the formation of any product possessing a detectable radioactivity. We must therefore suppose either (1) that uranium X is not in the uranium-radium series, (2) that long-lived new rayless products must exist in the series, or (3) that if uranium X changes directly into ionium the period of the latter must be greater than 30,000 years. There is good reason to believe that the last explanation may prove correct; so that to achieve the object for which the investigations were commenced still larger quantities of uranium must be dealt with, or the methods must in some way be greatly improved.

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XXXI. *The Ratio between Uranium and Radium in Minerals.* *By* FREDERICK SODDY, *M.A., F.R.S., and* RUTH PIRRET, *B.Sc.*[*]

MLLE. GLEDITSCH (*Compt. Rend.* 1909, cxlviii. p. 1451; cxlix. p. 267), in a reexamination of the ratio of uranium and radium in minerals, found small but distinct variations in the ratio for Ceylon thorianite, Joachimsthal pitchblende, and French autunite. Thorianite being probably a very old mineral and autunite a very recent one, the results suggested that the older the mineral the greater the ratio of radium to uranium. Neither Boltwood nor Strutt in their original determinations of this ratio refer to autunite, but the latter included thorianite (Phil. Mag. 1905, ix. p. 599; Proc. Roy. Soc. 1905, A. lxxvi. p. 88). Mlle. Gleditsch first separated the radium chemically from the minerals before estimating it; and it seemed very desirable to repeat the work, determining the radium in the usual way, without carrying out this separation. This has been done for specimens of the three minerals mentioned, the radium having been estimated by comparison of the amount of radium emanation generated, after periods of accumulation of a month or longer, in solutions of the minerals containing a fraction of a milligram of uranium preserved in sealed flasks. For Joachimsthal pitchblende we employed standards I. and V., previously used for calibrating the electroscope, and described by one of us in an earlier paper (Phil. Mag. 1909, xviii. p. 849), where a full description of the method of estimating the radium is given. So far attention has been mainly directed to thorianite; for, as Mlle. Gleditsch

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[*] Communicated by the Authors.

points out, it is more difficult to explain why a mineral should possess a greater than normal ratio of radium to uranium than the reverse. But the results with this mineral are not yet decisive. However, the results with autunite are of interest in connexion with the subject discussed in the preceding paper, so that it seems advisable to give an account of what has so far been done. The thorianite solution for the radium estimations was made by dissolving sixty milligrams of the powdered mineral in nitric acid, which had been distilled over barium chloride, diluting without filtering to a known weight and sealing up a known fraction, determined by weighing. The specimen of thorianite used left about 3·5 per cent. of residue insoluble in nitric acid. Previous experiments had shown that this residue, when examined in an electroscope, was practically free from radioactive matter. No β-activity whatever could be detected in the insoluble residues from 16 grams of the thorianite, used in the analyses, which had been sealed up in test-tubes for four months. Therefore neither uranium nor radium could have been present in appreciable amount.

The autunite employed was of Portuguese origin and consisted of beautiful crystals of the pure mineral in a clayey matrix. Twenty grams were used, and the whole of the autunite, consisting of about 40 per cent. of the total mineral, was dissolved out in hydrochloric acid. The residue was sealed up in a test-tube. After a month no β-activity whatever could be detected from the tube, showing that the whole of the uranium and radium had been dissolved. In the hydrochloric acid solution the uranium was estimated in one part and the radium in another.

Estimation of Uranium in Thorianite.—The method mainly employed was based upon the one described by Boltwood (Am. J. Sci. 1908, xxv. p. 269), and used by him in estimating the amount of uranium in many minerals (including thorianite) containing uranium and thorium. We found however that, as described, it was impracticable for the following reason. The solution of the mineral in nitric acid after removal of the lead with sulphuretted hydrogen is evaporated to dryness at 110°. In Boltwood's description the uranium is mainly removed from the dry residue by extraction with pure dry ether. The part insoluble in ether is then dissolved in dilute nitric acid, treated with oxalic acid to remove thorium and other rare earths. After removal of oxalic acid by ignition the dissolved residue is treated with ammonium carbonate and sulphide to remove iron &c. and the uranium, recovered from the filtrate by boiling, is joined to that from the ether extraction. However, we found that the ether extract contains actually more thorium than uranium. This was proved for the aqueous solution of the evaporated ether extract, both by precipitating with oxalic acid and by tests on the amount of thorium emanation generated. So the thorium and other rare earths were precipitated with oxalic acid from both the ether extract and residue. But it was found that the extraction was quite unnecessary, the same results being obtained whether it was employed or not. The uranium finally in some cases was precipitated by ammonium sulphide, and weighed as U_3O_8 after ignition in oxygen; in others, as phosphate by microcosmic salt and sodium thiosulphate (Brearley, Analytical Chemistry of Uranium, p. 7).

Five analyses were performed of the uranium which gave results comprised between 19·74 and 20·56 per cent. of uranium. The mean, which agreed well with the three most satisfactory determinations, was 20·0 per cent.

For autunite the uranium was precipitated as phosphate by microcosmic salt and sodium thiosulphate in presence of free acetic acid.

Ratio of Radium to Uranium.—The results are given in the following table. In the first column is given the name of the mineral, in the second the quantity of uranium in the solution employed, in the third the leak of the electroscope in divisions per minute, and in the last the leak per milligram of uranium. If the ratio of uranium to radium is the same for all minerals, the figures in the last column should be constant.

Mineral.	Uranium (milligrams).	Leak.	Leak per mg. Uranium.
Pitchblende	0·308 0·149	20·3 9·7	65·9 65·1 Mean 65·5
Thorianite	0·613	41·5 41·1	67·7 67·0 67·4
Autunite	0·834	24·3	29·1

Thus the ratios for thorianite and pitchblende come out very nearly the same, the thorianite being about 3 per cent. higher than pitchblende; while for autunite the ratio is very low, being less than half (44·5 per cent.) of that of pitchblende.

The measurements, therefore, so far as they have gone bear out those of Mlle. Gleditsch, in that they show the ratio is not constant in the three minerals. But pitchblende and thorianite are so near that the difference can scarcely be regarded as significant. It must be remembered that the figures for pitchblende depend upon the accuracy of the uranium estimation in the standards prepared previous to this work, for the purpose of calibrating the electroscope. There is no reason to doubt the accuracy of these analyses, but the results call for further measurements with other samples of both minerals before the matter can be considered settled. The specimen of thorianite selected was the purest,—that is to say, the one containing the least foreign matter insoluble in nitric acid,—of many which have been examined. But its uranium content is unusually high, and the specimen in this respect cannot be considered representative. One curious circumstance should be recorded. In the paper immediately preceding this it is shown that the constant of the electroscope has changed apparently since these pitchblende standards were first prepared. This change was actually discovered in the course of the present work. The ratio of radium to uranium in thorianite appeared, using the original value of the constant of the instrument, to be about 18 per cent. higher than for pitchblende, which is almost exactly what Mlle. Gleditsch found. But a redetermination with the old standards brought to light the change of sensitiveness of the electroscope; and although the corrected ratio is still higher for thorianite than for pitchblende, the difference is so small that it cannot be accepted without further confirmation. The point at issue is rather a fine one, and calls for a degree of accuracy not easily obtained in such measurements.

As regards autunite, however, the variation in the ratio for the specimen examined (of Portuguese origin) is far greater than that found by Mlle. Gleditsch for French autunite. The Portuguese autunite has little more than half the radium in the French autunite. The natural explanation of these results is that the mineral is of so recent formation that the uranium-radium series is not yet in equilibrium. In the preceding paper it is shown that the period of ionium is *at least* 35,000 years; and if the autunite examined were of very recent formation, this result is to be expected. The extremely recent formation of autunite is indirectly borne out by the work of Marckwald and Keetman (*Chem. Ber.* 1908, xli. p. 49), who could not find any lead in a crystal of autunite, though ·01 per cent. could have been detected. Recently J. A. Gray (Phil. Mag. 1909, xviii. pp. 816 and 937) has estimated the amount of lead in autunite spectroscopically to be only of the order of ·005 per cent. Assuming a direct change of uranium into lead, this quantity should be formed in a million years*. The results of Mlle. Gleditsch and ourselves with autunites therefore can be taken as confirmatory evidence of the existence of at least one intermediate body of very long period between uranium and radium. Incidentally they indicate that Portuguese autunite is considerably more recent than the French mineral, and indeed it would appear not improbable that the Portuguese mineral has been laid down within a period not very many times longer than that covered by historical records.

In the present state of the subject the possibility has to be taken into account that the two α-particles, known from the work of Boltwood (Am. J. Sci. 1908, xxv. p. 269), to be expelled from uranium may be due to two successive changes. The similar low range of these two α-particles is an argument, according to Rutherford's rule (Phil. Mag. 1907, xiii. p. 110), that the second change cannot be a very rapid one; and we are therefore faced with the possibility that uranium may be a mixture of two elements of atomic weights 238·5 and 234·5, which, like ionium, thorium, and radio-thorium, are chemically so alike that they cannot be separated. Now, if the element of atomic weight 234·5 had a period at all comparable to uranium, the ratio of uranium to radium must vary with the age of the mineral, both for very recent and for very old minerals, as Mlle. Gleditsch's results indicate. In this case the estimate of the minimum period of ionium given in the last paper, which depends on there being only one long-lived intermediate body, would not necessarily be fallacious, for by hypothesis uranium and its first product are so alike chemically that they cannot be separated.

To obtain evidence on this point the specific α-activities of specimens of uranium oxide separated from the three minerals were compared. On the view suggested, the specific α-activity of the uranium from autunite should be lower than that from pitchblende, and the latter should be lower than that from thorianite. Within 5 per cent. the specific α-activities of all three substances proved to be the same. The small differences can be well explained by experimental error and by the fact that in some of the preparations the β-radiation has not yet reached equilibrium. This, therefore, is fairly conclusive evidence that the variations in the uranium-radium ratio cannot be due to two successive slow α-ray changes in uranium itself.

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* The correction to 10,000 years on p. 937 of the same volume must be supplemented by a second correction bringing back the value to that first stated.

XXXII. *On the Statistical Theory of Radiation.*

By Prof. Sir J. LARMOR, *F.R.S.*[*]

IN the Philosophical Magazine for July (p. 122) Prof. H. A. Wilson, in a valuable review of my recent paper on the statistical theory of natural radiation[†], concludes that its procedure does not really evade the main difficulty, that an atomic constitution of energy must be implied in such investigations. One of the positions advanced in the paper was that the magnitude of the element of energy needed for the statistics might be chosen at will, provided the size of the elementary cell was chosen in a fixed proportion to it. Though such a theory has, and must have on the most favourable view, imperfect and provisional features, it does not appear to me that Prof. Wilson has established this formidable addition to their number, and for the following reason.

Using his notation, the heads of the argument there set out, perhaps too briefly[‡], were as follows. If S is entropy and W is the number of ways in which the system can be arranged in the actual state, then

$$\begin{aligned} S &= k \log W \\ &= k \log W_1 W_2 \ldots W_n, \end{aligned}$$

where $W_1, W_2 \ldots$ are the numbers for the parts of the system. If the first part contains n_1 elements of energy each of amount ϵ_1, contained in N_1 cells, and similarly for the others, then the total energy is

$$E = \epsilon_1 n_1 + \epsilon_2 n_2 + \ldots \epsilon_r n_r.$$

The natural state of an isolated system is the one that makes S maximum subject to E remaining constant. This requires

$$\frac{1}{\epsilon_1}\frac{\partial S}{\partial n_1} = \frac{1}{\epsilon_2}\frac{\partial S}{\partial n_2} = \ldots = \vartheta,$$

where $\epsilon_1 \delta n_1 = \delta E_1, \ldots$. Thus ϑ is a quantity the same for all the parts of a system which is in equilibrium of exchanges of energy: in fact if absolute temperature T is defined by the Clausius formula $dS = dE/T$, then ϑ is T^{-1}. Also the working out of the actual value of W_1 leads to

$$\frac{\partial S}{\partial n_1} = k \log\left(1 + \frac{N_1}{n_1}\right).$$

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[*] Communicated by the Author.

[†] Roy. Soc. Proc. 1909, vol. lxxxiii. A. pp. 82–95.

[‡] Errata should be noted: on p. 92 ϑ should be T; on p. 93 the factor $8\pi/\lambda^4$ should be $\lambda^4/8\pi$.

Thus, finally, for the distribution of energy among the parts of the system we have the formula (Planck's)

$$E_1 = n_1\epsilon_1 = \frac{N_1\epsilon_1}{e^{k\epsilon_1/T}-1}.$$

The argument of Prof. Wilson is that $E_1(=n_1\epsilon_1)$ as thus determined cannot be independent of the size of the energy-element ϵ_1, because ϵ_1 is the only variable that enters except N_1, which measures the extent of the system, so that any change of ϵ_1 must change the value of E_1, even though $\epsilon_1 N_1$ is kept constant: for example, if ϵ_1 is taken very small, the formula becomes

$$E_1 = N_1 k^{-1} T,$$

which represents the law of equipartition. But this unwelcome conclusion is evaded simply by recognizing that the value of k must be some function of the size of the energy-element which is taken as the basis of the statistics; it would indeed be strange if it were otherwise. If $k\epsilon_1$ remains finite as ϵ_1 diminishes, the equipartition is not attained unless T is very great. We shall find that it is $k\epsilon_1$ that is to be taken as constant when ϵ_1, the statistical element for any given type of energy, is changed.

The *two* independent constants in the formula are in fact $N_1\epsilon_1$ and $k\epsilon_1$. Their ratio $N_1 k^{-1}$ is equal to the gas-constant. That universal quantity, and $N_1\epsilon_1$ (say α) which is the ratio of the energy-element to the extent of a cell, are what affect the distribution and are thus of pre-determined values; but there seems to be nothing that demands a definite magnitude of the energy-element itself.

On the Boltzmann form of the theory of probability of distributions of energy among the molecules of gases, k turned out indeed to be the gas constant. On the present form of theory, which involves distribution of elements of disturbance with their appropriate energies in the containing system as mapped out into cells, instead of mere collocation of elements with regard to one another, this conclusion need not hold. We may probe this point further. It is known as a fact that, under ideal conditions, equable partition is very nearly attained as regards the translatory and rotatory parts of the energy of the molecules of a gas. This requires that, if ϵ_r is the value of ϵ corresponding to each of the translatory or rotatory types of freedom, it must prove to be so small compared with $\epsilon_1, \epsilon_2, \ldots$ that the exponent $k\epsilon_r/T$ is also small; for that is needed in order to lead to this law of approximately equable partition, in the form

$$E_r = n_r \epsilon_r = N_r k^{-1} T.$$

In this special result the value of the element of energy ϵ_r has become eliminated. Also $N_r k^{-1}$ must be the gas constant R; and since $N_r \epsilon_r$ must be α, another universal constant, we have $k\epsilon_r = \alpha/R$. Hence in this case of simple gas-theory the value of k should be inversely as the scale of magnitude of the elements of energy chosen; and the size of a standard cell should be directly as that element. And this result must be universal.

Thus the conclusion is, briefly, that to render the entropy independent of the scale of minuteness of sub-division of the statistics, as is natural, we have only to define it as $k \log W$, where the value of k (if we decide to retain it in the formulas) must vary directly as this amount of sub-division, or inversely as the scale of sizes of the elements of energy that are employed in the analysis. But, on the other hand, if k had the same value whatever be the scale of the statistics that is adopted, conclusions such as those of Prof. Wilson regarding the magnitude of the ultimate element of energy would necessarily follow.

To connect formally the values of ϵ, thus demanded by experimental knowledge for gas-theory, with those that obtain for the types of radiant energy, would involve a rather long argument. But the present type of theory works out for the domain of radiation as above, and it is readily seen that it works out for the domain of gas theory on the ordinary lines as indicated in the paper referred to; while a bridge can be constructed between the two, as there suggested, by noting that both for translatory and rotatory motions in gas-theory and for radiation of long wave-length, the principle of equipartition is practically effective, so that we may take advantage of Prof. Lorentz's train of ideas connecting these equipartitions by a calculation of the amount of the natural radiation from a thin metallic plate, considered as arising from the collisions of the moving free electrons that are required by its electric conductivity.

The existence of another universal physical constant (α), in addition to that of gas-theory, has been postulated without any explanation as yet. But its existence is independent of these statistical theories; and it thus seems to have come to stay in some form or other. In fact it was early pointed out by Wien and by Thiesen that the value $\lambda_m T$, where λ_m is the wave-length of maximum radiation at temperature T, and which is by Wien's displacement-law a universal constant, suffices and is required, in conjunction with the other recognized universal constants of nature, to establish an absolute system of fundamental units of mass, length, and time ; its dimensions are therefore not expressible in terms of those of other universal constants, and it must have an independent existence of its own.

Cambridge, July 4, 1910.

XXXIII. *The Amount of Thorium in Sedimentary Rocks. II. Arenaceous and Argillaceous Rocks.* *By* J. Joly, *F.R.S.*[*]

IN this paper the results of thorium measurements applied to detrital sedimentary rocks are given. The method used has been described in previous papers (Phil. Mag. May and July 1909). The rock is ground to a fine powder and passed through a sieve of 100 mesh to the inch. It is then mixed with from 2½ to 3½ times its weight of mixed carbonates (thorium-free) and fused in a closed platinum crucible till effervescence ceases. The melt is thrown while fluid into a platinum dish, and what remains in the crucible chilled and broken out. The fragments are then ground to a coarse powder in a mortar and leached in hot water over the water-bath. After standing all night the cold supernatant liquid is removed by decantation. The residue is ground to a paste in the mortar ; about 100 c.c. of water added, and finally 80 to 100 c.c. of strong HCl (thorium-free) rapidly stirred in. The final solution is seldom quite limpid. I have not found, however, that the presence of a small amount of precipitate interferes with the liberation of the emanation. Known quantities of a thorite solution added to such rock solutions, or mixed with the rock-powder before its decomposition in the crucible, produce the same effect upon the electroscope, sensibly, as do limpid aqueous solutions containing the same quantity of thorium.

The alkaline solution, which is poured off the insoluble part of the melt, contains very little thorium ; in most cases none that can be detected with certainty under the conditions of the experiment, whether the solution is acidified or not. The examination of the alkaline solutions has, therefore, not been carried out in every case. The investigation is tedious and generally indecisive, many hours of

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[*] Communicated by the Author.

observation being required (the electroscope being observed when the solution is alternately in ebullition and at rest) to detect with certainty a change amounting to a small fraction of a scale-division per hour. It may, I believe, be accepted as certain that what error may arise from confining the examination to the acid solution is very small, not more than a few per cent.

Table I. contains only arenaceous and conglomeratic rocks; mainly sandstones of various characters and ages. The greensandstone is, of course, a rock differing from the others in mode of origin. The sandstones are for the greater part constituted of residual quartz or of quartz and felspar, derived from older rocks. As the quartz is, itself, probably of very low thorium content, it is not surprising that these rocks are generally poor in thorium when contrasted with many igneous rocks. They are, however, much more radioactive than the calcareous rocks, in which, in most cases, the thorium emanation cannot be detected even when considerably larger quantities of rock are used in the experiments (Phil. Mag. July 1910).

TABLE I.

		Thorium. grm. $\times 10^{-5}$ per gram.
1.	Greensandstone. Werl, Westphalia. Cretaceous. (15)	0·20
2.	Sandstone. Obernkirchen, Teutoburger Wald. Wealden. (15)	0·30
3.	„ Vlotho, Westphalia. Keuper. (10)	1·14
	„ „ „ „ (17)	1·02
4.	„ (red). Heidelberg, Baden. Bunter. (20)	0·12
5.	„ Remiremont, Vosges. „ (20)	0·91
6.	„ Westhofen, Westphalia. Carboniferous. (15)	0·74
7.	„ Freienohl, „ „ (15)	0·61
8.	Quartz Conglomerate. Donebate, Co. Dublin. Old Red Sandstone. (14).	0·33
9.	Grauwacke-Quartzite. Allrode, Harz. Lower Devonian. (16)	0·74
10.	Quartzite (Taunus). Schlangenbad, Nassau. Lower Devonian. (15)	0·34
11.	Sandstone (red). Loch Torridon, Scotland. Torridonian. (19)	0·27
12.	Quartzite-schist. Western Spessart. Archæan (?). (17)	0·32
	Mean	0·54

In the above table the weight in grams of material dealt with is given in brackets.

The finer-grained detrital rocks—slates and shales—are, in contradistinction to the sandstones, derived from the more soluble and friable constituents of the primary rocks: such constituents as are reduced by denudative actions most readily to small dimensions. They are on this account precipitated furthest from the land, and represent materials from which the more resistant grains have been sorted by gravity. As the latter are generally quartz or felspar, and hence substances which in most cases are poor in radioactive constituents, it is to be expected that the argillaceous group of detrital rocks would reveal a more considerable richness in thorium than the arenaceous. Table II. shows that this is, indeed, the case. Comparison with Table I. shows that only two of the sandstones, Nos. 3 and 5, have quantities of thorium equal to those generally prevailing in the argillites. A few surface materials of recent date are included in the table. These possess the same degree of richness in thorium.

Table II.

		Thorium. grm. $\times 10^{-5}$ per gram.
1.	Brick-Earth. Rosslare, Co. Wexford. Recent. (18)	1·13
2.	Clay. Friesdorf, Bonn. Recent. (15)	0·91
3.	Loess. Heidelberg. Pleistocene. (18)	1·04
4.	Bundnerschiefer (folded). Piz Ot, Ober Engadin. Jurassic. (15)	0·91
5.	Schiste Lustré. Simplon Tunnel. Jurassic. (15)	1·04
6.	Red Marl. Ballymurphy, Co. Antrim. Keuper. (12)	0·14
7.	Roofing Slate. Wissenbach, Nassau. Upper Devonian. (15)	1·12
8.	,, ,, Caub, on the Rhine. ,, ,, (16)	1·40
9.	Slate. Valentia, Co. Kerry. Devonian. (15)	1·30
10.	,, (dark Killas). Cornwall. ,, (15)	1·16
11.	Grauwacke. Wipperfürth. Rhen-Prussia. Middle Devonian. (15)	2·40
12.	Clay-Slate. Mägdesprung, Harz. Lower Devonian. (15)	0·87
13.	,, ,, Weilburg, Nassau. Devonian. (14)	1·17
14.	Slate (green). Kingscourt, Co. Cavan. Silurian. (15)	1·30
15.	Phyllite (green). Lössnitz, Saxony. Lower Silurian (?). (15)	1·94
16.	Shale (black). Moffat, Scotland. Silurian & Ordovician. (10)	1·00
17.	Roofing Slate. Penrhyn, N. Wales. Cambrian. (16)	0·96
18.	Slate (Oldhamia). Bray Head, Co. Wicklow. Cambrian (?). (15)	0·82
	Mean	1·14

The highest result obtained, the Grauwacke No. 11, was checked by a second examination of the preparation, when the first result was almost exactly confirmed. The lowest, the Keuper Marl No. 6, refers to a material deposited under continental conditions, probably in inland waters, and is therefore of somewhat different character to the others. It contains very little calcium carbonate. Excluding this material, the general mean for the argillaceous group rises to $1·20 \times 10^{-5}$ gram thorium per gram. It will be noticed that there is a remarkable sameness in the foregoing results: fifteen rocks vary between the limits 0·82 and 1·40.

The results which I have already published (Phil. Mag. July 1909), when dealing with the St. Gothard rocks, are reproduced below. These rocks are regarded as for the greater part of sedimentary origin, although highly altered, and of Mesozoic age. Some are calcareous, some quartzose. It is, therefore, difficult to classify them with the materials grouped in the foregoing tables. The general means are, for the same reason, somewhat misleading. After subtracting from those of the Usernmulde two rocks of calcareous character, the mean for the Usernmulde (9 rocks) is $1 \cdot 10 \times 10^{-5}$. The mean for the Tessinmulde exclusive of the dolomite (7 rocks) $0 \cdot 53 \times 10^{-5}$. The first is in close agreement with that of Table II.: the second is too low; but the origin of some of the more basic rocks in the Tessinmulde is sufficiently doubtful to deprive the result of much of its weight.

Table III.

	Usernmulde.	Thorium. gram $\times 10^{-5}$ per gram.
1.	Usern gneiss. (11·14)	1·4
2.	Quartz-schist. (9·6)	1·1
3.	Black lustrous slate. (8·0)	0·2
4.	Grey cipolin. (9·47)	0·4
5.	Quartzitic cipolin. (11·36)	0·4
6.	Black lustrous slate. (10·66)	1 0
7.	Usern gneiss. (9·1)	1·3
8.	Sericite-schist. (8·0)	1·7
9.	Black lustrous schist (7·84)	2·4
10.	Quartz-mica. (8·16)	<0·3
11.	Usern mica-gneiss. (8·38)	0·5
	Tessinmulde.	
12.	Hornblende-schist. (8·64)	<0·3
13.	Calcareous mica-schist. (9 02)	0·5
14.	Hornblende " " (7·99)	0·6
15.	Amphibole garnet mica-schist. (8·38)	1·0
16.	Quartz-schist (9·5)	<0·3
17.	Amphibole mica-schist. (9·17)	0·5
18.	Quartz " " (8·8)	0·5
19.	Dolomite. (8·66)	0·4

If we assume that the results on sedimentary rocks, recorded in this and the previous paper on the subject, may be accepted as approximately representative, we find that whereas the calcareous rocks show a small, almost negligible, quantity of thorium, the detrital sediments contain easily measured amounts of thorium in almost every case; the argillaceous group having almost double the amount contained in the arenaceous group. The former may be taken as approximating to $1{\cdot}3\times10^{-5}$, making allowance for some small amount in the alkaline solutions; the latter to $0{\cdot}6\times10^{-5}$ gram per gram.

Accepting the estimate cited by F. W. Clarke ("A Preliminary Study of Chemical Denudation," Smithsonian Miscellaneous Collections, vol. lvi. No. 5, June 1910) that the calcareous rocks compose 5 per cent., the arenaceous 15 per cent., and the argillaceous 80 per cent. of the sedimentaries, my results on thorium measurements (assuming $0{\cdot}06\times10^{-5}$ to represent the mean for the calcareous rocks) give for the sedimentary rocks generally a thorium content of $1{\cdot}16\times10^{-5}$ gram per gram.

July 11th, 1910.

XXXIV. *The Magnetic Balance of MM. P. Curie and C. Cheneveau.* *By* C. Cheneveau, *with an Appendix by* A. C. Jolley [*].

THIS apparatus is intended for the measurement of the coefficient of specific magnetization, or the susceptibility or permeability of feebly paramagnetic or diamagnetic bodies [†].

Principle and Theory of the Apparatus.

The body whose magnetic properties are to be determined is suspended from one end of the arm of a torsion balance. By means of this balance the force is measured, which is experienced by the body when placed in a non-uniform magnetic field, produced by a permanent magnet whose lines of force cross the space occupied by the body. The method of calculating this force will first be briefly indicated.

Suppose that the body is placed at a point O in a field of direction Oy and of intensity H_y. The force f which tends to move the body will be normal to the direction of the field,

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[*] Communicated by the Physical Society: read April 22, 1910.

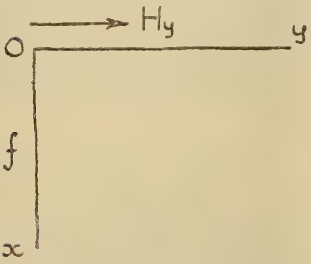
[†] The coefficient of specific magnetization K is the ratio of the intensity of magnetization $\mathcal{J}=\frac{M}{m}$ (where M is the magnetic moment and m the mass of the body) to the magnetizing field. The magnetic susceptibility $\kappa=K\Delta$, where Δ is the density of the body, and the permeability is obtained from the susceptibility by the relation $\mu=1+4\pi\kappa$.

i. e. in the direction Ox (fig. 1). If $\mathcal{J}$ is the intensity of specific magnetization, the value of the force is *

$$f=m\mathcal{J}\frac{\partial H_y}{\partial x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$\frac{\partial H_y}{\partial x}$ representing the space variation of the field.

Fig. 1.



As we are only concerned with feebly magnetic bodies, the demagnetizing force arising from the magnetization of the body is negligible, and we may assume that the intensity of magnetization is proportional to the field. If we denote the constant ratio between the intensity and field, or *coefficient of specific magnetization*, by K, we have

$$\mathcal{J}=KH_y, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

consequently combining equations (1) and (2)

$$f=KmH_y\frac{\partial H_y}{\partial x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Let us first suppose that the magnet producing the magnetic field is at a considerable distance from the body. Then $H_y=0$, and by (3) the force is zero.

The body being always situated at O, let the magnet be brought up to the position I (fig. 2). If the force f is one of attraction the body is of course paramagnetic, if of repulsion, diamagnetic †.

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* We have $f=\frac{\partial W}{\partial x}$, $W=MH_y$, and $M=\mathcal{J}m$.

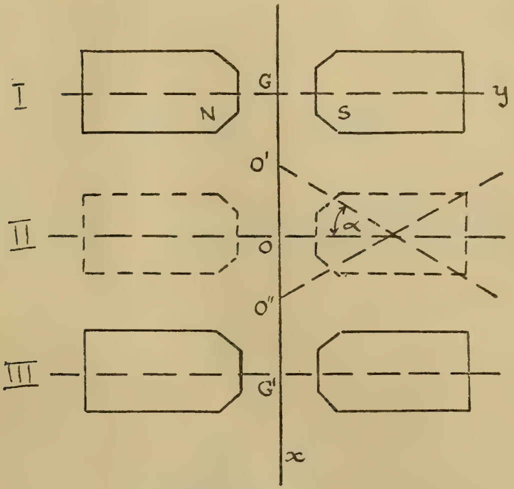
Hence $f=m\mathcal{J}\frac{\partial H_y}{\partial x}$.

† If the sense Ox is taken as positive and we employ the true formula for the force, $f=-\frac{\partial W}{\partial x}$ the negative sign for the force indicates attraction and the positive sign repulsion.

Suppose first that the body is paramagnetic.

When the magnet is situated so that the body O coincides with the centre G, the force will again be zero, as $\frac{\partial H_y}{\partial x}$ is zero at the centre (position II, fig. 2).

Fig. 2.

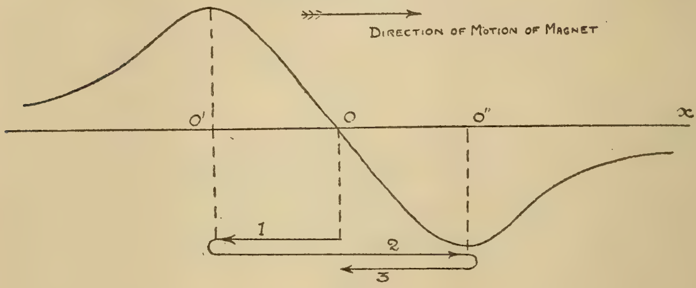


Hence the force f is zero when $x=\infty$ and $x=0$ and it passes through a *maximum* in the interval, which occurs at a certain point O′ where the product of the field H_y by its gradient $\frac{\partial H_y}{\partial x}$ is a maximum.

If the magnet is continually turned in the same sense of rotation, so that its centre G passes through the point O and arrives at G′ (position III, fig. 2), we observe that the force, which was nil at O, reaches a *minimum* or negative maximum at a point O″ symmetrical with O′, relatively to O, and becomes zero again after the magnet is withdrawn far from the body.

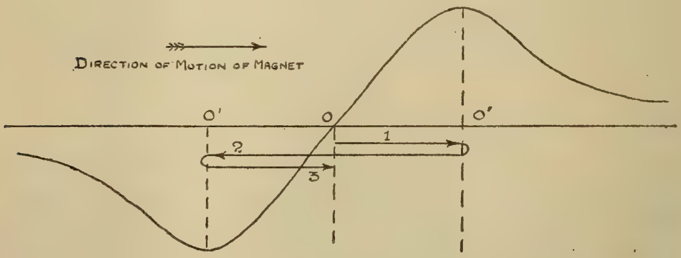
Hence the curve in fig. 3 shows the variation of the force f with the displacement x. The body is first displaced in the direction of the arrow marked 1 from O to O′, where it stops and moves back with the magnet along the arrow marked 2 to O″, where it again stops and afterwards returns to O, as shown by the arrow 3.

Fig. 3.



It is easy to explain in a similar manner the motions of a diamagnetic body which will of course be the reverse of the above, as the force is opposite in sign. Fig. 4 shows the curve in this case.

Fig. 4.



At every instant the action of the force is balanced by the torsion of the balance wire. If c is the moment of torsion per unit angle, and α the maximum deviation of the arm at O or O′ (fig. 2), the equilibrium condition is

$$fl=c\alpha, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

if l is the length of the balance arm.

If the deviation is measured by lamp and scale,

$$\alpha=\frac{\mathrm{D}}{2\mathrm{L}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

D being the deflexion of the spot upon the scale, and L the scale distance.

Hence from equations (3), (4), and (5)

$$\mathrm{K}m\mathrm{H}_y\frac{\partial \mathrm{H}_y}{\partial x}l=c\frac{\mathrm{D}}{2\mathrm{L}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

from which

$$\mathrm{K}=\frac{c\mathrm{D}}{2ml\mathrm{LH}_y\frac{\partial \mathrm{H}_y}{\partial x}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This formula (7) thus permits the *absolute value* of the coefficient K to be determined for a body if the other quantities are accurately determined. By an analogous method P. Curie * has determined the absolute value of the coefficient of specific magnetization of water.

But the apparatus is especially adapted for relative measurements, and in this case it becomes extremely simple and practical.

If we have a body of unknown coefficient K and of mass m, we have from equation (6)

$$\mathrm{K}m\mathrm{H}_y\frac{\partial \mathrm{H}_y}{\partial x}l=\frac{c\mathrm{D}}{2\mathrm{L}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For a body of known coefficient K′ and mass m' occupying the same volume

$$\mathrm{K}'m'\mathrm{H}_y\frac{\partial \mathrm{H}_y}{\partial x}l=\frac{c\mathrm{D}'}{2\mathrm{L}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Hence by division

$$\frac{\mathrm{K}}{\mathrm{K}'}\cdot\frac{m}{m'}=\frac{\mathrm{D}}{\mathrm{D}'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Equation (10) thus enables K to be determined.

It is evident that it is much more convenient to measure the displacements D and D′ of the spot corresponding to the angular deviations 2α and $2\alpha'$ between the two positions O′ and O″ of the body (fig. 2), for, without altering equation (10), the displacements of zero are eliminated and the accuracy of measurement doubled.

If the body is placed in a tube of glass or other substance, this tube being subjected like the body under test to the magnetic forces, an experiment must be made with the tube alone, and the effect due to the tube represented by a displacement of the spot D″ added or subtracted.

---

* P. Curie, *Annales de Chimie et de Physique*, 7ᵉ Série, t. v. p. 344 (1895).

We thus have

$$\frac{K}{K'}\cdot\frac{m}{m'}=\frac{D\pm D''}{D'\pm D''}\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \quad (11)$$

Whence

$$\frac{K}{K'}=\frac{D\pm D''}{D'\pm D''}\cdot\frac{m'}{m}\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \quad (12)$$

This formula is not corrected for the effect due to the magnetization of the air; the exact formula may be obtained as follows:

Let κ' and κ'' be the susceptibilities of the substance taken as standard, assumed to be paramagnetic, and of the air respectively. Let Δ' be the density of the comparison body, and A a constant of the apparatus. In reality the exact expression for the force when one deals with the standard body is

$$f'=(\kappa'-\kappa'')\frac{m'}{\Delta'}A=\left(K'-\frac{\kappa''}{\Delta'}\right)m'A, \quad . \quad . \quad (13)$$

since

$$K'=\frac{\kappa'}{\Delta'}.$$

When a measurement is made with a paramagnetic body of susceptibility κ and density Δ the true value of the force in this case is

$$f=(\kappa-\kappa'')\frac{m}{\Delta}A=\left(K-\frac{\kappa''}{\Delta}\right)mA. \quad . \quad . \quad . \quad (14)$$

Dividing (14) by (13) we have

$$\frac{f}{f'}=\frac{K-\frac{\kappa''}{\Delta}}{K'-\frac{\kappa''}{\Delta'}}\cdot\frac{m}{m'}$$

or

$$\frac{f}{f'}\frac{m'}{m}=\frac{K-\frac{\kappa''}{\Delta}}{K'-\frac{\kappa''}{\Delta'}}\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \quad (15)$$

If we put $r=\frac{f}{f'}\frac{m'}{m}$; this is the approximate ratio of the coefficients of specific magnetization K and K′ previously determined by the aid of formula (12)*.

---

* We have in fact, from what has been proved above,

$$fl=KmA=B(D\pm D''),$$
$$f'l=K'm'A=B(D'\pm D'');$$

A and B as well as l being constants; whence

$$\frac{f}{f'}=\frac{Km}{K'm'}=\frac{D\pm D''}{D'\pm D''}; \qquad \frac{fm'}{f'm}=\frac{K}{K'}=\frac{D\pm D''}{D'\pm D''}\cdot\frac{m'}{m}.$$

From (15)

$$r=\frac{K-\frac{\kappa''}{\Delta}}{K'-\frac{\kappa''}{\Delta'}};$$

$$K-\frac{\kappa''}{\Delta}=rK'-r\frac{\kappa''}{\Delta'};$$

$$\frac{K}{K'}=\frac{\kappa''}{K'\Delta}+r-r\frac{\kappa''}{K'\Delta'};$$

$$\frac{K}{K'}=r\left[1+\frac{\kappa''}{K'}\left(\frac{1}{\Delta r}-\frac{1}{\Delta'}\right)\right], \quad . \quad . \quad . \quad (16)$$

in which

$$r=\frac{D\pm D''}{D'\pm D''}\cdot\frac{m'}{m}.$$

When the comparison body is water

K' exactly $=-0{\cdot}79\times 10^{-6}$ (P. Curie).

As for air the susceptibility $\kappa''=0{\cdot}0322\times 10^{-6}$.
If r is *positive* we have for a paramagnetic body

$$\frac{K}{K'}=-r\left[1+0{\cdot}041\left(\frac{1}{r\Delta}+1\right)\right],$$

and for a diamagnetic body

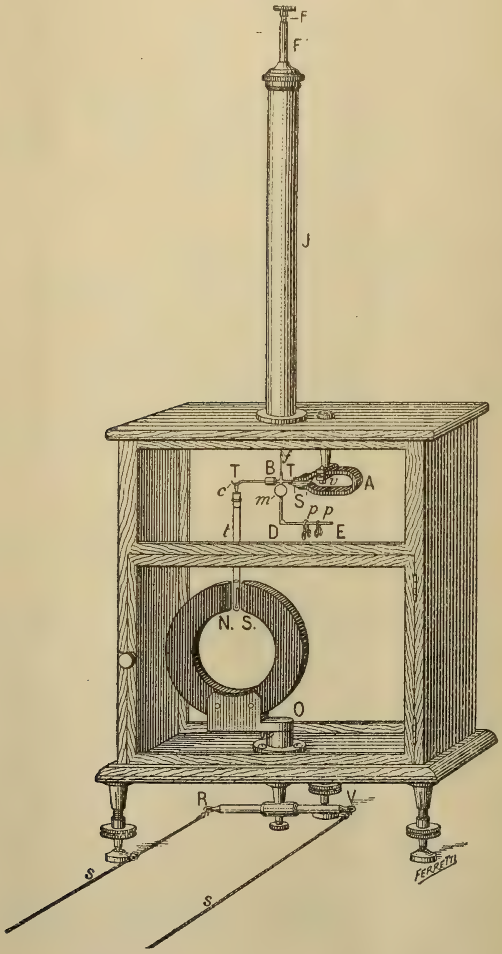
$$\frac{K}{K'}=r\left[1-0{\cdot}041\left(\frac{1}{r\Delta}-1\right)\right].$$

Hence the apparatus lends itself very readily to relative determinations, and if we take water as the standard body ($K'=-0{\cdot}79\times 10^{-6}$) it enables us to obtain an absolute value of the coefficient of specific magnetization of a body.

But the comparison substance may be a liquid or solid other than water, and such that its coefficient of magnetization is of the same order of magnitude as that to be determined. A choice can be made from the tables of magnetic constants. It is convenient if the masses of the bodies compared correspond to the same volume; on this account the tube containing the substance is always filled to a given mark. When the substances tested are very strongly magnetic, a smaller length may be employed, but in that case it is absolutely necessary that the comparison substance should have the same length.

The apparatus could be made still more sensitive with the aid of an electromagnet. On the other hand, with a torsion wire of larger diameter, the magnetic properties of iron or other ferro-magnetic metals and alloys could be determined. It would doubtless suffice to use an extremely fine wire of the metal, and to employ the method of experiment and the corrections already proposed by P. Curie in a work on the magnetic properties of bodies (*loc. cit.* p. 5, note 1).

Fig. 5.



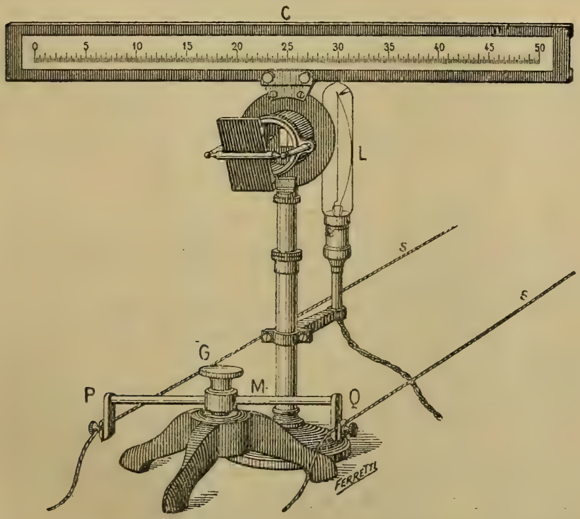
Description of the Instrument, Magnetically Damped Form.

The arm of the torsion-balance is formed by a rod TT (fig. 5), which carries from one of its two extremities a hook c, from which the glass tube t, which contains the body, can be suspended. To this end the glass tube is closed by a cork carrying a metallic ring which hangs on the hook *c*. The tube *t* is therefore in a vertical position. On the other end of the arm TT is fixed a copper sector, S′, which moves between the poles of a fixed damping magnet A. To vary the sensitiveness the torsion-wire can be changed, and the damping varied by the position of the copper sector in the field.

On the horizontal arm TT is fixed a vertical copper strip which carries a hook to which the torsion-wire *f* ($\frac{1}{10}$ mm. platinum) is attached. Below, this strip is turned at right angles as shown by the portion DE parallel to TT. Balance is obtained partly by the aid of a small copper cylinder B, sliding on the rod TT, when the tube is empty, and partly by copper or aluminium riders, *pp*, to compensate for the weight of the solid or liquid material which fills the tube to the level marked.

The displacement of the magnet N.S. is obtained by a movement of rotation around an axis O; this movement is smoother than the sliding motion of our earlier model. The movements of the torsion-balance are followed by the observer upon a divided scale C. (fig. 6). For this purpose a 2-metre radius concave mirror *m* is attached to the balance-arm, and the image of a straight filament is employed. The displacement of the magnet is effected by a controller M (fig. 6) fixed in

Fig. 6.



front of the scale, which consists of a horizontal rod PQ turning about a vertical axis in a heavy base, and furnished with a large milled head G, which can be turned by the observer. This rod is provided with two clamps P and Q, which are attached by two cords to two rings R and V on a similar rod attached to the axis of the magnet NS. If the cords are initially arranged so that the rods PQ and RV are parallel, the position of the magnet is at once determined by the direction of the rod PQ, and it can be turned either by the milled head G, or preferably by holding the two cords *ss* like reins.

The advantage of employing a rectilinear filament lamp (such as is made by the Pintsch Gluhlampenfabrik in Berlin) is considerable in practice, as the spot is always visible on the scale even if the torsion-arm is not perfectly balanced horizontally.

Appendix.

By the courtesy of M. Cheneveau and the Cambridge Scientific Instrument Co., we have been able to set up and test the performance of one of these balances in the laboratories of the Northampton Institute.

The instrument was of the magnetically damped type described above, and was used with a lamp and scale at some two metres distant from the mirror.

No attempt was made to obtain absolute values of the coefficients of specific magnetization; but relative determinations only were made, using as a standard substance distilled water, and assuming for it the value

$$K' = -0{\cdot}79 \times 10^{-6},$$

as found by M. Curie and given above.

The results obtained are set out in the accompanying table, and show some interesting figures.

The first portion of the table contains figures for a few materials selected quite at random in order to test the behaviour of the balance. Of these the first five are chemically pure liquids, and all exhibit diamagnetic qualities.

The four samples of aluminium are all magnetic, and we have not been able to get a sample which is less magnetic than the first of these. The eleven samples of brass indicate the range over which the magnetic qualities vary, while some of the samples examined, but not here tabulated, have been too magnetic to be used in the apparatus without changing the suspension.

It is interesting to note that during some inductance tests

NCE.	Den Δ
....	9·0
....	8·7
....	8·7
....	8·8
....	8·8
....	8·8
....	.
....	.
ogel	8·9
......	.
......	.
2	8·9
....	8·9
r, 2 A	9·0
....	8·9
....	.
....	8·9
....	8·6
belenhutte . .	8·6
....	8·6
....	8·2

Effect of Volume on Value of K.

NICKELIN, I.

ss, *m*.	K.
198	$2{\cdot}04\times10^{-6}$
985	1·99
784	2·16
583	2·23
385	2·03
187	2·11
989	2·13
789	2·14
592	2·18
393	2·18
192	2·41

EXTRA PRIMA.

·21	$2{\cdot}1\times10^{-6}$
·434	1·52
·635	1·6
·836	1·52
·033	1·66
·233	1·29
·435	1·38
·637	1·29
·835	1·28
·033	1·19
·237	1·23
·437	1·13
·634	1·07
·834	1·09

Effect of Length on Value of K.

COPPER.

Length.	K.
5 cm.	$0{\cdot}404\times10^{-6}$
4·5	0·446
4·0	0·516
3·5	0·642
3·0	0·828
2·5	0·71
2·0	0·895
1·5	1·093
1·0	1·46
0·5	2·37

EFFECT OF ACID TREATMENT.

COPPER.

Mass, *m*.	K.
2·545 gr.	$1{\cdot}16\times10^{-6}$
After Treatment with Hot Conc. HCl :—	
2·542	0·765
Further Treatment with HCl :—	
2·540	0·774

SUBSTANCE.	Density, Δ.	Coefficient of Specific Magnetization, K.
Water	1·0	$-0\cdot79\times10^{-6}$
Alcohol	0·79	−0·78
Amyl Alcohol	0·815	−0·929
Benzene	0·85	−0·962
Luxor Oil	0·8	−0·594
Methyl Ether	0·725	−0·785
Aluminium	2·67	$1\cdot19\times10^{-6}$
,,	..	1·79
,,	..	2·03
,,	..	2·99
Brass	8·1	$-0\cdot026\times10^{-6}$
,,	..	3·95
,,	..	0·3
,,	..	0·09
,,	..	0·083
,,	..	2·02
,,	..	1·94
,,	..	0·232
,,	..	3·09
,,	..	4·05
,,	..	2·45
Copper	8·9	$0\cdot707\times10^{-6}$
,,	..	0·455
,,	..	1·06
,,	..	0·68
,,	..	0·54
,,	..	0·36
,,	..	0·83
,,	..	0·537
,	..	−0·097
Tin	7·3	$0\cdot151\times10^{-6}$
Zinc	6·9	$0\cdot043\times10^{-6}$
,,	..	0·212
,, (Pure)	..	0·224

SUBSTANCE.	Density, Δ.	K.	Specific Resistance, Microhms per cm. cube at 0° C. ρ.	Temperature Coefficient °/ₒ at 17° C.	Thermo E.M.F. to Cu Microvolts per ° C.
Nickelin, I	9·09	$4\cdot88\times10^{-6}$	43·13	0·00245	37·5
Nickelin, 1	8·77	3·75	40·62	0·021	20·0
Nickelin, 5	8·79	2·11	39·29	0·0187	19·06
Nickelin, 13	8·82	5·76	39·73	0·021	20·75
Extra Prima	8·8	2·1	29·35	0·028	16·55
Platinoid	8·83	1·75	33·62	0·0224	23·52
,,	..	1·61			
,,	..	1·63			
Constantan Vogel	8·99	9·67	47·06	−0·00122	37·5
,,	..	10·25			
,,	..	9·72			
Constantan, 12	8·97	12·37	48·3	0·001437	35 75
1A 1A	8·97	9·23	50·7	−0·0029	39·12
German Silver, 2 A	9·06	6·77	42·89	0·00385	35·75
New Metal	8·97	6·87	51·10	−0·0038	35·8
,,	..	6·77			
Eureka	8·96	..	47·4	0 0048	40·6
Manganin, 14	8·61	28·05	36·62	0·00175	1·4
Manganin Isabelenhutte	8·6	28·7	39·14	0·00176	1·44
Rheotan	8·61	..	47·55	0·024	13·8
Superior	8·24	..	81·024	0·1148	7 44

Effect of Volume on Value of K.

NICKELIN, I.

Mass, *m*.	K.
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Effect of Length on Value of K.

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2·0	0·895
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1·0	1·46
0·5	2·37

EFFECT OF ACID TREATMENT.

COPPER.

Mass, *m*.	K.
2·545 gr.	$1\cdot16\times10^{-6}$

After Treatment with Hot Conc. HCl :—

2·542	0·765

Further Treatment with HCl :—

2·540	0·774

in progress in the laboratory, circumstances compelled us to use brass conductors, and the results obtained were higher than those given by calculations based on theory. This could only be accounted for by assuming a permeability for the brass greater than unity, and although the magnetism in the metal was not detectable by a fairly sensitive magnetometer, it was readily shown when samples of the conductors were tested in the balance.

Nine samples of copper are tabulated, and one only is diamagnetic, again emphasizing the difficulty of obtaining really non-magnetic conductors.

The tin sample was chemically pure and is also magnetic. Of the three samples of zinc the first two are ordinary commercial sheet metal, and the third one is a rod of chemically pure metal for use in standard cells.

The next portion of the table is devoted to an examination of the series of resistance alloys, whose electrical properties were investigated by the writer some time ago and published by Dr. Drysdale in connexion with his paper upon the Comparison of Standard Resistances, before the British Association at Leicester, 1907.

The first point which strikes one in connexion with these is the fact that every alloy is magnetic, but that those alloys containing relatively a large proportion of the magnetic metal nickel, *i. e.* Nickelines, are among the least so. The first sample is very different from the other three, and we have reason to believe that the second and fourth samples are of the same manufacture although obtained from different firms.

The samples of Platinoid fall into this group with properties very comparable with the Nickelines, and the material sold under the trade name of Extra Prima probably also belongs to this group.

The Constantans come next in order, being more magnetic than the Nickelines, and it is not difficult to see that the material catalogued as 1A1A belongs to this group of alloys, together with the alloy supplied to us under the title of New Metal, while the sample German Silver 2A, but for its high density and positive temperature coefficient, would also be classed among the Constantans.

Eureka is a resistance material which is often classed as a Constantan, but the balance easily disproves this, as it shows it to be so magnetic that observations would have had to be made with a stiffer suspension than we were using, and this, coupled with its positive temperature-coefficient, rule it out of the group.

Superior and Rheotan behave like steels in the apparatus and probably contain considerable quantities of iron in their composition.

The magnetic behaviour of Manganin is remarkable, it being, with the exception of the last two alloys and Eureka, the most magnetic of all the materials examined. This is of particular interest in view of its almost universal adoption for the construction of accurate resistances, but it is not altogether unexpected when we remember that the remarkable Heusler alloys have a Copper-Aluminium Manganese composition.

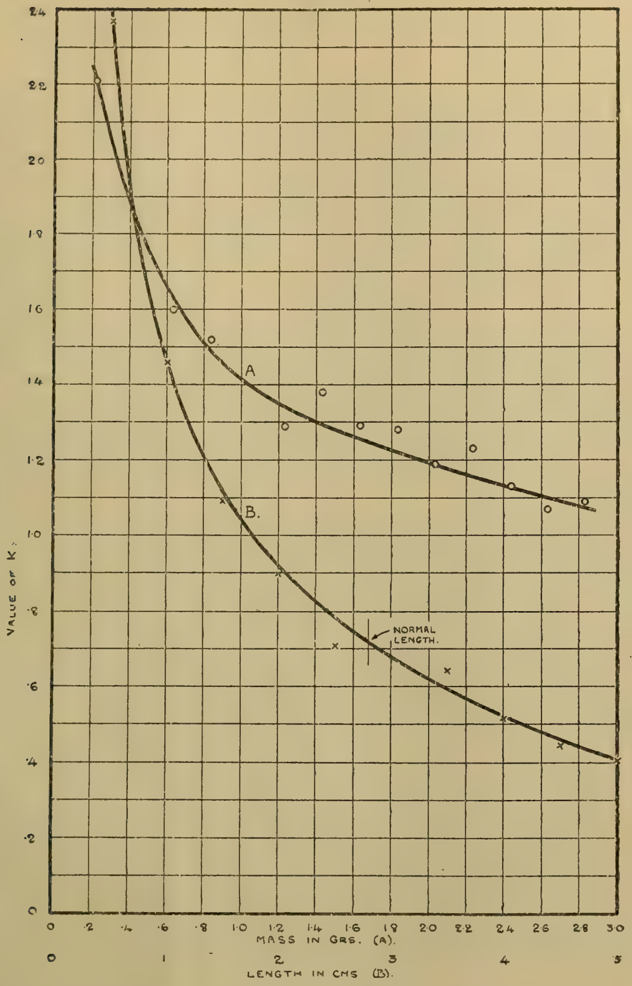
The figures in the rest of the table indicate the variation in the value of K, with increase in mass of the specimen and increase in length. In the first case the sample, in the form of a bare wire 1 mm. in diameter, was cut up into standard length (approx. 2·8 cms.), and successive lengths of measured mass were introduced into the tube until it would hold no more; it will be observed that the value of K tends to diminish as the mass increases. (Curve A, Extra Prima, fig. 7.)

The apparatus is, of course, very sensitive to the length of specimen, and an extreme range of length was taken in a wire of 1 mm. diameter, and the results are shown in the curve B (copper).

The difficulty of obtaining non-magnetic copper has already been referred to, and every instrument-maker knows how difficult it is to wind a really non-magnetic D'Arsonval coil. In order to see how far this is dependent upon surface conditions a sample of copper was taken and treated with concentrated hydrochloric acid and re-tested, and it was found that the value of K was reduced to nearly one-half, and that further treatment had but little effect.

From these results it will be seen that there is a considerable field of usefulness for the balance. Firstly, for examining the materials to be used in the construction of standard apparatus where the permeability becomes of first importance. Secondly, in grading and examining alloys whose properties are materially dependent upon minute traces of alloying constituents which are so difficult to estimate by chemical means, and which play such an important part in their electrical behaviour. Thirdly, it could well be used to maintain the standard of purity in the commercial production of such a metal as Aluminium, whose chief impurity is iron, the last traces of which are so difficult to remove.

Fig. 7.



In conclusion the writers' thanks are due to Mr. A. F. Burgess, B.Sc., for his help in the experiments and calculations.

XXXV. *Typical Cases of Ionization by X-Rays.* *By* CHARLES G. BARKLA, *M.A., D.Sc., Professor of Physics, King's College, London* *.

IN a letter to 'Nature' (April 15, 1909) and in a short preliminary paper on "Phenomena of X-Ray Transmission" (Proc. Camb. Phil. Soc. May 17, 1909) the writer showed that many apparent anomalies of ionization might be explained in terms of a few simple laws, and that so far as experiments had then gone, the behaviour of one substance might be regarded as typical of all. Further experiments have confirmed these conclusions, but as accurate measurements of ionization involve the study of absorption, secondary X-radiation and secondary corpuscular radiation, the publication of the results in detail cannot yet be undertaken. It is sufficient for the present to study the results of experiments on two substances, carbonic acid gas and ethyl bromide vapour, as these show all the marked phenomena hitherto observed.

Secondary X-radiations from Fe, Ni, Cu, Zn, As, Se, Br, Sr, Mo, Ag, Sn, and Sb—with special treatment in some cases—furnished homogeneous beams of X-rays which varied considerably in penetrating power. The most penetrating radiation dealt with was seventy times as penetrating as the most absorbable. The absorption of these radiations by Al, together with the substances which emitted them, is shown in Table I. λ is defined by the equation $I=I_0e^{-\lambda x}$ during transmission through aluminium, $\frac{\lambda}{\rho}$ is tabulated because it is a constant for a given radiation and given absorbing substance whatever the density of that absorbing substance.

In studying the results of experiments on ionization it is necessary to consider the ionizing effects of:—

(*a*) Radiations from the walls of the ionization chamber:

(1) Scattered X-rays—(one type of secondary X-rays);
(2) Transformed X-rays—(secondary X-rays characteristic of the radiating elements);
(3) Corpuscular rays—(secondary rays consisting of ejected electrons).

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* Communicated by the Author. The expenses of this research have been partially covered by a Government Grant through the Royal Society.

(*b*) Radiations from the gas or vapour studied :

(4) Scattered X-rays ;
(5) Transformed X-rays ;
(6) Corpuscular rays.

A few notes on each of these are necessary before attempting to interpret the results of experiments :—

(1) The energy scattered by light-elements has been studied by the writer. This radiation being of the same type as the primary produces the same relative ionizations as the primary. As it is not directed in a parallel beam, however, there must be a small error in the correction for absorption as applied to the primary beam. The error introduced is, however, exceedingly small.

(2) No characteristic X-radiation of penetrating power between the extreme limits of the primary radiations used is emitted by Al—the material of the ionization chamber. Extremely "soft" radiations, if they produce an appreciable ionization, are included in the correction applied for the corpuscular radiation from Al.

(3) The secondary corpuscular radiation from Al produced an appreciable ionization in some cases. Correction has been made for this from the results given by Mr. Sadler [*]. The maximum correction was about 20 per cent. of the total ionization.

(4) The energy of the rays scattered by the gas was, in these experiments, always a negligible fraction of the energy of primary radiation and consequently produced a negligible ionization.

(5) The secondary X-rays known to be emitted by the elements in ethyl bromide produced in the ionization chamber used not more than about 1 per cent. of the total ionization. The ionization produced by exceedingly soft secondary X-rays is unknown. It is included in what will be called the direct ionization of the X-rays.

(6) The corpuscular radiations from the elements in ethyl bromide will be discussed later.

The homogeneous beams of X-rays were passed through air, O, CO_2, SH_2, SO_2, coal-gas, N_2O, C_2H_5Br, CH_3I, Se_2Cl_2, $SnCl_2$. After correcting for absorption in the ionized gas, and for the effects of secondary corpuscular radiation from the walls of the ionization chamber, the results given in the following Table were obtained from experiments on air, carbonic acid, and ethyl bromide mixed with air.

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[*] Phil. Mag. March 1910, pp. 637-356.

TABLE I.

Source of homogeneous X-radiation.	Absorption of X-radiation in Al $\left(\frac{\lambda}{\rho}\right)$*.	$\frac{\text{Ioniz. in } CO_2}{\text{Ioniz. in air}}$.	$\frac{\text{Ioniz. due to } C_2H_5Br}{\text{Ioniz. in air}}$.	Ionization in CO_2 at 76 cm. pressure.	Ionization due to C_2H_5Br at 11·6 cm. pressure.
				[Numbers purely relative]	
Fe	88·5	1·42	29·5	125·7	571
Ni	59·1	1·385	30	81·9	387
Cu	47·7	1·39	30·2	66·3	315
Zn	39·4	1·36	31·1	53·6	268
As	22·5	1·376	30·2	31	148·5
Se	18·5	1·35	29·8	25	120
Br	17·4	—	30·9	—	117·5
Sr	13	1·4	106·7	18·2	303
Mo	4·7	1·42	133	6·7	137
Ag	2·5	1·38	153	3·45	83·5
Sn	1·57	1·4	175	2·20	60·2
Sb	1·2	1·42	166	1·72	44

* The majority of these absorptions were determined by Barkla and Sadler, that for Br radiation by Chapman.

Column 1 gives the source of the ionizing X-radiation; column 2 the absorbability of each radiation in aluminium; column 3 the ratio of ionizations* in carbonic acid and air at the same pressure and temperature; column 4 the ratio of the ionization due to ethyl bromide in air saturated with ethyl bromide vapour at 0° C. to the ionization in air at the same pressure (11·6 cm. of mercury) and temperature as the ethyl bromide. [Possibly this is not equal to the ratio in pure ethyl bromide and air at the same pressure. The ionizations in vapours when pure and when mixed with gases will shortly be dealt with.]

An examination of the above results shows that the ionization in carbonic acid gas is proportional to the ionization in air throughout this wide range of penetrating power. Similar results have been obtained with O, SH_2, SO_2, N_2O, and coal-gas, though in some of these the variations from proportionality were greater than in CO_2.

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* The term ionization is a somewhat ambiguous one. Unless otherwise stated the relative ionizations in gases mean the relative ionizations in films of the gases, so thin that the change of intensity of the beam of X-rays in transmission is negligible.

A similar relationship is found in the case of C_2H_5Br for radiations not more penetrating than the secondary X-radiation characteristic of Br. $\left[\frac{\lambda}{\rho} \text{ in Al} = 17{\cdot}4.\right]$

As the radiation is made more penetrating, the relative ionization rises rapidly at first and more slowly afterwards. It probably approaches a constant though much higher value than was obtained with the more absorbable radiations.

Similar features have been observed in CH_3I, $SnCl_2$, and Se_2Cl_2.

These variations in relative ionization are similar to the variations in absorption of the ionizing radiation *. For the absorption in a given element is approximately proportional to the absorption in other elements until the radiation becomes of more penetrating type than that characteristic of the absorbing element, when it begins to rise rapidly and finally approaches a higher proportionality.

Similar changes take place in the intensity of the secondary homogeneous radiation † emitted by an element when subject to a primary radiation whose penetrating power is gradually increased, except that primary radiations softer than that characteristic of the element exposed, excite no secondary X-radiation of this particular penetrating power.

Mr. Sadler ‡ has recently shown that as the penetrating power of the primary radiation increases, secondary corpuscular radiation begins to be emitted at the same critical point by the particular element subject to the radiation. The intensity increases rapidly with an increase in penetrating power at first, then much more slowly.

The variations of $\frac{\text{ionization in } CO_2}{\text{ionization in air}}$ and $\frac{\text{ionization in } C_2H_5Br}{\text{ionization in air}}$ are shown in fig. 1, in which these ratios are plotted as ordinates—(on different scales for convenience)—and the absorbability of the radiations $\left(\frac{\lambda}{\rho} \text{ in Al}\right)$ as abscissæ. It will be noticed that owing to crowding of very penetrating radiations at one side, the curve for C_2H_5Br turns upward again.

As the ionization in air diminishes with increased penetrating power of the radiation, the variations in ionization

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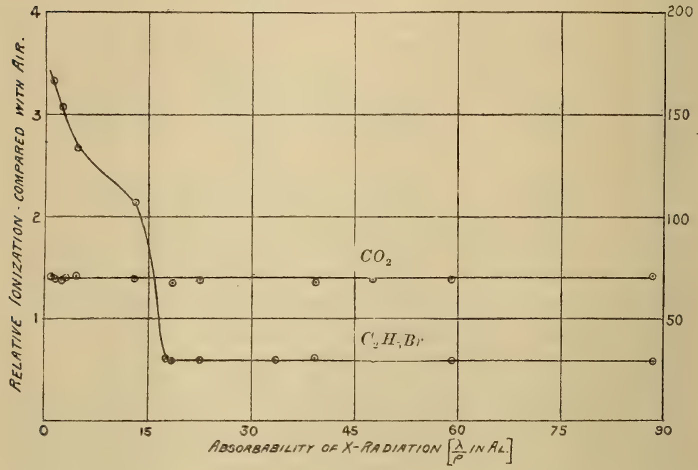
* Barkla and Sadler, Phil. Mag. May 1909, pp. 739-760.

† Barkla and Sadler, Phil. Mag. Oct. 1908, pp. 550-584; Phil. Mag. May 1909.

‡ Sadler, Phil. Mag. March 1910, pp. 337-356.

are more correctly indicated if we assume that the absorption of various beams of X-rays in air is proportional to the

Fig. 1.



ionization produced in air. With this assumption we get the relative values for the ionizations produced by the various primary beams of equal intensity as given in columns 5 and 6 (Table I.).

The curves exhibiting the relation between the ionization in a thin film of gas or vapour and the absorbability of the X-radiation are given in fig. 2. The accuracy of course depends upon the truth of the assumption made, but of the marked features there can be no doubt. These curves should be compared with those showing the variation of absorption in various elements with variation in penetrating power of the X-rays used *.

The marked deviation from simple proportionality of ionization in C_2H_5Br to ionization in air or to absorbability of the primary radiation is thus due to the presence of Br, which has a characteristic radiation within the range of penetrating power used in these experiments.

Similar deviations occur in the case of CH_3I at the particular penetrating power characteristic of the secondary radiation from I, in the case of $SnCl_2$ at that characteristic of Sn, and in Se_2Cl_2 at that characteristic of Se. Carbon,

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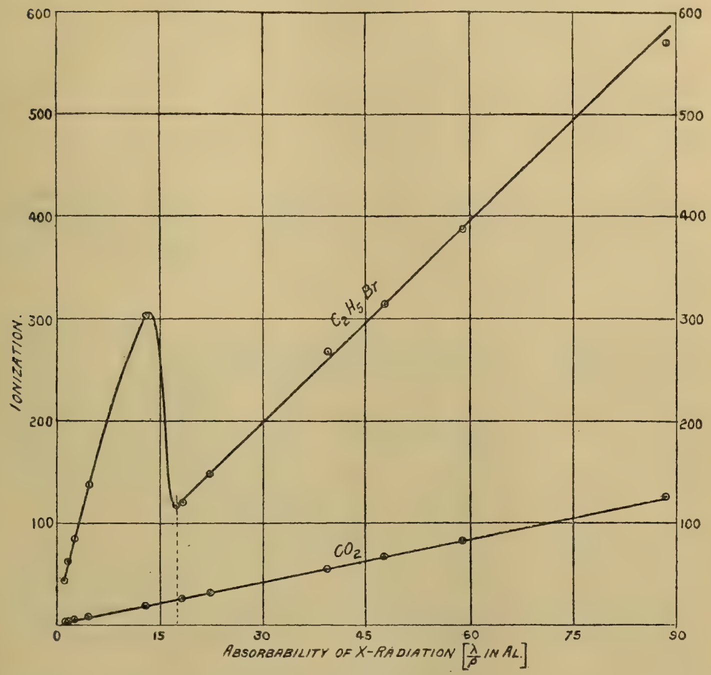
* Barkla and Sadler, Phil. Mag. May 1909, pp. 739–760; Barkla, Proc. Camb. Phil. Soc. May 1909, pp. 257–268.

hydrogen, and chlorine have no characteristic radiations within the range of penetrating power used.

Fig. 2.



The results may be stated thus :—

Every element has its own characteristic secondary X-radiations, which it emits when exposed to X-radiations of more penetrating type, in agreement with Stokes's Law of Fluorescence. This characteristic line spectrum in X-rays determines the variation in intensity of secondary X-radiation from the element, the variation in absorption of X-rays in the element, the variation in ionization in the element, the variation in intensity of corpuscular radiation from the element, as the penetrating power of the X-radiation is varied.

Thus if we pass a beam of X-rays of gradually increasing penetrating power through two substances A and B in the gaseous state, then when the X-radiation has not a penetrating power close, on the more penetrating side, to that of the radiations characteristic of any element in A or B, the absorption in A is approximately proportional to the absorption in B, the ionization in A proportional to the ionization in B, and the intensity of secondary X-radiation already excited in A proportional to the intensity of secondary X-radiation already excited in B. But as the penetrating power of the primary X-radiation becomes just greater than that of the radiation characteristic of an element in A say, this new type of X-radiation begins to be emitted by A, the absorption of the primary radiation in A begins to increase, the ionization in A begins to increase, the intensity of corpuscular radiation from A begins to increase. All these increases occur together, and they are, in general, very considerable in magnitude. There is every indication of all these quantities ultimately settling down to proportionality again with the corresponding quantities in B, though in this higher ratio.

The question naturally arises as to the possibility of the great increase in ionization being produced not by the direct action of the primary rays, but of the secondary rays—(X or corpuscular)—which are connected with the increase in ionization. It may easily be shown that the secondary X-radiation did not produce more than a very slight increase. The effect of the corpuscular radiation will, however, be considered as it leads to an interesting result.

During the transmission of X-rays through a gas, each thin layer of gas, unless within about 1 millimetre of the boundary in these experiments, is subject to the corpuscular radiation from two thick plates of its own substance—one on each side.

Let λ and λ' be the coefficients of absorption of the primary X-radiation and of the secondary corpuscular radiation respectively in the gas or vapour, as defined by the equations

$$I=I_0e^{-\lambda x} \quad \text{and} \quad I'=I_0'e^{-\lambda' x}.$$

Let k' be the coefficient of transformation of X-radiation into corpuscular radiation, as defined by the equation

$$dE'=k'I\,dx.$$

dE' being the total energy of the primary radiation of unit cross-sectional area transformed into corpuscular radiation per second in a layer of depth dx.

If f_1 is the fraction of this directed towards the face of incidence of the primary beam, the total intensity of this corpuscular radiation emerging from a thick layer through its face of incidence

$$=\int f_1 d\mathrm{E}' e^{-\lambda' x}\,;$$

$$=\int_0^\infty f_1 k' \mathrm{I} e^{-\lambda' x} dx\,;$$

$$=f_1 k' \mathrm{I}_0 \int_0^\infty e^{-(\lambda+\lambda')x} dx\,;$$

$$=f_1 k' \frac{\mathrm{I}_0}{\lambda+\lambda'}\,.$$

Similarly the intensity of corpuscular radiation from a thick layer of gas proceeding from the face of emergence of the primary beam is

$$f_2 k' \frac{\mathrm{I}_0}{\lambda'-\lambda},$$

where f_2 is the fraction directed towards the emergent face, and I_0 is here the intensity of primary radiation emerging from the thick layer.

Each thin layer of gas is thus exposed to corpuscular radiation of total intensity

$$k' \mathrm{I}_0 \left[\frac{f_1}{\lambda'+\lambda}+\frac{f_2}{\lambda'-\lambda}\right].$$

In the cases we are considering λ is negligible in comparison with λ'.

Therefore each layer of gas is exposed to corpuscular radiation of intensity

$$k' \mathrm{I}_0 \frac{(f_1+f_2)}{\lambda'}=\frac{k' \mathrm{I}_0}{\lambda'}\,.$$

$$\therefore\ \frac{\text{Intensity of corpuscular radiation producing ions}}{\text{Intensity of primary X-radiation producing ions}}=\frac{k'}{\lambda'}\,.$$

If the coefficients of ionization of the two types of radiation (primary X and secondary corpuscular) in the gas itself are i_r and i_r', as defined by the equations

$$dn=i_r \mathrm{I} dx \quad \text{and} \quad dn'=i_r' \mathrm{I}' dx,$$

where dn and dn' are the numbers of ions produced in a layer of gas of thickness dx by primary and secondary corpuscular radiations of intensities I and I′,

then $$\frac{dn'}{dn}=\frac{k' i_r'}{\lambda' i_r},$$ which therefore

$$=\frac{\text{Ionization by secondary corpuscular radiation}}{\text{Ionization by primary X-radiation}}\,.$$

Now Mr. Sadler has determined the total ionization produced in air by the corpuscular radiation from the incident face of plates of various substances compared with the ionization produced by the exciting X-radiation in a layer of air 1 centimetre thick. Call this R_1.

The total ionization of corpuscular radiation

$$=\int_0^\infty i_a' I' dx,$$

[i_a' is the ionization coefficient of corpuscular radiation *in air*]

$$=\int_0^\infty i_a' I_0' e^{-\lambda_a' x} dx,$$

$$=i_a' \frac{I_0'}{\lambda_a'}=\frac{i_a'}{\lambda_a'}\cdot\frac{f_1 k' I_0}{\lambda'},$$

$$\therefore \qquad R_1=\frac{i_a' f_1 k' I_0}{\lambda_a' \lambda} \div I_0 i_a,$$

$$=f_1 k' \frac{i_a'}{i_a}\cdot\frac{1}{\lambda' \lambda_a'}.$$

$$\frac{n'}{n} \text{ therefore equals } \left\{\frac{1}{f_1}\frac{i_r'}{i_r}\frac{i_a}{i_a'}\lambda_a'\right\} R_1.$$

Now $\frac{i_a}{i_r}$ in the case considered is the ratio of ionization in air to ionization in air and ethyl bromide, when the corpuscular radiation is not excited.

This $=\frac{1}{7 \cdot 5}$ approximately.

$\frac{i_r'}{i_a'}$ is the ratio of ionization in air and ethyl bromide to that in air, produced by the corpuscular radiation alone.

This is very approximately equal to

$$\frac{\text{density of air and } C_2H_5Br}{\text{density of air}}=1 \cdot 6.$$

λ_a' is the absorption coefficient in air of the corpuscular radiation from Br (or anything else) excited by the particular primary radiation.

Take the case of ionization by the radiation from Ag.

$$\lambda_a'=8 \cdot 8 \text{ approximately.}$$

(See Sadler's paper on "Homogeneous Corpuscular Radiation," Phil. Mag. March 1910.)

R_1 is the quantity defined; and by interpolation can be shown to be about ·8 for Br. For the mixture of air and ethyl bromide used in these experiments R_1 would be less than this, as $\frac{k'}{\lambda'}$ is less, the active substance Br being diluted.

Assuming the absorption of the corpuscular radiation to be dependent simply on the quantity of matter passed through, R_1 becomes ·3 approximately.

For f_1 we will take the value found by Mr. Sadler, $\frac{1}{3}$, as approximately correct.

$$\frac{n'}{n} \text{ therefore} = 3 \times 1{\cdot}6 \times \frac{1}{7{\cdot}5} \times 8{\cdot}8 \times {\cdot}3 = 1{\cdot}7 \text{ approximately.}$$

We should thus conclude that the ratio of ionization due to ethyl bromide to ionization in air at the same pressure would, owing to the emission of corpuscular radiation, increase from 30 to about 80 when using the homogeneous radiation from silver.

From column 4 of Table I. it will be seen that the increase observed in the ionization produced in ethyl bromide when the ionizing X-radiation was made more penetrating than the secondary X-radiation characteristic of bromine was from about 30 to 153 for the radiation from silver. Thus quite a considerable portion of the observed increase might be attributed to the corpuscular radiation. The exact proportion cannot be given with certainty.

On the other hand, Mr. Crowther[*], from a study of the ionization in ethyl bromide at low pressures, concludes that no appreciable portion of the ionization is due to very soft secondary radiations, such as these corpuscular radiations.

It should be observed that we have assumed that the emission of corpuscular radiation is not affected by the state of the bromine, that is, that the corpuscular radiation is an atomic phenomenon simply. Further experiments are being made by the writer to test these conclusions.

The results of experiments may be briefly stated thus:—

From the results of observations on ionization in many gases and vapours complete regularity in behaviour has been found. It is necessary and sufficient to know the penetrating power of the characteristic secondary X-radiations emitted by the constituent elements to determine the way in which the ionization in a gas or vapour varies with the penetrating power of the ionizing radiation. (See fig. 2.) In other words, it is necessary and sufficient to know the X-ray line spectra for the constituent elements. No anomalous ionization by X-rays has been observed.

A much fuller account of the experiments will be published later.

My thanks are due to Mr. G. H. Martyn, B.Sc., for his most valuable assistance throughout the experiments.

Wheatstone Laboratory,
King's College.

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[*] Roy. Soc. Proc. A. lxxxii. pp. 103–127.

XXXVI. *On the Motion of a Particle about a Doublet.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a recent paper* Sir J. J. Thomson investigates the motion of an electron about a doublet. I have recently been examining this same motion, and, as I have arrived at very different conclusions from those of Sir J. J. Thomson, a brief statement of my results may not be out of place.

The equations of motion of this particular problem admit of complete integration, providing, I think, the only instance in particle dynamics of a soluble problem in which the orbit is not confined to one plane.

As stated by Sir J. J. Thomson, the equations of motion are

$$\frac{d^2r}{dt^2}-r\sin^2\theta\,\dot{\phi}^2-r\dot{\theta}^2=-\frac{2Me}{m}\frac{\cos\theta}{r^3}, \quad . \quad . \quad (1)$$

$$\frac{d}{dt}(r^2\dot{\theta})-r^2\sin\theta\cos\dot{\theta}\phi^2=-\frac{Me}{m}\frac{\sin\theta}{r^2}, \quad . \quad . \quad (2)$$

$$\frac{d}{dt}(r^2\sin^2\theta\,\dot{\phi})=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and these have the obvious first integrals of momentum and energy,

$$r^2\sin^2\theta\,\dot{\phi}=n, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\tfrac{1}{2}(\dot{r}^2+r^2\dot{\theta}^2+r^2\sin^2\theta\,\dot{\phi}^2)=\mathrm{E}+\frac{Me}{m}\frac{\cos\theta}{r^2}. \quad . \quad . \quad (5)$$

Equations (2) and (3) give

$$(r^2\dot{\theta})\frac{d}{d\theta}(r^2\dot{\theta})=r^2\frac{d}{dt}(r^2\dot{\theta})=-\frac{Me}{m}\sin\theta+\frac{n^2\cos\theta}{\sin^3\theta},$$

leading to the integral

$$\tfrac{1}{2}r^2\dot{\theta}^2=\frac{Me}{m}\frac{\cos\theta}{r^2}-\frac{n^2}{2r^2\sin^2\theta}+\frac{\mathrm{C}}{r^2}, \quad . \quad . \quad . \quad (6)$$

in which C is a constant of integration. From this and (5),

$$\tfrac{1}{2}\dot{r}^2=\mathrm{E}-\frac{\mathrm{C}}{r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

of which the integral is

$$r^2=\frac{\mathrm{C}}{\mathrm{E}}+2\mathrm{E}t^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

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[*] "On the Theory of Radiation," Phil. Mag. xx. p. 244.

If E is negative the particle falls into the doublet after a finite time. The case in which $E=0$ is exceptional, and will be considered later. In all other orbits r passes through a single minimum value $r_0(=\surd(C/E))$, after which the particle passes to infinity, arriving with velocity $v_0(=\surd(2E))$. The changes in r are precisely those which occur when a particle describes a straight line distant r_0 from the origin, with a uniform velocity v_0.

The remaining integrals are best obtained in terms of a subsidiary variable χ given by

$$r=r_0 \sec \chi, \quad \ldots \ldots \quad (9)$$

$$t=\frac{r_0}{v_0}\tan \chi, \quad \ldots \ldots \quad (10)$$

these equations being mutually consistent with (8). The value of $d\chi$ is $r_0 v_0 dt/r^2$, and on changing the variable from t to χ, equation (8) yields the integral

$$\chi=\int\frac{d\theta}{\left(1+\frac{Me}{Cm}\cos\theta-\frac{n^2}{2C}\operatorname{cosec}^2\theta\right)^{\frac{1}{2}}},$$

which gives a relation of the type

$$\cos\theta=\wp\left\{\sqrt{\left(\frac{Me}{4Cm}\right)}\chi+\alpha\right\}.$$

and on evaluating ϕ from (4) the integration is complete.

The special case of $E=0$ gives motion in a sphere $r=r_0$. All the equations of motion are satisfied if $r=r_0$ together with

$$\dot{\theta}^2=\frac{2Me}{mr_0^4}\cos\theta-\frac{n^2}{r_0^4\sin^2\theta}.$$

Provided $n^2<\frac{4Me}{3\sqrt{3}m}$ there will be two real angles θ_1, θ_2 for which $\dot{\theta}$, as given by this equation, vanishes; when n^2 has the critical value, the angles θ_1 θ_2 coincide in the angle $\theta=\tan^{-1}\sqrt{2}$. There are therefore an infinite number of possible spherical orbits for each value of r_0, each orbit being confined to a belt of the sphere lying between the cones θ_1, θ_2. Any small departure from spherical motion will be represented by giving to E a value slightly different from zero. For such an orbit it is clear from equation (8) that r ultimately becomes infinite or zero, showing that the original orbit was unstable.

Thus it appears that in addition to the circular orbits in the cone $\theta = \tan^{-1} \sqrt{2}$, there are an infinite number of other periodic orbits, and also that all these orbits are unstable, results which appear to be subversive of the physical theory suggested by Sir J. J. Thomson.

Yours faithfully,
Cambridge, July 4, 1910. J. H. JEANS.

XXXVII. *Notices respecting New Books.*

Bulletin of the Bureau of Standards. Vol. 6. No. 3. February 1910. Washington: Government Printing Office.

THIS part contains three important papers on Radiation: Selective Radiation from various solids, by W. W. Coblentz; Luminous efficiency of the Firefly, by H. E. Ives and W. W. Coblentz; Luminosity and Temperature, by P. G. Nutting. The first is a continuation of a detailed examination of the emission curves of very various bodies and contains the curves. The second paper gives the luminous efficiency of a glow-lamp as ·43 per cent., while that of a firefly is 96·5 per cent. (allowance being made for the variation of visual sensibility with the wave-length). The third paper discusses the connexion between luminosity and temperature, making use of the author's visibility function,

$$V = V_0 \exp. (-\kappa (\lambda - \lambda_m)^2).$$

A fourth article is a theoretical and experimental study of the Vibration Galvanometer by Frank Wenner; another deals with an experimental study of the specific heat of some calcium chloride solutions between −35° C. and +20° C.; measured in part by a continuous flow method and partly with the use of a Dewar vessel containing the brine into which heat is admitted electrically. The investigation was undertaken owing to the extensive use of calcium chloride brine as a circulating medium in refrigerating plants.

The last article is by E. Buckingham on the definition of an ideal gas. To the present reviewer there is something nugatory about all such discussions, it being somewhat arbitrary as to what the criteria of ideality should be, as soon as we attempt anything more scientific than the application of Boyle's and Charles' laws. But Mr. Buckingham's article is well worth a detailed consideration as it makes clear many things which are often treated very loosely in discussions on this subject; and though some of these matters have been explained before, it does not appear to be unnecessary to repeat them.

XXXVIII. *Intelligence and Miscellaneous Articles.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I AGREE with Dr. Kleeman (Phil. Mag. 1910, xx. p. 248) that evidence can be cited from his own work and that of others against the view that the γ-rays are homogeneous. The question, as he points out, is an intricate one, and there exists a real inconsistency in the experimental results, different lines of work leading to opposite conclusions. The alterations of the properties of the γ-rays, and the diminution of their absorption-coefficients ("hardening") by previous screening of the rays, are certainly opposed to the view that the rays are homogeneous. Dr. Kleeman, however, scarcely does justice to the evidence we advanced in Part II. of our paper (Phil. Mag. 1910, xix. p. 725), for the belief that the γ-rays are homogeneous. According to him this evidence depends on the use of a formula "which like other absorption formulæ can only approximately represent the facts," and which does not take any account of the production of secondary radiation or of scattering of the primary without change of nature. This criticism is singularly at fault. The formula we used for the absorption of the γ-rays of radium over a semicircular arc from a point source placed at the centre of a truncated hemisphere of absorbing metal, as we employed it in our experiments, is, unlike other absorption formulæ, mathematically exact and is deduced from the three definite postulates, (1) that the γ-rays are homogeneous and exponentially absorbed, (2) that scattering of the primary radiation does not take place, (3) that no (penetrating) secondary radiation is produced in the metal. The formula could not hold true if either of the three postulates were false. Nevertheless the theoretical formula agreed nearly perfectly with the experimental results for the case of lead, with the same value for the absorption coefficient as had been found in numerous other experiments. For zinc the formula also held for thicknesses greater than 2 cm., the results clearly indicating that here a penetrating secondary radiation was produced. When the complicated character of the theoretical expressions, involving as they do two exponential integral terms, is borne in mind, the almost perfect agreement between the theoretical and experimental results for lead cannot be dismissed as lightly as Dr. Kleeman indicates.

I take this opportunity of putting right an error arising out of a reference we made (p. 730) to some work of Bragg and Madsen. We deduced theoretically that the transformation of a fraction, varying from zero to unity, of the absorbed primary into a penetrating secondary radiation by different metals would result in variations in the ionizations observed with great equivalent thicknesses of different metals in the ratio of rather more than 2 : 1, which agreed with what we had found. We alluded to the fact that Bragg and Madsen had obtained a similar 2 : 1 ratio; but, as Professor Bragg has pointed out to me, secondary penetrating rays cannot have been the cause of their results, which they ascribe to variation in the absorbabilities of (secondary) β-rays in different materials. A part of our variation must be similarly accounted for, so that whether secondary penetrating rays had any influence remains to be proved.

Glasgow, July 5th, 1910. FREDERICK SODDY.

To the Editors of the Philosophical Magazine.

GENTLEMEN,— June 21, 1910.

In a paper entitled "On the Electrostatic Effect of a Changing Magnetic Field" by J. M. Kuehne appearing in the April 1910 number, the author attributes to me an effort to observe this effect described in my paper published in the *Physikalische Zeitschrift* (vi. p. 474, 1905). In my paper I distinctly disclaimed any effort to observe this effect, and pointed out that the experiment aimed to show that a plan suggested by Kolacek could not be expected to yield any positive results.

Very truly yours,
JOHN B. WHITEHEAD.
Professor of Applied Electricity.

Johns Hopkins University,
Baltimore, Md.

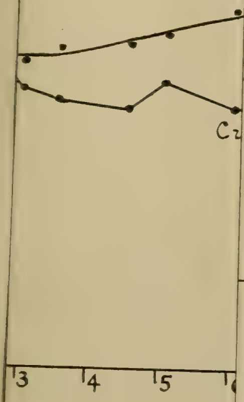
To the Editors of the Philosophical Magazine.

GENTLEMEN,— May 25, 1910.

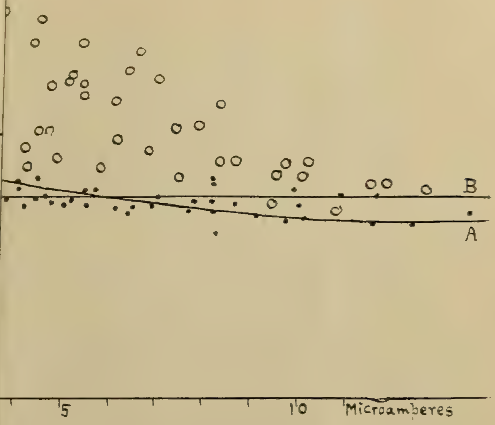
In connexion with my note "On the Laws regarding the Direction of Thermo-electric Currents enunciated by M. Thomas" (*Bulletin de la Classe des Sciences* of the Académie Royale de Belgique, No. 8, p. 903), which appeared in the April number (Phil. Mag. xix. p. 508), Professor E. van Aubel, of the University of Ghent, has called my attention to a note of his in the "Chronique et Correspondance" columns of the Paris *Revue générale des Sciences* for December 30th, in which the observations of Jäger and Diesselhorst are used to disprove the laws promulgated by M. Thomas in almost the same way as I use them in my note. I regret that I was not acquainted with Professor van Aubel's note when I sent mine to the Physical Society of London on January 8th, as I should have been glad to know that the disagreeable duty of criticising M. Thomas's theory had already been discharged.

I am, Yours truly,
CHARLES H. LEES.

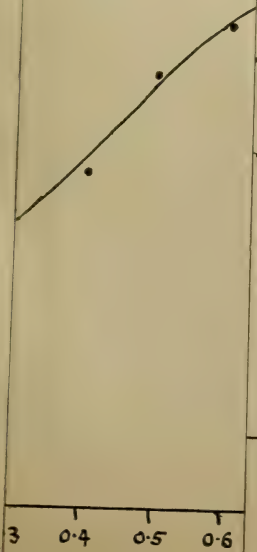
Curves IV.



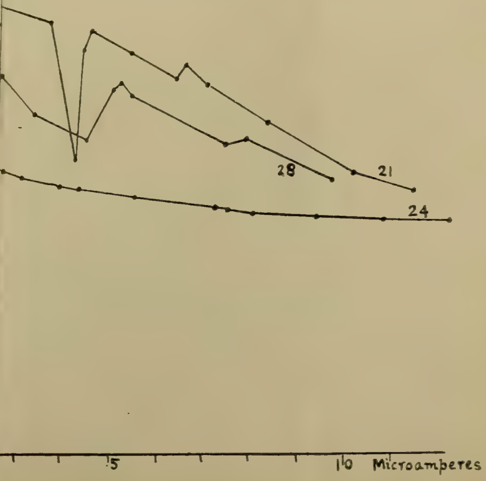
Curves VI.



Curves V.

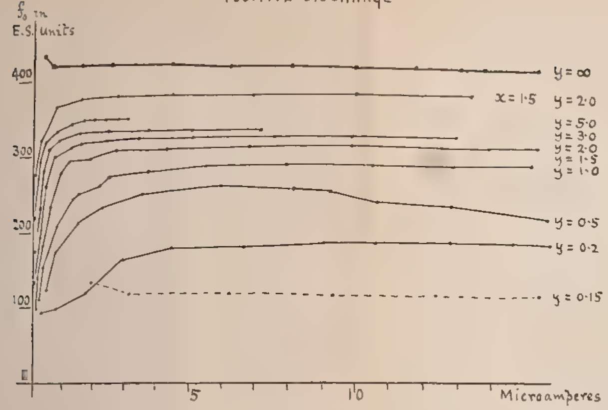


Curves VII.



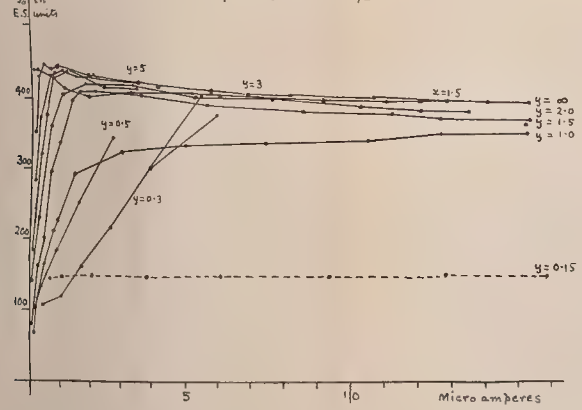
Curves I.

POSITIVE DISCHARGE

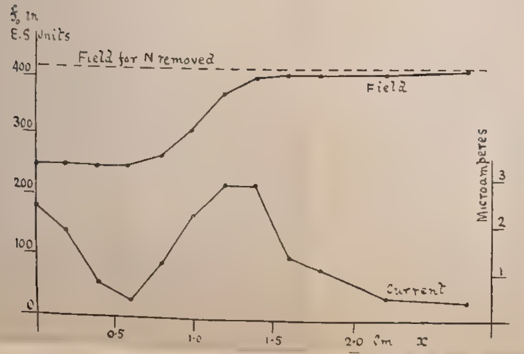


Curves II.

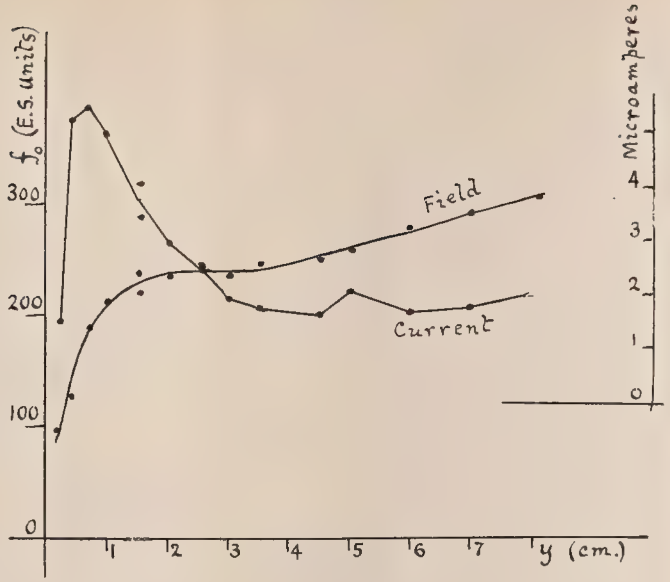
NEGATIVE DISCHARGE



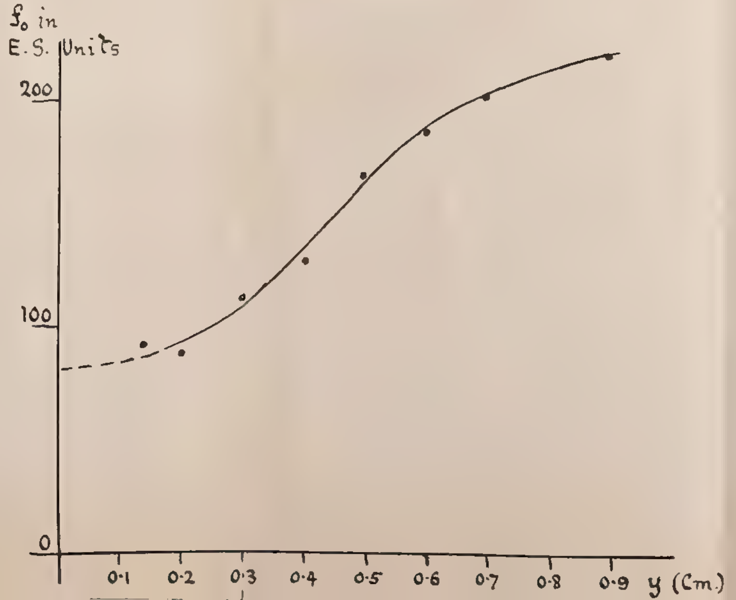
Curves III.



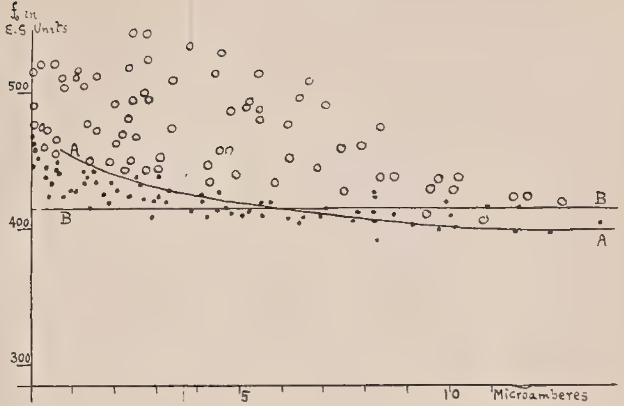
Curves IV.



Curves V.



Curves VI.



Curves VII.

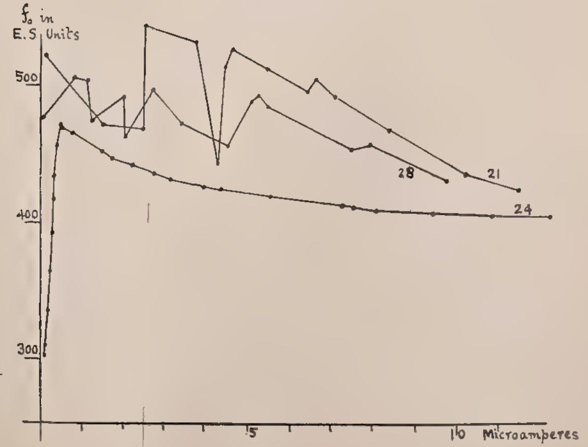


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Fig. 7.

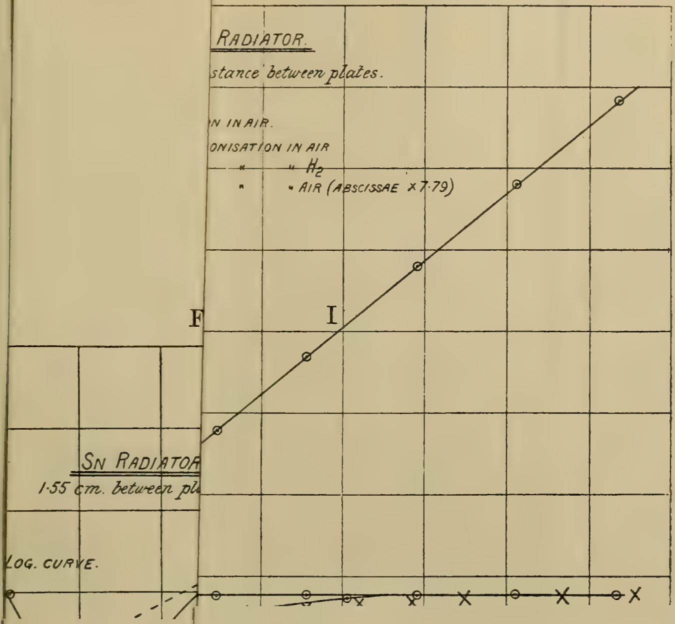


Fig. 4.

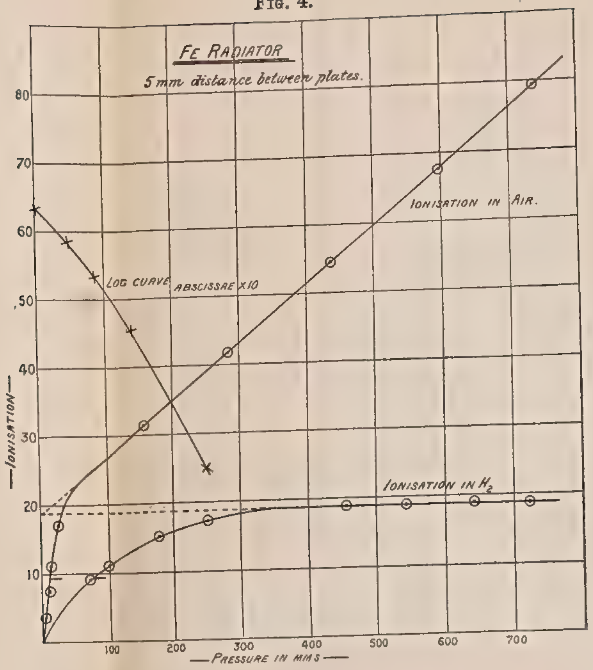


Fig. 5.

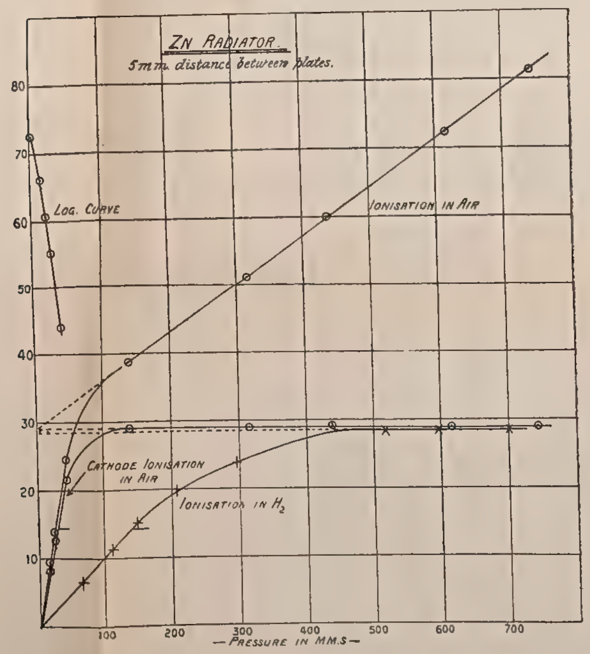


Fig. 6.

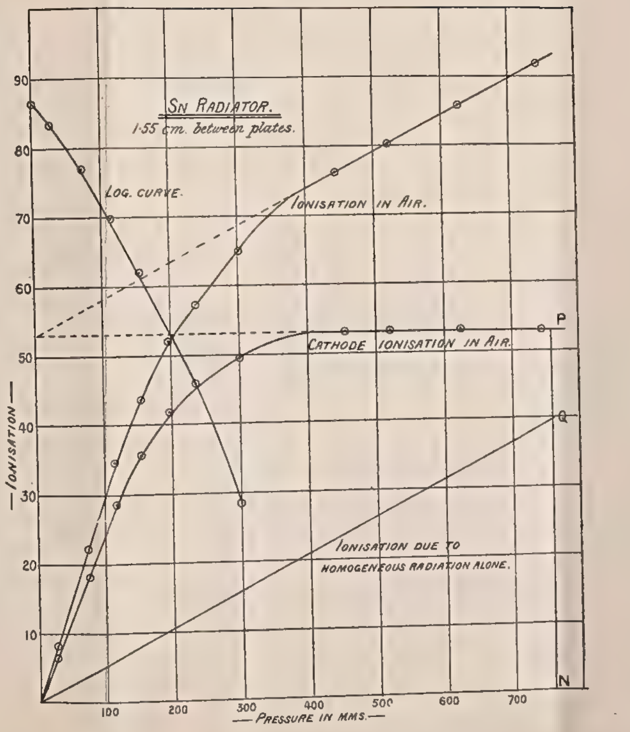


Fig. 7.

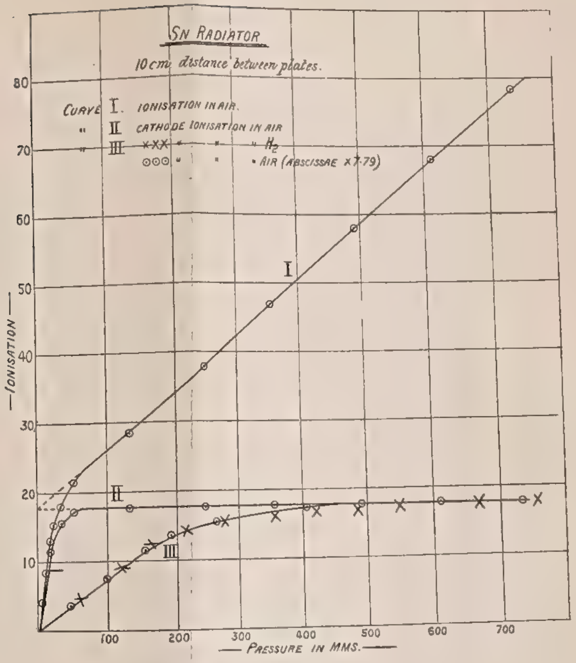
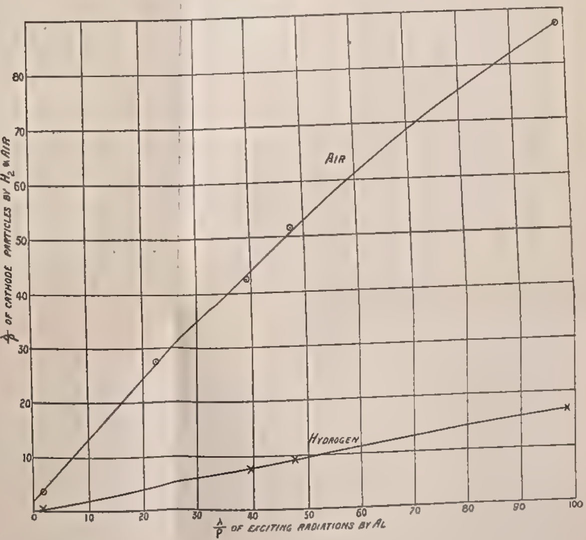


Fig. 8.



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XXXIX. *The Consequences of the Corpuscular Hypothesis of the γ and X Rays, and the Range of β Rays.*

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Introduction.

IN the following pages I have first restated briefly the case for the corpuscular hypothesis of the X and γ rays. I have then attempted to show the consequences to be

(1) A simple view of the history of the X or γ ray.
(2) The absence of true secondary radiation.
(3) A true additive principle in radioactive phenomena.
(4) The absence of specular reflexion.
(5) The inability of X and γ rays to ionize directly; the effect is indirect, the real agents being the secondary cathode and β rays.
(6) The general principle that if one radiant entity (α, β, γ, X, or cathode ray) enters an atom, one and only one entity emerges, carrying with it nearly all the energy of the entering entity.
(7) A natural division into three groups of the phenomena attending the passage of each radiant entity through matter. These groups relate to (*a*) rectilinear movements during which energy is spent so long as ionization is being produced; (*b*) special encounters with atoms on account of which deflexions or scatterings take place without appreciable loss of energy; (*c*) transformations (γ into β, cathode into X, &c.).

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[*] Communicated by the Author.

(8) The simple solution of at least two useful ionization problems. The second of these leads to a ready determination of the relative average ranges of β rays in various materials (the range being defined as the total length of the track when straightened out). These fit in very well with results obtained indirectly by H. W. Schmidt, and so furnish a general explanation of the form of the absorption curves of β rays.

THE idea that X and γ radiations are both to be regarded as consisting of streams of discrete entities has gained ground steadily in the last year or two. Sir J. J. Thomson looks upon the X ray as a kink in the one tube of force by which he represents all the properties of the electron. According to present knowledge the γ ray is of the same nature as the X ray, so that an hypothesis regarding the nature of the one must be taken to apply to the other also. J. Stark has recently developed* the theory, based on the work of Planck, that an X ray is a bundle of energy travelling without alteration of form. This differs from Thomson's theory in at least one important particular because the latter involves a change of form †. I have myself found it convenient to regard the X ray as a negative electron to which has been added a quantity of positive electricity which neutralizes its charge, but adds little to its mass.

Whatever view may be taken of the nature of the entity, the acceptance of the corpuscle idea modifies our views of the phenomena attending the passage of rays through matter, and alters the language which we use in describing experimental results. I think that it leads to a marked gain in simplicity, and my object in writing this paper is to show, if I can, that this is the case.

It will be convenient to begin with a brief statement of the main arguments for the entity hypothesis, though this plan involves some little repetition of similar statements previously given. For this purpose it will be best to use the results of recent investigations, since they are most fitted to serve as a foundation for the case, although I would not undervalue the older arguments which first suggested the discrete form of the X ray.

When a pencil of γ rays is directed normally upon a thin plate, for example a plate of aluminium one or two millimetres in thickness, β rays spring out from both sides of the

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* *Phys. Zeit.* x. p. 902 (1909); xi. p. 24 and p. 179 (1910).

† Phil. Mag. Feb. 1910.

plate[*], but very many more are found on the side of the plate from which the γ rays emerge than on the side through which they enter. In fact experiment shows that their distribution is just such as should be found if, when they are first formed, they simply prolong the line of motion of the γ rays, and if their subsequent movements are due to the usual scattering which β rays undergo. Cooksey[†] has shown that the same lack of symmetry is to be found in the cathode radiation which is caused by X rays.

It is also found that the speed of the β ray, which is caused by a γ ray, is independent of the nature of the atom in which it originates, but is directly connected with the quality of the γ ray. Again the parallel effect is to be observed with X rays, as is evident from the work of Dorn, Innes, and others, who have made it clear that the speed of the cathode rays which originate when X rays fall upon atoms depends rather on the nature or quality of the X rays than on the kind of atom. But the most accurate and complete proofs of these principles have been recently given by Beatty[‡] and by Sadler[§].

These facts are of fundamental importance when we come to discuss the source from which the β-ray energy is drawn. If it comes from the atom, as was first supposed, we have a trigger effect: the γ ray is to be considered as precipitating an explosion[||]. But if this were the case we should expect (1) that the direction of motion of the shot, viz. the β ray, would have no connexion with the direction of motion of the γ ray which merely pulled the trigger of the gun; (2) that the speed of the β ray would not depend on the quality of the ray, but on some property of the atom corresponding to the charge in the gun. The actual conditions are exactly the reverse. If we examine the alternative hypothesis, viz. that the energy of the β ray is brought to it by the γ ray, and the atom is merely the cause of a transference of energy, we find a perfectly satisfactory explanation. The momentum of the electron is a persistence of the momentum of the γ ray, and its energy is derived from the ray; the electron, therefore, continues the line of flight of the γ ray with a speed which has nothing to do with the atom to which the transformation is due, and depends entirely on the quality of the γ ray.

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[*] Bragg and Madsen, Trans. Roy. Soc. of South Australia, Jan. and May 1908; also Phil. Mag. May and Dec. 1908.

[†] 'Nature,' April 2, 1908.

[‡] Proc. Camb. Phil. Soc. vol. xv. pt. v. p. 416.

[§] Phil. Mag. March 1910.

[||] 'Conduction of Electricity through Gases,' 2nd ed. p. 320.

We therefore conclude that the energy of the β ray is derived from that of the γ ray, and similarly the energy of the cathode ray from that of the X ray. We are then in a position to take into account another experimental result. The velocity of the cathode particle ejected by the X ray is found to be the same, or nearly the same, as that of the cathode particle in the original X-ray tube. There is no doubt as to the approximate truth of this statement, though accurate experiment is wanting. Now there can be no question of the storage of X-ray energy in an atom until there is enough to provide for the ejection of a cathode ray, for then the nature of the atom would again be of influence, and we should revert to all our previous difficulties. One X ray must be enough to provide one cathode ray. Nor does it seem possible to suppose that the energy of several cathode particles can be stored up in an atom until there is enough to produce one X ray; for amongst other considerations there would then be no apparent reason why the speed of the cathode ray should influence the quality of the X ray so directly as it does. Hence the X ray cannot have more energy than was possessed by the cathode particle in the X ray bulb. Put the two statements together and we find that one cathode ray impinging on an atom may produce one X-ray and no more, and in its turn the X ray through impact on an atom (not necessarily the first it meets) produces one cathode ray and no more, handing on its energy and its direction of motion.

It is this conclusion which seems fatal to the spreading pulse theory. The latter taught us that when an electron was arrested the energy set free travelled out in all directions through space on an ever enlarging surface. We now find that we must have the energy of the X ray confined within very narrow bounds which are not to widen as the X ray travels, so that when at last the transference of energy takes place the energy is all in one spot ready for the sudden change. The speed of the cathode ray caused by the X ray is the same no matter where it comes into being. We cannot allow the energy of the X ray to spread even a little. The ray is to be considered as a minute entity of some sort, its energy as it travels being always bound up in an unaltering volume of atomic magnitude at the most.

This is a brief statement of the case for the entity hypothesis, containing only one main line of argument. Many subsidiary considerations are omitted. It is worth observing that it turns on questions regarding energy.

We must of course ask what we lose by the adoption of the new hypothesis, with the consequent abandonment of the spreading pulse theory. Only one thing of value: viz. the easy explanation of the partial polarization of a primary beam of X rays, and of the more complete polarization of secondary beams. Those who would maintain that the entity contains a wave-motion within it might argue that there is no loss of this kind; but such a position would seem unsound until there is a clear expression of the meaning and properties of an entity or bundle of energy with a wave-motion inside it. It is to be observed that the polarization of light is a very complex phenomenon which is capable of the closest examination, and that the undulatory theory of light explains it with great exactness. It is possible to overrate the importance of the ability of the pulse theory to explain the polarization of X rays, because it may be imagined that in this case also a complex effect is successfully accounted for. As a matter of fact the polarization of X rays is quite a simple effect and bears but a meagre resemblance to the polarization of light; there are, for example, none of the elaborate and beautiful effects of crystals. The polarization of the X ray consists only in the fact that if it is deflected it is more liable to move in one particular plane passing through its line of flight than in another: a billiard ball with side on does as much, or more exactly still, a spinning tennis ball.

If we accept the entity hypothesis the processes of the X-ray tube assume a new aspect. We gain in precision of statement and in clearness of outlook. The stream of cathode rays is directed against the anticathode; we no longer say, somewhat vaguely, that part of the energy goes in heat, part in secondary cathode radiation, part in X rays. We must not imagine a cathode ray to ricochet hither and thither among the atoms of the anticathode radiating X-ray energy at every turn. No doubt it does so radiate some energy, but the amount is trifling, and has nothing to do with X rays. We must rather say, that when each cathode particle strikes the anticathode it may fritter away its energy into a form which finally takes that of heat, or it may be splashed back against the glass wall of the tube, and cause phosphorescence and other effects, or, again, it may disappear (not necessarily at its first meeting with an atom, nor before it has spent any of its energy), and the complete disappearance of the cathode ray as such will then be simultaneous with the production of the X-ray entity. In the last case the entity starts off on its straight line course endowed with a penetration which the cathode ray did not possess. When it meets an atom, there is an overwhelming probability that it will go through without effect; but it may be deflected, and again it may in its turn be replaced by a cathode ray like the original one. We may think of the whole affair as the history of a small quantity of energy carried first in the X-ray bulb by a cathode ray, transformed into the energy of an X ray, with perhaps further reconversions; frittered away while it takes the cathode ray form, carried intact while it has the X-ray form, until finally it has all been spent.

It is never reinforced at any stage of its journey, for there is no unlocking of the internal stores of atomic energy, according to the most recent experimental evidence. Both Bumstead and Angerer, working independently, found there was no trace of a difference in the amount of heat generated by a stream of X rays in two different metals, such as would be expected if any part of the heat were due to atomic energy set free by the X rays. Moreover, no arrangement of screens or reflectors about a stream of X or γ rays causes any increase in the total ionization produced by the stream, so far as we have been able to discover. It is only possible to increase it in one place at the expense of a decrease in another. In this sense at least there is no such thing as "secondary radiation."

The term "secondary radiation" is largely used, and is often quite satisfactory; but it may have many meanings not all of which are true to fact. It is convenient for the time to continue the argument of this paper in the form of a discussion of the circumstances under which the use of the term is justified. For it is obvious that as long as we retain the idea that secondary radiations may add themselves to primaries, tertiaries to secondaries, and so on, we are oppressed with the sense of a complexity which must add greatly to our difficulties. If, on the other hand, we can permit ourselves to think that there is no indiscriminate addition of this kind, but that the appearance of each individual secondary entity is marked by the simultaneous disappearance of a primary entity; further, that the secondary inherits the energy of the primary, and, in some cases, its direction of motion; and further still, that the secondary can for all practical purposes be looked upon as a continuation of the primary, sometimes modified in form, then we obtain a simplification worth having. Let us, therefore, consider the matter a little more in detail.

When the electron, as a β or a cathode ray, dives into an atom and is thereby deflected, as is occasionally the case, the electron moves off in a new direction, but it can hardly be called a new ray. We may call it a secondary ray if we please, but we may just as well say that every molecule of a gas is a primary molecule before a collision, a secondary afterwards, a tertiary after two collisions, and so on; and it would be worse than useless to do so. Again, when Geiger shows that an α particle may be deflected or scattered he does not speak of a secondary α ray. When an X ray entity is transformed by an atom's action into a cathode ray, or a γ ray into a β ray, we may speak of the new rays as secondary rays, and now the term is really convenient; but it must not be taken to mean too much. There is a change of form of the entity, and that is all. When an X ray entity is deflected in passing through an atom, or is "scattered" in the usual phrase, the term secondary radiation is really inappropriate, because it is but the X ray entity swinging off in a new direction. Barkla has shown that when primary X radiation falls upon any metal (from Cr to Ag at least), so long as the penetrating powers of the primary exceed a certain limit peculiar to that metal, a homogeneous X radiation is emitted which is characteristic of the metal, and is less penetrating than the primary. Here the term secondary would seem to have a real meaning, for we wish to describe the fact that a primary X ray entity possessing energy of any amount above a certain minimum is replaced by a secondary X ray entity possessing an energy characteristic of the particular metal, and always less than that of the primary. The effect is simple enough to be described in this way, for energy considerations show that it can only be a case of one entity replacing another, not of two or three replacing one, nor of one being added to the original. It is not clear, however, that a transformation of this kind actually occurs, a transformation, that is to say, which makes the primary differ so much from the secondary that a real difference is to be recognized by the use of different terms. I hope to be able to show later that there are good grounds for presuming a double transformation, the first stage being a conversion of the primary X ray into a cathode ray stage, during which a loss of energy occurs, and the second a reconversion into the X-ray form. In any case it is enough for the present that the secondary must draw its energy from the primary, and the appearance of the former implies the disappearance of the latter.

There is another case which must be considered specially. McClelland[*] has explained certain of his experiments on the

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[*] Proc. Roy. Soc. lxxx. p. 501 (1908).

scattering of β rays by supposing a real secondary radiation to be added to a reflected primary. The experiments are simple. When a stream of β rays falls at an angle of, say, 45° upon an aluminium plate, it is found that the β rays which leave the plate on the incidence side are not distributed symmetrically about a normal to the plate, but show a maximum in a direction which is separated by the normal from that of the incident stream. When the plate is of lead or any other substance having a high atomic weight, the effect is much less marked. In fact it looks as if there was a confused specular reflexion at the surface of the plate coupled with a radiation scattered in all directions. McClelland therefore divides the scattered rays into two groups, the first of which consists of β rays from the primary stream reflected by the surface of the plate like light by a mirror, the second of a set of true secondary rays.

Let us first consider the question of specular reflexion. All the evidence we have regarding the actions and reactions between atoms and radiant entities shows that each atom when in collision with an entity has to bear the shock alone: it receives no support from its neighbours, even when they form parts of the same molecule, *a fortiori* when they are only neighbouring atoms in the surface of a plate such as McClelland used. It is this which makes radioactive measurements independent of physical and chemical conditions. The point seems to be firmly established now, for though at times evidence has been brought forward which has at first appeared to contradict the principle, more careful examination has always shown the evidence to have been mistaken. The principle may be expressed by the statement that the action of a molecule on one of the radiant entities is the sum of the effects of the actions of its component atoms, no allowance for constitutive influences being necessary. One or two examples will be sufficient.

The stopping power of a molecule for α rays is the sum of the stopping powers of the individual atoms of the molecule. During 1908 I measured as carefully as possible the stopping powers of a number of gases which were prepared in a very pure state by Dr. Rennie and Dr. Cooke of the Adelaide University. The range of the α particle can be measured to much less than one per cent. The additive principle was found to be true within the errors of experiment; both for stopping powers measured with respect to Ra C, and those measured with respect to the α particles of Ra A. The two sets are not quite the same[*].

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[*] Bragg, Phil. Mag. April and Sept. 1907.

Again, the absorption and scattering coefficients of liquids and compounds for β rays have lately been the subject of careful measurement by Schmidt[*] in Giessen, and by Borodowsky[†] in Manchester, and the additive principle was fully confirmed in this case also.

A radiant entity, therefore, acts on one atom at a time; and if its direction of motion is altered by a collision, the alteration is determined by the mutual relations of the entity and the atom alone. Neighbouring atoms have nothing to do with it, and it is quite immaterial whether or no there is a surface close by which separates one lot of atoms from another. On the other hand, specular reflexion, such as the reflexion of light in a mirror, depends on the conjoint action of the atoms of the reflecting surface. It cannot be supposed, therefore, that one part of the scattered β radiation examined by McClelland consists of rays reflected like light: and this being so, it is probable that the description of the remainder as a true secondary is wrong also. In fact there is a much more direct explanation of the whole effect.

When an entity passes into an atom there is a chance of deflexion through any given angle. Radii may be drawn from the atom, each representing by its length the chance of deflexion into the direction in which it is drawn. The extremities of these radii will lie on a surface the form of which will represent graphically the probable results of the encounter ; and its form will vary with the atom, with the nature of the entity, its speed, and so forth. As a rule the lighter the atom the more eccentric is the oval surface. The surface is one of revolution, the axis being the original line of motion of the entity. A section through the axis will therefore express all there is to express ; and such a section may be called a "deflexion oval." It must be one of the objects of experiment to determine the forms of the deflexion ovals in all possible cases, for clearly, until we know the probable results of an encounter between a given entity and a given atom, we cannot calculate the result of the attempt of an entity to pass through a plate which is an aggregate of many atoms ; in other words, we are not in a position to calculate with safety the absorption coefficients or reflexion coefficients of β rays. Although we do not yet know the exact form of the oval when a β ray impinges on an atom, we do know that it is far more eccentric for an aluminium atom than for a lead one. The heavy atom is much more likely to swing round the electron than the light one ; when

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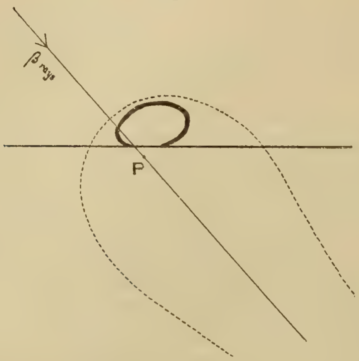
[*] *Phys. Zeit.* xi. p. 262 (1910).

[†] Phil. Mag. April 1910.

a stream of β rays falls upon a lead plate far more are turned back than when the plate is made of aluminium.

Suppose that β rays fall on an aluminium plate, as in the figure. Suppose one of the rays to be scattered by some atom in the plate at P. The chances of deflexion in various

Fig. 1.



directions are represented by the radii of the deflexion oval, which is roughly drawn as a dotted line. The chances of emergence have now to be taken into account; the deflected ray has less chance of getting out the more parallel is its line of movement to the surface. Each radius of the oval must be multiplied by a factor approaching the form $e^{-d \sec \theta}$, where d is the depth of the atom below the surface and θ is the inclination of the radius to the surface normal. The ends of the radii thus obtained lie on a new surface which is similar to McClelland's; its section is indicated by the firm curved line in the figure. It is in the right sense asymmetrical with respect to the normal; and the asymmetry is greater for light atoms than for heavy, because the lighter the atom the more eccentric is the oval. Thus McClelland's results are explained without the necessity of introducing the two hypotheses of specular reflexion and true secondary radiation with all the complexities they bring in their train.

Yet there is one way in which a sort of secondary β radiation might occur. Can an electron in flight so collide with another as to give it a large share of its energy, so that one β ray is replaced by two of much less penetrating power? There is no obligation to think so at present; but the case is worth considering, for it simplifies matters very much if we can conclude that no such obligation is likely to arise. There is however, not much to guide us. We may to some extent argue from the behaviour of other entities. An α particle has a considerable speed, say 2×10^9 cm./sec., and as an atom of helium it must contain several electrons, yet we never find in the gas traversed any electrons moving with a speed of more than a few volts: that is to say, we find only δ rays. Again, one α ray never gives rise to two α rays: nor one X ray to two X rays, so far as we can see. The enquiry really resolves itself into the difficult question of the way in which ionization comes about. There are indications that it is not a straightforward process in which the moving entity drives out the electron from the atom by direct collision, because, in the case of the α particle at least, the energy spent is not always proportional to the ionization produced—there must be an intervening link; and because, as already said, the ejected electrons all seem to have speeds of the same low order. There is indeed little certain information on these points, and it can only be said that to all appearances ionization is the result of the passage of entities through molecules, and that the observed facts can be expressed on the simple hypothesis that there is a gradual drain on the energy of the entity but no large change at any one encounter with an atom. Of course it may well be asked, what then does happen when one electron moves so directly upon another that we may expect a collision such as occurs when one billiard ball strikes another? But then we have here preconceived ideas of volumes, surface contacts, and elasticities, which we must not carry over to the case of electrons encountering each other. There is really nothing to compel us to handle such electrons as anything more than mere centres of force: if we give them dimensions, it is only to make them have the right amount of electromagnetic mass. Even when we take this view we have no sure ground on which to base a calculation as to the probable result of an encounter, because the electrons in the atom cannot be considered separately; each one is backed up by unknown linkages with positive electricity and with the general framework of the atom, as we know from the fact that the scattering of β rays depends very greatly on the atomic weight of the scattering material. To sum up, there is nothing to be said against, and something to be said in favour of, the simple hypothesis that the β particle gradually spends energy along its track, but does not lose any material portion of its energy on account of the violent deflexions to which it is frequently subjected. Its career is like that of an α particle with many more deflexions in it, though there is nothing at present to prove that if the track were straightened out the length of it would be constant, as in the case of the larger entity, the range of which can be found with precision. We may think of the β particle as possessing an average range in a given material, best expressed perhaps as a weight of material crossed. For purposes of definition we may suppose the track to be the axis of a cylinder of a small cross-section s; then if ds is the weight of the cylinder, d is the range. I hope to be able to show presently that it is possible to find the relative values of d for given β rays in various substances.

We have already sufficient information to give us some idea of the lengths of the short portions which make up the total range. The work of Madsen[*] shows that such β particles as have been turned aside from a main stream passing normally through an aluminium sheet ·004 cm. thick are not likely to experience a second deflexion in the same plate. Thus β particles of a speed approximating to that of light must often go through a tenth of a millimetre of aluminium without deflexion, or through the equivalent 20 cm. of air. Similar conclusions may be drawn from an earlier paper by Crowther[†]. Crowther does indeed state that the scattering of a pencil of β rays is complete when it has passed through ·015 cm. of aluminium; but he uses the term in a special sense relating to the details of his experiment. It does not mean that after going through such a plate the stream of β rays has lost all sense of direction, and the various rays are heading every way; for his figures show that 30 per cent. of the rays which emerge from the plate and were originally directed normally upon it retain so much of their original direction as to be grouped about the emergent normal in a cone of a semi-vertical angle between 4° and 5°. The solid angle of such a cone is about $\frac{1}{250}$ of that of a hemisphere.

I have now considered one by one several possible causes of complexity; and I would conclude that on the whole they can be put aside as having at present no obvious existence. In this way we arrive at a comparatively simple idea of the history of the radiant entity whatever its kind, α, β, γ, X, or cathode ray. In each case there is an initial store of energy communicated to the entity: the subsequent motion is rectilinear, varied by encounters which change the direction of the motion but not its energy: ionization, if it takes place at all, takes place along the track; and it is in this way that the energy is drawn upon. The form of the entity may change, γ into β, X into cathode ray, and so on; but there is so little change in anything but form that practically we may assume a continuity of existence.

[*] Phil. Mag. Dec. 1909.

[†] Proc. Roy. Soc. March 1908, lxxx. p. 186.

There are therefore three main subjects of measurement in respect to each entity: (*a*) the expenditure of energy along the path, (*b*) the form of the deflexion oval, (*c*) the chance of conversion of form. Let us consider to what extent these measurements have been made, and also some methods of making them.

Let us take the α particle first. The case is an especially simple one because there is no conversion of form, and very little chance of deflexion until the speed has greatly diminished and the range is nearly completed. Hence the particle's properties are almost entirely expressed when its range is determined; and this has been done with some thoroughness. The feeble but very interesting deflexions which do take place have been measured by Geiger. Our knowledge of the α particle is fairly complete in the sense that we know what to expect when any given screen is placed in the path of any given stream of radiation. We may go on to consider some of the other radiations of which we know less.

The X and γ rays have also their special points of simplicity, but they form an almost exact antithesis to the α rays. Here it appears that the expenditure of energy along the track is either negligible or non-existent. The rays do not ionize directly. Nor is the deflexion oval a very important thing. The most important feature is the chance of transmutation of form, the X ray being sometimes replaced by a cathode ray, the γ by a β ray.

The argument that the X or γ entity spends no energy along its track arises simply from the fact that it produces a cathode or a β ray of the same speed, no matter how much material it has already traversed. It cannot keep its energy intact while traversing matter and at the same time cause ionization which involves the expenditure of energy. Gases which are crossed by X and γ rays are ionized, but that is because they produce cathode and β rays respectively: and these latter do the work. Of course it may be said that the conversion of one X ray into one cathode ray is ionization: and so it is; but it is natural to keep this solitary and peculiar event distinct from the general ionization of the gas along the track of an entity.

This deduction seems to afford an opportunity for putting our hypothesis to the proof. What experiments have been made from which we may determine whether or no X and γ rays ionize gases directly?

McLennan describes an experiment (Phil. Mag. Dec. 1907) in which he shot γ rays through two ionization-chambers, one made of lead, the other of lead lined with aluminium, and compared the ionization current in the two cases. He supposed that the ionization could be assigned to two sources, one the direct action of the γ rays on the gas, the other the secondary rays caused by the γ rays to issue from the metal sides of the chamber. The former would be the same for the two chambers, let it be called I_P: the second would not, let it be I_{SL} for the chamber which is all lead, and I_{SA} for the one which is lined with aluminium. He then assumed that $I_{SA}=\cdot 286\times I_{SL}$, since Eve had shown that when γ rays fell on lead and aluminium plates the returned β rays were in the proportion of 100 to 28·6.

Thus:

$$I_P+I_{SL}=90\cdot 05 \text{ (total ionization in the lead chamber).}$$
$$I_P+I_{SA}=49\cdot 5 \text{ (the aluminium lining having been inserted).}$$
$$I_{SA}=\cdot 286\times I_{SL}.$$

Hence he found that $I_P=33\cdot 05$, $I_{SL}=57\ 00$, $I_{SA}=16\cdot 3$; and concluded that I_P, that is to say the result of the direct action of the γ rays upon the gas, was very considerable.

The source of error in this calculation is the assumption that $I_{SA}=\cdot 286\times I_{SL}$. It was not known at that time that this relation only holds in respect to the β radiations from the front face on which γ rays fall: the β radiations which issue from the face of a plate from which γ rays are emerging may even be greater for aluminium than for lead: and McLennan's results depended on both incidence and emergence rays. It was not right to use Eve's figures, which referred to a special case of incidence rays; and there is no contradiction of the deduction we have drawn from the entity hypothesis, viz. that I_P is zero.

Again, W. Wilson records * measurements of the ionization in an electroscope made partly of aluminium and partly of brass when the pressure of the air was varied from one to forty atmospheres: the γ rays came from RaC. He supposes that "the total ionization due to the secondary β rays at different pressures will be given by $B(1-e^{-\lambda ap})$ where B is a constant, p the pressure and λ the coefficient of absorption," and further that "the ionization due to the γ rays will be given by a term of the form Ap, where A is a constant." He then finds that B must be 6·6 times A, and that the ionization due to the secondary rays is therefore several times the ionization due to the direct action of the γ rays on the gas. This is of course nearer than McLennan's result to what we now expect, but it still ascribes some effect to the direct

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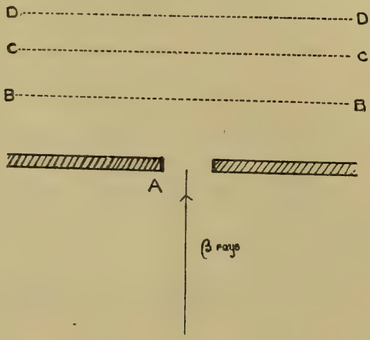
* Phil. Mag. Jan. 1909.

action of the γ rays. The fact is, however, that the division of the ionization into these two terms is not quite right, even supposing the ionization due to the γ rays to include the ionization due to the β rays generated by the γ rays in the gas.

Let us consider so far as we can what should be the amount of ionization in a gas through which γ rays are passing, assuming the entity hypothesis and its consequences. There are two cases at least in which the solution is fairly easy and satisfactory. The easier one is the case of an ionization vessel lined completely with any material, provided only that it is so thick that β rays cannot cross it. The other is the case of a large but shallow ionization vessel, the top and bottom of which consist of two parallel plates, one of which is made of a substance having about the same atomic weight as the air which the vessel contains. Let us take the latter case first.

It simplifies considerations of this kind to remember that the spacing of atoms plays a subordinate part in them. Suppose, for example, that a stream of β rays passes up normally to a plate through an opening in it at A, and that

Fig. 2.



B, C, and D are imaginary surfaces in the air parallel to the plate. The β rays cause a certain ionization in the air between the planes B and C. It would make no difference in this amount if the air between C and D were compressed into a thin layer lying along C or indeed anywhere above it, so long as the air between B and C remained in a uniform layer between and parallel to B and C. It would be the same even if air were brought down from above C and laid in a layer along C in such quantities that no β rays could get through it; or if a plate composed of atoms of nearly the same weight as the air atoms were placed along C. If the distances of the planes from A were b, c, and d, and if we might assume the β rays to be spent exponentially with a space coefficient λ, the ionization between the planes B and C would be $\mathrm{I}(e^{-b\lambda}-e^{-c\lambda})$ in all the cases just described, I being the initial energy of the radiation as it comes through the hole at A. There is no need to trouble about secondary radiation from a plate at C containing light atoms only, even though we know that atoms of carbon and oxygen can return some β rays: all such effects are already fully accounted for in the formula.

Consider now a stream of γ rays passing normally upwards through the lower plate bounding such an ionization-chamber. The upper plate can be made of cardboard, or some material having approximately the same average atomic weight as air.

Let k be the absorption coefficient of the material of the plate for γ rays in the sense that rays of energy I lose an amount of energy $k\mathrm{I}dx$ in passing normally through a sheet weighing dx grams per sq. cm.: k is then the weight absorption coefficient. The meaning of this is to be that the energy $k\mathrm{I}dx$ becomes energy of β rays which at the start continue the line of motion of the γ rays.

Let λ be the similar coefficient of the plate for β rays such as these γ rays produce. This means that when a layer of the same material as the plate, weighing x grams per sq. cm. is placed normally to a stream of β rays of energy I, the energy which gets through the plate and is spent in ionizing the air on the other side is $\mathrm{I}e^{-\lambda x}$. It is worth observing that if some other gas, say a heavy one like methyl iodide, were substituted for the air, the gas would return more of the radiation into the plate, so that more would be spent in the plate and less in the gas: it might be said that the absorption of a plate depended on the gas or other material above it.

Let k' and λ' be the corresponding coefficients for the γ and β rays in air.

The β rays originated in a layer of weight dx, which is at such a distance down in the plate that a layer of weight x lies above it, will have an energy $k\mathrm{I}e^{kx}dx$, where I is the energy which the γ rays possess as they enter the ionization-chamber. These β rays at first move directly upwards towards the chamber, and a certain fraction, viz. $e^{-\lambda x}$, of their energy is transmitted across the layer x into the ionization-chamber. The whole energy emerging is therefore $\int_0^t k\mathrm{I}e^{(k-\lambda)x}dx$; and if the plate is thick enough to stop all β rays we may put the thickness t equal to infinity. The emerging energy of β rays is therefore $k\mathrm{I}/(\lambda-k)$, which may practically be simplified to $k\mathrm{I}/\lambda$, since k is usually so small compared with λ.

The ionization produced in the ionization-chamber may be taken as $k\mathrm{I}(1-e^{-\lambda'\mathrm{D}})/\lambda$, where D is the depth of the chamber multiplied by the density of the air. This is not strictly correct, because some of the β rays will strike against the side walls, which we cannot do without, and will not spend so much energy in the layer of air (of weight D) as they ought to do according to the definition of λ'. If we had a material which threw back all β rays completely, we could avoid this error; but there is no such material. It can be lessened by having a wide and shallow chamber. There is an error of a different nature in that λ' was defined with reference to rays striking a layer of air normally, whereas the β rays emerging from the plate will be moving in all directions. But it is not worth while to attempt to avoid such errors just now: it is probably a still greater error to have assumed an exponential law, and our object is to obtain a theoretical result accurate enough to tell us what we should look for.

We have now to take into account the ionization due to the β rays produced by the γ rays in the air of the chamber. This may be done by direct calculation, or in the following way which seems interesting.

If the plate which forms the base of the chamber were replaced by a plate of nearly the same atomic weight as the air in the chamber, the γ rays would then pass through the same sort of atoms throughout their course. Considering a short path of the course in which there is no great absorption of the γ rays, strata of equal weight convert equal quantities of γ-ray energy into β-ray energy, and will show equal ionization even though the ionization in any stratum is not wholly due to the β rays made in that stratum. The energy spent on ionization in any stratum is practically equal to the γ-ray energy converted in that stratum: thus the ionization in this particular ionization-chamber is measured by $k'\mathrm{DI}$: the λ' does not come in. If we now replace the bottom plate of constants k' and λ' by the plate of constants k and λ, we add a source of ionization amounting to $k\mathrm{I}(1-e^{-\lambda'\mathrm{D}})/\lambda$, but we take away a source of ionization amounting, by the same rule, to $k'\mathrm{I}(1-e^{-\lambda'\mathrm{D}})/\lambda'$. We also provide a plate which turns back more effectively some of the β rays made in the air of the chamber and in the plate at the top, but these are not many and we may neglect them. Thus the ionization in the chamber is expressed by

$$I\left\{Dk'+\left(\frac{k}{\lambda}-\frac{k'}{\lambda'}\right)(1-e^{-\lambda'D})\right\}.$$

If $k/\lambda=k'/\lambda'$ the expression becomes IDk' simply: and the relation between ionization and pressure, measured by D, becomes a linear equation. If k'/λ' is greater than k/λ the curve is convex to the pressure axis, and if less it is concave. So far as I know, no experiments have ever been carried out with an ionization-chamber of this form in which γ rays have been employed to ionize air at different pressures. In the experiments of Kaye and Laby * the ionization-chamber was wholly made of one metal aluminium: in those of W. Wilson† it was partly of brass and partly of aluminium. If the γ rays have been hardened by a lead screen, k and k' are nearly equal, in fact the absorption coefficients of a number of substances are nearly the same. Now the β ray absorption coefficients are somewhat smaller for light atoms than for heavy, so that k/λ is less than k'/λ' and the curve, in the case I have considered, should be slightly convex to the pressure axis. When the top and bottom plates are both of aluminium, it should be slightly concave, as will be shown presently: Kaye and Laby found this to be the case.

In the case of γ rays, $\lambda'D$ is generally small, unless the pressure of the air in the chamber is very great: the expression then becomes

$$I\left\{\frac{Dk\lambda'}{\lambda}+\left(\frac{k'}{\lambda'}-\frac{k}{\lambda}\right)\frac{\lambda'^2D^2}{2}\right\}.$$

There is a term in this expression which is proportional to D and therefore to the pressure, but it does not represent exactly the action of the γ rays on the air, as some have supposed. Nor does it represent the action of the secondary rays from the walls entirely. And again it has sometimes been stated that a term proportional to the square of the pressure will be required to represent the ionization due to the β rays made by the γ rays in the gas. Clearly this is not quite true.

In the case of X rays k is usually so much greater than k' that the latter may be neglected, and $\lambda'D$ is so large that $e^{-\lambda'D}$ is negligible also. The exponential term is only to be retained when the pressure of the gas is so low that the cathode rays originating in the walls of the chamber can get across it in

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* Phil Mag. Dec. 1908.

† Phil. Mag. Jan. 1909.

appreciable quantities. At ordinary pressures the formula becomes $I(Dk' + k/\lambda)$.

In this form it may be tested experimentally. It may be well to repeat that this formula is deduced on the supposition that X rays do not ionize a gas directly, but indirectly through the intermediate action of the cathode rays produced by the X rays in the metal through which they enter and in the gas which they cross. The term Ik/λ represents the effect due to the cathode rays from the metal; IDk' represents the effect due to the cathode rays formed in the gas. The first of these can be determined by experiment in a given case; the second can be calculated from the first when measurements have been made of k/k', λ, and D. If then the ionization produced by the X rays in the gas (directly or indirectly) is also found experimentally, it can be seen whether the calculated indirect effect is sufficient to account for it all, or whether there is something left over which must be ascribed to the direct action of the X rays.

I have made a number of experiments of this kind and have found that the results were always to be explained on the supposition that there was no direct action of the X rays. An example will show the usual extent of the agreement.

An ionization-chamber was made of brass, lined with aluminium to avoid disturbances due to the secondary X rays of brass, and again with paper to cut out the secondary cathode rays from the aluminium. The chamber was cylindrical, 3·6 cm. deep and 10 cm. in diameter. A pencil of primary X rays was passed in along the axis through an opening 1 cm. in diameter. When a card was placed over the opening, and nine thicknesses of silver-foil placed on the card on the side next the ionization-chamber, the current was 150·0 on an arbitrary scale: when the foils were placed the other side of the card the current was 70·3. The difference 79·7 was due to the cathode rays from the silver: *i. e.* we may take Ik/λ to be 79·7. The absorption coefficient k was then found by placing various thicknesses of silver under the card, and measuring the current in each case. The curve obtained when the results were plotted was not far from exponential, and gave k equal to 43·2 for the primary rays after passing through 9 foils. The absorption coefficient required is that which measures the conversion into cathode ray energy, excluding secondary X rays. It is therefore better to put the absorbing sheet close to the ionization-chamber so that secondary X rays may be taken in, though there is still some error due to the difference in quality of the primary and secondary rays. The absorption coefficient for the β rays in silver was found by placing one, two, four, eight, and twelve silver foils on the side of the card next the chamber and observing the gradual rise in the cathode ray effect: this gave λ equal to 3550. The quantity k was not found directly. The absorption coefficient of card was determined by experiment to be 2·28: card may be taken as cellulose, $C_6H_{10}O_5$; and the figures given by Thomson, 'Conduction of Electricity through Gases,' p. 307, may be used to show that the coefficient of air must be greater than that of cellulose in the proportion of 8 to 7. In this last calculation the absorbing power of H is neglected, which possibly makes the ratio too large; but there are no data from which to determine the error; it must be small, This gives $k'=2{\cdot}61$. Lastly $D=3{\cdot}6\times{\cdot}0012={\cdot}00432$.

Hence
$$\begin{aligned} \mathrm{ID}k' &= \frac{\mathrm{I}k}{\lambda}\,.\,\lambda\,.\,\mathrm{D}\,.\,\frac{k'}{k} \\ &= 79{\cdot}7\times 3550\times{\cdot}00432\times\frac{2{\cdot}61}{43{\cdot}2} \\ &= 73{\cdot}8; \end{aligned}$$

whereas the ionization actually found, when the card was next the chamber and the nine silver foils on the outside of the card, was 70·3 as already stated. In this case therefore the ionization was somewhat overaccounted for.

Generally the other experiments gave results of much the same kind; it would not be justifiable to expect more accurate confirmation under present conditions.

The ordinary primary ray which was used in these experiments might well be replaced by one of the streams of homogeneous X rays which Barkla has shown us how to obtain from various metals. Recent papers by Beatty* and by Sadler† actually give results from which the desired information may be obtained in part, but neither author has had occasion to measure the value of λ. Moreover there is no published determination of k', the absorption coefficient of homogeneous X rays by air. Mr. Sadler has been good enough to tell me that he finds $k'=9\ 3$ for copper rays. Using this value, and taking λ in silver to be the same as λ in air, though it is probably greater, I find that on Beatty's results about two-thirds of the ionization can be ascribed to cathode rays: the figures of the latter author give a rather smaller proportion. The agreement would be better if a larger value were assumed for λ. Moreover these rays are

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* Camb. Phil. Soc. Proc. vol. xv. pt. v.

† Phil. Mag. March 1910.

peculiarly liable to spend only a part of their energy in producing cathode radiation in the metal through which they enter ; some of the energy is spent on secondary X radiation ; or, which comes to the same thing effectively, some of the cathode radiation is liable to be reconverted into X radiation. In this way the measurement of $\mathrm{I}k/\lambda$ becomes too small.

There is another method by which it is sometimes sought to separate the ionization effect due to secondary β rays from the supposed effect due to the direct action of the γ rays upon the gas, viz. the method of the magnetic field. Kleeman *, for example, has tried in this way to deflect from the ionization-chamber all secondary β rays, and has been able to reduce the ionization current to less than half its original value. Finding, however, that a considerable effect remained which he was unable to remove with the strongest magnetic fields at his disposal, he has concluded that this must be due to the direct action of the γ rays upon the gas.

The effect of a magnetic field is, however, a very difficult question to solve. It is to be remembered that the field may actually increase a β-ray effect in some ways while it lessens it in others. A β-ray path in the chamber may be lengthened by its being forced into a circular form, and the ionization due to the particle be made greater. Moreover, β particles are scattered by impact on the atoms of the surfaces upon which the magnetic field deflects them, and by successive impacts may travel considerable distances in spite of the field : for the field does no more than convert the rectilinear portions of the path into circular portions ; it has no influence on the direction which the particle will take after an impact. It cannot be asserted that the results obtained by the magnetic deflexion method are yet capable of clear interpretation : further work in this direction is much wanted.

Crowther has described an experiment from which he has drawn the conclusion that X rays passing through a gas ionize it directly, and that consequently the cathode rays made by the X rays in the gas have no appreciable ionizing effect. He passed a fine pencil of X rays between two parallel plates so as to touch neither of them, and measured the ionization for various pressures of the gas. He found it to be very nearly proportional to the pressure : if cathode rays from the atoms of the gas were responsible for some of the ionization, the ionization due to them ought to show a marked decline as soon as the pressure of the gas is low enough to permit them to strike either of the plates, and so to leave their paths in the gas unfinished. He could not find

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* Proc. Roy. Soc. lxxxii. 1909, p. 358.

a deficiency from the proportionality to pressure, as already said, and hence his conclusion.

But it is clear that this experiment proves too much. One of the gases he used was methyl iodide. If X rays strike iodine atoms there is a very large conversion into cathode rays, as may be shown easily by scattering a little iodoform on a card through which X rays are entering an ionization-chamber when the current may be doubled under quite usual conditions. When the thinnest sheet of tissue-paper, equivalent to 1·5 cm. of air, is laid over the iodoform, this extra radiation is absorbed and the current returns to its former value. It is a clearly established principle that the effect of an atom upon an X ray is the same, no matter whether the atom is part of a solid or of a gas. Consequently there is a large production of cathode rays in the vapour of methyl iodide through which X rays are passing*, and a considerable fraction of the ionization of the gas is caused by these cathode rays. The amount can be calculated on the principles laid down above; but even if the complete accuracy of such a calculation be denied, it is still clear that the cathode ray ionization is large. Yet Crowther found there was none at all. Again, Mr. Edmonds has shown in this laboratory that if a hole is made in one of the parallel plates of Crowther's experiment and a piece of wire gauze placed over it, cathode rays pass through the hole from the X-ray stream in quantities which show a large increase as soon as the pressure of the air is sufficiently lowered. The distance from the X-ray stream to the window is about a centimetre, and the ionization current which is measured on the side of the gauze away from the stream increases rapidly relatively to the ionization in the air through which the X rays are passing: at first there is even an absolute increase in spite of the lowering of the pressure. The relation of the increase to the pressure alterations is just such as would be expected if the ionization outside the gauze window was due to cathode rays made in the X-ray stream and passing through the meshes in the gauze.

If the ionization of the gas in an ionization-chamber across which γ rays are passing is caused wholly by the β rays coming out of the walls of the vessel or out of the atoms of the gas, then, since the former of these sources of β rays is usually far more important than the latter, the ionization is

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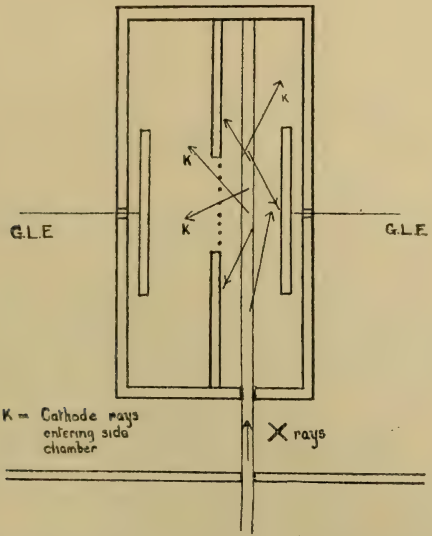
* It is worth observing that in a mixture of methyl iodide and any gas of small atomic weight the iodine atoms would be responsible for a large ionization, but only a fraction of the ions would be formed from the methyl iodide molecules.

due to an agent which does not change when the gas is changed, viz. the β rays from the vessel walls. The relative ionizations in different gases due to the γ rays must be the same as the relative ionizations due to β rays; and this is found to be the case very exactly, unless there is such a mass of gas in the chamber that the second source of β rays becomes important. This occurs when the gas contains heavy atoms like those of iodine. The "atomic ionizations" by β and by γ rays are set out below and show the close parallelism. They are taken from a paper by Kleeman *.

Fig. 3.



	H.	C.	N.	O.	S.	Cl.	Br.	I.
β.........	0·18	0·46	0·475	0·58	1·60	1·44	2·67	4·10
γ.........	0·18	0·46	0·45	0·58	1·60	1·44	2·81	4·50

If any part of the ionization in the gas were due to a direct action of the γ rays, and we were to reject the simple explanation just given, we should certainly find it extraordinarily difficult to explain the almost exact similarity of these two rows of figures. This would be the case on the entity hypothesis: if the γ rays were supposed to be spreading pulses,

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* Proc. Roy. Soc. lxxix. p. 220, Feb. 1907.

differing therefore in every imaginable way from β rays, an explanation would surely be hopeless.

Considering all this evidence for and against the existence of a direct ionization of a gas by X and γ rays, I would conclude that the entity hypothesis leads us to expect that there is no such effect, that many experiments fall in readily with this view, and that others are quite likely to show a like agreement when obvious defects have been removed.

Let us therefore accept this simplification, provisionally at least; and let us go on to consider a second problem of the ionization-chamber which may then be taken in hand with some success: the problem of the chamber of any form made wholly of any one substance.

Suppose a block of any material to be crossed by a stream of γ rays, and let us try to estimate so far as we can the whole length of track covered by β rays in any element of volume in a second, irrespective of direction. The number will in the first place depend on the strength of the γ radiation in the neighbourhood of that element of volume: after allowing for that, it will depend on two things only, (*a*) the number of β rays originated in each unit weight of the substance, *i. e.* the absorption coefficient of the γ rays by the substance, (*b*) the weight of material traversed by each β ray before it disappears. If different β particles traverse different amounts of material, the average is to be taken: we may call such average the average range, or briefly the range. The important thing to observe is that the range need not be all in one straight line: the β particle may make any number of twistings and turnings during its total path, and the range is the length of the path if it were straightened out, or rather the weight of material which the particle traverses. The deflexion oval and the scattering which the oval represents do not come into consideration at all. Let us say that k is the absorption coefficient of the γ rays and d the range, then the sum of the tracks of β rays in a unit volume is directly proportional to $\mathrm{I}kd$, I being the intensity of the γ rays. It may be of some service to give an analogy. If k points were taken at random in each square centimetre of a sheet of paper, and a line of length d were drawn from each point, then the quantity of ink used and the quantity of ink on each square centimetre would be just the same, on the average, whether the lines were straight or curved or made up of any number of short pieces so as to be zigzag in form. The ordinary coefficient of absorption of β rays is a compound of d, and of the dimensions of the deflexion oval. We are here dealing with a much simpler thing. If we take different substances and take I to be always the same, the "β ray density" in each substance is represented relatively by kd.

Suppose a cavity to be made in the substance. This makes no difference whatever in the value of kd anywhere in the metal, even on the borders of the cavity. This follows from the fact that every β particle has to cross a weight d of the substance: crossing the cavity does not count in its total path. The only inaccuracy in this statement arises from the fact that the value of I may not be the same in all parts of the substance that border on the cavity. It will be found to have little importance so far as our present purpose is concerned, and we will not take it into account. Then we can say that just as many β rays cross each unit volume of the cavity as would cross it if it were filled with substance of the kind considered, or of any other substance having the same kd. The shape of the cavity is immaterial. We may in fact take it to be the inside space of an ionization vessel, provided only that the walls are thick enough to prevent the passage of β rays either way.

It is curious but not uninstructive to consider that if we had a substance with no k, but with the power of reflecting every β ray that fell upon it, and made a closed vessel of the substance, and shot γ rays across it, we should then get the following results. If a vacuum existed in the vessel, kd would be zero: if a single atom of any ordinary substance were placed in the vessel, kd would in time mount to its full value for that substance, and would not increase if the one atom were added to by putting in any number of like kind. If atoms of other kinds were inserted, there would be a compromise, the density of β rays becoming $\Sigma k/\Sigma(1/d)$.

To go back to the cavity in the substance traversed by γ rays, the introduction of air into it makes little difference in the value of kd in different parts of it unless the kd of the substance differs considerably from the kd of air, and there is so much air that an appreciable fraction of β-ray energy is used up when a stream of such rays tries to cross the cavity. Hence the cavity must not be so big, nor the pressure of air inside it so great, that this source of inaccuracy becomes serious. If there were any doubt about it in a given case, it could be tested by varying the pressure of the air; if the relation between pressure and ionization required a curved line to represent it, it would be necessary to use the initial portion of the curve for which the pressure is small. This precaution is usually unnecessary, and we may take the ionization in the air of the cavity as proportional to kd. If, therefore, we make a number of ionization vessels of different materials but the same form, and cause γ rays to pass into them, the amount of ionization produced inside becomes a measure of the *kd* of that substance. The experiment may conveniently be carried out by making a thick lead ionization-chamber and inserting different linings. The γ rays must of course be kept at the same strength inside each lining, or if not any differences must be allowed for.

Mr. H. L. Porter has recently carried out some experiments for me in this way, the results of which are shown in the table below. The first column gives the material of the lining, and the second its thickness, which was enough to give the true value of *kd* in all cases except perhaps those of aluminium and cardboard. The third column gives the results obtained when the γ rays had to pass through little more than the lead wall of the ionization-chamber, which was 0·47 cm. thick, and the fourth the results when the rays had to pass through a screen of lead 1·1 cm. thick in addition. The figures are corrected for differences in volume and for differences in the strength of the γ rays due to absorption in the linings.

I. Metal.	II. Thickness of screen.	III. Ra unscreened.	IV. Ra screened.
Lead	...	100	100
Tin	·16	58	68
Zinc	·21	47	55
Iron	·155	45	54
Aluminium	·21	40	49
Card	·24	39	46

The height of the chamber, which was cylindrical in form, was 15 cm., and the diameter 9 cm. The radium was placed on the axis of the cylinder, 10 cm. away from one end.

The differences between the figures in the last two columns are really due to a change in the relative value of lead only. The rays have been so hardened by passing through the extra cm. of lead that the absorption coefficient of the lead lining has fallen to the same value as that of the other metals. In the first case there is a special production of softer β rays by the lead which does not take place in the second.

In these experiments the strength of the γ rays is not the same all over the cavity as it ought to be; but the inequality cannot have much influence on the relative values of *kd* for the different linings. Mr. Porter finds that the figures are indeed somewhat altered when the radium is moved about into different positions, but the alterations are such as would be expected from the variations in the quality of the γ rays. In some positions the γ rays pass more obliquely through the walls, and therefore through a greater thickness of lead, so that they are so much the more hardened.

When all allowances for error are made we still have a set of figures which show with considerable accuracy the relative values of *kd* in certain substances, and, since *k* is practically the same for all of them, the relative values of *d*, the range of the β particle. It may be well to point out once more that this range does not give directly the power of penetrating screens of different metals; and indeed it varies in the opposite direction. The power of penetration depends also on the form of the deflexion oval which represents the scattering effect. In the definition of the range, and in the experiment which measures it, scatterings or reflexions, or so-called secondary radiations, have no part at all. In fact these experiments allow us to investigate separately one of the three main subjects of measurement already referred to, viz. the expenditure of energy along the track of the β particle, since this must determine the length of the track.

In order to complete a proper set of investigations of the β particle phenomena, it is further necessary to find the form of the deflexion oval in all cases. This may be done by observing the scattering of the β rays in various directions as they pass through very thin plates, since in such cases the scatterings are due to one encounter with an atom in each case, as Madsen has shown (*loc. cit.*). The third subject of measurement is the conversion of form: so far as we know this is unimportant in the case of the β ray, but it is just possible that an effect of this kind has been overlooked.

Until satisfactory investigations have been made under these heads, it is impossible to find true foundations for calculation of the effects to be observed when sheets of material are placed over a substance emitting β rays, that is to say, of the so-called absorption coefficients. For these coefficients must necessarily vary in a complicated manner from material to material and thickness to thickness, since they are involved functions of the range and of the scattering. It is too much to attempt a theory of the absorption of β rays until these intermediate steps have been hewn into shape. H. W. Schmidt has tried to fill up the gap by arguing back from a large number of measurements of absorption and of scattering coefficients †. He has defined two constants which he has called the "reflexion" and the "true absorption" coefficienst. The former really represents roughly the facts of the deflexion oval, the oval being reduced to its axis, and the atom placed at various positions upon it; the latter represents the expenditure of energy along the path. His two constants actually stand approximately for the two independent subjects of measurement which we have seen to be important in the case of the β ray. It is therefore very interesting to compare his calculated values of the true absorption coefficient with the quantity d, which should be approximately in the inverse ratio. To what extent this is due is shown in the following table. The second column gives the values which Schmidt‡ calculated for the true absorption coefficients of the β rays of uranium, *i. e.* the values of his α/D. I do not think the values for radium are available. But it must be quite allowable to use the former instead of the latter, since the β rays of radium do not differ much in penetrating power from the β rays of uranium; while the values of α/D for uranium and for actinium are very much the same relatively to one another, and yet the β rays of actinium are much less penetrating than those of uranium. The third column gives the relative values of kd, or practically of d, and the last the product of the figures in the two preceding columns.

Substance.	α/D.	kd.	$\alpha/\mathrm{D}\times kd$.
Lead	1·69	100	169
Tin.....................	2·14 (2·40)	68	145 (163)
Zinc	3·00	55	165
Iron	3·08	54	166
Aluminium	3·26	49	160
Card	3·32*	46	153

* Calculated as for carbon from later figures given by Schmidt.

The uniformity of the figures in the last column is only broken seriously by tin. Strange to say, the value 2·14 which Schmidt gives for tin is quite out of line with the values he gives for all the other metals; if these values are plotted and a value for tin obtained from the curve we get

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† See also McClelland and Hackett, Dublin Trans. 1907. ix. p. 37.

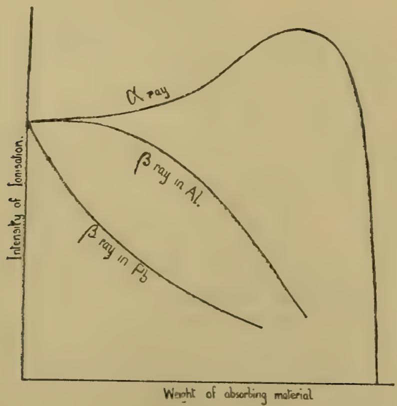
‡ *Ann. d. Phys.* xxiii. p. 671 (1907); *Jahrb. d. Rad.* 1908, p. 451.

2·40, which leads to a value 163 in the last column. Schmidt's values of α/D for the β rays of actinium do not show this irregularity in the case of tin.

The values of *d* are clearly less for the smaller atomic weights. The whole track of a β particle in lead is actually greater, weight for weight, than in aluminium. Yet as is well known a β particle can penetrate a heavier screen of aluminium than of lead. The reason is that the lead atoms turn back the β particles so much more than the lighter atoms do. In lead the particle finishes its course much more closely to its starting-point; it is really a longer course, but there are many more turns in it.

It is easy to see that there will consequently be considerable differences in the "absorption curves" of different materials; *i. e.* the curves which show the relation between the thickness of a screen placed normally to the path of a stream of β rays, and the ionization in a chamber on the other side, a chamber which the rays can usually cross. A β ray going through aluminium behaves rather more like an α particle than when it goes through lead, since it is less liable to deflexion in the former case, and the α particle has very few departures from a straight line course. The absorption curve of the β ray in aluminium should, therefore, be more like that of an α particle than the curve of β ray in lead. Now the α particle actually causes more ionization when screens are placed in its path, unless the screen is too thick, than when it is unimpeded; that is to say, the curve which is plotted with thickness of screen as abscissa and ionization on the other side of the screen as ordinate rises at first; subsequently it falls rapidly

Fig. 4.



to the axis of x. Experiment shows that the absorption curves for β rays in aluminium screens do really possess a trace of this peculiarity, for they fall slowly at first and much more quickly afterwards. On the other hand, the absorption curve for lead is more like an exponential curve, which is to be expected since scattering is the most prominent cause of absorption.

Sir J. J. Thomson has recently published (Proc. Camb. Phil. Soc. xv. part v. p. 465) a theory of the "scattering of rapidly moving electrified particles." It seems to me to be inapplicable to the actual case because it considers scattering to be due to a multitude of small deflexions experienced by the particle in passing by the various centres of positive and negative force in the atoms, all the centres acting independently of each other. Apart from the question as to whether it is likely that the positives and negatives do not interfere with each other's actions, the argument is limited to cases where the total deflexion is so small that the particle has hardly moved from its original direction when it emerges on the other side of the screen. This is necessary because the deflexion is taken to be the average of a number of deflexions, and the reasoning tacitly assumes that all these deflexions are grouped symmetrically about the original direction of the particle throughout the whole of the transit of the particle across the absorbing layer. The scattering of a pencil of β rays is looked upon as a gradual opening out of the whole pencil, and the calculations refer to a state in which the absorbing layer is so thin that only slightly scattered rays are worth considering. Actually there is no such state; however thin the plate the highly scattered rays are in a certain proportion to the slightly scattered rays, which does not alter as the thickness of the layer is increased, unless the thickening is carried too far. From the very first large deflexions must be considered. The many slight deflexions which the β particle experiences along the comparatively straight portions of its track are of no real consequence; little more than in the case of the α particle. Moreover, while the plate is still fairly thin, another important effect comes in, viz. the loss of speed; and it is by the mutual interplay of these two that the differences in the absorption curves are caused. Crowther (Camb. Phil. Soc. Proc. xv. 5, p. 442) shows absorption curves of aluminium and of platinum. The curves show the special characteristics just discussed; but I think it is only by accident that the aluminium curve fits the formula derived by Sir J. J. Thomson. The curve for platinum will not fit the theory in the same way, and

Crowther supposes that secondary radiation must be present and be responsible for the want of agreement; but there does not seem to be any good reason for selecting secondary radiation as the cause of the error. On the other hand, the entity hypothesis leads naturally to a simple explanation of the general form of the curves both of aluminium and of platinum.

In the case of β and cathode rays there is very little accurate knowledge of the third of the phenomena which I have tried to distinguish above, viz. the conversion of form. The conversion of β rays into γ rays is often doubted altogether; but it can hardly be safe to deny it, for if the number of γ rays produced by a given number of β rays were relatively as few as the X rays produced by a stream of cathode rays, the effect produced by the γ rays would be almost imperceptible. The conversion of cathode rays into X rays is, however, a very obvious and common process, and it is rather striking that so little work has been done to discover the laws of it. It would be a great help to know whether there is a critical speed or more than one critical speed at which an electron should strike an atom in order to get an X ray effect. Let us suppose that there is a speed which it is necessary for a cathode ray falling on a given atom to possess in order that the conversion may take place, which does not seem at all unlikely considering the general behaviour of X ray tubes. Let us suppose, further, that the critical speed increases with the atomic weight, for which also there is something already to be said. Then we seem to have a reasonable chance of explaining the very remarkable phenomena of the homogeneous secondary X radiations which Barkla has discovered. The explanation given by Barkla himself is not at all in accord with the arguments which I have tried to state above. He supposes the primary pulse to shake an atom in passing and make it give out its own characteristic quivers. But this suggests that a single primary X ray is the cause of many secondary X rays.

We have to explain why one single primary entity—an X ray—is replaced by one secondary X ray entity after collision with a certain atom, the energy of the secondary being characteristic of the atom not of the primary, and its direction of motion being also independent of the primary, *i. e.* of the direction of motion of the primary. We have to explain further why the X ray emitted by zinc can excite the copper atom to emit its own characteristic X ray, and why the reverse does not take place, the copper X ray is not able to excite the zinc X ray. Let X rays from zinc, that is to say secondary X rays coming off a plate of zinc on which sufficiently hard X rays are falling, be made to strike a plate of copper. Their energy is gradually converted into that of cathode rays, which possess a certain definite power of penetration, *i. e.* a certain definite speed (or perhaps average speed) as Sadler has shown. These cathode rays possess more than the critical speed for copper; we may imagine them to scatter in the zinc, losing all sense of original direction very quickly and falling in speed. When they reach the critical speed for copper and the maximum conversion of form takes place, the characteristic X rays of copper will flash out in all directions. If they pass this speed without conversion their energy is spent merely on the copper atoms, transforming itself in the usual ways into heat. But if X rays produced by some means in a copper plate are allowed to fall on a zinc plate, and there form cathode rays, the speed of these latter rays is below the critical speed for zinc, and no X rays characteristic of zinc are produced. Thus all Barkla's effects are qualitatively explained. Until the conversion of cathode ray energy into X ray energy has been more fully investigated, such an hypothesis can be no more than a provisional one, but it seems simple and reasonable, and suggests promising lines of research.

In the foregoing pages I have tried to follow out the consequences of adopting the "entity hypothesis" of X and γ rays, and to show how we are led to modify our views of well known theories and our interpretations of well known experiments. Since there is so much to consider, the discussion has, I fear, been rather lengthy; but I think the result is simple. We are to think of each entity as possessing initially a certain store of energy which it spends gradually as it goes along, the result being ionization of the material through which it passes; there are no sudden accessions or withdrawals of energy; the path is not necessarily straight, but made up of a number of small pieces more or less straight, the deflexions or turnings being the results of intra-atomic collisions; the β rays are very liable to such deflexions, and the cathode rays even more so. Certain conversions of form may take place, γ into β, X into cathode ray, and so on; but in such cases the energy is handed on, and in some cases at least the momentum. The essence of it all is the recognition of the individuality of each entity which is to be followed by itself from its origin through all its changes of direction and sometimes its changes of form, until its gradually diminishing energy becomes too small to render it distinguishable.

XL. *On Hysteresis Loops and Lissajous' Figures, and on the Energy wasted in a Hysteresis Loop.* *By* Professor SILVANUS P. THOMPSON, *D.Sc., F.R.S.* *

[Plate VI.]

§ 1. PROBABLY many physicists have attempted to find an explanation of the forms of the looped curves which express the hysteresis exhibited by iron and steel when subjected to cycles of magnetization. Physical explanations to account for their general shape have indeed been given by Ewing and by Hopkinson. Neither of these pioneers, however, offered any mathematical equations to express their forms; nor, so far as appears, has any other person yet found any, though M. Pierre Weiss has put forward an electronic theory to account for the principal features.

According to Ewing's molecular hypothesis of magnetism, the act of magnetization consists in the orientation into a common direction of the axes of the elementary magnets constituted by the iron molecules which, when the mass of iron is in the unmagnetized state, are miscellaneous in their directions, the molecules being then arranged in groups within which the individuals are so oriented as to satisfy amongst themselves their various polarities in a more or less stable equilibrium. When a small magnetizing force is applied and gradually increased, the individual elementary magnets are at first merely slightly deflected towards the line of the magnetizing force, but still remain in their various groups. With larger magnetizing forces and increased deflexions of individual elements, the groupings, or some of them, become unstable, and break up as instability is reached; the elements of the group then suddenly swinging round into a new configuration more nearly in alignment with the impressed magnetic force. The less stable groups will be first affected, the more stable afterwards, and the most stable will be the last to swing into alignment. When all or nearly all the groups have thus been broken up, any further increase in the magnetizing forces can produce but little effect, though an infinite magnetizing force might be needed to produce absolute alignment of every element. To deduce from this hypothesis an expression for the ascending curve of magnetization, it might be possible to apply the statistical method, under the assumption that the number and variety of the groupings is enormously great. The ratio $d\mathfrak{B}/d\mathfrak{H}$ would represent at each stage the differential permeability of the

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* Communicated by the Physical Society: read July 8, 1910.

specimen, or the rate (per unit of magnetizing force) at which the magnetization was proceeding; and this would at every stage be proportional to the probable number of groups that were coming into alignment, and to the magnitude of the aligning force. The expression would thus assume the form

$$\frac{d\mathfrak{B}}{d\mathfrak{H}} = a \, . \, \epsilon^{-(\mathfrak{H}-b)^2};$$

where a and b are constants, the one denoting the maximum value of $d\mathfrak{B}/d\mathfrak{H}$, the other the particular value of $\mathfrak{H}$ at which that maximum is reached. The difficulty of integrating this expression is not the only objection to it; for it would at best give only the ascending curve of magnetization, and additional assumptions would need to be made before it could be adapted to express the descending branch.

§ 2. Hysteresis loops, as found by experiment, can however be considered from a wholly different standpoint. Whatever the law connecting $\mathfrak{B}$ and $\mathfrak{H}$, the area enclosed by the loop measures the amount of energy lost in the iron in the cycle of magnetic operations; the value, in ergs per cubic centimetre, being $\frac{1}{4\pi}\int \mathfrak{B} \, . \, d\mathfrak{H}$. Let it be assumed that the variations of $\mathfrak{H}$ are such that $\mathfrak{B}$ passes from the value $+\mathfrak{B}_1$ to $-\mathfrak{B}_1$ and back, through a regular cycle of values according to the expression

$$\mathfrak{B} = \mathfrak{B}_1 \cos \theta;$$

then, in general, the variations of $\mathfrak{H}$, though they go through a cycle, will not be capable of being expressed by any such simple form, otherwise the shape of the hysteresis loop would be simply an ellipse, or, in the limiting case, a straight line. The fact that the magnetizing current (and therefore the magnetizing force) in choking coils and transformers does not follow a simple sine or cosine function is well known to all electrical engineers. In these instruments, if worked from a source of alternating electromotive force in which the wave-form of the supply is a pure sine-curve, the wave-form of the flux in the core, and therefore of the flux-density $\mathfrak{B}$ in the core, will also be a pure sine-curve having a lag of exactly 90° with respect to the impressed voltage curve. Or if the impressed voltage is expressed by the equation

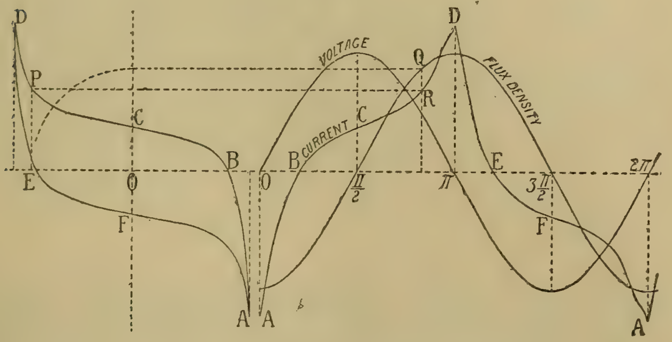
$$V = V_0 \sin \theta,$$

the flux-density will be given by the equation

$$\mathfrak{B} = - \mathfrak{B}_0 \cos \theta.$$

But the current will not be capable of being expressed in any such simple fashion *. It has also long been known how these curves of magnetizing current are related to the hysteresis loop. If the form of the hysteresis loop is known, then the form of the magnetizing current can be deduced graphically. An example will be found in Kapp's 'Transformers' (1908), fig. 56, p. 106. Assuming that the flux-density follows the equation given above, let it be plotted as a curve, with maximum ordinate equal to that of the hysteresis loop. Consider any point on this curve, or the point on the loop having the same ordinate; then the ordinate at the same instant on the current curve will be (on some scale) proportionate to the abscissa of the same point of the hysteresis loop; whence it follows that the current curve can be constructed, point by point, through the entire cycle. This process is followed here, save that for convenience the hysteresis loop is turned over through a right angle, so that the values of $\mathfrak{B}$ are taken as abscissæ, and those of $\mathfrak{H}$ as ordinates. In fig. 1 the hysteresis loop A B C D E F selected, has been taken from Ewing's classical memoir of 1885.

Fig. 1.



Relation of Current Curve to Hysteresis.

Assuming a closed magnetic circuit, and an impressed voltage of a pure sine form, marked V, the flux-density curve is a sine-curve lagging 90° behind the voltage-curve. Then the current curve is derived by taking any point P on the

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* For a good example of a current curve, see Fleming's 'Alternate Current Transformer,' fig. 186, vol. i. p. 543 (edition of 1896). These irregular current curves seem to have been first observed by Ryan; see 'Transactions of the American Institute of Electrical Engineers,' vol. iii. Jan. 10, 1890. See also the 'Electrician,' vol. xxiv. p. 239, and p. 263, January 1890, and vol. xxv. p. 312, July 25, 1890.

hysteresis loop, projecting it by first turning its abscissa through a quadrant about the centre O, then tracing along horizontally to the point Q on the flux-density curve, where a vertical line QM is dropped. Then a horizontal line projected from P cuts QM in R, giving thus the corresponding point on the current curve, the peak of which, corresponding to the cusp of the loop, occurs at the time when the flux-density curve is a maximum, and when the voltage curve is at its zero.

It will be seen that the wave-form of the current curve reflects, in a certain way, the form of the hysteresis loop. If the loop is sharply cusped, the wave-curve will have corresponding sharp peaks. In fact, the loop consists of the two halves of the wave-curve, folded back one upon another, but with the ordinates differently spaced, exactly as if the wave-curve had been wrapped around a cylinder[*] and projected upon a plane cutting the cylinder diametrically through the two peaks of the curve.

Now this current curve can be subjected to harmonic analysis, and its harmonic constituents discovered. Each constituent will be a pure sine-curve or cosine curve. If each such constituent be drawn, and then be projected back by reversal of the process by which the wave-curve was obtained, the several constituents will reappear as separate closed curves; and by the summation of these the original hysteresis loop can be reconstituted. It thus appears that *any hysteresis loop can be analysed into an harmonic series of closed curves corresponding to the various terms in the analysis of the current wave.* An examination of these constituents of the hysteresis loop is the principal object of this communication.

§ 3. In this graphic process, which is equivalent to wrapping the periodic curve around a cylinder, the area of the projected curve is equal to the integral, over the whole period, of products obtained by multiplying each ordinate by the sine of the angle at which it stands in the wave-curve; abscissæ in that curve being reckoned as values of angles. (The origin of the cycle is taken where the curve has its negative peak.) In symbols this is equivalent to

$$\int_0^{2\pi} \sin\theta \,.\, \psi(\theta) \,.\, d\theta.$$

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[*] As in the graphic method of harmonic analysis of Clifford described by Perry in Proc. Phys. Soc. vol. xiii.

Now $\psi(\theta)$, the function which represents the current-curve, may by Fourier's theorem be expanded into the series

$$A_1 \sin\theta + A_3 \sin 3\theta + A_5 \sin 5\theta + \ldots\ldots A_n \sin n\theta$$
$$+ B_1 \cos\theta + B_3 \cos 3\theta + B_5 \cos 5\theta + \ldots\ldots B_n \cos n\theta.$$

Odd terms only are present, as in all alternating current work; and there is no constant term, because the mean ordinate is already zero.

The constituent terms in the area of the hysteresis loop correspond therefore to the integrated products of $\sin\theta$ into the successive terms of the above series.

§ 4. To investigate the form of the constituent elements of the loop, let us consider a simple harmonic motion $x = \mathrm{X}\sin\theta$, where θ stands for $2\pi ft$, f being the fundamental frequency, and X the amplitude. This motion is to be compounded, at right angles, with another simple harmonic motion

$$y = \mathrm{Y}_n \sin(n\theta + \phi_n);$$

where Y_n is the amplitude, ϕ_n a possible angle of phase-difference, and n any (odd) integer giving the order of the harmonic. We have then to find an expression for the curve of which x and y are the coordinates. For simplicity we deduce the expressions where $n=1$, $n=3$, and $n=5$, that is for the first, third, and fifth terms of the constituent elements.

First Term (Fundamental); $n=1$.

We have

$$\frac{x}{\mathrm{X}} = \sin\theta, \quad \ldots\ldots\ldots \quad (1)$$

$$\frac{y}{\mathrm{Y}_1} = \sin(\theta + \phi_1). \quad \ldots\ldots\ldots \quad (2)$$

Multiplying both sides of (1) by $\cos\phi_1$, we have

$$\frac{x}{\mathrm{X}}\cos\phi_1 = \sin\theta \, . \cos\phi_1.$$

Also

$$\frac{y}{\mathrm{Y}_1} = \sin\theta \, . \cos\phi_1 + \cos\theta \, . \sin\phi_1.$$

Subtracting this equation from the preceding, we have

$$\frac{x}{\mathrm{X}}\cos\phi_1 - \frac{y}{\mathrm{Y}} = -\cos\theta \, . \sin\phi_1. \quad \ldots\ldots \quad (3)$$

Multiplying (1) by sin ϕ_1, we get

$$\frac{x}{X}\sin\phi_1 = \sin\theta \, . \sin\phi_1 . \quad \ldots\ldots \quad (4)$$

Squaring (3) and (4), and adding them gives us

$$\left(\frac{x}{X}\right)^2 + \left(\frac{y}{Y_1}\right)^2 - 2\frac{xy}{XY_1}\cos\phi_1 = \sin^2\phi_1 . \quad . \quad (5)$$

This is the equation to an ellipse, such as is represented by fig. 2 (Pl. VI.). According to the values given to ϕ_1 there arise three principal cases.

Case (i.). If

$$\phi_1 = \frac{\pi}{2} \quad \text{or} \quad 3\frac{\pi}{2},$$

then

$$\sin\phi_1 = \pm 1 \quad \text{and} \quad \cos\phi_1 = 0,$$

and the equation becomes

$$\frac{x^2}{X^2} + \frac{y^2}{Y_1^2} = 1.$$

This is the equation to an ellipse set orthogonally with respect to the coordinate axes as in fig. 3 (Pl. VI.).

Case (ii.). If

$$\phi_1 = 0, \quad \sin\phi_1 = 0, \quad \text{and} \quad \cos\phi_1 = 1,$$

and the equation becomes

$$\frac{x^2}{X^2} + \frac{y^2}{Y_1^2} - 2\frac{xy}{XY_1} = 0,$$

whence

$$y = +\frac{Y_1}{X}x,$$

which is the equation to a straight line into which the ellipse shrinks as in fig. 4 (Pl. VI.). But its length is limited by the prior expressions, since x and y cannot exceed X and Y_1 respectively.

Case (iii.). If

$$\phi_1 = \pi, \quad \sin\phi_1 = 0, \quad \cos\phi_1 = -1,$$

and the equation becomes

$$\frac{x^2}{X^2}+\frac{y^2}{Y_1^2}+2\frac{xy}{XY_1}=0,$$

or

$$y=-\frac{Y_1}{X}x,$$

which is a straight line sloping the reverse way as in fig. 5.

For all other values of ϕ the ellipse takes some intermediate form. The sine-component of the first term in the harmonic analysis of the current curve corresponds to the orthogonal ellipse; the cosine-component to the oblique line form. All the intermediate forms of the ellipse could be obtained by wrapping a sine-curve of period T around a cylinder of diameter T/π and projecting in appropriate directions upon planes parallel to the axis of the cylinder the apparent outline of the sine-curve.

THIRD TERM (Third Harmonic) ; $n=3$.

Here the two equations are

$$\frac{x}{X}=\sin\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{y}{Y_3}=\sin(3\theta+\phi_3), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$=\sin 3\theta\,.\,\cos\phi_3+\cos 3\theta\,.\,\sin\phi_3. \quad . \quad . \quad (2\,a)$$

But

$$\sin 3\theta=3\sin\theta-4\sin^3\theta,$$

by known trigonometrical relations.

Inserting for $\sin\theta$ its value from (1), we get

$$\sin 3\theta=\frac{3x}{X}-\frac{4x^3}{X^3}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Substituting this value in (2 *a*), we deduce

$$\left(\frac{3x}{X}-\frac{4x^3}{X^3}\right)\cos\phi_3-\frac{y}{Y_3}=-\cos 3\theta\,.\,\sin\phi_3. \quad . \quad . \quad (4)$$

Also multiplying (3) by $\sin\phi_3$, we have

$$\left(\frac{3x}{X}-\frac{4x^3}{X^3}\right)\sin\phi_3=\sin 3\theta\,.\,\sin\phi_3. \quad . \quad . \quad . \quad (5)$$

Squaring (4) and (5), and adding, we get

$$\left(\frac{3x}{X}-\frac{4x^3}{X^3}\right)^2+\left(\frac{y}{Y_3}\right)^2-2\left(\frac{3x}{X}-\frac{4x^3}{X^3}\right)^2\frac{y}{Y_3}\cdot\cos\phi_3=\sin^2\phi_3. \quad (6)$$

This is the equation to a figure having the general form of fig. 6 (Pl. VI.), which is indeed the well-known Lissajous' figure, compounded of two vibrations the frequencies of which are as 1 : 3. It could be obtained by taking three complete sine-waves, each of period T/3, and wrapping them around a cylinder of diameter T/π.

Again there arise three cases :—

Case (i.). If $\phi_3=\frac{1}{2}\pi$ or $\frac{3}{2}\pi$, then

$$\sin\phi_3=\pm 1 \quad \text{and} \quad \cos\phi_3=0,$$

and then the equation becomes

$$\left(\frac{3x}{X}-\frac{4x^3}{X^3}\right)^2+\left(\frac{y}{Y_3}\right)^2=1.$$

Here the figure is symmetrical with respect to the axes, as in fig. 7. It is, for the third term, what the orthogonal ellipse is for the first term.

Case (ii.). If $\phi_3=0$, then

$$\sin\phi_3=0, \quad \cos\phi_3=1,$$

and the equation reduces to

$$\frac{3x}{X}-\frac{4x^3}{X^3}-\frac{y}{Y_3}=0.$$

Here the trilobate form has shrunk to the form of the curved line (fig. 8) precisely as the ellipse shrank to the oblique line of fig. 4. This line is subject to the limitations that x and y cannot exceed X and Y_3, respectively.

Case (iii.). If $\phi_3=\pi$, then

$$\sin\phi_3=0, \quad \cos\phi_3=-1,$$

and the equation becomes

$$\frac{3x}{X}-\frac{4x^3}{X^3}+\frac{y}{Y_3}=0,$$

the graph of which is fig. 9.

FIFTH TERM (Fifth Harmonic); $n=5$.

The two equations now are

$$\frac{x}{X} = \sin\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

$$\frac{x}{Y_5} = \sin(5\theta+\phi_5), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

$$= \sin 5\theta \,.\, \cos\phi_5 + \cos 5\theta \,.\, \sin\phi_5. \quad . \quad . \qquad (2a)$$

But

$$\sin 5\theta = 5\sin\theta - 20\sin^3\theta + 16\sin^5\theta.$$

Inserting for $\sin\theta$ its value in (1), we get

$$\sin 5\theta = \frac{5x}{X} - \frac{20x^3}{X^3} + \frac{15x^5}{X^5}. \quad . \quad . \quad . \quad . \qquad (3)$$

Substituting this value in (2 *a*), we deduce

$$\left(\frac{5x}{X} - \frac{20x^3}{X^3} + \frac{16x^5}{X^5}\right)\cos\phi_5 - \frac{y}{Y_5} = -\cos 5\theta \,.\, \sin\phi_5. \quad . \qquad (4)$$

Also multiplying (3) by $\sin\phi_5$, we have

$$\left(\frac{5x}{X} - \frac{20x^3}{X^3} + \frac{16x^5}{X^5}\right)\sin\phi_5 = \sin 5\theta \,.\, \sin\phi_5. \quad . \qquad (5)$$

Squaring (4) and (5), and adding them, we get

$$\left(\frac{5x}{X} - \frac{20x^3}{X^3} + \frac{16x^5}{X^5}\right)^2 + \left(\frac{y}{Y_5}\right)^2 - 2\left(\frac{5x}{X} - \frac{20x^3}{X^3} + \frac{16x^5}{X^5}\right)\frac{y}{Y_5} \,.\, \cos\phi_5 = \sin^2\phi_5.$$

This is the equation of the general Lissajous' figure of the fifth order, representing the result of compounding two vibrations having relative frequencies of 1 : 5, and a general form like fig. 10 (Pl. VI.).

As before, three cases arise:—

Case (i.). If $\phi_5 = \frac{1}{2}\pi$ or $\frac{3}{2}\pi$, then

$$\sin\phi_3 = \pm 1 \quad \text{and} \quad \cos\phi_5 = 0,$$

and then the equation becomes

$$\left(\frac{5x}{X} - \frac{20x^3}{X^3} + \frac{16x^5}{X^5}\right)^2 + \left(\frac{y}{Y_5}\right)^2 = 1,$$

which is symmetrical as in fig. 11.

Case (ii.). If $\phi_5=0$, then

$$\sin\phi_5=0,\quad \cos\phi_5=1,$$

and the equation reduces to

$$\frac{5x}{\mathrm{X}}-\frac{20x^3}{\mathrm{X}^3}+\frac{16x^5}{\mathrm{X}^5}-\frac{y}{\mathrm{Y}_5}=0,$$

corresponding to fig. 12, subject to limitations as before.

Case (iii.). If $\phi_5=\pi$, then

$$\sin\phi_5=0,\quad \cos\phi_5=-1,$$

and the equation is

$$\frac{5x}{\mathrm{X}}-\frac{20x^3}{\mathrm{X}^3}+\frac{16x^5}{\mathrm{X}^5}+\frac{y}{\mathrm{Y}_5}=0,$$

which is the equation to fig. 13.

§ 5. *The Higher Terms. Generalized expression for the Lissajous' curve of the* n*th term.*

The expression for any higher term has the general form

$$\mathrm{G}_n^2+\left(\frac{y}{\mathrm{Y}_n}\right)^2-2\mathrm{G}_n\frac{y}{\mathrm{Y}_n}\cdot\cos\phi_n=\sin^2\phi_n,$$

which reduces in the case of symmetry to

$$\mathrm{G}_n^2+\left(\frac{y}{\mathrm{Y}_n}\right)^2=1,$$

and, in cases where $\phi_n=0$, to

$$\mathrm{G}_n\pm\frac{y}{\mathrm{Y}_n}=0,$$

in which expressions G_n is written for the series

$$\mathrm{G}_n=n\frac{x}{\mathrm{X}}-\mathrm{C}_3\frac{x^3}{\mathrm{X}_3}+\mathrm{C}_5\frac{x^5}{\mathrm{X}^5}-\mathrm{C}_7\frac{x^7}{\mathrm{X}^7}+\ \dots\ +\mathrm{C}_n(-1)^{\frac{n-1}{2}}\cdot\frac{x^n}{\mathrm{X}^n};$$

where

$$\mathrm{C}_r=\frac{n(n^2-1^2)(n^2-3^2)\ \dots\dots\ (n^2-\overline{r-2}^2)}{\lfloor r},$$

where r is an odd number greater than unity.

§ 6. It is now possible to restate the proposition at the end of § 2 in the following way. *Any hysteresis loop can be* *analysed into an harmonic series of Lissajous' figures* of the kind considered in the §§ 4 and 5.

A number of examples of hysteresis loops were chosen, and subjected to harmonic analysis, to ascertain what constituents were present. The loops chosen relate to various kinds of iron and steel, hard and soft, solid and laminated, taken by various methods; a wide selection being made in order to ascertain the physical significance of the several constituent terms.

In carrying out the analysis the author used the simple approximate method described by him to the Physical Society, Dec. 9, 1904, vol. xix. Proc. Phys. Soc. p. 443, based on an arithmetical process originated by Archibald Smith and generalized by Runge in the *Zeitschrift für Mathematik und Physik*, vol. xlviii. p. 443, 1903. It was found that for the present purpose it sufficed to ascertain the harmonic sine and cosine terms up to the eleventh, and therefore to employ twelve equidistant ordinates in the half-period. The work proceeded on the lines of the simple schedule given by the author on p. 448 of his former paper, with a slight modification to enable the origin of abscissæ to be taken not at the point where the ordinate has zero value, but at that point where the ordinate has its negative maximum. At first the values of the twelve ordinates required for the analysis were taken from the current curve plotted, as explained above in § 2, from the hysteresis loop. But it was seen that it was unnecessary to draw the current curve, and that the values of the ordinates might be taken direct from the hysteresis curve, by taking them not equidistant, but at places corresponding to equidistant points in the axis of abscissæ of the wave-curve, which points, when the curve is wrapped round a cylinder, will no longer appear equidistant.

§ 7. The following are the results :—

Example I. fig. 14, Pl. VI., Ewing's hysteresis loop for pianoforte steel wire, in state of normal temper, being fig. 11, pl. lviii. of Philosophical Transactions, 1885.

The analysis of the values of $\mathfrak{H}$ gives the following coefficients of the harmonics up to the eleventh order :—

Sine Terms.	Cosine Terms.
$A_1 = 32\cdot2$	$B_1 = -45\cdot4$
$A_3 = 7\cdot1$	$B_3 = -20\cdot6$
$A_5 = 0\cdot7$	$B_5 = -10\cdot8$
$A_7 = -0\cdot7$	$B_7 = -5\cdot7$
$A_9 = -0\cdot05$	$B_9 = -4\cdot1$
$A_{11} = -0\cdot06$	$B_{11} = -3\cdot4$

It will be seen that the values of the sine terms beyond A_5 are negligible, and are not greater than the errors due to the approximate nature of the method. The cosine terms are all negative and of decreasing values for the successive orders. In the Plate the wave-curve has been given for comparison, and on it the components A_1, A_3, B_1, B_3, and B_5 have been plotted in dotted wave-curves. For comparison with the hysteresis loop its chief components have also been drawn in dotted lines: the ellipse corresponding to A_1; the trilobate curve of A_2; the oblique straight line of B_1, and the curves for B_3 and B_5.

Example II. fig. 15, Pl. VI., Ewing's loop for annealed iron wire, being fig. 5 of plate lviii. of Phil. Trans. 1885.

The analysis gives:—

$$\begin{array}{ll} A_1 = 3{\cdot}98 & B_1 = -7{\cdot}38 \\ A_3 = 2{\cdot}14 & B_3 = -4{\cdot}74 \\ A_5 = 1{\cdot}36 & B_5 = -2{\cdot}04 \\ A_7 = 0{\cdot}88 & B_7 = -3{\cdot}78 \\ A_9 = 0{\cdot}16 & B_9 = -2{\cdot}14 \\ A_{11} = 0{\cdot}14 & B_{11} = -1{\cdot}90 \end{array}$$

The ellipse and the straight line, corresponding respectively to A_1 and B_1, have been added in dotted lines in the figure.

Example III. fig. 16, Pl. VI., Ewing's loop for annealed iron wire, being fig. 6, plate lviii. of the same memoir.

The analysis gives:—

$$\begin{array}{ll} A_1 = 4{\cdot}2 & B_1 = -35{\cdot}4 \\ A_3 = 1{\cdot}8 & B_3 = -25{\cdot}5 \\ A_5 = 0{\cdot}7 & B_5 = -17{\cdot}9 \\ A_7 = 0{\cdot}2 & B_7 = -\ 6{\cdot}7 \\ A_9 = 0{\cdot}3 & B_9 = -\ 4{\cdot}5 \\ A_{11} = 0{\cdot}2 & B_{11} = -\ 0{\cdot}5 \end{array}$$

Example IV. fig. 17, is taken from Lord Rayleigh's paper in the Phil. Mag. xxiii. pp. 225–245, 1887, or Scientific Papers, ii. p. 593, and is the loop obtained with very small magnetizing forces on a specimen of "rather hard Swedish iron."

The analysis gives:—

$$\begin{array}{ll} A_1 = 0{\cdot}553 & B_1 = -1{\cdot}022 \\ A_3 = 0{\cdot}038 & B_3 = -0{\cdot}094 \\ A_5 = 0{\cdot}006 & B_5 = -0{\cdot}046 \\ A_7 = 0{\cdot}002 & B_7 = -0{\cdot}025 \\ A_9 = 0{\cdot}005 & B_9 = -0{\cdot}023 \\ A_{11} = 0{\cdot}000 & B_{11} = -0{\cdot}012 \end{array}$$

Example V.

The next example is taken from a memoir of K. Ångström in the 'Proceedings' of the Royal Swedish Academy of Sciences, 1899, p. 257, where the curves are given without any scale-values. They relate to a rod of steel containing 0·2 per cent. of carbon. Fig. 18 was observed by a magnetostatic method, fig. 19 by using an alternating current of 20 periods per second, fig. 20 by using one of 60 periods per second.

The analyses, on an arbitrary scale, are :—

Fig. 18.

$A_1 = 0{\cdot}57 \qquad B_1 = -7{\cdot}29$
$A_3 = 0{\cdot}01 \qquad B_3 = -0{\cdot}59$
$A_5 = -0{\cdot}02 \qquad B_5 = -0{\cdot}40$
$A_7 = -0{\cdot}005 \qquad B_7 = -0{\cdot}23$
$A_9 = -0\ 01 \qquad B_9 = -0{\cdot}24$
$A_{11} = 0{\cdot}07 \qquad B_{11} = -0{\cdot}24$

Fig. 19.

$A_1 = 2{\cdot}31 \qquad B_1 = -8{\cdot}45$
$A_3 = 1{\cdot}08 \qquad B_3 = -0{\cdot}42$
$A_5 = 0{\cdot}44 \qquad B_5 = -0{\cdot}04$
$A_7 = 0{\cdot}16 \qquad B_7 = 0{\cdot}02$
$A_9 = 0{\cdot}05 \qquad B_9 = -0{\cdot}07$
$A_{11} = 0{\cdot}04 \qquad B_{11} = -0{\cdot}07$

Fig. 20.

$A_1 = 2{\cdot}74 \qquad B_1 = -8{\cdot}57$
$A_3 = 1{\cdot}21 \qquad B_3 = 0{\cdot}16$
$A_5 = 0{\cdot}10 \qquad B_5 = 0{\cdot}33$
$A_7 = -0{\cdot}09 \qquad B_7 = 0{\cdot}23$
$A_9 = -0{\cdot}04 \qquad B_9 = -0{\cdot}01$
$A_{11} = 0{\cdot}09 \qquad B_{11} = -0\ 03$

The small scale of the original drawings of these three loops makes the values of the higher harmonics quite unreliable. But the comparison is of interest as showing the effect of eddy-currents in the substance of the rod in widening the loops, and in increasing both A_1 and A_3.

§ 8. *Work done in the cycle.*—It was early pointed out by Warburg and by Ewing that the work spent in carrying the iron through a cycle of magnetizing operations was represented by the area of the hysteresis loop. We now consider this from another point of view.

Whatever work is spent in magnetizing the iron is derived from the electric energy which is imparted by the circuit, and this, at any instant, is proportional to the product of the current and potential at that instant. If the voltage is represented by the expression

$$V = V_0 \sin pt,$$

where p stands for $2\pi f$, and if the current, being some periodic function of the time, is represented as

$$C = \psi(pt),$$

then the element of work imparted to the circuit during time dt being $CVdt$, the work given to the iron (if the copper resistance is negligible) during one cycle will be

$$V_0 \int_0^T \sin pt \,.\, \psi(pt) \,.\, dt.$$

But $\psi(pt)$ consists (see § 3) of a series of harmonic sine and cosine terms. The quantities which will be formed by multiplying the members of that series by $\sin pt$, and integrating each product over a whole period, will fall under three kinds, the values of which are known, viz.:—

$$\text{(i.)} \quad \int_0^T \sin pt \,.\, A_n \sin npt \,.\, dt = 0, \text{ (except when } n = 1\text{);}$$

$$\text{(ii.)} \quad \int_0^T \sin pt \,.\, B_n \cos npt \,.\, dt = 0, \text{ (in all cases);}$$

$$\text{(iii.)} \quad \int_0^T A_1 \,.\, \sin^2 pt \,.\, dt = A_1 \,.\, \frac{T}{2}.$$

That is, *the only work done in the cycle* is that done by that constituent of the current which is in phase with the voltage, namely, its fundamental sine-term. *All other constituents are wattless.* And since the area of the loop represents the work done, it follows that the area of the hysteresis loop is equal to the area of the orthogonal ellipse which is its fundamental constituent of the sine series. *The true and fundamental form of every hysteresis loop is therefore an orthogonally placed ellipse.* All departures from that form are wattless—are mere distortions which involve no expenditure of energy. The area of the hysteresis loop is proportional to the maximum value of $\mathfrak{B}$ and to the amplitude of the first sine term into which the values of $\mathfrak{H}$ (corresponding to the values of the current) can be analysed. If the value of the amplitude of that sine-term be denoted by $\mathfrak{H}_1$, then the area of the loop is accurately given by the expression $\frac{\pi}{4} \times \mathfrak{B}_{\text{max.}} \times \mathfrak{H}_1$; being the area of the fundamental elliptical constituent. To test this conclusion the areas of the three loops, figs. 18, 19, and 20 were planimetered for comparison with the values of A_1:

	Planimeter reading.	A_1.	Ratio.
Fig. 18	33·8	0·57	594
Fig. 19	140·	2·31	605
Fig. 20	167·5	2·74	610

All the constituent curves belonging to the higher orders have zero areas; the lobes formed by the crossing of their outlines being alternately positive areas and negative areas. This is only another way of saying that the integrals (i.) and (ii.) above are always zero. As for those of form (ii.), they are obviously so, as all cosine constituents shrink up to mere lines.

§ 9. *Presence of Eddy-Currents.*

If the hysteresis loop has been produced by some slow process, absence of eddy-currents may be assumed. But this is by no means the case when alternating currents of ordinary frequencies are used, even if the iron be finely laminated. It therefore remains to be seen how the presence of eddy-currents will affect the size and form of the hysteresis loop. The eddy-current, being a secondary current, will be of pure sinusoidal form only if the inducing electromotive force be of a pure sinusoidal form, and if the resistance and permeability be constant also. But it is not necessarily in phase with the impressed electromotive force, but may lag by magnetic reaction ; and indeed, as is already known, lags by different amounts at different depths below the surface of the iron. Assuming equal permeability and resistance in the different layers, the effect of the eddy-current will be represented with sufficient accuracy by a sine-curve lagging by an amount that will depend on conditions into which there is no need here to enter. For here, again, the only effective component—effective that is in the sense of involving expenditure of energy—is the sine-component in phase with the voltage ; and the element which the sine-component contributes to the loop is an orthogonal ellipse. So far as it lags it possesses a cosine-component, and this contributes to the loop only an oblique line, shearing the loop over ; but this constituent is wattless. Harmonic analysis cannot of itself distinguish as to how much of the fundamental elliptical constituent of the loop, or of the fundamental sine-component of the magnetizing current, is due to eddy-currents, and how much to hysteresis. It is, indeed, already known * that the effect of eddy-currents is to widen out the loop elliptically.

§ 10. *Effect of the Higher Sine-Constituents.*

The presence of the third harmonic has been noted in § 7 above. Indeed, it is usually present. A fine example is afforded by the curve, fig. 21, which is taken from Fleming's 'Alternate Current Transformer,' vol. ii. p. 486 (edition of 1892), which affords the following analysis :—

Fig. 21.

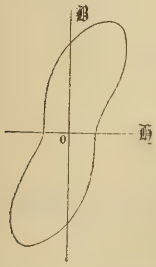


Fig. 22.

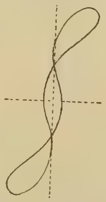
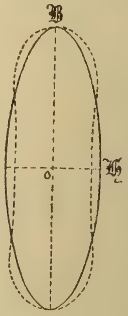


Fig. 23.



$$\begin{array}{ll}
A_1 = 11{\cdot}23 & B_1 = -11{\cdot}87 \\
A_3 = 1{\cdot}71 & B_3 = -\ 0{\cdot}72 \\
A_5 = -\ 0{\cdot}74 & B_5 = +\ 0{\cdot}23 \\
A_7 = +\ 0{\cdot}62 & B_7 = +\ 0{\cdot}07 \\
A_9 = -\ 0{\cdot}29 & B_9 = +\ 0{\cdot}22 \\
A_{11} = +\ 0{\cdot}03 & B_{11} = +\ 0{\cdot}57
\end{array}$$

In the memoir of Ångström already quoted, a curious curve, fig. 22, nearly a pure third harmonic is given, having been found by him as a differential hysteresis loop representing the difference between two steel rods, one having 0·2 per cent. the other 0·8 per cent. of carbon.

It is obvious that the effect of superposing a third-term sine-constituent upon the fundamental ellipse will be to narrow it at the middle. It will widen it toward the ends, the widening beginning at a distance of 0·134 of the semi-major axis from the ends, as in fig. 23.

If sine-constituents were present, of all orders, in the following proportions,

$$A_1=1,\ A_3=\tfrac{1}{3},\ A_5=\tfrac{1}{5}\ldots\ldots A_n=\frac{1}{n},$$

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* See Ångström, *op. citat.*; and Heinke, *Die Electrophysik* (1904), p. 500.

the form of the loop would become a pure rectangle, as fig. 24.

Fig. 24.

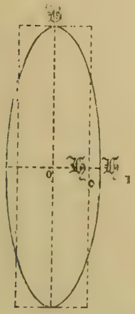
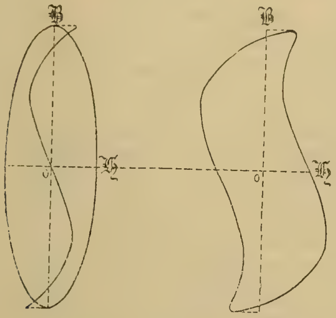


Fig. 25.



The half-width of any static hysteresis loop, which is commonly taken (following Hopkinson) as a measure of the coercive force, is independent of all the cosine terms, and is in all cases equal to $A_1-A_3+A_5-A_7+A_9-$ &c.

For loops of equal height (that is equal maxima of flux density) the coercive force is not proportional to the work spent in the cycle; for the work spent in the cycle is represented by the area of the loop, and as shown above, this is invariably proportional to A_1, while the coercive force is represented by the sum of the series named in the previous sentence. Since in static hysteresis loops the fifth and higher terms are practically absent, the coercive force is proportional to A_1-A_3.

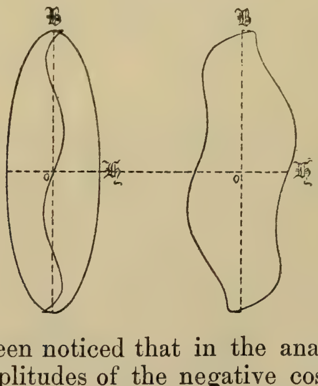
§ 11. *Effect of the Cosine-Constituents.*

As already seen, the fundamental cosine-constituent is an oblique line. It is in reality a double line, traversed upwards during half the cycle, and downwards during the other half. The effect of superposing this constituent upon the fundamental ellipse is to shear it over. Cosine-components are always negative, corresponding to lagging constituents of the wave-curve. They shear the $\mathfrak{B}$–$\mathfrak{H}$ curve over toward the right, on the ascending side. If a mass of iron undergoing magnetization is traversed by an air-gap, or is constituted as a non-closed magnetic circuit, the reaction of the air-gap brings a lagging constituent into the magnetizing current, imposing a negative cosine-constituent upon the loop, and shearing it over.

The presence of negative cosine-constituents in hysteresis loops is specially marked in those beaked forms which are obtained when the magnetization has been pushed to high degrees of saturation: the diminished permeability of the material resulting in a diminished reactance, and therefore in a disproportionate increase in the magnetizing current. This is well seen on examination of the analysis of figs. 14, 15, and 16. Cosine terms of the higher orders are responsible for the distortion of the ellipse into the characteristic two-beaked form. Fig. 25 shows the result of superposing a negative third cosine-constituent upon the ellipse. But this particular figure, resembling a capital **S**, could not result from any experiment, as neither the ascending nor the descending half is single-valued. No experimental curve* could, on ascending from the point where it crosses the $\mathfrak{H}$ axis, curve backwards toward the $\mathfrak{B}$ axis, and then recurve from that axis. Such a curve would be unstable; and the ascending branch could, at most, ascend parallel to the $\mathfrak{B}$ axis before turning to the cusp. Is it too remote to speculate that the vertical portions of the loops experimentally found for soft iron really do represent instabilities, and mask the true forms of the loops?

The superposition of a negative fifth-order constituent is shown in fig. 26; but, again, the only possible cases must be such as to yield single-valued resultants.

Fig. 26.



It will have been noticed that in the analyses of some of the loops the amplitudes of the negative cosine terms appear in a descending set of values. If these amplitudes are of relative magnitudes as $1:\frac{1}{2}:\frac{1}{4}:\frac{1}{8}$ &c., the resultant curve will have its middle portion truly vertical. Fig. 27 gives a

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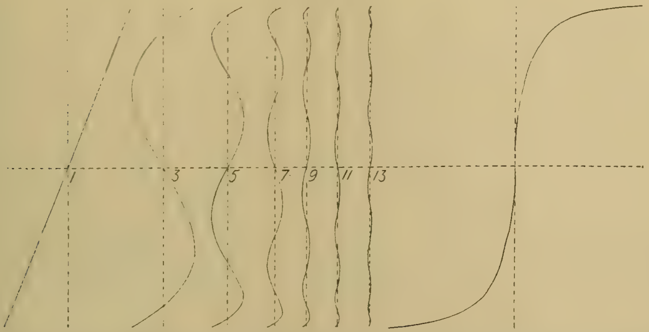
* See, for example, P. Holitscher (*Inaug. Diss.*, Zürich, 1900), "Experimentelle Untersuchungen über den remanenten Magnetismus des Eisens," plate 6.

set of such curves up to the thirteenth order, together with their resultant. If this resultant is then superposed on a fundamental ellipse, the result is a characteristic two-beaked loop.

Fig. 27.



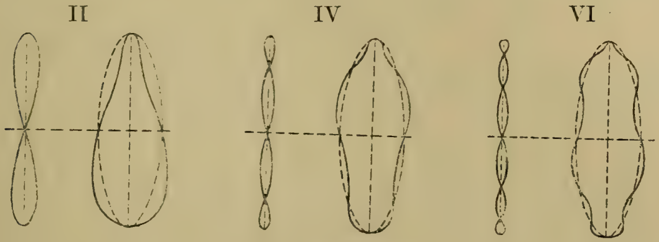
The horizontal length from the cusp to the vertical axis (*i. e.* the amplitude of $\mathfrak{H}$ at its maximum) is in all cases equal to

$$B_1 + B_3 + B_5 + B_7, \text{ \&c.}$$

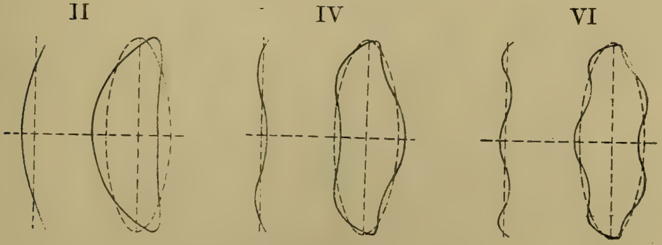
§ 12. *Effect of Harmonic Constituents of Even Orders.*

If constituents of even orders could exist, they would produce distortions of the loop, such as are shown in fig. 28. No such distortions have ever been observed.

Fig. 28.



Sine Components.



Cosine Components.

§ 13. Hysteresis is commonly regarded as an irreversible process, and as such involving a degradation of energy into heat. But in view of the present analysis of the hysteresis loop it is necessary to revise this opinion. In the first place, no energy is wasted in producing any cosine component of the loop. In the case of the first cosine term—the oblique line—the distortion is a mere shear. True energy is spent in half the cycle in producing the magnetic flux, but that energy is returned to the magnetizing circuit during the other half of the cycle, exactly as it is in the case of the production of a magnetic flux in a solenoid devoid of iron. The like is true of the higher cosine-components. Also the sine-components higher than the first represent reversible processes. The only component which represents an irreversible process is the fundamental sine-component, the ellipse, itself due to that component of current which is in phase with the voltage. This irreversible part is due in detail to an energy-waste which at every instant is proportional to the square of the magnetizing current, and is in phase with it. True hysteresis waste accompanies the current, and does not either lag behind it nor precede it. True hysteresis does not cause any lag in the current, being necessarily simultaneous with it. True, the curve of the flux-density always lags 90° behind the voltage curve, and therefore 90° behind the effective component of the current curve. Of the reversible components, it is the first cosine term which is concerned in the lag of the current, and the lagging component of current is wattless. The higher cosine-components conjointly produce additional lags, and are also wattless. The higher sine-components, also wattless, do not cause any lag of the current as a whole. The name "hysteresis" was originally given [*] to the phenomenon to connote an effect which lagged behind its cause. The term is now usually restricted to the phenomenon of energy-waste. But the energy-waste does not involve or produce any phenomenon of lag. On the contrary, as it is a simultaneous phenomenon, its presence actually produces an advance in the phase of an otherwise lagging current. The greater the reluctance of the magnetic circuit, the greater the angle of lag. The less the permeability which enters into that reluctance the greater is the angle of lag. The lagging components, that is the cosine-components of the loop, so far as they are not due to eddy-currents, depend solely upon the reduction of the permeability of the iron during the process of the cycle of magnetization. The lag is in fact due to components other than the fundamental component which represents the true hysteresis.

[*] Ewing, Phil. Trans. 1885, pt. ii. p. 524.

XLI. *On the Precise Effect of Radial Forces in opposing the Distortion of an Elastic Sphere.* *By* J. Prescott, *M.A., Lecturer in Mathematics, Manchester School of Technology*[*].

THIS question is part of a more general one which is worked out very fully in Love's 'Theory of Elasticity' (arts. 170–178). Since, however, there is an important error in Love's solution, an error of principle and not of calculation merely, I have presumed in this paper to point out the error and give the correct solution. It is all the more necessary to point out the error because, not being a very obvious one, it might pass a long time unnoticed in such an excellent book as Love's.

It is supposed that straining forces act on a solid homogeneous sphere which have a potential of the form $V+U$, where $V=f(r)$ and U is the sum of several spherical solid harmonics. Then it is reasonable to assume, as in Love, that the radial displacement will be composed of solid harmonic terms also.

Let us suppose that the matter which, in the unstrained sphere, was distributed over the sphere of radius r_0, is now distributed over the surface whose equation is

$$r=r_1+\sigma,$$

r_1 being constant for each shell, and σ being a small quantity which is a function of r_1 and angular co-ordinates. The equation (1) is thus the equation of a family of nearly spherical surfaces with r_1 as parameter.

Let us also suppose that the coordinates of a particle on the surface whose parameter is r_1 are x_1+u, y_1+v, z_1+w where x_1, y_1, z_1 are the coordinates of a point on the sphere of radius r_1.

It will be seen from the above that we are considering the displacement of every particle to be composed of two distinct parts, namely (1) one in which every shell which was spherical in the unstrained state and had a radius r_0, is strained into a shell of radius r_1; and (2) displacements measured from the strained spherical surface. Now the radial forces with potential V will produce a radial strain, and the other type of strain can be produced by the harmonic forces.

We will now suppose that the radial forces, if acting alone, would produce the radial displacement from r_0 to r_1, which, we shall assume, is not sufficiently large to alter the density appreciably, or to affect the elastic properties of the sphere. If now we completely ignored the radial forces we could find

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[*] Communicated by the Author.

the additional displacements due to the harmonic forces, and it might appear that these would be the displacements represented by u, v, w above. But if the radial forces are very much larger than the harmonic forces, it is obvious that they have the effect of reducing the deviations from the mean sphere. When any spherical shell is distorted from the spherical form the particles of the shell are in places where the radial forces are unequal, and thus differential forces are brought into play which are of a similar type to those of the harmonic forces.

The difficulty arises from the fact that x, y, and z are used with double meanings. In the expressions for the potential of the external forces and for those forces themselves, they mean space-coordinates. Thus if V denotes the potential of the external forces, we suppose V expressible in terms of these space-coordinates thus

$$\mathrm{V}=\mathrm{F}(x, y, z),$$

and the forces are derived from this by differentiation and expressible in the form

$$\mathrm{X}=-\frac{\partial \mathrm{V}}{\partial x}=-\mathrm{F}_x(x, y, z), \text{ \&c.}$$

Now there is a second meaning to x, y, and z. They are used as the distinguishing coordinates of a particle of the elastic body even after the body is strained. They are the space-coordinates of the position of the particle before strain. The space-coordinates after strain are represented by $x+u$, $y+v$, and $z+w$. It is clear, therefore, that the x-force at the point occupied by the particle whose distinguishing coordinates are (x, y, z) is, after the strain, $\mathrm{F}_x(x+u,\ y+v,\ z+w)$. Now these external forces at the point $(x+u, y+v, z+w)$ are in equilibrium with the stresses at that point. But the stresses are regarded as functions of the distinguishing coordinates of the particles of the body; so that if $\mathrm{P}=\phi(x, y, z)$ is one of these stresses, we mean by $\phi\ (x, y, z)$ the stress at that point of the body which was at (x, y, z) before strain, and which is at $(x+u,\ y+v,\ z+w)$ after strain. Thus in the equations of equilibrium we must express the stresses in terms of (x, y, z) and the external forces in terms of $(x+u, y+v, z+w)$, and that is my method.

In most problems the external forces in the displaced positions would differ so little from those in the original positions, that it would be superfluous to take account of the difference. But in the problem considered here the difference in the case of the radial forces is of the same order of magnitude as the harmonic forces. Professor Love does not neglect this difference, but he allows for it in a wrong way. Instead of modifying the bodily forces throughout, he assumes that the difference is properly accounted for by treating the bodily forces on the matter displaced outside the original bounding surface as if it were a surface-traction. This is a consequence of regarding the coordinates which occur in the equations of equilibrium as the space-coordinates of the particles of the strained body; whereas, as I have pointed out, they are the space-coordinates of the particles of the unstrained body. Surface-tractions are forces applied at the boundary of the body, and not forces applied at that surface which was the boundary in the unstrained state.

When the harmonic forces do not act, the radial force acting on the spherical shell whose new radius is r_1, has a potential $f(r_1.)$ But when the spherical shell is strained to the surface whose equation is

$$r=r_1+\sigma$$

the radial force acting at different points of this shell is derived from the potential

$$\begin{aligned}V&=f(r_1+\sigma)\\&=f(r_1)+\sigma f'(r_1),\text{ nearly.}\end{aligned}$$

The first term of V is the one that causes radial strain, and it has no effect whatever on the value of σ. Since, in the rest of the paper, we shall only be concerned with the deviation of the shells from the spherical form, we can ignore this term both in the differential equations and in the boundary conditions.

But the second term in V causes displacements from the mean spheres; and if its magnitude is of the same order as that of the harmonic forces, it must be added to the potential of these forces.

We shall assume that

$$\sigma=\Sigma\epsilon_n Q_{n+1},$$

where ϵ_n is a small coefficient and Q_{n+1} is a spherical solid harmonic of order $n+1$.

We shall write r, x, y, z instead of r_1, x_1, y_1, z_1, to save labour in writing wherever no ambiguity can arise.

In problems concerning the tidal action of the sun and moon on the earth and the action of "centrifugal force" due to the earth's rotation $f(r)$ is proportional to r^2; and therefore we may put $f'(r_1) = \mathrm{K}r_1$. Thus the term which has to be added to the potential of the non-radial force is

$$\mathrm{W} = \mathrm{K}r_1 \Sigma \epsilon_n \mathrm{Q}_{n+1}.$$

We have now to find particular integrals of the equations of equilibrium due to the term W, and to determine its contribution to the boundary conditions.

The equations of equilibrium are three such equations as

$$(\lambda + \mu)\frac{\partial \Delta}{\partial x} + \mu \nabla^2 u + \rho \frac{\partial \mathrm{W}}{\partial x} = 0, \quad . \quad . \quad . \quad . \quad (4)$$

the symbols used having the same meaning as in Love's book.

We shall obtain particular integrals by assuming that

$$u = \frac{\partial \phi}{\partial x}, \quad v = \frac{\partial \phi}{\partial y}, \quad w = \frac{\partial \phi}{\partial z}.$$

Then equation (4) gives

$$(\lambda + 2\mu)\nabla^2 \frac{\partial \phi}{\partial x} + \rho \frac{\partial \mathrm{W}}{\partial x} = 0, \quad . \quad . \quad . \quad (5)$$

whence

$$(\lambda + 2\mu)\nabla^2 \phi = -\rho \mathrm{W}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Now if W_{n+1} denotes a solid harmonic of order $(n+1)$ we know that

$$\nabla^2(r^p \mathrm{W}_{n+1}) = p(2n + p + 3) r^{p-2} \mathrm{W}_{n+1}. \quad . \quad . \quad (7)$$

By putting $p = 3$ in equation (7) we see that the solution of (6) is

$$\phi = -\frac{\mathrm{K}\rho r^3}{\lambda + 2\mu} \cdot \Sigma \frac{1}{6(n+3)} \epsilon_n \mathrm{Q}_{n+1}. \quad . \quad . \quad . \quad (8)$$

This gives

$$u = -\frac{\mathrm{K}\rho}{\lambda + 2\mu} \cdot \frac{\partial}{\partial x} \Sigma \frac{r^3}{6(n+3)} \epsilon_n \mathrm{Q}_{n+1}. \quad . \quad . \quad (9)$$

and two similar expressions for v and w.

Also

$$\Delta = \nabla^2 \phi$$

$$= -\frac{\mathrm{K}\rho r}{\lambda + 2\mu} \Sigma \epsilon_n \mathrm{Q}_{n+1}. \quad . \quad . \quad . \quad (10)$$

If there are no surface tractions one of the boundary conditions is

$$\lambda x\Delta+\mu\left\{\frac{\partial\zeta}{\partial x}+r^2\frac{\partial}{\partial r}\frac{u}{r}\right\}=0, \quad . \quad . \quad . \quad (11)$$

where

$$\zeta=xu+yv+zw$$

$$=-\frac{\mathrm{K}\rho r^3}{\lambda+2\mu}\Sigma\frac{n+4}{6(n+3)}\epsilon_n\mathrm{Q}_{n+1}.$$

The terms contributed to the left-hand side of (11) by the particular integrals we have just found are

$$-\frac{\mathrm{K}\rho}{\lambda+2\mu}\Sigma\epsilon_n\left\{\lambda xr\mathrm{Q}_{n+1}+\mu\frac{n+4}{6(n+3)}\frac{\partial}{\partial x}(r^3\mathrm{Q}_{n+1})\right.$$

$$\left.+\mu\frac{n+2}{6(n+3)}\frac{\partial}{\partial x}(r^3\mathrm{Q}_{n+1})\right\}$$

$$=-\frac{\mathrm{K}}{\lambda+2\mu}\Sigma\epsilon_n\left\{\lambda xr\mathrm{Q}_{n+1}+\tfrac{1}{3}\mu\frac{\partial}{\partial x}(r^3\mathrm{Q}_{n+1})\right\}$$

$$=-\frac{\mathrm{K}\rho}{\lambda+2\mu}\Sigma\epsilon_n r\left\{(\lambda+\mu)x\mathrm{Q}_{n+1}+\tfrac{1}{3}\mu r^2\frac{\partial\mathrm{Q}_{n+1}}{\partial x}\right\}$$

$$=-\frac{\mathrm{K}\rho r}{\lambda+2\mu}\Sigma\epsilon_n\left\{(\lambda+\mu)\frac{r^2}{2n+3}\left[\frac{\partial\mathrm{Q}_{n+1}}{\partial x}-r^{2n+3}\frac{\partial}{\partial x}\left(\frac{\mathrm{Q}_{n+1}}{r^{2n+3}}\right)\right]\right.$$

$$\left.+\tfrac{1}{3}\mu r^2\frac{\partial\mathrm{Q}_{n+1}}{\partial x}\right\}.$$

Now we want to make every term in the preceding expression into a spherical solid harmonic, and since it is the surface value of the expression that occurs in the boundary condition we may put a (the value of r at the surface) for r wherever we choose.

In solid harmonics the preceding expression becomes

$$-\frac{\mathrm{K}\rho a}{\lambda+2\mu}\cdot\Sigma\epsilon_n\left\{\left(\frac{\lambda+\mu}{2n+3}+\frac{\mu}{3}\right)a^2\frac{\partial\mathrm{Q}_{n+1}}{\partial x}-\frac{\lambda+\mu}{2n+3}r^{2n+5}\frac{\partial}{\partial x}\left(\frac{\mathrm{Q}_{n+1}}{r^{2n+3}}\right)\right\}.$$

In the case of tidal forces or "centrifugal force" the only significant part of K is $-\frac{g}{a}$. With this value of K the above expression becomes

$$\Sigma\epsilon_n\left\{a_n'\frac{\partial\mathrm{Q}_{n+1}}{\partial x}+b_n'r^{2n+5}\frac{\partial}{\partial x}\left(\frac{\mathrm{Q}_{n+1}}{r^{2n+3}}\right)\right\},$$

where

$$a_n' = \frac{1}{3}\frac{g\rho}{\lambda+2\mu}\frac{3\lambda+2(n+3)\mu}{2n+3}a^2,$$

$$b_n' = -\frac{g\rho}{\lambda+2\mu}\cdot\frac{\lambda+\mu}{2n+3}.$$

The above two terms should replace two similar terms given in the boundary condition in Love (Art. 177). The values of the coefficients differ, however, from those in Love's work.

In order to express the functions Q_{n+1} in terms of the potentials of the given forces it is necessary to equate the radial displacements found in the problem, measured from the mean sphere, to the assumed displacements, viz. $\Sigma\epsilon_n Q_{n+1}$.

Now the radial displacement is $\frac{1}{r}\cdot\{xu+yv+zw\}$, and the part contributed to this by the differential terms of the radial forces is

$$-\frac{K\rho r^2}{\lambda+2\mu}\cdot\Sigma\frac{n+4}{6(n+3)}\epsilon_n Q_{n+1}.$$

The value of this at the surface, where $r=a$, is

$$+\frac{g\rho a}{\lambda+2\mu}\Sigma\frac{n+4}{6(n+3)}\epsilon_n Q_{n+1}.$$

The corresponding terms in Love (Art. 177) are

$$(A+3Ha^2)\Sigma\epsilon_n Q_{n+1}.$$

where

$$H = \frac{1}{10}\cdot\frac{g\rho}{a(\lambda+2\mu)},$$

$$A = -\frac{5\lambda+6\mu}{3\lambda+2\mu}Ha^2.$$

Substituting these values for A and H the above terms become

$$\frac{\rho g a}{\lambda+2\mu}\cdot\frac{2\lambda}{5(3\lambda+2\mu)}\Sigma\epsilon_n Q_{n+1},$$

which again differs from the expression I have found above. The error here arises from the same misconception concerning the part played by radial forces as that from which the error in the boundary conditions arises.

The rest of the work is the same as in Love's book, and thus it is unnecessary to give it here.

The erroneous theory and my theory give exactly the same results for an incompressible sphere, but there is a difference in the results for a compressible solid. I will give here the correct result when a disturbing force, which has a potential W_2, acts on a sphere and the value of the ratio $\frac{\lambda}{\mu}$ is unity.

The radial displacement is

$$\epsilon_1 Q_2 = \frac{225\vartheta}{275+(99\frac{3}{8})\vartheta} \frac{W_2}{g},$$

where

$$\vartheta = \frac{g\rho a}{\mu}.$$

The result given by the incorrect theory (Love's 'Elasticity,' Art. 183) is

$$\epsilon_1 Q_2 = \frac{225\vartheta}{275+93\vartheta} \frac{W_2}{g}.$$

XLII. *Note on the preceding Paper.* *By* A. E. H. Love[*].

MR. PRESCOTT'S criticism of my solution is to the effect that I have not used correct expressions for the body forces. The right way to obtain expressions for the components of the body force at a point, say P, is to express the potential at P in terms of the coordinates of P and differentiate the expression so obtained with respect to the coordinates of P. What Mr. Prescott does is to differentiate (with respect to the coordinates of P) the potential at that point Q to which the particle that was initially at P is displaced. I do not know of any justification for this procedure.

Mr. Prescott's argument in the paragraph of his paper beginning "Now there is a second meaning to x, y, z" seems to me to be unsound. Whenever, as in this problem, it is necessary to distinguish the forces that act upon the body in the strained and unstrained states, the coordinates x, y, z that occur in the equations of equilibrium must be taken to be the

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[*] Communicated by the Author.

coordinates of a point of the body when in the state in which it is held by the forces, not those of the same particle of the body when in the state that it would have if the forces were not acting. This meaning is shown at once to be correct by examining the proof of the equations of equilibrium as given, for example, in the second edition of my book on 'Elasticity,' Articles 44, 54.

The incriminated solution was given in the first edition of my book and omitted from the second edition, because in the meantime I had found that it was unsatisfactory. The problem is concerned with an elastic solid body held in a nearly spherical shape by its own gravitation and by external forces. The nearly spherical body is taken to represent the Earth. The type of the external forces is such as to include tide-generating force as a particular example. In the solution in question it is assumed that the stress by which the self-gravitation of the body, supposed truly spherical, is balanced throughout the body, is correlated, according to Hooke's Law, with a state of strain, and that this strain can be expressed by means of a displacement according to the ordinary method of the theory of Elasticity. According to this method the body is regarded as capable of existing in two states: the first, a sphere free from gravitation, and therefore also free from stress; the second, a gravitating sphere. The calculated displacement is that by which the particles would pass from their positions in the first state to their positions in the second state. It is essential to the success of the method that the strain and and displacement so calculated should be small quantities. When the calculation is effected it is found that, unless the material can be treated as incompressible, this condition is not satisfied. In Mr. Prescott's notation and words, the displacement required to change r_0 into r_1 does alter the density appreciably and affects the elastic properties of the sphere. The assumption in regard to the nature of the stress, by which the self-gravitation of the sphere is balanced, is therefore in general untenable, and the solution fails. Mr. Prescott's would fail for the same reason even if his argument which is criticized above were correct. As I have pointed out in the second edition of my book and elsewhere, the Earth must be regarded as a body in a state of "initial stress." This view has been advanced also by Lord Rayleigh (Proc. Roy. Soc. vol. lxxvii. p. 486, 1906). The solution given in the first edition of my book needs correction, but not in the sense indicated by Mr. Prescott.

XLIII. *On the Shape of the Molecule.* *By* R. D. KLEEMAN, *D.Sc., B.A., Mackinnon Student of the Royal Society* *.

THE shape of a molecule is usually assumed to be spherical and its diameter calculated on this supposition. One of the formulæ used is $L=\frac{3}{4}N\pi\sigma_1^2$, where L denotes the mean free path of the molecule, σ_1 the radius of its sphere of action, and N the number of molecules per c. c. at standard temperature and pressure. The value for σ_1 is usually taken as the diameter of the molecule. L is usually obtained from experiments on diffusion or viscosity, and N from a knowledge of *e*, the electric charge on an ion.

But the assumption that the molecule is spherical in shape is not admissible. Thus Meyer in his 'Kinetic Theory of Gases' shows that the cross-section of an atom, which is proportional to σ_1^2, is an additive quantity relating to the atoms composing the molecule. Meyer shows that this is only possible if the atoms of the molecule lie approximately on a plane. It is difficult to see how under the circumstances the molecule can be spherical in shape. Especially since using the values of the cross-section of molecules given by σ_1^2, and the fact that the volume of an atom according to Traube † is proportional to the square root of the atomic weight, it has been shown by the writer ‡ that the atom must be approximately spherical in shape.

The object of this paper is to give a method by means of which direct information as to the shape of the molecule may be obtained.

At the absolute zero of temperature the molecules have no motion of translation, and the apparent space occupied by a molecule or atom is its true volume. Now the densities of liquids at corresponding states are the same fraction of their density at the critical state to within a few per cent. The densities may therefore also be said to be the same multiple of their densities at the absolute zero. The relative molecular volumes of the molecules of liquids at corresponding states are therefore the same as the relative volumes at the absolute zero.

Further it is probable that the relative values of σ_1^2 or σ_1 given by the above equations can only be legitimately compared at corresponding temperatures. The value of σ_1 does not represent merely the real cross-section of the molecule, but the cross-section modified (usually increased) by the field of force surrounding the molecule.

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* Communicated by the Author.

† *Phys. Zeit.* p. 667, Oct. 1909.

‡ "On the Shape of the Atom," Phil. Mag. July 1910, p. 229.

Now the writer has shown * that the radius of the sphere of action of the force of attraction of different molecules is the same fraction of their radius at the absolute zero. He had also previously shown † that the attraction between two molecules is given by the expression $(\Sigma\sqrt{m_1})^2\frac{1}{z^5}\phi\left(\frac{z}{x_c},\beta\right)$, where $\Sigma\sqrt{m_1}$ denotes the sum of the square roots of the atomic weights of the atoms composing a molecule, z is their distance of separation, x_c is their distance of separation at the critical state, and $\beta=\frac{T}{T_c}$ where T denotes temperature. From this it follows that at corresponding states, $\phi\left(\frac{z}{x_c},\beta\right)$ will be the same for all liquids, and the radii of the sphere of action of different molecules at corresponding temperatures therefore the same fraction of their radii at the absolute zero. We shall therefore be on much safer ground if we compare values of σ_1 or σ_1^2 at corresponding states.

Let the relative values of σ_1^2 be determined for a number of different molecules and also their molecular volumes in the liquid state, both at corresponding temperatures. Then if V denotes the molecular volume, the ratio $\frac{V}{\sigma_1^3}$ will be the same for all liquids if the molecules are spherical in shape, for V is then proportional to σ_1^3. But if it is not spherical in shape the ratios are not necessarily the same, and we shall be nearer the truth in supposing the molecule an oblate spheroid of which $\frac{V}{\sigma_1^2}$ is proportional to an axis of the generating ellipse. If we denote $\frac{V}{\sigma_1^2}$ by σ_2, then $\frac{V}{\sigma_1^3}=\frac{\sigma_2}{\sigma_1}$. A set of calculations of this nature has been carried out, and the results are contained in Table I. They correspond to $\frac{349\cdot7}{556\cdot1}T$. The relative values of σ_1 were calculated by means of the equation $\sigma_1=\left(\frac{mv}{4\pi\eta}\right)^{1/2}$, where m denotes the molecular weight, v the velocity of translation of a molecule, and η the coefficient of viscosity. In this equation, v was put proportional to $\left(\frac{T}{m}\right)^{1/2}$, and then σ_1 is proportional to $\frac{(mT)^{1/4}}{\eta^{1/2}}$. The coefficient of viscosity corresponding to the

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* Phil. Mag. p. 480, June 1910.

† Phil. Mag. pp. 788–792, May 1910.

temperature $\frac{349{\cdot}7}{556{\cdot}1}\,\mathrm{T}_c$ was calculated from the formulæ given in Landolt and Börnstein's Tables, 5th edition. The molecular volume V is proportional to $\left(\frac{m}{\rho}\right)$. Column 8 contains the relative values of $\frac{\rho\sigma_1{}^3}{m}$ or $\frac{\sigma_2}{\sigma_1}$, the ratio of the axis of the circular section of the spheroid to the axis at right angles to the section.

TABLE I.

Name of Substance.	Abs. Temp. T.	ρ.	$\eta\times10^7$	$\frac{m}{\rho}$.	$\frac{(m\mathrm{T})^{1/4}}{\eta^{1/2}\times10^{7/2}}$ or relative values of σ_1.	Relative values of $\frac{m}{\rho\sigma_1{}^2}$ or σ_2.	Relative values of $\frac{\rho\sigma_1{}^3}{m}$ or $\frac{\sigma_2}{\sigma_1}$.	$\frac{(\Sigma m^{1/3})^{3/2}}{\Sigma m^{1/2}}$ or $\frac{\sigma_2}{\sigma_1}$.
Carbon tetrachloride CCl_4	349·7	1·5030	1950	102·4	·3449	683·9	5·044	2·22
Ethyl oxide... $C_4H_{10}O$	293·9	·7123	745·2	103·9	·4448	524·9	8·474	3·61
Benzene .... C_6H_6	353·1	·8145	1057	95·76	·3962	610·1	6·494	3·28
Methyl formate $C_2H_4O_2$	306·2	·9553	997·9	62·82	·3686	462·3	7·975	3·76
Ethyl propionate $C_5H_{10}O_2$	343	·8308	1074	122·7	·4173	705·2	5·917	3·86
Chloroform ... $CHCl_3$	335·2	1·3935	1905	85·78	·3242	816·2	3·972	2·66

It will be seen that the values of this ratio are by no means constant, showing that the shape of the molecule is far from being spherical.

The absolute value of the ratio $\frac{\sigma_2}{\sigma_1}$ for a molecule cannot be calculated, because we do not know the absolute molecular volume of a molecule. But this ratio can be approximately obtained as follows. The writer has shown * that the diameter of an atom is proportional to $m^{1/6}$, and its cross-section therefore proportional to $m^{1/3}$. The cross-section of the molecule coinciding with the plane in which the atoms lie will therefore be $\Sigma m^{1/3}$, and its radius is therefore proportional to $\sqrt{\Sigma m^{1/3}}$. Now the volume of the molecule according to Traube is proportional to $\Sigma m^{1/2}$, and the length of the axis at right angles to the circular section is therefore $\frac{\Sigma m^{1/2}}{\Sigma m^{1/3}}$. The ratio of the two axes is then $\frac{(\Sigma m^{1/3})^{3/2}}{\Sigma m^{1/2}}$.

The values of this ratio have been calculated and are given in the 9th column of Table I. It will be seen that they bear

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* *Loc. cit.*

approximately the same relation to one another as the relative values of $\frac{\sigma_2}{\sigma_1}$ given in the 8th column. It is also seen that the axis at right angles to the plane in which the atoms lie is, as we should expect, much smaller than an axis in that plane. Thus it appears that the atoms of a molecule lie approximately in one plane.

We should expect, however, from this that the ratio for ethyl propionate given in the 8th column should be greater than that for any of the other substances given in the table. But this is not the case. Thus the atoms of an ethylpropionate molecule do not lie altogether in a plane. If the atoms are in rotation round the centre of the molecule, we should expect that greater stability would be secured if, in a molecule containing many atoms, the latter did not lie exactly in a plane.

We may therefore conclude that instead of supposing the molecule a sphere, we shall be nearer the truth in supposing it an oblate spheroid of which the ratio of the axis of the circular section to that at right angles to this section is given by $\frac{(\Sigma m^{1/3})^{3/2}}{\Sigma m^{1/2}}$.

The values of this ratio have been calculated for a number of compounds, and are contained in Table II. It is very probable that it may be possible to connect them with other properties of the substances such as crystalline form, and therefore a table of their values seems useful.

It is of interest to inquire whether the shape of the molecule changes with temperature. From the equation $\eta = \frac{mv}{4\pi\sigma_1^2}$ we see that if the radius of the sphere of action, σ_1, is independent of the temperature, η is proportional to v, and therefore to $T^{1/2}$, since v is proportional to $T^{1/2}$. Experiment, however, shows that η is approximately proportional to the first power of the temperature, so that σ_1 must be a function of the temperature. If there is no field of force surrounding the molecule this would indicate that the volume of the molecule changes with the temperature. If, however, we regard the molecules as centres of force, their apparent cross-section will change on account of the increase in the velocity of the colliding molecules with temperature. Maxwell on this supposition proved that the force of attraction varied inversely as the fifth power of the distance from the centre of the molecule. We thus see that the variations of

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* *Loc. cit.*

η with temperature do not furnish any information as to the change of shape of the molecule with temperature, because we do not know to what extent σ_1 depends on the field of force round the molecule. The same also applies to the variation of the coefficient of diffusion with temperature, because this also depends on σ_1, the radius of the sphere of action.

TABLE II.

	$\frac{(\Sigma m^{1/3})^{3/2}}{\Sigma m^{1/2}}$.		$\frac{(\Sigma m^{1/3})^{3/2}}{\Sigma m^{1/2}}$.		$\frac{(\Sigma m^{1/3})^{3/2}}{\Sigma m^{1/2}}$.		$\frac{(\Sigma m^{1/3})^{3/2}}{\Sigma m^{1/2}}$.
H_2	1·415	HCl	1·276	CO_2	1·712	NH_3	1·865
CO	1·414	Cl_2	1·416	N_2O	1·729	C_2H_4	2·301
NO	1·412	H_2O	1·601	SO_2	1·726	CH_3Cl	2·023
O_2	1·415	H_2S	1·522	CH_4	2·116	N_2	1·410
				C_2N_2	2·004	C_2H_5Cl	3·874

Methyl alcohol	CH_4O	2·282	Formic acid	CH_2O_2	2·116
Ethyl alcohol.........	C_2H_6O	2·802	Acetic acid	$C_2H_4O_2$	2·656
Propyl alcohol	C_3H_8O	3·240	Propionic acid......	$C_3H_6O_2$	3·109
Butyl alcohol	$C_4H_{10}O$	3·500	Butyric acid	$C_4H_8O_2$	3·505
Isobutyl alcohol ...	$C_5H_{12}O$	3·975	Iovalerianic acid ...	$C_5H_{10}O_2$	3·849
Amyl alcohol.........	$C_6H_{14}O$	4·294			
Methyl formate......	$C_2H_4O_2$	2·656	Iodo benzene	C_6H_5I	3·134
Methyl acetate	$C_3H_6O_2$	3·109	Bromo benzene ...	C_6H_5Br	3·230
Ethyl acetate.........	$C_4H_8O_2$	3·505	Chloro benzene ...	C_6H_5Cl	3·259
Ethyl propionate ...	$C_5H_{10}O_2$	3·862	Fluor benzene	C_6H_5Fl	3·289
Ethyl butyrate	$C_6H_{12}O_2$	4·189	Pentane	C_5H_{12}	3·875
Ethyl valerianate ...	$C_7H_{14}O_2$	4·494	Octane	C_8H_{18}	3·821
Isobutyl butyrate ...	$C_8H_{16}O_2$	4·778	Mercury	Hg	1·000
Isobutyl valerianate	$C_9H_{18}O_2$	5·046	Iodine	I_2	1·416

One point calls for remark at this place. The law of force surrounding a molecule is usually determined from the variations of the coefficient of viscosity or diffusion with temperature, on the assumption that the molecule behaves as a centre of force. But this assumption is objectionable since a molecule or an atom must possess an *actual* volume. The writer* has shown that if the atom is spherical in shape the cross-section is proportional to $m^{1/3}$, *i.e.*, if σ_1^2 represents the true cross-section of the molecule, $\frac{\sigma^2}{m^{1/3}}$ is constant. This is approximately realized. On the other hand the chemical attraction of one atom on another is considerable, and must influence the apparent radius σ_1 of a molecule. Thus the writer has shown that this attraction is

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* *Loc. cit.*

such that two atoms on collision may rotate round their centre of gravity with their previous velocity of translation, separated by a distance equal to their diameter. It appears, therefore, that the value of σ_1 is really a complex quantity, and its apparent variations cannot be ascribed to the molecule behaving simply as a centre of force. This method of determining the law of force surrounding a molecule is therefore scarcely admissible.

Some information whether the shape of a molecule changes with temperature can be obtained from the following considerations. The writer has shown from the phenomena of surface-tension that the attraction between two molecules in a liquid is given by the expression $\frac{1}{z^5}(\Sigma m^{1/2})\,.\mathrm{K}$, where K is a constant which has the same value for all liquids at corresponding states and z is the distance of separation of the molecules. Now since corresponding temperatures are not equal to one another, this suggests that the dependence of K on temperature is not direct but indirect; that is, it is not due to a decrease of the attractive power of each atom, but to a change in their configuration. A change in configuration produces a change in the law of force. If the energy of rotation of a molecule increases with the energy of translation, as is usually supposed, the molecule would contract with rise of temperature if there is equilibrium between the forces of attraction and the centrifugal forces. It seems probable that this is what happens.

Cambridge, May 16, 1910.

XLIV. *Note on the Finite Vibrations of a System about a Configuration of Equilibrium. By* Lord RAYLEIGH, *O.M., F.R.S.*[*]

THE theory of the infinitesimal free vibrations of a system, depending on any number of independent coordinates, about a position of stable equilibrium has long been familiar. In my book on the 'Theory of Sound' (2nd ed. vol. ii. p. 480) I have shown how to continue the approximation when the motion can no longer be regarded as extremely small, and the following conclusions were arrived at :—

(*a*) The solution obtained by this process is periodic, and the frequency is an even function of the amplitude (H_1) of the principal term ($\mathrm{H}_1 \cos nt$).

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[*] Communicated by the Author.

(*b*) The Fourier series expressive of each coordinate contains cosines only, without sines, of the multiples of nt. Thus the whole system comes to rest at the same moment of time, *e.g.* $t=0$, and then retraces its course.

(*c*) The coefficient of cos rnt in the series for any coordinate is of the rth order (at least) in the amplitude (H_1) of the principal term. For example, the series of the third approximation, in which higher powers of H_1 than H_1^3 are neglected, stop at cos $3nt$.

(*d*) There are as many types of solution as degrees of freedom; but, it need hardly be said, the various solutions are not superposable.

One important reservation (it was added) has yet to be made. It has been assumed that all the factors, such as $(c_2-4n^2a_2)$*, are finite, that is, that no coincidence occurs between an harmonic of the actual frequency and the natural frequency of some other mode of infinitesimal vibration. Otherwise, some of the coefficients, originally assumed to be subordinate, become infinite, and the approximation breaks down.

I have lately had occasion to consider more closely what happens in these exceptional cases; and I propose to take as an example a system with two degrees of freedom, so constituted that the frequencies of infinitesimal vibration are exactly as 2 : 1. In the absence of dissipative and of impressed forces, everything may be expressed by means of the functions T and V, representing the kinetic and potential energies. In the case of infinitely small motion in the neighbourhood of the configuration of equilibrium, T and V reduce themselves to quadratic functions of the velocities and displacements with constant coefficients, and by a suitable choice of coordinates the terms involving *products* of the several coordinates may be made to disappear. Even though we intend to include terms of higher order, we may still avail ourselves of this simplification, choosing as coordinates those which have the property of reducing the terms of the second order to sums of squares. We will further suppose that T is completely expressed as a sum of squares of the velocities with *constant* coefficients, a case which will include the vibrations of a particle moving in two dimensions about a place of equilibrium. We may then write

$$T=\tfrac{1}{2}a_1\dot{\phi}_1^2+\tfrac{1}{2}a_2\dot{\phi}_2^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$V=\tfrac{1}{2}c_1\phi_1^2+\tfrac{1}{2}c_2\phi_2^2+V_3+\ldots, \quad . \quad . \quad . \quad (2)$$

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* See below.

where

$$V_3=\gamma_1\phi_1^3+\gamma_2\phi_1^2\phi_2+\gamma_3\phi_1\phi_2^2+\gamma_4\phi_2^3, \quad . \quad . \quad (3)$$

giving as Lagrange's equations

$$a_1 d^2\phi_1/dt^2+c_1\phi_1+3\gamma_1\phi_1^2+2\gamma_2\phi_1\phi_2+\gamma_3\phi_2^2=0, \quad . \quad (4)$$

$$a_2 d^2\phi_2/dt^2+c_2\phi_2+3\gamma_4\phi_2^2+2\gamma_3\phi_1\phi_2+\gamma_2\phi_1^2=0. \quad . \quad (5)$$

To satisfy these equations we assume

$$\phi_1=H_0+H_1\cos nt+H_2\cos 2nt+H_3\cos 3nt+\ldots \quad . \quad (6)$$

$$\phi_2=K_0+K_1\cos nt+K_2\cos 2nt+K_3\cos 3nt+\ldots \quad . \quad (7)$$

In general we may take as one approximate solution

$$\phi_1=H_1\cos nt, \quad \phi_2=0 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

with

$$n^2=c_1/a_1 ; \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and in proceeding to a second approximation we may regard all the other coefficients as small relatively to H_1. On this supposition the 4th and 5th terms in (4) may be omitted, so that ϕ_1 is separated from ϕ_2. Substituting from (6) and equating the terms containing the various multiples of nt, we get

$$c_1 H_0+\tfrac{3}{2}\gamma_1 H_1^2=0,$$

$$(c_1-n^2a_1)H_1=0,$$

$$(c_1-4n^2a_1)H_2+\tfrac{3}{2}\gamma_1 H_1^2=0 ;$$

so that

$$\phi_1=-\frac{3\gamma_1 H_1^2}{2c_1}+H_1\cos nt-\frac{3\gamma_1 H_1^2}{c_1-4n^2a_1}\cos 2nt, \quad . \quad (10)$$

with

$$c_1=n^2a_1,$$

as in the first approximation. In like manner

$$c_2 K_0+\tfrac{1}{2}\gamma_2 H_1^2=0,$$

$$(c_2-n^2a_2)K_1=0,$$

$$(c_2-4n^2a_2)K_2+\tfrac{1}{2}\gamma_2 H_1^2=0.$$

Thus, if c_2 differs both from n^2a_2 and from $4n^2a_2$, we have

$$\phi_2=-\frac{\gamma_2 H_1^2}{2c_2}-\frac{\gamma_2 H_1^2}{2(c_2-4n^2a_2)}\cos 2nt. \quad . \quad . \quad (11)$$

But if

$$c_2 - n^2 a_2 = 0,$$

the inference that $K_1 = 0$ does not follow ; and if

$$c_2 - 4n^2 a_2 = 0,$$

the terms in $\cos 2nt$ in (10), (11) assume infinite values. Accordingly these two cases demand further consideration. We will commence with that where

$$c_2 - n^2 a_2 = 0,$$

that is, where both modes of infinitesimal vibration have the same frequency.

We must now discard the supposition that $\phi_2 = 0$ approximately and be prepared to allow K_1, as well as H_1, to be quantities of the first order of smallness. The other coefficients in (6), (7) are still of the second order at least. Substituting in (4), (5) and retaining only terms not above the second order, we get

$$\begin{aligned} &c_1 H_0 + (c_1 - n^2 a_1) H_1 \cos nt + (c_1 - 4n^2 a_1) H_2 \cos 2nt + \ldots \\ &\qquad + 3\gamma_1 H_1^2 \cos^2 nt + 2\gamma_2 H_1 K_1 \cos^2 nt + \gamma_3 K_1^2 \cos^2 nt = 0, \\ &c_2 K_0 + (c_2 - n^2 a_2) K_1 \cos nt + (c_2 - 4n^2 a_2) K_2 \cos 2nt + \ldots \\ &\qquad + 3\gamma_4 K_1^2 \cos^2 nt + 2\gamma_3 H_1 K_1 \cos^2 nt + \gamma_2 H_1^2 \cos^2 nt = 0; \end{aligned}$$

whence

$$c_1 H_0 + \tfrac{1}{2}(3\gamma_1 H_1^2 + 2\gamma_2 H_1 K_1 + \gamma_3 K_1^2) = 0, \quad . \quad (12)$$

$$c_2 K_0 + \tfrac{1}{2}(3\gamma_4 K_1^2 + 2\gamma_3 H_1 K_1 + \gamma_2 H_1^2) = 0, \quad . \quad (13)$$

$$(c_1 - 4n^2 a_1) H_2 + \tfrac{1}{2}(3\gamma_1 H_1^2 + 2\gamma_2 H_1 K_1 + \gamma_3 K_1^2) = 0, \quad . \quad (14)$$

$$(c_2 - 4n^2 a_2) K_2 + \tfrac{1}{2}(3\gamma_4 K_1^2 + 2\gamma_3 H_1 K_1 + \gamma_2 H_1^2) = 0. \quad . \quad (15)$$

Also

$$H_3, \text{\&c.}, K_3, \text{\&c.} = 0.$$

These equations, arising from the terms independent of t and proportional to $\cos 2nt$, $\cos 3nt$, &c., determine H_0, K_0, H_2, K_2, &c. when H_1, K_1, and n are known. The term in $\cos nt$ gives further

$$H_1(c_1 - n^2 a_1) = 0, \quad K_1(c_2 - n^2 a_2) = 0.$$

Thus when

$$n^2 = c_1/a_1 = c_2/a_2, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

K_1 as well as H_1 is an arbitrary quantity of the first order. And this completes the solution to the second approximation.

When the process is pursued to the next stage, the ratio H_1/K_1 may become determinate. In illustration of this let us suppose that V is an even function of both ϕ_1 and ϕ_2. Thus $V_3=0$, and

$$V_4=\delta_1\phi_1^4+\delta_3\phi_1^2\phi_2^2+\delta_5\phi_2^4. \quad . \quad . \quad . \quad (17)$$

Using this as before, we obtain

$$H_0=0,\quad K_0=0,\quad H_2=0,\quad K_2=0,\quad H_4\,\&c.=0,\quad K_4\,\&c.=0.$$

To determine H_3, K_3 we have

$$(c_1-9n^2a_1)H_3+\delta_1 H_1^3+\tfrac{1}{2}\delta_3 H_1 K_1^2=0, \quad . \quad . \quad (18)$$

$$(c_2-9n^2a_2)K_3+\delta_5 K_1^3+\tfrac{1}{2}\delta_3 K_1 H_1^2=0. \quad . \quad . \quad (19)$$

Also from the terms in cos *nt*

$$H_1[c_1-n^2a_1+3\delta_1 H_1^2+\tfrac{3}{2}\delta_3 K_1^2]=0, \quad . \quad . \quad (20)$$

$$K_1[c_2-n^2a_2+3\delta_5 K_1^2+\tfrac{3}{2}\delta_3 H_1^2]=0. \quad . \quad . \quad (21)$$

Equations (20), (21) can be satisfied by supposing either H_1 or K_1 to vanish while the other remains finite. Thus if $H_1=0$, (20) is satisfied and (21) gives

$$c_2-n^2a_2+\tfrac{3}{2}\delta_3 H_1^2=0, \quad . \quad . \quad . \quad . \quad (22)$$

determining n. From (19) we see that in this case $K_3=0$, while H_3 is given by (18) with $K_1=0$.

There is also another solution in which both H_1 and K_1 are finite. Since by supposition

$$c_2/a_2 = c_1/a_1,$$

$$\frac{2\delta_1 H_1^2+\delta_3 K_1^2}{\delta_3 H_1^2+2\delta_5 K_1^2}=\frac{c_1-n^2a_1}{c_1-n^2a_2}=\frac{c_1}{c_2}, \quad . \quad . \quad . \quad (23)$$

which determines K_1^2/H_1^2, and then either (20) or (21) gives n^2. Equations (18), (19) determine H_3, K_3 with two alternatives according to the sign of K_1/H_1.

In certain cases the ratio K_1/H_1 may remain arbitrary; for example, if

$$c_2 = c_1 \quad\text{and}\quad 2\delta_1 = 2\delta_5 = \delta_3,$$

making V_4 a complete square.

The other class of cases demanding further examination arises when

$$c_2/a_2 = 4c_1/a_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

and it requires that K_2 should be treated as a quantity of the first order as well as H_1, the remaining coefficients being still of the second order. The substitution of (6), (7) in (4), (5) then gives

$$\begin{aligned} c_1 H_0 + (c_1 - n^2 a_1) H_1 \cos nt + (c_1 - 4n^2 a_1) H_2 \cos 2nt + \ldots \\ + 3\gamma_1 H_1^2 \cos^2 nt + 2\gamma_2 H_1 K_2 \cos nt \cos 2nt \\ + \gamma_3 K_2^2 \cos^2 2nt = 0, \quad . \quad . \quad . \quad (25) \end{aligned}$$

$$\begin{aligned} c_2 K_0 + (c_2 - n^2 a_2) K_1 \cos nt + (c_2 - 4n^2 a_2) K_2 \cos 2nt + \ldots \\ + 3\gamma_4 K_2^2 \cos^2 2nt + 2\gamma_3 H_1 K_2 \cos nt \cos 2nt \\ + \gamma_2 H_1^2 \cos^2 nt = 0. \quad . \quad . \quad . \quad . \quad (26) \end{aligned}$$

From the terms independent of t we get

$$2c_1 H_0 + 3\gamma_1 H_1^2 + \gamma_3 K_2^2 = 0, \quad 2c_2 K_0 + \gamma_2 H_1^2 + 3\gamma_4 K_2^2 = 0; \quad . \quad (27)$$

from the terms in $3nt$

$$(c_1 - 9n^2 a_1) H_3 + \gamma_2 H_1 K_2 = 0, \quad (c_2 - 9n^2 a_2) K_3 + \gamma_3 H_1 K_2 = 0; \quad . \quad (28)$$

from the terms in $4nt$

$$(c_1 - 16n^2 a_1) H_4 + \tfrac{1}{2}\gamma_3 K_2^2 = 0, \quad (c_2 - 16n^2 a_2) K_4 = \tfrac{3}{2}\gamma_4 K_2^2;. \quad . \quad (29)$$

while coefficients with higher suffixes than 4 vanish. Further, from the terms in nt, $2nt$

$$(c_1 - n^2 a_1) H_1 + \gamma_2 H_1 K_2 = 0, \quad (c_2 - n^2 a_2) K_1 + \gamma_3 H_1 K_2 = 0, \quad . \quad (30)$$

$$(c_1 - 4n^2 a_1) H_2 + \tfrac{3}{2}\gamma_1 H_1^2 = 0, \quad (c_2 - 4n^2 a_2) K_2 + \tfrac{1}{2}\gamma_2 H_1^2 = 0. \quad . \quad (31)$$

These equations determine H_0, K_0, K_1, H_2, H_3, K_3, H_4, K_4 as functions of H_1 and K_2 of the second order, when n is known. To find n and the ratio K_2/H_1 we have the first equation of (30) and the second of (31). With regard to (24) these may be written

$$c_1 - n^2 a_1 + \gamma_2 K_2 = 0, \quad . \quad . \quad . \quad (33)$$

$$\frac{c_2}{c_1}(c_1 - n^2 a_1) K_2 + \tfrac{1}{2}\gamma_2 H_1^2 = 0; \quad . \quad . \quad . \quad (34)$$

of which the first may be considered to determine n. Eliminating $(c_1 - n^2 a_1)$, we get

$$K_2/H_1 = \pm\sqrt{(c_1/2c_2)}. \quad . \quad . \quad . \quad . \quad (35)$$

This completes the solution to the second order of small quantities.

If $V_3 = 0$, the above solution reduces itself to that of the first approximation. In this case, especially if V is an even function of ϕ_1 and ϕ_2, see (17), a solution, correct to the third order of small quantities, is readily developed; it is hardly necessary to give the details.

In 'Theory of Sound' (*loc. cit.*) I remarked upon the failure of the simple theory to deal with the apparently simple problem of the vibrations in one dimension of a column of gas, obeying Boyle's law, and contained in a cylindrical tube with stopped ends. So far as I am able to see, the present extension does not help the matter. In this case there are an infinite number of coincidences between natural frequencies of infinitesimal vibration and harmonics of the fundamental vibration. From what we know of the behaviour of *progressive* waves of finite amplitude, it is perhaps not surprising if no solutions exist of the character contemplated. Probably after the lapse of a finite time discontinuity will ensue.

Terling Place, Witham, Aug. 8.

XLV. *Vibration Curves of Violin Bridge and Strings.* *By* EDWIN H. BARTON, *D.Sc., F.R.S.E., Professor of Experimental Physics, and* THOS. F. EBBLEWHITE, *B.Sc., Heymann Exhibitioner, University College, Nottingham* [*].

[Plates VII.–IX.]

FOLLOWING the work of one of us and others [†], the present paper deals with the simultaneous motions of a violin bridge and the strings. The violin being mounted horizontally in the usual position of playing, the vertical motions of each upper corner of the bridge are recorded, also the motions of the same corners lengthwise of the strings. Each string is dealt with separately and its vibration simultaneously with that of the bridge recorded photographically. Further, the strings were excited at various places by bowing, plucking, striking, &c., seventy-two photographic records being now presented.

Comparing this work with that on the violin belly (August 1909), the following points may be noted here:—

1. The vibrations of the bridge show more variety of form than those of the belly.

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[*] Communicated by the Authors.

[†] Phil. Mag. July 1905, pp. 149–157; Dec. 1906, pp. 576–578; April 1907, pp. 446–452; Aug. 1909, pp. 233–240.

2. Each of the strings gives considerable motion to the bridge in spite of the presence of the other three strings which are not sounding, whereas previously only the G-string gave appreciable motion to the part of the belly under examination.

3. The distribution of the bridge's motion seems to be somewhat intricate. Thus a certain corner of the bridge would scarcely stir in one direction under the influence of a given string excited in a certain manner, but went extremely well under the influence of another string or the same string excited differently. These circumstances may be due to the asymmetry of the stresses and structure of the violin.

4. In some cases the motion of the bridge lengthwise of the string shows a frequency double that of the string, although such a phenomenon had not been detected by the previous work on the belly.

This point has some interest in connexion with the work of Mr. J. W. Giltay and Prof. M. de Haas [*] of Delft.

EXPERIMENTAL ARRANGEMENTS.

The mounting of the violin was all through as in fig. 2 of Plate iv., Phil. Mag. Aug. 1909. The optical arrangements were also on the same general lines as before, so that the string's motion is recorded in the positive print by a dark line on a light ground, the motion of the bridge being recorded below it by a white line on the dark ground. It should be noted here also that great steadiness of the arc light was obtained by the use of a Leitz Lilliput arc lamp in which the positive carbon is horizontal. The plates used throughout were the Barnet Orthochromatic, Fast, Backed, and were developed by the Barnet formula.

Vertical Motions of the Bridge.—For the vertical motions of the E-string corner of the bridge the arrangements were almost precisely those shown in figs. 1–5, Plate iv. of the last paper (Phil. Mag. Aug. 1909), the only essential modification being that the leg of the optical lever *m* rested on the bridge instead of on the belly.

For the vertical motions of the G-string corner the arrangements were of the same nature, but the other side of the violin was turned towards the lamp and plate.

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[*] "On the Motion of the Bridge of the Violin," *Konink. Akad. v. Wetenschappen, Amsterdam,* Proc. xii. pp. 513–524, Jan. 26, 1910. Also Science Abstracts, No. 404, Mar. 1910.

The respective magnifications in the two cases were as follows :—

Part of Bridge under Examination.	Actual Magnifications on quarter-plate negative.		Ratio of Magnifications on any print.
	String's Motion.	Bridge's Motion.	
E-string Corner	2·2	598·3	271
G-string Corner	2·1	603	287

Longitudinal Motion of Bridge.—For the motions of the E-string corner of the bridge lengthwise of the strings, the arrangements adopted are shown diagrammatically in fig. 1 (Pl. VII.) and in perspective from a photograph in fig. 2 (Pl. VII.).

Referring to fig. 1, the arc lamp and condenser are indicated by A L, and C, from which part of the beam passes direct to H, a screen pierced by a small hole. The light from H reaches a concave mirror *m* on the optical lever, and is thence converged to the point R on the sensitive plate PP, which is shot along the rails INA in the dark room. This gives on the lower part of the plate a record of the bridge's motion, which in the positive prints appears as a white line on a dark ground.

Let us now follow the other part of the beam from the arc lamp. This is reflected by the pair of plane mirrors M_1 M_2 to the vertical slit S, from which the light falls upon the lens L_1, which focusses a real image of the slit on the string in use at 12 or 13 cm. from the nut, 32 cm. being the length of the vibrating portion of the strings from nut to bridge. The light is then reflected by the plane mirror M to the lens L_2, which gives on the plate at R a real image of the slit crossed by the shadow of the string; it accordingly leaves a record of the string's motion, which in the positive prints is a dark line on a light ground. This image is on the upper part of the plate, precisely over that from the optical lever *m*. Thus a comparison of the two records gives information as to the relative phases of the vibrations of string and bridge.

Let us now examine more closely how the bridge's motion is recorded. Fig. 3 (Pl. VII.) shows on a larger scale the bridge of the violin with the optical lever somewhat out of place, for clearness sake. The clamp CC is fixed at a corner of the violin which is specially free from vibrations, and carries the adjustable bracket BBBBB, at the end of which is the table T. This table has the hole H and the slot S for carrying the two upper conical feet of the optical lever, thus forming its horizontal axis. The lower foot F of the lever, when held in position by an elastic band, presses on the plane P of the bridge, P being a piece of microscope-cover glass fastened on with shellac.

Magnification of Bridge's Longitudinal Motion.—As the optical lever is now used in an oblique position, the magnification requires special examination. Referring again to fig. 1, we see that as the bridge moves lengthwise of the string the lever is made to rotate about the axis mA through a small angle $d\phi$ say. Thus the normal mN to the mirror changes to the position mN' where N′ is above N and not shown in the diagram. But since the incident beam IHm is at rest when N rises to N′, the reflected image R will rise to R′ say where IN′R′ is a straight line. Now it was previously shown (Phil. Mag. April 1907, p. 448) that

$$\frac{RR'/AR}{NN'/AN}=\frac{2\tan\alpha}{\tan\alpha-\tan\theta}, \quad \ldots\ldots \quad (1)$$

where α is the angle AmN and θ is the angle NmR.

But the angle

$$NN'/AN = d\phi = \frac{h}{l}, \quad \ldots\ldots \quad (2)$$

where h is the displacement of the foot F of the optical lever and l is its distance from a line through the two upper feet which fit in the hole and slot and so form its axis.

For the case shown where the E-string corner of the bridge is under test, the dimensions were as follows :—

$$AR = 14 \text{ cms.}, \quad \alpha = 16^\circ\, 3', \quad \theta = 12^\circ\, 33', \quad l = 0{\cdot}68 \text{ cm.}$$

Thus the linear magnification, on the negative, of the bridge's motion is given by

$$\frac{RR'}{h}=\frac{AR}{l}\cdot\frac{2\tan\alpha}{\tan\alpha-\tan\theta}=\frac{14}{0{\cdot}68}\times 8{\cdot}846 = 182{\cdot}1.$$

For the same arrangement the string's motion was magnified 2·1 times. Hence the relative magnification which is the same in any reproduction is 86·7.

For the G-string corner of the bridge, all the arrangements were similar but reversed laterally and a new optical lever used. The dimensions and magnifications were then as follows :—

$$\mathrm{AR} = 13 \text{ cms.}, \quad \alpha = 11^\circ\ 27', \quad \theta = 7^\circ\ 5', \quad l = 0{\cdot}68 \text{ cm.};$$

$$\frac{\mathrm{RR}'}{h} = \frac{\mathrm{AR}}{l} \cdot \frac{2\tan\alpha}{\tan\alpha - \tan\theta} = \frac{13}{0{\cdot}68} \times 5{\cdot}29 = 101{\cdot}1.$$

The string's motion was magnified *twice* ; hence the ratio of the two or the relative magnification, which is undisturbed by reproduction, is 50·5.

The value 101·1 of the magnification of the bridge's motion was substantially confirmed by introduction of a fragment of blown glass under the foot of the optical lever, the consequent displacement of the spot being measured and the thickness of the glass determined by a spherometer.

The foot of the optical lever which touched the plane on the bridge was made hemispherical on an oilstone, the work being tested by a microscope. In like manner the other two feet, which rested in the hole and slot, were made truly conical.

As to the interpretation of the abscissæ and ordinates of the curves on the prints,

(1) the beginning of the time is in all cases at the left side ;

(2) the ordinates for the string's motion are always inverted, *i. e.* an upward motion of the shadow of the string means a motion of the string towards the belly of the violin ;

(3) the ordinates for the vertical motion of the bridge are also inverted ; and

(4) for the longitudinal motions of the bridge an upward ordinate denotes a displacement of the bridge towards the "nut," *i. e.* towards the peg-box of the violin.

Asymmetry of the Violin.—The necessity for dealing with both the upper corners of the violin bridge suggested itself to us on account of the well-known asymmetry of such instruments ; for the strings are lower in pitch, and therefore slacker, on one side and tighter on the other, the pitches being respectively g, d', a', e'' on Helmholtz's notation. Thus the G-string side of the bridge has less pressure from the string on its upper edge and less where its foot touches the belly than is the case for the E-string side. Further, because of this asymmetry of the tensions and pressures of the strings, the body of the violin is asymmetrical also.

Fig. 4, reproduced from a photograph of the Old English violin in use, shows by chalk-marks on the belly the positions of (1) the bass bar and (2) the sound-post. The former is a little bar of wood glued inside the belly and lying under the space between the G and D strings and extending almost the whole length of the belly. The position of the sound-post is shown by the circle under the E string and just below the corresponding foot of the bridge. The sound-post is a little straight piece of wood extending from the belly to the back of the violin, and held in place simply by the pressure and consequent friction. In this view the optical lever is again shown slightly displaced and tied to the strings, the adjustable bracket being still in position.

Results.

The results obtained are exhibited in Pls. VIII. & IX. by the 72 photographs, which naturally fall into four groups or series according to the motion of the bridge concerned and the corner of it under examination. The violin was the one used in the former paper, and the strings were in this work used "open" and always at concert pitch. The circumstances under which each photographic record was obtained are briefly indicated at the margin against each print. The place of excitation of the string is indicated by the fraction of its length from the bridge at which it was bowed, plucked, or struck. "Plucked" indicates plucked with the finger-tip ; "struck" indicates the use of a pencil with several thicknesses of washleather, to form a soft pad ; the plectrum referred to as sometimes used in plucking was simply a pencil-point. The "wooden hammer" referred to is simply the pencil without the pad. The strings not in use were still in position and at concert pitch. They were in their equilibrium position if behind that in use, but if in front they were tied down to the neck as though being stopped by the fingers as in playing. We may now note various special points in connexion with some of the individual prints.

Vertical Motion of E-string corner of Bridge. (Upper part of Pl. VIII.)—Figs. 1 and 2 show the G-string's motion to be of small vertical amplitude but with Fourier's series to infinity, the bridge's motion being of very large amplitude and of quite different character. The two show by their general similarity the satisfactory working of the experimental arrangements, which remarks apply likewise to the next three figures (3–5) ; here, however, the curves for the string are rounded, as the forcing of the bow is absent.

Figs. 6 and 7, on the other hand, where the harsher treatment is used, show a marked difference in behaviour of both string and bridge. It is noticeable that figs. 1–11 all deal with the motions of a corner of the bridge due to the strings most remote from it. The other strings when bowed or plucked scarcely move this corner vertically, but did so to a slight extent if struck. These results are given in figs. 12–14.

Vertical Motion of G-string corner of Bridge. (Lower part of Pl. VIII.)—Figs. 15–17, for the G-string bowed, by their close similarity, give another proof of the satisfactory working of the apparatus. The string has again only a moderate vertical amplitude and shows the two-step zigzag, while the bridge's motion is large and of striking character. Figs. 18–23, in which the G-string is struck or plucked, again show the rounded curves instead of the sharp peaks always present when the string is well bowed.

With this corner of the bridge it was again found that no considerable vertical motion could be produced by any but the G-string, the E string giving nothing appreciable. The D and A strings were also ineffective when plucked. Figs. 24–26 give the best results obtained for the D-string, and figs. 27 and 28 for the A-string which was only effective when bowed.

Longitudinal Motion of E-string corner of Bridge. (Upper part of Pl. IX.)—Figs. 29 and 30 are not, like most of the others, true displacement-time curves, because we here failed to secure a simple vertical motion of the spot of light on the plate. Hence the abscissæ which should denote time simply are here complicated by the horizontal component of the spot's motion. In other words, the axes are now oblique instead of, as usual, rectangular. Figs. 32 and 33, showing the effects of bowing the A-string, are closely analogous to figs. 27 and 28 produced by the same excitation. Fig. 37, in which the A-string is plucked, shows a striking vibrational curve much slower than that of the string and apparently due to some vibration of the instrument as a whole. This is interesting in the light of a similar phenomenon noticed recently by Mr. G. H. Berry in work on the sound-board of the pianoforte (Phil. Mag. April 1910). Other examples of this slow vibration in the present work occur in figs. 31, 50, 60, 66, and 71.

Figs. 38 and 39, in which the D-string was bowed, show a moderate motion of the bridge though the string is scarcely moving vertically. It may, however, have had a fair horizontal motion, which is of course unrecorded by the photograph ; indeed it is obviously difficult to produce by bowing much vertical motion of the middle strings (D and A). The motions of the bridge in these prints are seen to be highly complicated ; the traces are, however, true displacement-time curves.

Figs. 40 and 42 show similar complicated motions of the D-string when plucked at a seventh ; figs. 41 and 43 also forming a second but different pair for plucking at one-fourth. It may be noted that the D is the thickest of the four strings.

In figs. 44 and 45 we have the G-string bowed, and so obtain again the characteristic two-step zigzag. The bridge's motions are here represented by traces which, though so strange, are true displacement-time curves and show a resemblance to the other bowed sets of this series, figs. 29 and 30, 32 and 33, 38 and 39.

The remaining figures of this series deal with the G-string plucked or struck. Of these, fig. 47 shows the bridge's motion to have the pitch of the string with very little appearance of the presence of the octave. In figs 46 and 50 the octave is quite distinct in the bridge's motion ; while in figs. 48 and 49 the octave is paramount, the fundamental not being evident at all. In this last respect these two are unique among all the prints hitherto obtained. An approach to this state of things is however seen in various other cases, as, for example, in figs. 44 and 45.

Longitudinal Motion of G-string corner of Bridge. (Lower part of Pl. IX.)—Figs. 51 and 52, for the G-string bowed, do not give pure displacement-time curves for the bridge's motion, as here again we did not succeed in securing a purely vertical motion of the spot of light on the plate. Figs. 53–57 deal with the G-string struck or plucked, and call for no special remark.

Figs. 58 and 59, for the D-string bowed, are again affected by an oblique motion of the spot of light on the plate. The next figure, showing a superposed slow motion, has already been referred to. Fig. 62 shows, by accident, the very beginnings of the vibrations of the D-string plucked and the consequent motion of the bridge. The plate was unintentionally shot rather too soon ; hence the greater part of it shows only the string and bridge at rest in the displaced or drawn-aside positions due to plucking, the initial motions of each on letting go being also seen at the right margin of the print.

In figs. 64 and 65 the curves for the bridge's motion are again complicated by a slight sideways motion of the spot of light on the plate. Figs. 66–68 show the very small longitudinal motions of the bridge obtainable by striking or plucking the A-string. Fig. 69, with a smaller motion of the string excited by the plectrum, gives a larger motion of the bridge. The last three figures (70–72) show the only appreciable motions obtainable for this corner of the bridge by exciting the E-string. Fig. 72 is very remarkable in that the string's motion, though entirely vertical, leaves so small a record, and yet the longitudinal motion of the other corner of the bridge is quite considerable.

Univ. Coll., Nottingham,
June 29th, 1910.

XLVI. *The Ionization produced by the Splashing of Mercury.* *By* J. J. Lonsdale, *M.Sc.* (*Dunelm*), *B.Sc.* (*Lond.*).[*]

PREVIOUS work on the ionization produced by splashing, or by bubbling gas through liquids has usually been carried out with liquids having considerable vapour pressure [†]. The results show that the ions produced generally move with a very small velocity, varying from a few mms. to ·001 mm. per second under a potential gradient of one volt per cm. The question is whether these small velocities are due to the condensation of the vapours on the ions, or whether, as Bloch [‡] suggests, the ions are of a kind altogether distinct from the usual Röntgen ray ions. With a view to gaining evidence on this point, I have investigated the ionization produced by splashing mercury, as there will be little condensation in this case. As the mechanism of the production of ions by the splashing process is not clear, various other points have received attention.

The apparatus used is shown in fig. 1. The splash-chamber consisted of a wrought-iron cross-piece fitted with nipples, allowing the splash-plate or the upper iron tube to be readily removed. Mercury fell from the iron funnel A on to the plate B, and the ions so produced were pulled by an air current along two brass tubes, insulated from each other and carrying two insulated electrodes, C and D, placed axially in the tube. C and D could be connected when desired to a Dolezalek electrometer. The connexions were, of course, suitably screened by earthed conductors. With ebonite insulation certain irregularities were shown when the direction of the electric field was reversed in the space

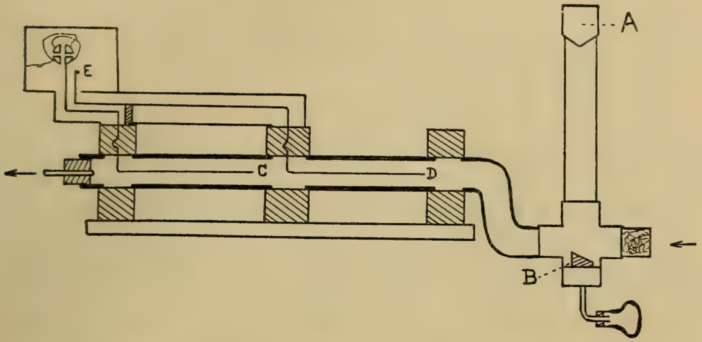
[*] Communicated by Dr. R. S. Willows.

[†] Kähler, *Ann. der Physik,* 1903, p. 1119. Aselmann, *Ann. der Physik,* 1906, p. 960.

[‡] Bloch, *Compte Rendus,* cxlv. p. 54.

surrounding C and D; paraffin, which largely reduced these irregularities, was therefore used. The brass tubes were connected to the insulated pole of a battery, the other pole of which was earthed, and the ions were driven over to C or D, originally earthed and connected to the electrometer.

Fig. 1.



As a preliminary investigation, it was deemed advisable to test if the ionization of the air was the same if the mercury struck the drop-plate in an electrified condition or not. If the dropper and the splash-plate are both earthed the mercury might be electrified in its passage through the air and so reach the plate in a charged condition. To test this, the dropper was placed above a long narrow cylinder provided with a hole just large enough for the stream to go through without splashing. The cylinder and leads were screened by an earthed outer cylinder. If any charge is given to the mercury on passing through the air, it will be carried in to the cylinder, the equal and opposite charge remaining in the air above. The ionized air-charge and the charge on the plate will be of equal amounts and opposite in sign, so that any current given to the electrometer will be due to air friction. Various heights were tried but no definite evidence of electrification was found.

Next the dropper was insulated on a block of wax, the splash-plate was earthed, and the currents were examined on the second electrode of the final apparatus. The current was taken when the dropper was earthed. Then the dropper and the mercury were charged to voltages varying from −390 to +390. Both positive and negative currents were examined, but no definite variations were found in the ionization currents. Thus in the after-work no variation of the ionization current could be attributed to the electrification of the mercury.

To ensure that no variation in the ionization was due to the variations in the state of the mercury, different samples were tried and the currents taken. If the mercury were purified by bubbling air through for a considerable time before using, the results showed no variation.

The effect of changing the surface on which the mercury splashed was also investigated. Previous investigators have stated that the material of the plate has no effect, at least if the plate is wetted by the liquid. The electrometer having a sensitiveness of about 800 mm. scale-divisions for a volt, the mercury splashing on iron gave a current of 120 mm. in 20 seconds due to positive ions. If the splash-plate were re-cleaned and polished the variation was very slight. The negative ionization was very much less. A voltage of about 200 volts was put on the second electrode in both cases. A platinum splash-plate gave under similar conditions a positive current of about 30 mm. in 20 seconds. The negative current was scarcely measurable. When mercury was dropped on mercury the positive current was very small, often nothing; the negative current was larger. Glass was tried as presenting points of interest. Very variable currents were observed, as might have been expected, owing to the field produced near the source by the electrification of the glass. If the glass plate was used once and then heated to discharge it, the results were in moderate agreement and gave a positive current of about 14 mm. in 20 seconds.

With the apparatus used it has been shown that the mobility of the ions is given by *

$$u=\rho\frac{(b^2-a^2)}{2Vt}\log_e\frac{b}{a},$$

where b is the radius of the outer tube;

a is the radius of the inner electrode ;

V is the voltage on the outer tube;

t the time taken by the blast to pass along the length of the electrode ;

ρ the ratio of the saturation currents on the second electrode, (1) when field V is on D ; (2) when there is no potential difference between D and the tube.

A first examination of the positive ions showed that the current gradually rose as the voltage increased and then remained constant between voltages of 85 and 150 volts.

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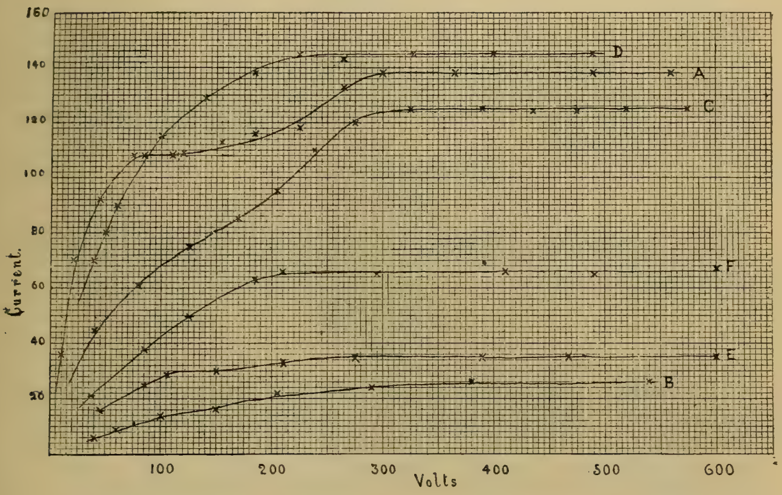
* J. J. Thomson, 'Conduction of Electricity through Gases,' p. 59.

Taking 85 volts as saturation voltage this gives with this apparatus a mobility for the slowest ions of ·013 cm. per volt-cm. for the positive ion.

A similar examination of the negative ionization gave the saturation voltage of the negative as about 300 volts, corresponding to a mobility of ·004 cm. per volt-cm. The fact of the negative ion having the least mobility appeared so remarkable that the positive current was again examined to see if it had really been saturated. 200 volts were placed on the first electrode and 200 on the second. A considerable current was found on the second electrode. The curve giving the relation between the current and the voltage was therefore investigated over larger ranges of voltages and had the appearance shown in fig. 2, curve A. A distinct flat part exists between voltages of about 100 to 150 volts and a further flat part from 300 volts onward. The upper part of the curve may be due to ions of small mobility or it may be due to neutral doublets, similar to those observed by Thomson in canal rays, which break up under the action of a field or from other causes. If ions of small mobility were present we should expect the curve to rise gradually, never showing a flat part until all the ions are removed, and, as is seen, this is not the form the curve takes. It cannot be due to the formation of ions by collision as generally understood, as this would require a field of 30,000 volts per cm.; the field

Fig. 2.



near the centre at the electrode was never greater than 3500 volts per cm.

The curve giving the relation between the current on the central electrode and the voltage on the outer tube when ions of varying mobilities are present :—

The velocities of the ions under a gradient of a volt-cm. are respectively	u_1, u_2, u_3, . .
The number of ions per c.c. of each kind .	n_1, n_2, n_3, . .
Saturation voltage of each ion (ascending order)	V_1, V_2, V_3, . .
The time for the air to pass the electrode .	t secs.
The measure of the blast	B c.c. per. sec.

Let r be the greatest distance from which an ion can be driven into the electrode by a voltage V, then

$$r^2-a^2=\frac{2Vtu}{\log_e\frac{b}{a}}.$$

Then in one second the ions will be driven into the electrode from the volume

$$\frac{B(r^2-a^2)}{(b^2-a^2)}.$$

If e is the charge on an ion, then the current due to a particular ion is

$$\frac{en(r^2-a^2)B}{(b^2-a^2)}.$$

The whole current due to any voltage V, when that voltage is less than V_1 the saturation voltage of the fastest ion, is

$$\frac{eB}{(b^2-a^2)}\{(r^2-a^2)n_1+(r^2-a^2)n_2+(r^2-a^2)n_3+\ldots\ldots\},$$

$$\frac{eB2t}{(b^2-a^2)\log_e\frac{b}{a}}(Vu_1n_1+Vu_2n_2+Vu_2n_3+\ldots\ldots),$$

or
$$C=k(Vu_1n_1+Vu_2n_2+Vu_3n_3+\ldots\ldots),$$

where k is constant, and as u and n are also constants this part of the curve is a straight line through the origin. If the voltage lies between V_1 and V_2 then the current

$$=k(V_1u_1n_1+Vu_2n_2+Vu_3n_3+\ldots\ldots).$$

This part of the curve is also a straight line. When a voltage above V_n is reached the current will be given by

$$k(V_1u_1n_1+V_2u_2n_2+V_3u_3n_3+\ldots\ldots),$$

where the forms Vun are constant. This will be a straight line parallel to the axis of x. Thus the curve should gradually rise, never showing a flat part until all the ions are removed. The curve evidently has not this form in curve A in fig. 2.

Further, if a voltage above 300 volts is put on the first electrode, then there should be no current on the second, since beyond this voltage the curve is flat. Thus a voltage of 342 volts should drive all the ions on to the first electrode, but in most cases observed (the exceptions are given later), a current was found on the second of such a size that if it had been due to free ions it should have shown on the saturation curve. The numbers below show this: they refer to different sets of observations with different electrometer sensibilities, different heights of fall, &c., but the bracketed pairs were taken under the same conditions except that the field was reversed.

V_1 the voltage on the first electrode;
V_2 the voltage on the second electrode;
c the current observed on the second electrode when the given voltage V was on the first;
C the current observed on the second electrode when the first was earthed.

V_1.	V_2.	c.	C.
598	598	9	277
−598	−598		−25
598	598	8	54
−598	−598	8	−18
600	600	7, 8, 7	43
−600	−600	8, 8	Small
544	544	5, 5	20
−544	−544	6, 4	0

The last result is remarkable. A capacity had been placed in parallel with the electrometer, and thus the saturation current for the positive ionization was only 20 mm. divisions in 20 seconds. The current due to the negative ionization when the first electrode was earthed could not be observed, yet when the field was put on the first electrode a current of 5 divisions was found. This appears to show that the field produces the ions from the doublets, if such are present. The initial leak of the electrometer could not be observed: it was certainly less than 1 mm. in 20 seconds. Examining these results, if we presume that they are due to slow ions, then from the dimensions of the apparatus the mobilities of both the positive and negative ions must be less than ·0018 cm. per volt-cm. It is worthy of note that no matter how largely the total current C may differ in a given pair of observations for the positive and negative ions, c is practically the same for either sign. This is what we should expect if the current is due to the breaking up of doublets.

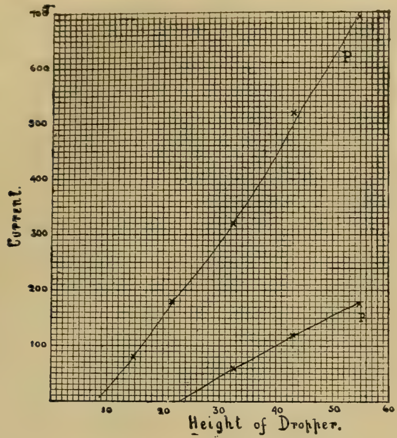
The saturation curve with negative ions is shown on fig. 2, curve B. No departure from the usual form of saturation curve was found with these ions, but the smallness of the current may account for this. The second flat part does not always appear even with positive ions. Whenever this is missing, then all the ions can be taken out on the first electrode by a voltage of about 100 volts.

The ionization currents vary with the height of the drop, the other conditions remaining the same. The investigation was made in the following way:—A definite height of drop being taken, the current for positive and negative ions was observed on the second electrode with the first earthed. Then a voltage of 114 volts was placed on the first electrode. As this voltage is on the flat part of the curve first occurring, the faster positives will be driven on to the first electrode. If the highest voltage is then placed on the second electrode, the ions giving rise to the upper part of the curve will be driven on to the electrode. The results averaged and reduced to a sensitiveness of the electrometer of about 1000 mm. per volt are given below:—

Height of dropper	H cms.
Voltage on the first electrode	V_1
Voltage on the second electrode	V_2
The total current due to negative ions	N
The total current due to positive ions	P
The positive current when the voltage V_1 is on the second electrode	p

The results are plotted on fig. 3.

Fig. 3.



H.	V_1.	V_2.	P.	*p*.	N.
53·8	114	596	690	180	−175
43	114	590	520	120	−118
32·4	112	596	320	60	−62
21·5	112	590	180	0	0
14·8	114	600	81	0	0
6	—	600	0	0	0

The numbers under *p* show the current on the last electrode with a field of about 590 volts, when the voltage V_1 is on the first: they therefore represent the ions causing the second rise in the saturation curve. For convenience we will call these the slow positive ions. The last column shows the total negative ions, and as is seen the slow positive are practically equal in amount to the negative ions. If, therefore, the doublet theory is correct, the negative ions arise altogether from the breaking up of doublets. This may perhaps account for the current-voltage curve of the negative ions showing no peculiarities, as the doublets may be broken up in continuously increasing amount. The numbers show that below a height of 21·5 cms. no slow positives are produced, and, as we should expect from the doublet theory, the negatives are also absent. In these cases the saturation curves show no peculiarities.

At the heights 14·8 and 21·5 voltages of 600 were placed on both electrodes, but no current could be observed on the last electrode. This shows that at these heights no doublets are formed. At a height of 6 cms. the mercury struck the plate without breaking into drops and no ions are produced. If the mercury is forced by pressure from the dropper, there is no ionization produced unless the mercury forms visible drops before striking the plate.

Professor J. J. Thomson has asked whether ions are first produced by splitting doublets, or are ions first produced and then doublets formed by the combination of positive and negative ions. These results at the lower heights show that ions are produced by dropping mercury without accompanying doublets. At greater heights both doublets and ions are produced. As we get the ions without doublets in certain cases it would seem that something more than ions is necessary to produce doublets.

With a view to further information on the subject of doublets at atmospheric pressure, the ionization produced by heating aluminium phosphate and lime was examined by the same apparatus. The salt to be heated was placed on a thin piece of platinum-foil in a wide glass tube and then heated electrically to a bright white heat. Air filtered by cotton-wool was drawn over the heated salt into the apparatus. The curves giving the relation between the current and the voltage shown on fig. 2, are the currents from aluminium phosphate, C and D, and from lime, E and F. It will be seen that there is a distinct kink in each at about the same voltages as the mercury curve, and the saturation voltage of the second part is the same as the saturation voltage of the negatives.

V.	C.
314	130
352	130
390	130
432	130
474	128
516	130
558	126
600	130
656	130

If the saturation curve be examined in the case of aluminium phosphate, the current does not vary by more than four divisions for voltages from 314 to 656. Yet if a voltage above 300 is put on the first electrode, and the current examined on the second, it is seen to be larger than the four divisions difference observed in the current on the first, from the following numbers. The first three lines refer to lime and the last to aluminium phosphate.

Positive saturation current on the first electrode	P
Negative saturation current on the first electrode	N
Positive current obtained with a voltage of 600 on the first electrode, the current being taken on the second electrode	*p*
Negative current similarly obtained	*n*

P.	*p*.	N.	*n*.
170	13, 14, 15	200	15, 15
79	13, 14	164	12, 16
175	19, 20, 20	224	19, 15, 16
114	9, 8, 8	145	9, 6, 7

The values for the positive and negative currents on the second electrode, with a large voltage on the first, show a remarkable equality despite the fact that the total positive and negative currents differ, although not to the same extent as the positive and negative currents produced by the splashing of mercury. If the mercury were allowed to splash and the air drawn through a tight cotton-wool plug 2 inches long before reaching the testing vessel, it was found that ions were still present. These, again, are exceedingly slow ions that have passed the plug, or else they have been produced from doublets after they have passed the plug. Similar results were obtained by Garret and Willows for the ions produced by the halogen compounds of zinc (Phil. Mag. 1904, vol. viii. p. 437).

Summary.

(1) Splashing mercury on an iron plate produces a large excess of positive ions over negative ions.

(2) A considerable proportion of these ions have a very small velocity.

(3) The amount of ionization depends on the nature of the surface on which the splashing is produced.

(4) The current-voltage curves for the positive ions show peculiarities which may be most readily explained by supposing the presence of neutral doublets, which are broken up by the field or other means. Below certain heights these doublets are not produced.

(5) Similar peculiarities in the saturation curves for the positive ions of aluminium phosphate and lime are also noticed.

(6) The negative ions from these three sources show no such peculiarities.

I have to thank Dr. R. S. Willows for the use of the Cass Physical Laboratory and much kindly advice and assistance.

XLVII. *Wiltshireite: a New Mineral.*
By Prof. W. J. Lewis, *M.A.*, *F.R.S.*[*]

DURING a recent visit to Binn (Valais) I obtained, amongst several other interesting specimens, one which gives on measurement a series of angles which leave little doubt that it has not been hitherto described. It is associated with a crystal of sartorite in a cavity in the well-known dolomite; and from its position it is probably of more recent origin. Its colour is for the most part tin-white, but a few of the facets have a russet tarnish. The crystals are small but piled on one another in almost absolutely parallel orientation, and the same facet on separate individuals gives in many cases a distinct single image, although some of the most important cases give two images separated by some ten minutes. So far only a crystallographic determination can be made, and its chemical composition must be left until further specimens are found, though it is highly probable that it is a lead sulpharsenite.

The faces 201, 302, 101, 001, and $\bar{1}01$ are smooth and bright, and give for the most part good images; they are all very small end-facets. The hemi-pyramids which occur in two homologous zones symmetrical to a symmetry-plane are also smooth and bright; and single images were got from several distinct and separate facets on different parts of the specimen. The faces in the vertical zone 100, 310, 320, 120, and 010, are strongly striated parallel to their edges, along which the crystals are elongated; they give good images in zones which likewise include pinakoids and hemipyramids, but direct observations over the vertical edges give very indifferent measurements.

The crystal belongs to the oblique system, and its elements

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[*] Communicated by the Author.

may be given as

$$100:101=48^\circ\ 47'{\cdot}\dot{3},\quad 100:001=79^\circ\ 16'$$

and $$001:011=46^\circ\ 25'{\cdot}75;$$

or by $\beta=79^\circ\ 16'$, and $a:b:c=1{\cdot}587:1:1{\cdot}070$.

The following are readings in important zones :—

	Computed.	Observed.
100 : 201	32° 37′·7	32° 36′
302	39 22	40 11
101	48 $47{\cdot}\dot{3}$	48 47
001	79 16	79 15
$\bar{1}01$	116 $24{\cdot}\dot{6}$	116 33
100 : 522	37 33	38 7
211	43 9	43 7
233	50 14	50 7
111	59 7	59 10
122	70 1	70 0
011	82 37·5	82 38
$\bar{1}22$	96 19	96 2
$\bar{1}11$	108 44	108 39
$\bar{2}11$	128 56	128 58
$\bar{5}22$	136 11	136 2
$\bar{1}01:\bar{2}12$	25 36	25 35
.. $\bar{1}11$	43 $46{\cdot}\dot{6}$	43 45
011 : 001	46 25·75	46 24
$0\bar{1}1:001$	,,	46 35
$\bar{0}11:011$	92 51·5	92 58

I propose for it the name of Wiltshireite, as a token of respect for the late Rev. Professor Thomas Wiltshire, Hon. Sc.D., at one time Professor of Mineralogy in King's College, London.

Cambridge, 13 August, 1910.

XLVIII. *Discussion of Results obtained at Kew Observatory with an Elster and Geitel Electrical Dissipation Apparatus from* 1907 *to* 1909. *By* C. Chree, *Sc.D., LL.D., F.R.S.*[*]

(From the National Physical Laboratory.)

§1. An ordinary Elster and Geitel dissipation apparatus has been in regular use at Kew Observatory since the end of 1906, and the Annual Reports for 1907, 1908, and 1909 have contained summaries of the results derived from it.

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[*] Communicated by the Author.

The present paper discusses the results in a more complete fashion. The observations have been taken at a fixed spot in the Observatory garden, and the instrument has been used in an invariable way with the cover on, following it is believed the original procedure approved by Elster and Geitel.

During the observations the instrument has stood on a stone pier 1·2 metres in height situated near the middle of the garden, at a considerable distance from any tree or building and freely exposed to the wind. The centre of the dissipation cylinder is 1·45 metres above the ground. The instrument has been wholly unprotected except by its own cover. No one is near the instrument unless when actually reading it, and when doing so the observer stands to leeward. Observations have been made only when it was dry, and when the wind permitted. During high winds the electroscope leaves are not sufficiently stationary, and after a little experience no observations were made under such conditions.

All the observations utilised here were taken between 2 and 4 P.M. The regular dissipation observations were preceded and followed by a leakage experiment, to determine how much of the apparent loss was due to defective insulation. There were usually three dissipation observations, each lasting 20 minutes ; the first and last being with charges of the same sign, the intermediate with a charge of opposite sign. If on one day there were two positive charge experiments, then on the next day there was only one. Thus the number of experiments with positive and negative charges was roughly equal, and the mean time of the experiments on the same day with the charges of opposite sign practically coincided. The mean monthly and annual results for the dissipation of positive and negative charges may thus be regarded as exactly corresponding to one another.

At the time of observation, the observer noted the amount of cloud (scale 0 to 10) and its type or types, also whether the sun was shining, and if so whether brightly or otherwise. He further noted the state of the atmosphere, whether clear, hazy, misty, or foggy, and the direction of the wind. Most of the observations were taken by Mr. E. G. Constable, the senior assistant in the Meteorological department. In his absence they were taken by Mr. E. Boxall, who is also an experienced meteorological observer. For the purposes of the present discussion, particulars have been derived from the curves of the self-recording instruments as to the mean values of temperature, barometric pressure, relative humidity, and electric potential gradient during each afternoon's observations.

§ 2. The values of a_+ and a_-, the percentage losses per minute of positive and negative charges, have been calculated from the formula

$$a/100 = \frac{1}{1-n} \cdot \frac{1}{t}\left\{\log\frac{V_t}{V_0} - \frac{1}{n}\log\frac{V_t'}{V_0'}\right\}, \quad . \quad . \quad . \quad (1)$$

where V_0 denotes the initial, V_t the final potential in the dissipation experiment, V_0' the initial and V_t' the final potential in the leakage experiment, both experiments being supposed to last t minutes, n denotes the ratio (capacity of electroscope alone)/(joint capacity of dissipator and electroscope). Unfortunately, n is a quantity which it is not easy to determine accurately, and while high precision in the value of n is unimportant in the leakage term inside the long bracket, supposing the insulation to be good, it is of course important in the factor $(1-n)^{-1}$ outside the bracket. When dealing with comparative results from the same instrument, Elster and Geitel, in some at least of their earlier work, omitted the factor $1-n$, using the notation E instead of a. The fact that E and a represented something more than a mere difference in notation was overlooked in the preparation of the tables of dissipation results published in the Kew Reports for 1907, 1908, and 1909. The values assigned there to a_+ and a_- really answer to E_+ and E_- in Elster and Geitel's notation, and thus presumably require multiplication by $(1-n)^{-1}$ to be comparable with values published for other stations. The value obtained for n in direct experiments at Kew was 0·3, the corresponding value of $(1-n)^{-1}$ being 1/0·7 or 1·43.

So long as the insulation is kept satisfactory the ascription of a wrong value to n practically alters all values of a_+ and a_- in the same proportion, and so is without influence on any conclusions that depend only on relative values. Such an error is for instance without effect on values of a_-/a_+ or on the annual variation observed in a_- or a_+.

§ 3. There is another question affecting the interpretation of the results.

Elster and Geitel assume "dissipation" to follow the law

$$dV/dt + \alpha V = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This is at least approximately true in air so long as the potential gradient is small, α being a measure of the conductivity. As the gradient, however, is raised, the curve in which abscissæ represent gradient and ordinates current departs markedly from a straight line, and then throughout a considerable gradient range remains practically parallel to the axis of abscissæ ("saturated" current condition). A further stage then presents itself which does not concern us.

Mache and v. Schweidler * assert, what seems to be now generally allowed, that the conditions in the Elster and Geitel instrument as ordinarily used are those of the "saturated" current. If so, then the true formula is

$$dV/dt + A = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A is proportional to the number of ions being generated in unit of time in unit of space surrounding the dissipator. This last formula leads to

$$A = (V_0 - V_t)/t, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where V_0 is the original value of the potential, and V_t its value after time t.

Let us compare this with the corresponding results from the equation assumed by Elster and Geitel, viz.

$$\alpha = (1/t) \log (V_0/V_t). \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Writing this $\alpha = -(1/t) \log \{1 + (V - V_0)/V_0\}$,

we see that as a first approximation, provided $(V_t - V_0)/V_0$ be small—as is normally the case at Kew—we have

$$\alpha = (1/t)\ (V_0 - V_t)/V_0 \,. \quad . \quad . \quad . \quad . \quad . \quad (6).$$

The formulæ (2) and (5) would apply to the ideal Elster and Geitel instrument in which the capacity of the electroscope is negligible, or $n = 0$. The result calculated from the right-hand side of (5) would represent $a/100$ in Elster and Geitel's notation. We see, however, that so long as the loss of charge in time t is small, we may to a close degree of approximation replace (5) by (6). If, then, the true law of loss of charge be not (2) but (3), the calculated value of $a/100$ is very approximately the true value of A/V_0, and so varies approximately as A—the number of ions being generated in unit of time—provided V_0 is constant.

In the Kew observations V_0 was not really a constant, but it seldom departed much from its mean value, which was about 180 volts for both the positive and negative charges.

It is unquestionably desirable that no doubt should exist as to the exact physical significance of observational quantities. It is doubtful, however, whether any one of the quantities measured in atmospheric electricity observations is wholly

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* *Die Atmosphärische Elektrizität*, pp. 63, 64.

unambiguous. And, on the other hand, there are the facts that Elster and Geitel instruments have had an extensive use on the continent, and that there is a larger mass of comparative data for a_+ and a_- than for any other atmospheric electricity element, except perhaps potential gradient.

It has thus seemed worth while to run an Elster and Geitel apparatus at Kew long enough to obtain fairly representative data, and having done so it has appeared desirable to analyse the results.

§ 4. Table I. (p. 480) gives results from the three years combined. N denotes the total number of days' observations. a_+ and a_- are the percentage losses per minute as derived from (1) with $n=0{\cdot}3$, t being almost invariably 20 minutes. $\bar{a}$ denotes the arithmetic mean $(a_+ + a_-)/2$, a quantity employed by some observers as a measure of dissipation. q represents the arithmetic mean of individual days' values of a_-/a_+, while q' stands for $(\Sigma a_-) \div (\Sigma a_+)$, where Σ denotes summation for all days of the month.

Of the three seasons, Winter is composed of four months November to February, Summer of May to August, and Equinox of the remaining four months.

The values assigned to the year and the seasons, except for q', are arithmetic means from the monthly values, but in the case of q' they are derived from the seasonal values of a_+ and a_- carried one significant figure further than in the table. Table I. gives also mean values corresponding to the times of the dissipation experiments for potential gradient P, screen temperature, barometric pressure, amount of cloud (scale 0 to 10), and relative humidity. Meteorological conditions vary so much that it appeared desirable to indicate their character. The pier carrying the dissipation instrument and all uninsulated parts of it were at zero (the Earth's) potential, and the electric field in the immediate neighbourhood was necessarily irregular. The values assigned to P are intended to refer to a spot in the open. They were derived from the electrograph curves by applying factors obtained by reference to absolute observations with a portable electrometer. The mean value of the factor was 1·41. This is higher than the values hitherto employed, recent experiments having shown that previous values were too low.

The values of a_+ and a_- are considerably lower than those recorded at most continental stations. The largest values actually measured during the three years were 1·80 for a_+ and 3·41 for a_-. The values obtained for q or q' are exceptionally large.

TABLE I.

	N.	a_+	a_-	$\bar{a}$.	q.	q'.	P.	Temperature Fahrenheit.	Barometric Pressure, inches.	Cloud.	Relative Humidity.
January	36	·346	·486	·416	1·56	1·42	400	41°·0	30·292	5·9	76
February	38	·326	·521	·423	1·78	1·60	357	44·1	30·209	6·1	69
March	30	·310	·486	·398	1·69	1·62	302	46·6	29·912	5·3	63
April	24	·434	·671	·552	1·79	1·68	224	54·6	29·897	4·8	56
May	37	·591	·871	·731	1·50	1·45	166	62·7	30·014	6·3	59
June	39	·753	·986	·870	1·45	1·32	166	65·2	30·043	6·3	60
July	39	·704	1·029	·867	1·53	1·46	149	69·1	30·061	6·0	59
August	29	·634	·984	·809	1·65	1·55	166	67·2	30·026	6·1	59
September	39	·623	·970	·797	1·79	1·56	221	63·6	30·003	5·6	66
October	34	·647	1·050	·848	1·73	1·62	182	59·7	29·850	5·4	70
November	37	·519	·787	·653	1·86	1·55	294	48·1	30·066	6·4	77
December	29	·610	·739	·674	1·27	1·23	362	42·4	29·960	6·0	79
Year	411	·541	·799	·670	1·63	1·47	250	55·4	30 028	5·8	66
Winter	140	·450	·633	·541	1·62	1·41	354	43·9	30·132	6·1	75
Equinox	127	·504	·794	·649	1·75	1·58	232	56·1	29·916	5·3	64
Summer	144	·671	·967	·819	1·53	1·44	162	66·0	30·036	6·2	59

§ 5. The large size of q and q' is due not to the existence of any considerable number of exceptionally high individual values of q, but to a persistent tendency of a_- to be substantially larger than a_+. This is readily seen by reference to Table II. The first line shows the total number of occasions when q lay within the limits specified, the second the percentages which these form of the whole 411 individual observations.

TABLE II.

q.	< 1.	1 to 2.	2 to 3.	> 3
Number of occasions	42	291	61	17
Percentage of total	10	71	15	4

Of the 42 days when a_+ exceeded a_- no less than 15 occurred in December or January. It is a curious fact, which may be worth noting, that low values of q seemed to have a tendency to occur on successive days. On one occasion values less than unity happened on 4, and on three occasions on 2 successive days.

Of the 17 days when q exceeded 3 only two occurred in the summer months May to August.

The largest value of q actually recorded was 8·9—in November 1907,—but in this and one or two other cases where q was exceptionally high or low, some doubt may reasonably be felt as to the accuracy of the result.

At Kew, a large value of q means usually a very small value of a_+, a small value of q a small value of a_-. Now individual observations cannot claim any very high precision, and when dissipation is small the loss due to defective insulation is apt to represent rather a high fraction of the total, so that the probable error in a low value of a_+ or a_- is very considerable.

§ 6. Table I. shows a well-marked annual variation in dissipation, though obviously a good many more years' observations would be required to give smooth results. Taking the mean of a_+ and a_-, we have the maximum dissipation in June and July and the minimum in January, February, and March. The annual variation is the opposite of that in P, but the difference between summer and winter is less pronounced. It should, however, be remembered that the results refer to only a small fraction of the day, viz., 2 to 4 P.M., and that if we were dealing with mean results from the whole 24 hours the annual variation in a_+ and a_- and the relation to P might be different.

We know that in the case of P the character of the regular diurnal variation varies with the season of the year. In summer, the element is between 2 and 4 P.M. notably below its mean value for the day, but at midwinter at this hour it is if anything above the mean. Thus the annual variation of P shown by Table I. differs from that shown by the 24-hour mean, in the direction of increasing the difference between summer and winter. In the case of a_+ and a_- it is at least as likely as not that the opposite is true.

In the case of q and q', annual variation if existent appears to be small, but whether accidentally or otherwise the four equinoctial months all give values above the mean.

§ 7. In order to see whether a_+ or a_- exhibited any parallelism to P or to any meteorological element, the days of each month of the three years were arranged in two equal groups, according to the value of the element under consideration. When temperature, for instance, was being considered, the two groups were composed respectively of the warmest and coldest days. If there happened to be an odd number of days of observation, the day which was central as regards temperature was omitted. Mean values were found for each of the groups, for temperature, a_+, a_-, a_-/a_+, and P, as well as the corresponding values of $(\Sigma a_-/\Sigma a_+)$. Calling these two mean values for any element from any one month of the year m and m', and distinguishing the three years by the suffixes 1, 2, 3, means

$$\mathrm{M}=(m_1+m_2+m_3)/3, \text{ and } \mathrm{M}'=(m_1'+m_2'+m_3')/3$$

were then calculated. The means of the 12 M's and the 12 M′'s were ascribed to the year as a whole, the means of the M's and M′'s for November, December, January, and February were ascribed to winter, and so on. The difference between the final means $\overline{\mathrm{M}}$ and $\overline{\mathrm{M}}'$ for the year, or for any season, was taken, and in the case of a_+, a_-, and P, this difference was expressed as a percentage of the mean value of the element for the season. The results thus found are given in Tables III. to VI.

TABLE III.—High Potential ∼ Low Potential.

	Differences as percentages of seasonal mean.				
	P.	a_{+}.	a_{-}.	q.	q'.
Year	+64	−18	−21	+4	−3
Winter	+64	−25	−28	+4	−3
Equinox......	+64	−24	−23	+5	+2
Summer......	+64	− 9	−11	+4	−3

TABLE IV.—High Temperature ∼ Low Temperature.

	Temperature Difference.	Differences as percentages of seasonal mean.				
		a_{+}.	a_{-}.	q.	q'.	P.
Year	8°·1	+12	+19	+ 7	+ 8	−15
Winter	7·7	+22	+27	− 4	+ 6	−31
Equinox......	8·4	+14	+31	+21	+17	− 2
Summer......	8·0	+ 4	+ 3	+ 2	− 1	+ 1

TABLE V.—High Pressure ∼ Low Pressure.

	Barometric Pressure Difference (inches).	Differences as percentages of seasonal mean.				
		a_{+}.	a_{-}.	q.	q'.	P.
Year	0·337	−25	−24	+ 1	+ 2	+17
Winter	0·875	− 2	− 6	−12	− 4	+ 9
Equinox......	0·323	−41	−28	+12	+14	+28
Summer......	0·313	−28	−31	0	− 3	+21

TABLE VI.—Much Cloud ∼ Little Cloud.

	Cloud Difference.	Differences as percentages of seasonal mean.				
		a_+.	a_-.	q.	q'.	P.
Year	5·3	+21	+21	−5	+1	−14
Winter	6·2	+32	+33	−8	0	−19
Equinox......	5·0	+18	+17	−6	−1	− 7
Summer......	4·7	+14	+18	−1	+3	−13

To elucidate Tables III. to VI., take Table IV. as an example, and consider the case of the "year." The means of the 12 monthly means derived from the groups of warmest and of coldest days were as follows :

	Temp.	a_+.	a_-.	q.	q'.	P.
From groups of warmest days ...	59°·4	·577	·876	1·70	1·52	229
From groups of coldest days ...	51·3	·513	·726	1·58	1·41	267
Excess on warmest days	+8·1	+·064	+·150	+0·12	+0·11	− 38
Corresponding mean values	...	·541	·799	1·63	1·47	250
Excess as percentage of mean ...	...	+12	+19	+7	+8	−15

§ 8. Before discussing Tables III. to VI. it is convenient to introduce two other Tables which present another aspect of the case. The comparison of groups of days, as already explained, was made for each of the 36 months of the three years. If a close connexion exists between a_+ or a_- and any of the other elements considered, then there ought to be a substantial majority of individual months in which the connexion appears. This is the aspect of the case that is dealt with in Table VII.

A value near 18 indicates little or no connexion. A value much above 18 indicates a marked tendency for the two quantities compared to be large together, while a value much under 18 signifies that the one quantity tends to be large

TABLE VII.—36 months taken individually.

	Number of months when largest value of				
	a_+.	a_-.	q.	q'.	P.
in group of days of highest P	9	10	20	20	—
,, ,, ,, temperature.	24	26	19	21	13½
,, ,, ,, pressure......	10	9	20½	20	28
,, ,, of most cloud............	25	28	15	17½	11

when the other is small. For instance, in 9 months the mean value of a_+ was larger in the group of days of highest potential, leaving 27 months in which the larger mean value of a_+ belonged to the group of days of lowest potential. The tendency is thus for high values of a_+ to be associated with low values of P, and conversely. A case in which the means from the two groups of days were exactly equal was counted as $\frac{1}{2}$.

If, instead of taking the three years separately we take them combined, we get the following results instead of those in Table VII. The number of months being now 12, the criterion for association is a decided departure from the figure 6.

TABLE VIII.—3 years combined.

	Number of months when largest value of			
	a_+.	a_-.	q.	P.
in group of days of highest P	0	1	7½	—
,, , ,, temperature.	8½	10	9	3
,, ,, ,, pressure......	3	3	7½	11
,, ,, of most cloud...	9	11	5	2

§ 9. The somewhat curious fact that the difference between the two mean values of P in Table III. was in each season exactly the same fraction of the mean seasonal value, makes the comparison especially instructive.

It is clear from Table VIII. that there is a distinct association, the whole year round, of high values of a_+ and a_- with low values of P, but this association according to Table III. is decidedly less marked in summer than in winter or equinox. There is, however, room for doubt whether the apparent difference between summer and the other seasons is real. It is due almost entirely to the one summer 1907. In all four months of that season, the group of days of largest P had the higher mean value of a_-, and in two cases out of four the higher mean value of a_+.

Tables VII. and VIII. both suggest that a_-/a_+ has a slight tendency to be large when P is high, but the numerical differences for q and q' in Table III. are too small to rely on and tend to differ in sign.

Tables IV., VII., and VIII. agree in associating large values of both a_+ and a_- with high temperature, but the apparent closeness of the association is widely different at the different seasons. It is conspicuous in winter, but tends to disappear in summer. In fact, when the three years are combined, the two hottest months July and August associate high values of a_+ and a_-, not with the higher but with the lower temperature group of days. Of the 24 individual months in Table VII. which associate high values of a_+ with high temperature, no less than 11 are contributed by winter, so that the two other seasons only contribute 13 out of a possible of 24. The association of high values of a_-/a_+ with high temperature is, according to Table IV., pronounced in equinox but not in the other seasons.

The relationship between temperature and potential presents closely similar features in its annual variation. It is marked in winter in Table IV., high temperature going with low potential, but not in equinox or summer. As Table VII. shows, high temperature was associated with low potential in 22½ of the 36 months, but no less than 11 of these were winter months, and an actual majority of summer months associated high temperature and high potential.

The apparent relation between dissipation and barometric pressure is in several respects the exact opposite of that with temperature. According to Table V., high pressure is at all seasons associated with low values of a_+ and a_-, but the association is much less apparent in winter than in summer. This fact is all the more striking because the mean pressure difference between the groups of days of high and low barometer was conspicuously large in winter. As shown in Table VII., the number of individual months which associate high values of a_+ and a_- with high pressure is appreciable, but winter is responsible for 6 out of 10 in the case of a_+, and for 5 out of 9 in the case of a_-. In only one out of 12 summer months was there an association of high values of a_+ and a_- with high pressure. Tables VII. and VIII. agree in indicating a tendency for high values of a_-/a_+ to be associated with high pressure ; but Table V. gives no support to this conclusion except in equinox. The association of high potential with high pressure is marked. According to Table V. it is reduced in winter, but still winter contributes 9 months out of the 28 in which the associationship appears.

Tables VI., VII., and VIII. agree in associating high values of a_+ and a_- and low values of P with the prevalence of much cloud. The apparent influence of cloud seems remarkably alike in a_+ and a_- according to Table VI. It appears greatest in winter, and is distinctly larger in the case of dissipation than in that of potential.

§ 10. The question of the influence of cloud is complicated by the facts that there are a number of different types, representing different meteorological conditions, and that the relative frequency of the various types varies with the season of the year. An attempt was made to ascertain whether the electrical phenomena associated with the different types of cloud differed. The difficulty at once presented itself that upper and lower clouds are usually both present, and that not infrequently there is more than one type represented, both in the lower and in the upper. There were, however, some types which occurred alone in a sufficient number of instances to warrant the hope that conclusions of fair reliability might be obtained. These were stratus (including ordinary low stratus and alto-stratus), cumulus (at all levels including fracto-cumulus, but not strato-cumulus), and cirro-stratus (at high levels). In a good many months there were no representatives of one or other of these types, and in many other months there were only one or two representatives. Thus the method of deriving mean values of dissipation and potential for days of each species of cloud in each month was unworkable. The plan adopted was to examine each day by itself, and classify separately the corresponding a_-, a_+, and P, according as the value was above or below the mean value for the month.

A difficulty, however, presented itself in the interpretation of the results. None of the three quantities a_-, a_+, or P has its values occurring symmetrically with respect to its arithmetic mean. Taking all the observations, the number of occasions having values larger than the mean is very decidedly less than the number having values below the mean.

Thus no inference can be drawn from the results for any particular type of cloud without considering the corresponding results from all days of observation. This comparison is made in Table IX. It gives the number of days of each class, the corresponding mean amount of cloud and the percentage of occasions in which the value of a_+, a_-, or P was above the average derived from all days of observation in the month to which the observation belonged. The results are given to the nearest 0·5 per cent.

Table IX.

Type of day.	Number of days.	Mean amount of cloud.	Percentage of cases when value above the monthly mean.		
			a_+.	a_-.	P.
All days	411	5·8	44·5	44·5	42
Days of Stratus	50	9·0	47	41	30·5
„ Cumulus......	88	5·1	38·5	51	31
„ Cirro-stratus.	85	5·4	46	39	40

In the cases of cumulus and cirro-stratus the mean amount of cloud is less than the mean from all days, but the difference is not large, so that any conspicuous peculiarity in the results for either class, if not "accidental," is presumably really dependent on the *type* of cloud. We thus infer that the presence of cumulus has a distinct tendency to be associated with low values of P and of a_+, but with high values of a_- and so of q. The presence of cirro-stratus seems to have exactly the opposite effect so far as dissipation is concerned, but the apparent association with high values of a_+ is at least doubtful. The apparent depression in P is also too small to possess much significance. Stratus appears to be associated with a slight rise in a_+ and fall in a_-, and a very decided fall in P. The amount of sky covered on days of stratus is, however, much larger than on an average day, so that the apparent effects on P and a_+ may be due to the quantity of cloud and not to its type. The examples of stratus were mostly from the winter months, and so from the season when Table VI. makes the influence of cloud on P largest.

§ 11. Amongst the other meteorological conditions considered were *bright* sunshine (as opposed to faint or no sunshine), clearness of the atmosphere (as opposed to haze or mist), and the limiting form of extreme clearness distinguished by the letter v (high visibility) in the meteorological records. Mean values of a_+, a_- &c. were got out for the days of bright sunshine in each month, and the algebraical residues remaining after subtracting from these the corresponding means from all the observations of the month were totalled for the 36 months. The mean of this sum of differences was finally expressed as a percentage of the mean value of the element for the three years. These percentages for the several elements appear in Table X. The same method was applied in the cases of clear atmosphere and of high visibility.

TABLE X.

	Number of days.	Percentage excess of element on representative day of special type.			
		a_+.	a_-.	q.	P.
Bright sunshine	125	−14	−15	0	+ 6
Clear atmosphere	144	+ 9	+12	− 1	−10
High visibility	24	+39	+21	−12	− 7

To illustrate the interpretation of Table X., take the case of bright sunshine. Out of the whole 411 days of observation there were 125 on which there was bright sunshine during at least the greater part of the dissipation experiment. On the average day of bright sunshine a_+ was 14 and a_- 15 per cent. below its mean value for the season, while P was 6 per cent. in excess of its mean value. There was no appreciable effect on q. The days of clear atmosphere include the 24 of high visibility. They exhibit the exact opposite of the phenomena exhibited by the days of bright sunshine, while the days of high visibility are specially conspicuous for the large values of the dissipation. Whether the apparent reduction of q on days of high visibility may not be in part at least "accidental" is open to some doubt, on account of the comparative fewness of the days. High visibility was mainly confined to summer months, no single example being encountered from November to March.

The difference apparent between days of bright sunshine and days of clear atmosphere may appear at first sight improbable, as one is apt to regard the two meteorological conditions as naturally coexistent. This, however, is by no means the case at Kew, more especially in the afternoon, when haze is a frequent accompaniment of sunshine.

§ 12. It was originally intended to treat relative humidity in the same way as temperature, pressure, and cloud, and this was actually done for one whole year. The mean electric results, however, from the groups of days of high and of low relative humidity were so closely alike for all the seasons that it appeared unnecessary to proceed further.

§ 13. The last meteorological element to be considered in detail was wind direction. In some months one direction was so dominant that grouping of days presented difficulties. Supposing the wind to be westerly on 9 days out of 11, little significance can be assigned to the numerical size of the difference between means derived from the 9 days and from the 11. Accident is likely to play too large a part. The method actually adopted was as follows : the days of each month were grouped under the four fundamental directions, N, E, S, and W. If the wind were N.W., or N.N.W., or W.N.W., it was grouped under both N and W. The values of a_+, a_-, q and P were then found for each of the four directions—or for all that were represented—for each month. Taking for example a_+, the direction giving the largest mean value was regarded as taking the first place in a competition, the direction giving the next largest mean value the second place, and so on. Out of the whole 36 months there were 19 on which the largest mean value of a_+ was associated with a South wind, as compared with 10, 4, and 3 respectively on which the largest value was associated with a West, a North, and an East wind. The second place on the list was taken 7 times by a South, 19 times by a West, 6 times by a North, and 4 times by an East wind. These results form the first two rows in Table XI. under a_+. The data for a_-, q, and P possess the same significance.

The sum of the figures for "first" and "second" always totals up to 36, but the same is not true of the figures for "third" and "fourth" because in some months not more than 3 or even than 2 wind directions were represented.

A glance at Table XI. shows a very pronounced association of high values of a_+ and a_- with southerly and westerly winds, and an equally pronounced association of high values of P with northerly and easterly winds. q seems to be independent of the wind direction.

The influence of wind direction on a_+, a_-, and P is much less marked in winter than in the other seasons. Winter contained 5 of the 7 months in which a_+ was highest with a N. or E. wind, 7 of the 9 months in which a_- was highest

Table XI.—Influence of Wind Direction.

Wind Direction.	a_+.				a_-.				q.				P.			
	N.	E.	S.	W.	N.	E.	S.	W.	N.	E.	S.	W.	N.	E.	S.	W.
Times first ...	4	3	19	10	4	5	16	11	8	9	10	9	10	22	2	2
second...	6	4	7	19	6	4	8	18	13	5	6	12	18	4	8	6
third ...	16	10	3	6	15	10	4	6	7	12	7	9	6	1	12	16
fourth...	10	13	5	1	11	11	6	1	8	4	11	6	1	3	12	12

with a N. or E. wind, and 3 of the 4 months in which P was highest with a S. or W. wind. Confining ourselves to firsts and seconds in Table XI., and combining East with North and West with South, we obtain the following figures for Winter (*i.e.* 12 months of the 36) :—

Number of	North and East.			South and West.		
	a_+.	a_-.	P.	a_+.	a_-.	P.
Firsts	5	7	9	7	5	3
Seconds........ ...	4	4	7	8	8	5

In the case of dissipation South and West have a distinct majority of seconds, but absolutely no majority of firsts.

The influence of wind direction is a complicated question. Kew Observatory is situated in a large park, which is bounded on the east by the extensive Kew Gardens, and to the north-east across the Thames lies Syon Park. No inhabited buildings are at all near in the direction from S.E. to N., while Isleworth approaches to within $\frac{1}{3}$ of a mile across the river in the N.W. direction. St. Margarets, the next suburb up the river, follows immediately on Isleworth, and extends to Twickenham. Richmond is about $\frac{2}{3}$ of a mile away in the direction from S. to S.E., and behind Richmond lie Richmond Park and Sheen Common. Thus there is a comparatively narrow fringe of houses—mainly dwelling-houses—extending round from N.N.W. through W. to S.E. within a mile radius, while from N.N.E. to E. there occurs the great mass of London, but few houses come inside a $1\frac{1}{2}$ mile radius. Sometimes when the wind is easterly the curtailment of daylight by London smoke is very apparent, but this is mainly in the winter months when the influence of wind direction, as we have just seen, is least decisive. If London smoke is the really effective influence, then the effect should be considerably dependent on the hour of the day, and when most marked at Kew should be least marked at a station to the east of London. A comparison of simultaneous results from Kew and such a station should be decisive. If the low value of the dissipation and the high value of the potential gradient at Kew arise from its proximity to London, then the electrical conditions in the heart of London itself are presumably highly abnormal, and it seems unlikely that great abnormality in any atmospheric condition will be without some influence on living objects exposed to it.

§ 14. B. Zölss has described a remarkable parallelism between dissipation and the size of the daily range of declination at Kremsmunster, and has explained this as a case of cause and effect, dissipation representing a vertical electric current, and declination change the consequent effect on the magnetic needle. If such a connexion could be definitely established, it would be a result of great physical importance. Zölss' conclusions are given without criticism in Mache and v. Schweidler's textbook of Atmospheric Electricity, and it thus appeared worth while seeing whether any confirmation was derivable from Kew results. One point deserving attention is that the dissipation observations at Kew covered only two hours, while the declination range represents magnetic changes during a larger fraction of the day.

The diurnal range of declination, as Zölss himself recognized, agrees with dissipation in being considerably larger in summer than in winter. If the two phenomena are compared in a way which does not eliminate annual variation, then a conclusion similar to Zölss' is practically certain to be reached. But when the effects of annual variation are eliminated by subdividing the observations of each month into two equal groups composed respectively of the days of largest and of least declination range, the Kew results at least afford no support to Zölss' conclusions. It appeared sufficient to consider one year, 1908. The final means derived from the 12 pairs of monthly groups were as follows :—

Groups.	Mean value of		
	Declination Range.	$\frac{1}{2}(a_{+}+a_{-})$.	P.
Days of largest declination range ...	17′·6	·549	210
,, least ,, ,,	9′·2	·581	216

The example of Zölss has been followed in taking the mean of a_+ and a_- as a measure of the dissipation.

The difference between the groups as regards declination range is most substantial, but the difference between the corresponding values of dissipation and of potential is too small to possess any certain significance, and, as it so happens, the smaller value of the dissipation appears in association with the larger value of the declination range.

As already explained, summaries of results obtained with the Elster and Geitel apparatus have been published for a number of stations abroad, and in most cases investigations have been made as to the apparent association with different meteorological conditions. For information on these points the reader is referred to A. Gockel's "Die Luftelektrizität" and to Mache and v. Schweidler's "Atmosphärische Elektrizität."

XLIX. *On the Stability of Superposed Streams of Viscous Liquids. By* W. J. Harrison, *B.A., Fellow of Clare College, Cambridge*[*].

§1. In this paper it is shown that, if two streams of viscous liquids are moving uniformly in laminar motion, one of which is superposed on the other, and both are of great depth, the motion will be unstable under certain circumstances for disturbances of the interface which are of greater wave-length than some determinate limit[†]. It is clear that if instability ensues in any particular case it will be for great wave-lengths, comparatively speaking, and not for small ones, since, in the latter case, the motion is equivalent to two streams flowing with the same uniform velocity, as far as the disturbance is concerned. Lord Rayleigh has found a similar result when treating the disturbances between two streams of a liquid moving in opposite directions with uniform velocity, but separated by a transition layer of liquid in which the velocity changes uniformly. He says, "It appears, therefore, that so far from instability increasing indefinitely with diminishing wave-length, as when the transition is sudden, a diminution of wave-length below a certain value entails an instability

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[*] Communicated by the Author.

[†] It ought to be clearly stated that the stability here discussed is only for the case of particular modes of disturbance, namely, those originating from a disturbance of the interface. The arguments of Osborne Reynolds would seem to show that the motion must be unstable for a general disturbance, as there are no lateral boundaries to determine a limit to the instability.

which gradually decreases, and is finally exchanged for actual stability"[*].

I have given below three methods of solving the equations of motion, of which only one has been employed. The other two are too cumbrous for practical use, though more rigorous. There still remains another method, which has the advantage of not needing the same assumptions for the purposes of approximation, and which is especially adapted for very viscous liquids, but can only be employed for disturbances of great wave-length. However, as the stability of the motion is determined by its stability for great wave-lengths, this method will furnish the precise information we need. I hope to develop this solution in a future paper.

§2. We shall confine the problem to two dimensions and take the origin of coordinates (x, y) in the undisturbed interface, the axis of x being in the direction of flow, the axis of y vertically upwards.

The equation which is satisfied by the stream function Ψ can easily be shown to be

$$\left(\nu\nabla^2 - \frac{\partial}{\partial t}\right)\nabla^2\Psi = \left(\frac{\partial\Psi}{\partial y}\frac{\partial}{\partial x} - \frac{\partial\Psi}{\partial x}\frac{\partial}{\partial y}\right)\nabla^2\Psi, \quad . \quad (1)$$

where ν is the kinematical coefficient of viscosity.

We shall take the undisturbed motion of the lower liquid to be given by

$$\psi_0 = \mathrm{B}y + \tfrac{1}{2}\mathrm{C}y^2.$$

This implies an infinite velocity at $y = -\infty$, but as we are only concerned with the condition near the interface this need not cause any serious trouble. Lord Rayleigh makes the same assumption in his work on motion past a corrugated wall[†].

For the upper liquid

$$\psi_0' = \mathrm{B}'y + \tfrac{1}{2}\mathrm{C}'y^2,$$

where we must have

$$\mathrm{B} = \mathrm{B}',$$

$$\nu\rho\mathrm{C} = \nu'\rho'\mathrm{C}',$$

by reason of the continuity of velocity and traction across the interface.

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[*] Scientific Papers, vol. i. p. 480; Proc. Lond. Math. Soc., xi. p. 63, 1880.

[†] Scientific Papers, vol. iv. p. 89; Phil. Mag. xxxvi. p. 368 (1893).

The complete solution will be given by

$$\Psi = \psi_0 + \psi, \quad \Psi' = \psi_0' + \psi',$$

where ψ, ψ' are due to small disturbances, whose squares are to be neglected.

We assume ψ to be of the form

$$\psi = \mathrm{F}(y)e^{ikx+\alpha t}.$$

On substitution for Ψ in (1), we obtain

$$\nu\left(\frac{\partial^2}{\partial y^2} - k^2\right)^2 \mathrm{F}(y) - \left(\alpha + \iota k\mathrm{B} + \iota k\mathrm{C}y\right)\left(\frac{\partial^2}{\partial y^2} - k^2\right)\mathrm{F}(y) = 0. \quad (2)$$

Writing

$$\left(\frac{\partial^2}{\partial y^2} - k^2\right)\mathrm{F}(y) = f(y),$$

we can put (2) into the form

$$\nu\left(\frac{\partial^2}{\partial y^2} - k^2\right)f(y) - (\alpha + \iota k\mathrm{B} + \iota k\mathrm{C}y)f(y) = 0. \quad . \quad (3)$$

§3. Before proceeding further with the solution of the problem, I wish to insert here the solution giving the form of the free-surface of a stream of uniform depth flowing over a corrugated bed, over which it is assumed that the liquid can flow without experiencing any resistance.

In equation (2) we have $\mathrm{C} = 0$, $\alpha = 0$.

It is easily shown that

$$\mathrm{F}(y) = a_1 e^{ky} + b_1 e^{-ky} + a_2 e^{\lambda y} + b_2 e^{-\lambda y},$$

where

$$\lambda^2 = k^2 + ik\mathrm{B}/\nu.$$

We may take the bed to be

$$y = -h + \beta_0 e^{ikx},$$

and the free-surface

$$y = \beta e^{ikx}.$$

Writing down the usual conditions

$$\Psi = -u_0 h, \quad p_{xy} = 0 \text{ at } y = -h + \beta_0 e^{ikx},$$

$$\Psi = 0, \quad p_{xy} = 0, \quad p_{yy} = \text{const. at } y = \beta e^{ikx},$$

and eliminating the constants, we obtain the relation between β and β_0 in the form

$$[\mathrm{P} \operatorname{cosech} kh - \mathrm{Q} \operatorname{cosech} \lambda h]\beta_0$$
$$= [\mathrm{P} \coth kh - \mathrm{Q} \coth \lambda h + gk^2/\nu]\beta,$$

where $$\mathrm{P} = k\nu(2k^2 + \iota k\mathrm{B}/\nu)^2,$$
$$\mathrm{Q} = 4k^4\lambda\nu.$$

This leads to a finite expression for β for all velocities of the stream, and also gives the difference of phase between the corrugation and the wave-profile. When the wave-length is small compared with the depth the solution differs widely from that in the case of a non-viscous liquid*. When the stream velocity is great the amplitudes in the viscous and the non-viscous cases are equal.

§4. There are two ways of rigorously solving the equation (3). The first is that which was given by Lord Kelvin in his paper on "Rectilineal Motion of Viscous Fluid between two Parallel Planes" †. But in order to adapt this method of solution to our problem it is necessary to employ very complicated integration of Fourier's type.

The second rigorous solution can be obtained in terms of the Bessel's functions $J_{\frac{1}{3}}$, $I_{\frac{1}{3}}$; this problem thus affords a second example of the use of these functions in physical analysis. The double integration involved in the solution of equation (2) from that of (3) can be expressed, first of all, as a triple integral and then reduced to a single integral by the aid of Dr. J. W. Nicholson's results in his paper "On the Relation of Airy's Integral to the Bessel's Functions" ‡.

But again the analysis involved in the use of these functions is too complicated, and we are forced to consider an approximate solution §.

§5. Returning to equation (2) we shall solve by successive approximation on the supposition that $ik\mathrm{C}$ is small compared with $\alpha + ik\mathrm{B}$. To satisfy this assumption it is not necessary in general that C should be small.

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* *Cf.* Lamb, Hydrodynamics, 3rd edition, p. 389.

† Phil. Mag. xxiv. p. 192 (1887).

‡ Phil. Mag. (6) xviii. pp. 6–17 (1909).

§ Since writing this my attention has been drawn to two papers by Prof. W. M'F. Orr in the 'Proceedings' of the Royal Irish Academy, 1907, in which he uses these functions in the similar but less complicated problems of the stability of motion of a single liquid flowing between parallel planes.

The solution suitable for the lower liquid is to a first approximation

$$F(y) = Le^{ky} + Ne^{\lambda y} = f_0(y),$$

where
$$\lambda^2 = k^2 + (\alpha + \iota kB)/\nu,$$

and the real part of λ is to be taken positive.

To a second approximation

$$F(y) = f_0(y) + f_1(y),$$

where we have

$$\left(\frac{\partial^2}{\partial y^2} - k^2\right)^2 f_1(y) - (\lambda^2 - k^2)\left(\frac{\partial^2}{\partial y^2} - k^2\right) f_1(y) = \frac{\iota kC}{\nu} y(\lambda^2 - k^2) Ne^{\lambda y}.$$

The particular integral is

$$f_1(y) = Py^2 e^{\lambda y} + Qye^{\lambda y},$$

where
$$P = ikC \,.\, N/4\lambda\nu,$$

$$Q = -\frac{(\lambda^2 - k^2) + 4\lambda^2}{\lambda(\lambda^2 - k^2)} \cdot \frac{\iota kC}{4\lambda\nu} N.$$

To a third approximation

$$f_2(y) = (Ry^4 + Sy^3 + Ty^2 + Wy)e^{\lambda y},$$

where
$$R = \iota kC\, P/8\lambda\nu, \text{ \&c.}$$

Thus for the lower liquid we assume

$$F(y) = Le^{ky} + Ne^{\lambda y}[1 + N_1 y + N_2 y^2 + N_3 y^3 + N_4 y^4],$$

where
$$N_1 = (Q + W)/N,$$
$$N_2 = (P + T)/N,$$
$$N_3 = S/N,$$
$$N_4 = R/N,$$

and the stream function becomes

$$\Psi = By + \tfrac{1}{2}Cy^2 + F(y)e^{\iota kx + \alpha t}.$$

For the upper liquid

$$F'(y) = L'e^{-ky} + N'e^{-\lambda' y}[1 + N_1' y + N_2' y^2 + N_3' y^3 + N_4' y^4],$$

and
$$\Psi' = By + \tfrac{1}{2}C'y^2 + F'(y)e^{\iota kx + \alpha t}.$$

§6. The conditions at the interface are

$$\left.\begin{aligned} \frac{\partial\Psi}{\partial x} &= \frac{\partial\Psi'}{\partial x} \\ \frac{\partial\Psi}{\partial y} &= \frac{\partial\Psi'}{\partial y} \\ p_{xy} &= p'_{xy} \\ p_{yy} &= p'_{yy} \end{aligned}\right\} y = 0,$$

where p_{xy}, p_{yy} are the tangential and the normal tractions at the interface.

From the first three we have

$$L+N = L'+N', \quad \ldots\ldots\ldots \quad (4)$$

$$kL+(\lambda+N_1)N = -kL'+(-\lambda'+N_1')N', \quad \ldots \quad (5)$$

$$\rho\nu[2k^2L+N(k^2+\lambda^2+2\lambda N_1+2N_2)]$$
$$= \rho'\nu'[2k^2L'+N'(k^2+\lambda'^2-2\lambda' N_1'+2N_2')] \quad . \quad (6)$$

From the two equations of motion

$$\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y} = -\frac{1}{\rho}\frac{\partial p}{\partial x}-\nu\nabla^2 u,$$

$$\frac{\partial v}{\partial t}+u\frac{\partial v}{\partial x}+v\frac{\partial v}{\partial y} = -\frac{1}{\rho}\frac{\partial p}{\partial y}-g-\nu\nabla^2 v,$$

we find

$$ik\left(\frac{p}{\rho}\right)_{y=0} = -gik\eta-(\alpha+ikB)(kL+\lambda N+NN_1)+ikC(L+N)$$
$$+\nu[\lambda(\lambda^2-k^2)+3\lambda^2 N_1-k^2 N_1+6\lambda N_2+6N_3],$$

where η is the elevation of the interface,

$$\eta = -ik(L+N)/(\alpha+ikB)$$
$$= -ik(L'+N')/(\alpha+ikB).$$

Now $$\left(\frac{p_{yy}}{\rho}\right)_{y=0} = -\left(\frac{p}{\rho}\right)_0+2\nu\left(\frac{\partial v}{\partial y}\right)_0$$
$$= -\left(\frac{p}{\rho}\right)_0-2\nu ik(kL+\lambda N+NN_1).$$

Thus we have as our final condition

$$\begin{aligned}\rho[&gk^2(\mathrm{L}+\mathrm{N})/(\alpha+\iota k\mathrm{B})+(\alpha+\iota k\mathrm{B})(k\mathrm{L}+\lambda\mathrm{N}+\mathrm{N}_1\mathrm{N})-ik\mathrm{C}(\mathrm{L}+\mathrm{N})\\ &-\nu\mathrm{N}\{\lambda(\lambda^2-k^2)+(3\lambda^2-k^2)\mathrm{N}_1+6\lambda\mathrm{N}_2+6\mathrm{N}_3\}\\ &+2\nu k^2\{k\mathrm{L}+(\lambda+\mathrm{N}_1)\mathrm{N}\}]=\rho'[gk^2(\mathrm{L}'+\mathrm{N}')/(\alpha+\iota k\mathrm{B})\\ &+(\alpha+ik\mathrm{B})(-k\mathrm{L}'-\lambda'\mathrm{N}'+\mathrm{N}_1'\mathrm{N}')-\iota k\mathrm{C}'(\mathrm{L}'+\mathrm{N}')-\nu'\mathrm{N}'\{-\lambda'(\lambda'^2-k^2)\\ &+(3\lambda'^2-k^2)\mathrm{N}_1'-6\lambda\mathrm{N}_2'+6\mathrm{N}_3'\}+2\nu'k^2\{k\mathrm{L}'+(-\lambda'+\mathrm{N}_1')\mathrm{N}'\}]\ . \quad (7)\end{aligned}$$

Now we can write the equations (4), (5), (6), (7) in the form

$$\begin{aligned}\mathrm{L}+\mathrm{N}&=\mathrm{L}'+\mathrm{N}',\\ k\mathrm{L}+n_1\mathrm{N}&=-k\mathrm{L}'-n_1'\mathrm{N}',\\ 2k^2\rho\nu\mathrm{L}+n_2\mathrm{N}&=2k^2\rho'\nu'\mathrm{L}'+n_2'\mathrm{N}',\\ l_1\mathrm{L}+n_3\mathrm{N}&=l_1'\mathrm{L}'+n_3'\mathrm{N}'.\end{aligned}$$

The eliminant of $\mathrm{L}_1\mathrm{N}_1\mathrm{L}_1'\mathrm{N}'$ is the required period equation,

$$\begin{vmatrix} k & n_1 & k & n_1' \\ 2k^2\rho\nu & n_2 & -2k^2\rho'\nu' & -n_2' \\ l_1 & n_3 & -l_1' & -n_3' \\ 1 & 1 & -1 & -1 \end{vmatrix}=0.$$

§7. We can approximate to the solution of this equation on the supposition that ν and ν' are both small. Now it may easily be shown that the term of highest order in n_1 is of the order $\nu^{-\frac{1}{2}}$, those in l_1, n_2, n_3 are of the order 1. Hence retaining the terms of the two highest orders only in the period equation, it reduces to

$$\begin{aligned}(l_1-l_1')(n_1n_2'+n_2n_1')+kn_2(-l_1-l_1'+2n_3')\\ +kn_2'(l_1+l_1'-2n_3)=0.\end{aligned}$$

The first approximation is given by

$$l_1-l_1'=0.$$

Now to our order of approximation

$$\begin{aligned}l_1&=(gk^2/\alpha_0+k\alpha_0-\iota k\mathrm{C})\rho,\\ l_1'&=(gk^2/\alpha_0-k\alpha_0-\iota k\mathrm{C}')\rho'.\end{aligned}$$

Hence

$$(\rho-\rho')gk^2+(\rho+\rho')k\alpha_0^2-\iota k(\mathrm{C}\rho-\mathrm{C}'\rho')\alpha_0=0,$$

where α_0 has been written instead of $\alpha+ik\mathrm{B}$.

This equation leads to the solution

$$\alpha_0 = \pm i[\{(\mathrm{C}\rho - \mathrm{C}'\rho')^2 + 4gk(\rho^2 - \rho'^2)\}^{\frac{1}{2}} \pm (\mathrm{C}\rho - \mathrm{C}'\rho')]/2(\rho + \rho')$$
$$= \beta(\text{say}),$$

like signs being taken together.

There are two modes propagated in opposite directions with different velocities relatively to the stream velocity at the interface. If $\mathrm{C}\rho = \mathrm{C}'\rho'$, we obtain the usual result.

For the purposes of the next approximation we have to substitute

$$\begin{aligned} n_1 &= (\alpha_0/\nu)^{\frac{1}{2}} - 5ik\mathrm{C}/4\alpha_0, \\ n_1' &= (\alpha_0/\nu')^{\frac{1}{2}} + 5ik\mathrm{C}'/4\alpha_0, \\ n_2 &= \rho\alpha_0 - 5ik\mathrm{C}\rho/2(\alpha_0\nu)^{\frac{1}{2}}, \\ n_2' &= \rho'\alpha_0 + 5ik\mathrm{C}'\rho'/2(\alpha_0\nu')^{\frac{1}{2}}, \\ n_3 &= gk^2\rho/\alpha_0, \\ n_3' &= gk^2\rho'/\alpha_0. \end{aligned}$$

In these approximate values the quantities R, S, T, W are not sufficiently important to contribute any term, and therefore might have been omitted. But this would have given the solution the appearance of being correct to the first power of $ik\mathrm{C}/(\alpha + ik\mathrm{B})$ only, instead of to the second, as we require it to be.

To a second approximation $\alpha_0 = \beta + \gamma$, where it is quite easily shown that

$$\gamma = \pm(1 \pm i)\frac{k\rho\rho'(\rho - \rho')(\nu\nu')^{\frac{1}{2}}[\mathrm{S}^{\frac{1}{2}} \pm (\mathrm{C}\rho - \mathrm{C}'\rho')]^{\frac{1}{2}}}{(\rho + \rho')^{\frac{3}{2}}(\rho\sqrt{\nu'} + \rho'\sqrt{\nu})} \times$$
$$\frac{4gk(\rho + \rho') + (\mathrm{C}\rho - \mathrm{C}'\rho')(\mathrm{C} + \mathrm{C}') \pm (\mathrm{C}' + \mathrm{C}')\mathrm{S}^{\frac{1}{2}}}{4gk(\rho^2 - \rho'^2) + (\mathrm{C}\rho - \mathrm{C}'\rho')^2 \pm (\mathrm{C}\rho - \mathrm{C}'\rho')\mathrm{S}^{\frac{1}{2}}},$$

where $$\mathrm{S} = (\mathrm{C}\rho - \mathrm{C}'\rho')^2 + 4gk(\rho^2 - \rho'^2).$$

With the exception of the first choice of signs, like signs are to be taken together.

This result can be verified by putting $\mathrm{C} = \mathrm{C}' = 0$. It then agrees with the former result * for two superposed fluids at rest, provided we take the negative sign in the first choice.

The sign of the real part depends upon that of

$$-\frac{4gk(\rho + \rho') + (\mathrm{C}\rho - \mathrm{C}'\rho')(\mathrm{C} + \mathrm{C}') \pm (\mathrm{C} + \mathrm{C}')\mathrm{S}^{\frac{1}{2}}}{4gk(\rho^2 - \rho'^2) + (\mathrm{C}\rho - \mathrm{C}'\rho')^2 \pm (\mathrm{C}\rho - \mathrm{C}'\rho')\mathrm{S}^{\frac{1}{2}}}.$$

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* Proc. Lond. Math. Soc., ser. 2, vol. vi. p. 399 (1908).

(*a*) $C\rho > C'\rho'$.

Now when k is very small

$$\left[\frac{4gk(\rho+\rho')}{C+C'}+(C\rho-C'\rho')\right]^2-S$$

$$=4gk(\rho+\rho')\{2(C\rho-C'\rho')-(\rho-\rho')(C+C')\}/(C+C')$$

$$=4gk(\rho+\rho')^2(C-C')/(C+C').$$

Thus the numerator can be negative when $C<C'$, but the denominator can never be negative. Hence the motion is unstable for disturbances of great wave-length when $C<C'$. Remembering that $C\rho>C'\rho'$, and that $\nu\rho C=\nu'\rho'C'$, these conditions are equivalent to $\nu'\rho'<\nu\rho$, and $\nu'>\nu$. These two inequalities are not inconsistent with $\rho>\rho'$, and hence under these circumstances the interface will be unstable for waves propagated in one direction of length greater than some limit.

(*b*) $C\rho<C'\rho'$.

As before, the denominator is always positive. The numerator corresponding to one mode will always be negative when k is small, and in consequence the interface will be unstable. Since $\nu\rho C=\nu'\rho'C'$, we have shown that, if $\nu'<\nu$, the motion is unstable for waves of great wave-length.

Thus putting the two cases together we have shown that,

if $\qquad \nu'\rho'<\nu\rho,\quad \nu'>\nu,$

or if $\qquad \nu'<\nu,$

the motion will be unstable for great wave-lengths. Taking into account the fact that $\rho'<\rho$, these two cases are both included in the inequality $\nu'\rho'<\nu\rho$.

There still remains the question of the validity of the assumption that ikC is small in comparison with $\alpha+\iota kB$, or α_0. Now from the expression for α_0 it is quite evident that this is satisfied, except when k is very large, without the necessity of assuming that C is small, if the C. G. S. system of units be used.

It is to be noticed that $(\alpha+ikB)$ and ikC are not of the same dimensions, and therefore the assumption that ikC is small compared with $(\alpha+ikB)$ may not lead to a solution valid when y is great. But this does not affect the form of the solution when y is small, which is all we require to know for the present purpose.

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L. *On the Nature of the Transition Layer between Two Adjacent Phases.* *By* WM. C. McC. LEWIS, *M.A., D.Sc., Physical Chemistry Laboratory, University College, London* *.

IT is well known that the "internal pressure" or "molecular pressure" in a liquid is included in the van der Waals' equation as the correction term $\frac{a}{v^2}$. Obviously the numerical values obtained for the internal pressure by the calculation of a and v will be average values obtaining throughout the bulk of the liquid. Let us denote such values by K_m. For the particular case of water at 0° C. van der Waals himself has calculated K_m to be 10500–10700 atmospheres †. There is another method, however, first proposed by Dupré (*Théorie Mécanique de la Chaleur*, Paris, 1869), viz., that K is the work required to remove *unit volume* from the surface layer in the form of very thin laminæ, and carry them outside the range of their mutual attraction. In other words, K is the internal work required to vaporize unit volume of the liquid at the given temperature. Lord Rayleigh in his work on "The Theory of Surface Forces" (Phil. Mag. xxx. p. 285, 1890; Scientific Papers, vol. iii. p. 396), states that "this view appears to be substantially sound." Assuming that the volume of one gram of water is approximately the same in the bulk of the liquid and in the surface layer one finds that for water at 0° C. the value for the internal pressure comes out to be about 25,000 atmospheres, *i. e.*, there is a large discrepancy between K_m and $K_{\text{Dupré}}$. Other substances show the same peculiarity, viz.:—

Ether	$K_m = 1300–1430$ atm.	$K_{\text{Dupré}} = 2426$ atm.
Ethyl alcohol......	$K_m = 2100–2400$,,	$K_{\text{Dupré}} = 7266$,,
Carbon disulphide	$K_m = 2890–2900$,,	$K_{\text{Dupré}} = 4704$,,

The differences are so large that they can hardly be regarded as accidental, so that one is forced to the conclusion that the internal pressure in the surface (call it K_s) is considerably greater than the average bulk value K_m. This

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* Communicated by the Author.

† An attempt at calculating how K_m varies with temperature is rendered very difficult owing to the fact that van der Waals' "a" is anything but constant. Thus, taking as our units atmosphere, litre, grammole, for pressure, volume, and mass respectively, the value of a at 0° C. is 3·467; at 100° C. $a = 3·29$ (according to Traube), and at the critical temp. 362°·4 C. $a = 5·77$ as calculated from the critical data. The inconstancy of "b" is even more marked, but does not concern us here.

further suggests that the *average* density in the surface layer (call it σ_s gram/c.c.) is larger than σ_m, the bulk value, though this conclusion really widens the difference between the two sets of values. As a matter of fact, as will be shown later, the values of K_s at ordinary temperature for water appears to be of the order of 50,000 atmospheres.

We can see the connexion between $K_m, K_s, \sigma_m, \sigma_s$ most clearly by making use of the Laplace expression for molecular attraction. The general expression developed by Laplace for the internal pressure is (employing the usual symbols)

$$K = \sigma^2 \int_0^{\infty = c} \psi(z) dz$$

(c is the range of molecular action).

For the bulk of the liquid, therefore,

$$K_m = \sigma_m^2 \int_0^{\infty} \psi(z)\, dz.$$

For the surface layer

$$K_s = \sigma_s^2 \int_0^{\infty} \psi(z)\, dz,$$

and therefore,

$$\sigma_s = \sigma_m \sqrt{\frac{K_s}{K_m}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This expression is, however, not much use to us as it stands, since it contains two unknowns, σ_s and K_s. For the same reason the value of σ_s cannot be obtained from what might be called a corrected form of the Dupré relationship. Thus σ_s is of course $\frac{1}{\nu_s}$, where ν_s is the average volume of 1 gram of the substance in the surface layer (the corresponding quantities in the bulk of the liquid being σ_m and ν_m). It is usual to call ν_m or ν_s "specific volumes." Further, if λ_i represents the internal latent heat of vaporization of 1 gram, then Dupré's relationship is

$$K_s = \frac{\lambda_i}{\nu_s}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

To determine ν_s or σ we must have recourse to Bakker's relationship—which also requires a slight modification if we are to regard ν_s and ν_m as differing in numerical value.

Bakker's Relationship.

Bakker *, in 1888, was the first to point out that the latent heat of vaporization is given by the expression

$$\lambda = \int_{\nu_{\text{fl}}}^{\nu_{\text{gas}}} \mathrm{K}dv + p(\nu_{\text{gas}} - \nu_{\text{fl}}),$$

where ν_{fl} denotes the specific volume of the liquid. In view of the considerations advanced above one can no longer speak of magnitudes as pertaining to the liquid state only, but must further specify whether bulk or surface. Evidently here we are dealing with surface quantities, so that with corresponding notation

$$\lambda = \int_{\nu_s}^{\nu_{\text{gas}}} \mathrm{K}_s dv + p(\nu_{\text{gas}} - \nu_s)$$

(λ is the latent heat, external and internal, per gram).

Further, van der Waals' equation gives us for the surface layer

$$\mathrm{K}_s = \frac{a}{\nu_s^2},$$

so that on integration the above expression becomes

$$\lambda = a\left(\frac{1}{\nu_s} - \frac{1}{\nu_{\text{gas}}}\right) + p\,(\nu_{\text{gas}} - \nu_s),$$

or approximately,

$$\lambda = \frac{a}{\nu_s} + \frac{\mathrm{RT}}{\mathrm{M}} \quad \text{or} \quad \lambda_i = \frac{a}{\nu_s}, \quad . \quad . \quad . \quad . \quad (3)$$

where M is the molecular weight of the liquid in the state of vapour.

The connexion between Bakker's relationship and Dupré's expression is obvious.

By means of equation (3) we can calculate ν_s knowing λ_i and a. This has been done for a number of chemical compounds given in the following table, which is partly taken from a list compiled by J. Traube †. The values refer to the boiling-point of the respective compounds.

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* G. Bakker, Dissertation, Schiedam, 1888.

† J. Traube, *Ann. d. Physik* [4] xiii. p. 300 (1902).

TABLE I.

Substance.	Molecular weight in grams.	$t°$ C.	λ. Cals. per gram.	λ_i.		a_t litre² atmos. unit of mass = gram mol.	a_K*. litre² atmos. unit of mass = gram mol.	a_t litre² atmos. unit of mass = 1 gram.	v_s in cc.	σ_s gram/cc.	σ_m gram/cc.	$\frac{\sigma_s}{\sigma_m}$
				Cals. per gram.	Litre atmos. per gram							
Mercury	200·3	360·0	62·0	55·3	2·322	8·68	—	0·0002164	0·09319	10·73	12·74	0·84
Isopentane	72·1	28·0	83·2	74·9	3·146	11·23	18·20	0·002160	0·6868	1·456	0·6115	2·48
n Hexane	86·1	69·0	79·4	72·2	3·032	15·37	24·58	0·002073	0·6837	1·462	0·6142	2·38
n Heptane	100·1	98·4	74·0	66·5	2·793	18·69	30·85	0·001865	0·6677	1·497	0·6139	2·44
n Octane	114·2	125·8	70·84	63·8	2·679	22·17	36·58	0·001700	0·6345	1·576	0·6120	2·57
Ether	74·1	34·8	84·5	76·2	1·814	10·56	17·44	0·001923	1·058	0·9432	0·695	1·36
Carbon tetrachloride .	153·8	76·2	46·35	41·8	1·756	12·04	19·20	0·0005114	0·2912	3·444	1·4802	2·33
Zinc chloride...........	260·3	112·5	30·53	27·6	1·159	16·05	26·94	0·0002368	0·2043	4·895	1·983	2·47
Benzene.................	78·04	80·25	93·45	84·4	3·544	11·13	18·36	0·001827	0·5154	1·940	0·811	2·39
Fluor-benzene	96·06	85·1	79·1	71·3	2·994	12·11	19·95	0·001312	0·4381	2·282	0·9433	2·42
Chloro-benzene....... .	112·45	132·0	72·0	64·8	2·721	15·51	25·54	0·001227	0·4508	2·218	0·9836	2·26
Methyl formiate	60·0	32·9	116·1	105·9	4·876	6·54	11·38	0·001817	0·3727	2·683	0·6569	4·08(?)
Ethyl acetate	88·1	75·9	86·7	78·8	3·309	11·79	20·47	0·001519	0·4590	2·179	0·8311	2·62
Methyl propionate ...	88·1	80·0	84·2	76·2	3·200	11·24	20·24	0·001447	0·4523	2·211	0·8422	2·62
Methyl alcohol	32·0	64·5	267·48	246·8	10·360	5·08	9·53	0·004963	0·4792	2·086	0·7475	2·79
Acetic acid...............	60·0	119·2	89·8	111·4	4·677	8·29	17·60	0·002302	0·3909	2·558	0·9372	2·73
Water.....................	18·0	100·0	536·5	495·2	20·800	3·29	5·77	0·01050	0·5048	1·981	0·9584	2·07

* a_K is the value of a at the critical temperature. These values are inserted for comparison with a_t. The remaining data are calculated from a_t.

It is evident from the foregoing table that the average surface densities are distinctly greater than the bulk densities—in fact, approximately 2·5 times the bulk density for the above-mentioned liquids.

In view of the apparent generality of the phenomenon of increased surface-density (over bulk) one is naturally led to inquire how far this may be connected with, or exert an influence upon, the molecular surface energy, which in the hands of Eötvös [*] from the theoretical standpoint, and later in the hands of Ramsay and Shields [†] from the experimental, constitutes the basis of all our numerical conceptions of molecular complexity, or state of aggregation in pure liquids. Eötvös showed that the temperature coefficient of the molecular surface energy would follow the same curve for all liquids. Having carried out experiments with ether he found that $\frac{d\gamma(\mathrm{M}v)^{\frac{2}{3}}}{dt}$ was constant over a wide range of temperature, and therefore of course this linear relationship should hold for all liquids. Since the expression includes the surface tension γ it is evident that in the first instance at any rate any deductions as to molecular state must be applied to the surface layer, and it is rather curious that the mean numerical value for "normal" liquids comes out 2·1, a number not differing much from the $\frac{\sigma_s}{\sigma_m}$ ratio 2·5.

It might therefore be thought at first sight that "molecular complexity" was simply a different degree of surface density, but that this is *not* so is amply demonstrated by the fact that such characteristically "non-associated" (normal) liquids as the esters and hydrocarbons (aliphatic and aromatic) have practically the same $\frac{\sigma_s}{\sigma_m}$ ratio as bodies such as water, methyl alcohol, and acetic acid, which are characterized by marked association. Further, Eötvös' original considerations, depending as they do upon general principles of corresponding states, would be practically independent of surface density changes as long as the surface was in equilibrium with the bulk, which of course is the case [‡].

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[*] Eötvös, Wied. *Ann.* xxvii. p. 448 (1885).

[†] Ramsay and Shields, *Zeitsch. für phys. Chemie,* xii. p. 433 (1893).

[‡] The form of Eötvös' expression does require a little modification, but the conclusions as to complexity will probably not be altered.

The Surface-density of Water and its variation with Temperature.

This has been measured, as in the previous case, by means of equation (3). The temperature range is from 0° to 100° C. The value of "a" is due to van der Waals*, namely, 3·467 (units : gram molecule, atmosphere, litre). When we take the gram as unit this number becomes 0·0107. It is regarded as constant throughout the range of temperature, which is approximately correct as long as we are sufficiently far distant from the critical temperature. (The value for a found for 100° C. is 0·0105 on the same units, *cf.* foregoing

Table II.—Water : Surface density.

Temperature ° C.	Bulk density, gram/c.c. σ_m.	Bulk Specific Volume, $V_m=\frac{1}{\sigma_m}$.	Latent heat, cals. per gram. λ.	$\frac{RT}{M}$ (when M=18). (cals.)
3·61	1·0000	1·0000	588·4	30·78
13·95	0·9993	1·0007	584·74	31·89
25·14	0·9971	1·0029	580·13	33·11
37·31	0·9935	1·0066	574·35	34·45
50·64	0·9880	1·0120	567·26	35·99
65·36	0·9807	1·0196	558·62	37·56
81·71	0·9707	1·0302	548·19	39·45
100·0	0·9587	1·0431	535·78	41·45

Temperature 0° C.	λ_1 in cals.	λ_1 in litre atmospheres.	V_s in c.c.	$\sigma_s=\frac{1}{V_s}$ gram/c.c.	$\frac{\sigma_s}{\sigma_m}$.
3·61	557·6	23·42	0·4568	2·189	2·189
13·95	552·9	23·21	0·4610	2·169	2·171
25·14	547·0	22·97	0·4658	2·147	2·153
37·31	539·9	22·68	0·4719	2·119	2·133
50·64	531·3	22·31	0·4796	2·084	2·109
65·36	521·1	21·89	0·4888	2·046	2·086
81·71	508·7	21·36	0·5009	1·996	2·056
100·0	494·3	20·76	0·5153	1·940	2·023

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* This value of "a" gives K_m : 10700 atmospheres at 0° C. (*Continuität*," etc.)

Table.) The values of the latent heat are those of Winkelmann, Wied. *Ann.* ix. p. 338 (1880).

It will be seen that σ_s and σ_m converge slightly with rising temperature. This convergence no doubt becomes abrupt as we approach the critical temperature, where of course $\sigma_m = \sigma_s = \sigma_{\text{vapour}}$.

The Internal Pressure of Water in the bulk of the liquid and in the surface-layer, and its variation with Temperature.

Having obtained values for the specific volumes in the surface-layer and bulk, we calculate the corresponding internal pressures by equation (1) or (2). The results are given in the following Table. I have here calculated the values of K_m and K_s, first assuming that van der Waals' constant a has the value 0·0107 (and remains constant); secondly, a is assumed to be 0·0178, its value for the critical temperature. The values of K_m and K_s are no doubt far from the truth when calculated on the second assumption, since the temperature range 0–100° C. is fairly far removed from the critical region (364° C.). Comparison is, however, instructive as showing how the want of constancy in a is magnified when applied to internal pressure values. If a were really constant, K_s and K_m should vary only as the respective specific volumes.

Table III.—Internal Pressure of Water at different Temperatures.

Temperature, 0° C.	$K_m = \frac{a}{v_m^2}$ (a=0·0107).	$K_s = \frac{a}{v_s^2}$ (a=0·0107).	$K_m = \frac{a}{v_m^2}$ (a=0·0178).	$K_s = \frac{a}{v_s^2}$ (a=0·0178).
	atmospheres.	atmospheres.	atmospheres.	atmospheres.
3·61	10,700	51,260	17,810	30,800
13·95	10,650	50,350	17,720	30,260
25·14	10,640	49,320	17,700	29,630
37·31	10,560	48,060	17,560	28,880
50·64	10,450	46,510	17,390	27,960
65·36	10,290	44,790	17,120	26,920
81·71	10,080	42,600	16,770	25,630
100·0	9,840	41,290	16,370	24,210

Calculation of the Heat-effect per unit surface area due to the surface change in density.

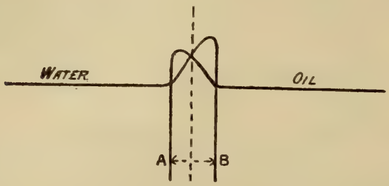
It is evident from Table II. that the surface-density approximates more nearly to the bulk density the higher the temperature. It follows therefore according to the principle of Le Chatelier that the density increase is accompanied by an evolution of heat.

The internal latent heat of vaporization is the amount required to remove one gram of the liquid from the surface-layer, and taking into account Stefan's law, the same amount of work accompanies the passage of one gram from the bulk of the liquid into the surface when new surface is formed thereby. In water at 0° C. this heat-effect is about 570 cals. Water suffers a density increase of 1·189 gram/c.c. as we pass from bulk to surface. If we take the thickness of the transition layer to be 5×10^{-6} cm. (Quincke's value for the average range of molecular action), then each unit of surface area corresponds to a surface slab of liquid 5×10^{-6} c.c. possessing a mass of $2{\cdot}189 \times 5 \times 10^{-6}$ gram. If there had been no surface-density changes the same slab would have had a mass of 5×10^{-6} gram. Each additional sq. cm. of surface is therefore associated with the transfer of $1{\cdot}189 \times 5 \times 10^{-6}$ gram of liquid. The heat-effect due to this quantity transferred would be 0·0034 cal. In this connexion one might draw attention to the value obtained experimentally by J. G. Parks (Phil. Mag. iv. p. 240, 1902) for the heat given out on moistening powders (such as silica) with water. The cause of the heat-effect is ascribed to surface-density changes in the water where solid and liquid meet. The heat evolution per sq. cm. of powder is 0·00105 cal.—a number which is of quite the same order of magnitude as that calculated for the case water/vapour.

The general structure of the Surface-layer.

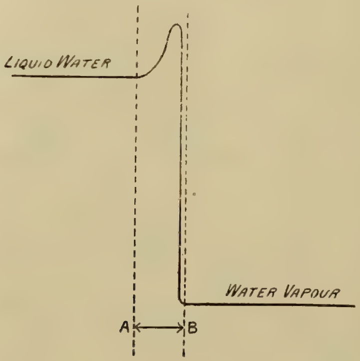
Willard Gibbs in his celebrated memoir was one of the first to point out that a surface-layer is in general heterogeneous, as, for example, oil in contact with water. The density changes of each phase do not consist in a steady and rapid fall or rise as we traverse the layer from one side to the other, but if the considerations put forward in this paper are correct the density of each phase will pass through a maximum before falling to zero. The water-oil case might be represented thus (fig. 1):

Fig. 1.



The vertical dotted line represents the imaginary mathematical "surface"; the distance AB represents the thickness of the heterogeneous layer, the horizontal lines representing the constant bulk densities on each side. For the case of a liquid in contact with its own vapour, we obtain (fig. 2):

Fig. 2.



The magnitudes denoted by σ_s and K_s are the *average* values over the layer as a whole—the actual values over any small portion of layer may be considerably greater or less than these.

Summary.

1. The values for the internal pressure in a liquid, as obtained by the Bakker-Dupré method of calculation, are considerably larger than those calculated from van der Waals's equation. A cause for this is sought in the assumption that the density in the surface-layer is greater than in the bulk.

2. A table is given showing the average values for the surface density of a number of liquids at their boiling-points.

3. A table is also given showing the variation of the surface density of water with temperature; the temperature variations of the internal pressure, both in the bulk of the liquid and in the surface-layer, are likewise tabulated.

4. The heat effect involved in this density change is calculated per unit area of surface and is found to be 0·0034 cal.—a quantity which agrees approximately with Parks' analogous determinations.

I should like to take this opportunity of expressing my indebtedness to Prof. W. B. Morton, the Queen's University, Belfast, and to Prof. A. W. Porter, University College, London.

LI. *On the Lagging of Pipes and Wires. By* ALFRED W. PORTER, *B.Sc., Fellow of, and Assistant-Professor of Physics in, University College, London; with an Addendum in conjunction with* Mr. E. R. MARTIN, *B.Sc.*[*]

THE effect of surrounding a pipe or wire with a lagging material does not seem to be perfectly understood. A coat of poor thermal conductivity may keep a hot pipe *cooler* than it would be without such a coat. The problem occurred to me a few years ago in working out examples to set to a class of senior students; but it is also a problem of practical importance, especially in connexion with laboratory apparatus. On looking the question up I find only a reference to such an effect in a paper by Professor Bottomley (Roy. Soc. Proc. vol. xxxvii. 1885), where it is shown experimentally that a difference of a degree or so can exist between two equal wires carrying the same current, one of them coated with a thin coating of various materials such as shellac, while the other is bare; the coated one being the cooler of the two. Such experiments as these give, however, an entirely inadequate notion of the possible magnitude of the effect as the sequel will show[†]. A striking experiment is to take a thin platinum wire and coat it at intervals with a thin layer of glass—which is easily fused round the wire. If a suitable current be now passed through the wire the uncoated portions may

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[*] Communicated by the Author.

[†] From a remark in Professor Bottomley's paper I gather that Lord Kelvin was aware of the anomalous results to be expected. The matter, however, seems to have dropped out of sight owing to the lack of success in obtaining any experimental support.

be made nearly white hot, while those parts which are covered with glass *do not even glow.* In such a case there are several hundreds of degrees difference in the temperature of neighbouring portions of the wire. This experimental result accounts for the platinum wire sealed into an ordinary incandescent lamp remaining as cool as it does.

The problem in its simplest form.

A cylindrical wire of good conducting material and radius a is surrounded by a concentric sheath of radius b and thermal conductivity k. The wire is heated by means of an electric current or otherwise to a constant uniform temperature by a rate of supply of heat H per unit length of the wire. Then if the thermal emissivity from the outside of the sheath is e we have

$$\begin{aligned} \mathrm{H} &= -k \, . \, 2\pi a \left(\frac{\partial \theta}{\partial r} \right)_a = -k \, . \, 2\pi r \frac{\partial \theta}{\partial r} \\ &= e \, . \, 2\pi b \theta_b, \end{aligned}$$

where θ_b is the temperature of the outside of the sheath, and $\left(\frac{\partial \theta}{\partial r} \right)_a$ is the slope of temperature in the sheath at its inner surface. The corresponding solution for the temperature of the wire is

$$\theta_a = \frac{\mathrm{H}}{2\pi} \left\{ \frac{1}{be} + \frac{1}{k} \log_\epsilon \frac{b}{a} \right\},$$

where θ_a is the temperature of the wire.

To find the effect of changing the thickness of the coating we differentiate this equation with respect to b: giving

$$\frac{\partial \theta_a}{\partial b} = \frac{\mathrm{H}}{2\pi} \left\{ -\frac{1}{b^2 e} + \frac{1}{kb} \right\}.$$

The effect then is to increase θ_a (for a given rate of supply of heat) provided that b is greater than k/e; the coating under these conditions acts as a lagger. But if b is less than this critical value the effect of its increase is reversed; the coating under these circumstances promotes the outward flow of heat. This critical value if it exists is *independent of the radius of the wire*; but it must be noted that since b can never be less than a, it is possible that for a particular wire it does not exist. To find out the likelihood of its occurrence we must examine the values of k and e which will probably enter into account.

The old values of the thermal conductivities of badly conducting materials still given in most text-books are mainly due to Forbes. They have been shown, however, to be completely untrustworthy. The values employed here are those obtained by Dr. C. H. Lees by Sir O. Lodge's method (Trans. Roy. Soc. A. vol. 183. 1892, p. 481).

With regard to the emissivity there is more indefiniteness as it depends, when the body is in air, not only upon the nature of the surface but upon its radius, as was first shown by Péclet. Provided, however, that we do not consider sheaths whose radius is very small, we may take ·0003 as a fair value.

The critical values of b are then as given in the following table :—

TABLE I.

Material.	Thermal conductivity.	Critical radius in centimetres.
Crown glass	·00243	8·1
Slate	·0047	16
Shellac	·0006	2
Para rubber	·00038	1·3
Gutta-percha	·00046	1·5
Paper	·00031	1·0
Asbestos paper	·00057	1·9
Cork	·00013	·4
Silk	·00022	·7
Cotton	·00055	1·8
Flannel	·00023	·8
*Magnesia (Pattinson's Light Calcined)	·00016	·5

* Hutton & Beard, Faraday Society, July 1905.

Here we have the somewhat startling result that coating a wire with glass up to 8 cms. radius is more and more detrimental to the maintenance of a high temperature in the wire the thicker the coat is within this range. For gutta-percha the range is up to 1½ cms., and so on for other substances.

If the coating has an outer radius greater than the critical one the action begins to reverse. But an examination of the formula shows that the improvement (from the point of view of effectiveness in lagging) is very slow, depending ultimately upon a logarithmic term. The result is that very considerable thicknesses must be attained before the temperature of the wire will become the same as if there were no lagging in it at all. This point is reached when

$$\frac{1}{be}+\frac{1}{k}\log b=\frac{1}{ae}+\frac{1}{k}\log a.$$

This second radius, which may be called the *neutral* radius for the particular bare wire, because for it the total temperature effect of the lagging material is zero, is not independent of the radius of the wire. It is not possible to express it, therefore, quite so simply. It is obvious, however, that it corresponds to the value of b for which the expression $\frac{1}{be}+\frac{1}{k}\log b$ has the same value as for the uncoated wire. If then the value of this expression be calculated for various values of b and be plotted against b, then the radius of the bare wire and the corresponding neutral radius are the two values of b for which the ordinates are equal. Corresponding values so read off from a curve are tabulated with sufficient accuracy in Table II.

TABLE II.—Para Rubber.

$k=\cdot0004$. $e=\cdot0004$.

Radius of bare wire.	Neutral radius.
·25 cm.	10 cm.
·32	5·8
·50	2·9
1·00	Critical 1·00

In order to test these results a thin platinum wire (·02 cm. radius) was coated along a part of its length with glass so that the outside radius was ·1 cm. When a current is passed through the wire the uncoated portion may be made nearly white-hot without any sensible glow occurring in the coated portions. This is the nature of the result to be expected even from the above simplified theory, for it gives

$$\frac{\text{Temperature excess of uncoated wire}}{\text{Temperature excess of coated wire}}=\frac{1}{a\left(\frac{1}{b}+\frac{1}{b_c}\log\frac{b}{a}\right)},$$

where $b_c\equiv$ the critical radius.

In the above case this ratio is 5 nearly. It should be observed in passing that the logarithmic term scarcely affects the ratio, and this will usually be so when b is small compared with the critical radius.

Thus if the uncoated is raised to 1600° C. the coated will be only at 330° C.

Deviations from simple theory.

Where the difference of temperature is so considerable it is of course not sufficient to consider the various data as independent of the temperature. In this experiment the same current passes through both portions of the wire, and therefore, owing to the change of specific resistance with temperature, the rate of generation of heat in equal portions is not the same. If α is the coefficient of increase of resistance with temperature, ρ_0 the specific resistance at atmospheric temperature, and C the current, the equation becomes

$$\theta_a = \frac{\rho_0(1+\alpha\theta_a)\,\mathrm{C}^2}{2\pi^2 a^2}\left\{\frac{1}{be}+\frac{1}{k}\log\frac{b}{a}\right\},$$

or

$$\frac{\theta}{1+\alpha\theta_a} = \mathrm{A}\left\{\frac{1}{be}+\frac{1}{k}\log\frac{b}{a}\right\}.$$

The critical radius is still $b=k/e$, but $\theta_a/(1+\alpha\theta_a)$, say Θ, takes the place of θ_a. Hence for the given wire and coat we have:

$$\Theta_{\text{uncoated}}/\Theta_{\text{coated}} = 5 \text{ nearly};$$

and if α be taken as ·004 this gives a temperature of about 50° C. for the coated portion when the uncoated is at 1600° C. The increase in the resistance with temperature has thus a very large intensifying action. The value of $(1+{\cdot}004\,\theta_a)$ may be called the "intensifying ratio" due to the resistance change. Its value for different values of θ_a is given in Table III.

TABLE III.

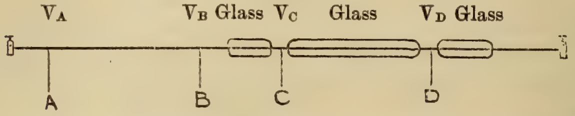
θ_a.	$1+{\cdot}004\,\theta_a$.
0	1
100	1·4
500	3·0
1000	5·0
2000	9·0

That is to say, a current which would maintain a wire at 200° excess with a given coat if the resistance remained constant (as it would do approximately in the case of an alloy) will heat it to 1000° C. in the case of a metal for which $\alpha={\cdot}004$ (as it approximately is for pure metals).

Experimental.

It was considered to be of value to determine the actual temperatures acquired by the different portions of the wire. For this purpose a wire was prepared with potentiometer leads A, B, C, D, arranged as in fig. 1.

Fig. 1.



The two short lengths of glass-covering eliminate the end-effects of the coated portion. The distance from A to B is made as nearly as possible equal to that from C to D. The differences of potential V_A-V_B and V_C-V_D when various steady currents (measured by a shunted Sullivan galvanometer) flow in the wire were determined by means of high resistance galvanometers which were calibrated for the purpose. The temperature coefficient of the platinum wire was determined, also the value of V_A-V_B corresponding to a measured *small* current—the wire being immersed in oil—in which case the wire was assumed to be at the temperature of the oil. From these data the temperatures of the two portions of the wire were calculated. There is no need to give the readings as only rough values were aimed at. The temperature-excesses (above 18° C. which was the room temperature) are given in Table IV.

Table IV.

Uncovered.	Covered.	Ratio.
832	152	5·5
702	117	6·0
112	32	3·5
87	15	5·8

The radius of the bare wire was ·015 cm. and of its covering ·235 cm.

Great as the ratio of excess temperatures is, it is not nearly as great a number as the "simple theory" requires, viz. 15. Still less does it come up to the requirements of the theory when allowance is made for resistance change. Similar observations were made on a nickel wire partly coated with gutta-percha. The results in this case are given in Table V.

Table V.—Nickel wire and Gutta-percha.

$a = {\cdot}025$ cm. $b = {\cdot}175$ cm.

Excess temperatures.

Uncovered.	Covered.	Ratio.
19	14	1·36
31	18	1·70
36	25	1·44
65	27	2·4
67	24	2·7
77	42	1·8
111	51	2·2

The simple theory would require a ratio of about 6.

The cause of the discrepancy is to be sought for in the variation of emissivity and thermal conductivity with the temperature, and in the case of emissivity with the radius also. The last cause is in fact exceedingly important in the case of wires so fine as those used in these experiments. The ratio Θ_a/Θ_b should in fact be more nearly

$$\frac{b}{a}\cdot\frac{\mathrm{E}_b}{\mathrm{E}_a},$$

than $\frac{b}{a}$, where E_b is the emissivity for the covering and E_a is that for the wire. In the case of the platinum wire at about 100° excess E_a is perhaps as much as 7 times E_b, hence a ratio of 15 is at once lowered to about 2.

The full and satisfactory consideration of the question requires, therefore, a complete knowledge of the variation of the various data with temperature. In the absence of this it scarcely seems worth while to develop the theory much further owing to the increased complication. The following formulation may, however, be found useful in case the question should be found of sufficient practical importance.

The differential equation to be solved is

$$k\frac{\partial\theta}{\partial r} = -\frac{\mathrm{H}}{2\pi r},$$

the solution of which is

$$K_a - K_b = \frac{H}{2\pi} \log \frac{b}{a},$$

where $$K_a = \int^a k d\theta.$$

Differentiating with regard to b we have

$$k_a \frac{d\theta_b}{db} = k_b \frac{d\theta_b}{db} + \frac{H}{2\pi b}.$$

Hence the critical radius is given by

$$\frac{d\theta_b}{db} = -\frac{H}{2\pi b k_b};$$

or since $$H = e \,.\, 2\pi b \theta_b,$$

$$\frac{1}{k_b b} = -\frac{d}{db}\left(\frac{1}{eb}\right),$$

where $$\frac{d}{db} = \frac{\partial}{\partial b} + \frac{d\theta_b}{db} \frac{\partial}{\partial \theta_b},$$

the values being those for b equal to the critical radius, and therefore

$$\frac{d\theta_b}{db} = -\frac{H}{2\pi b k_b}.$$

If we can neglect the variation of e with the radius at constant temperature as we can do when the radius ceases to be very small, the critical radius becomes

$$b_c = \frac{k_b}{e_b}\left(1 - \frac{H}{2\pi e_b k_b} \frac{\partial e}{\partial \theta_b}\right).$$

Thus the critical radius is seen to depend upon the rate of heat supply. The value in the simple theory is the value for a very slow supply of heat.

The above is worked out on the assumption that the value of H is constant.

ADDENDUM (*in conjunction with* Mr. E. R. MARTIN).

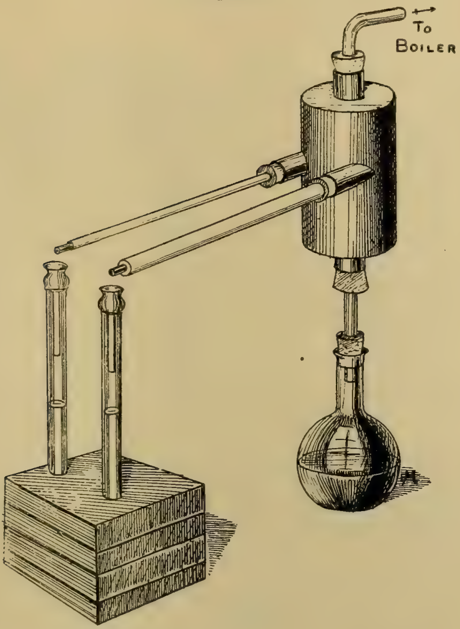
The lagging of steam-pipes.

A similar theorem to that proved above is, of course, valid also for the case of the condensation of steam in pipes. The amount of condensation is proportional to the escape of heat from the surface. We have as before

$$\theta_a = \frac{H}{2\pi}\left(\frac{1}{Eb} + \frac{1}{k} \log \frac{b}{a}\right).$$

In order to test this equation we have taken two thin brass tubes, each 30 cms. long and ·19 cm. external radius. These are inserted in a steam-trap (fig. 2) so that steam issues simultaneously from both. One of the tubes is coated in succession with increasing thicknesses of asbestos paper, while the other has throughout a single coating of asbestos paper, the object of this being to make the character of the surface as nearly as possible the same for both, and thus promote an equality in the values of the emissivity for them. Under the orifice of each tube is placed a collecting test-tube into which drops the steam which is condensed in the pipes. The amount collected from the more thickly coated pipe varies with the thickness of the coating. By taking the ratio of this amount to that collected from the thinly coated one, a value is obtained which may reasonably be taken as being more independent of varied conditions of the flow of the steam than if the value for a thin coating were determined once for all. The two tubes when coated each of them with a single layer did not correspond to equal condensation owing to some small difference of circumstance. The ratios obtained have subsequently been raised 5 per cent., so as to

Fig. 2.



change to unity the value corresponding to a single coat. This is merely equivalent to changing the standard to one which is more convenient for calculation. Several observations were made for each thickness; in the following table the mean values are alone tabulated:—

No. of Coats.	Outside radius.	Ratio of condensations $\frac{\text{Thick coat.}}{\text{Thin coat.}}$	R Ditto Reduced standard.
1	·234 cms.	·953	1·000
2	·275	·984	1·032
3	·318	1·068	1·122
4	·350	1·084	1·140
5	·397	1·099	1·154
6	·447	1·155	1·214
8	·514	1·234	1·296
10	·580	1·211	1·272
12	·671	1·180	1·239
14	·749	1·185	1·244
18	·890	1·161	1·217
—	1·194	1·070	1·125

The theoretic value for the ratio should be (assuming that the temperature at the external surface of the *brass* may be taken as constant throughout the experiments)

$$\text{Ratio} = \text{R} = \frac{\dfrac{1}{\cdot 234\text{E}} + \dfrac{1}{k}\log_\epsilon \dfrac{\cdot 234}{\cdot 19}}{\dfrac{1}{b\text{E}} + \dfrac{1}{k}\log_\epsilon \dfrac{b}{\cdot 19}},$$

where ·19 is the radius of the tube uncoated,
·234 „ „ with one coat,
E and k are emissivity and thermal conductivity of asbestos.
b = external radius of coated tube.

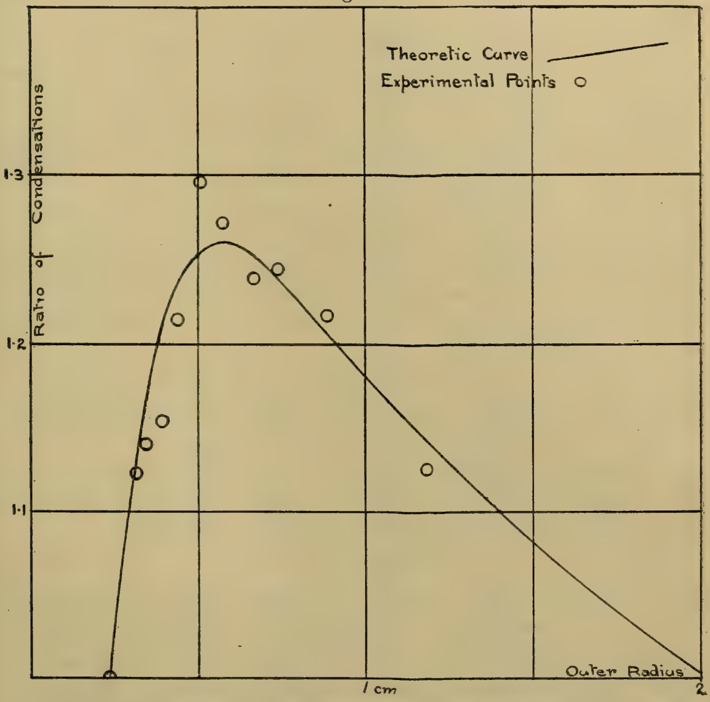
Now E and k both depend upon the excess temperature, and E depends also upon the radius. The experimental results are not accurate enough, however, to justify one in trying to take these variations into account. Assuming constancy in these data, it is easy to show that R should be a maximum when $b = \frac{k}{\text{E}}$. Now from the diagram the maximum is found to occur when b = ·57 cm. (about). The position of this maximum fixes the ratio of k to E. Putting the value of k derived from this value of b into the equation, the result is independent in any further way of both k and E ; the equation in fact becomes

$$R=\frac{\frac{1}{\cdot 234}+\frac{1}{\cdot 57}\log_\epsilon\frac{\cdot 234}{\cdot 19}}{\frac{1}{b}+\frac{1}{\cdot 57}\log_\epsilon\frac{b}{\cdot 19}}.$$

Thus it is unnecessary to know the absolute values of k and E, though we shall discuss these later on.

This theoretic equation is represented by the continuous curve on fig. 3. It will be seen that it corresponds with a fair amount of accuracy with the experimental values.

Fig. 3.



It was considered worth while to obtain the absolute values of the emissivity and conductivity of the asbestos paper employed. The former was obtained from the rate of cooling of a thinly coated bar, the temperatures being read by the thermoelectric potentiometer method. Plotting a curve of temperatures against time, and finding graphically the slope at the 100° point of the curve, the emissivity was calculated from the slope and the dimensions of the bar. The value so obtained was ·000275.

The thermal conductivity was measured by the slab method —a slab of about 300 sq. cm. area and of a thickness of ·245 cm. being pressed between a steam and a cold-water vessel. The temperatures of the cold water were read from minute to minute as they rose. Careful corrections were made for "radiation" loss from the cold vessel. Two distinct sets of readings were taken. The values of the conductivity obtained were ·000150 and ·000141 respectively. Taking the mean of these and employing the value obtained experimentally for the emissivity, viz. ·000275, the critical radius becomes ·527 cm. The value read off from fig. 3 is about ·57. The agreement is as good as was to be expected.

The conclusions to be drawn from these experiments are that:

(1) On narrow steam-pipes, up to about half a cm. external radius, the application of an asbestos coating encourages the escape of heat. This radius is below what may be termed engineering dimensions. But in experimental apparatus it is not at all an unusually small radius; and for such pipes the application of lagging is a delicate question.

(2) When the radius is much smaller than this critical value, the coat must have an external radius much greater than half a centimetre before the lagging efficiency is as good as without a coat at all. Thus, the curve would seem to show that the escape of heat is the same for external radii of ·24 cm. and 2·0 cms.

LII. *Relations between the Physical Properties of Liquids at the Boiling-Point.* *By* D. Tyrer[*].

A SIMPLE relation exists between the latent heat of vaporization of a liquid and the molecular volume at the boiling-point. The relation may be expressed

$$LM = K\sqrt[3]{V},$$

where L is the latent heat of a liquid at its boiling-point, V the molecular volume at the boiling-point, M the molecular weight, and K a constant. This relation, which may for the present be regarded as empirical, holds with a fair degree of accuracy for most classes of substances. In the Table given below the values of the molecular volumes are the mean values of the results chiefly of Kopp, Pierre, Schiff, Thorpe, Gartenmeister, and Young. In the last column are given the latent heats calculated according to the above equation, the value of K having been taken as 1583. This figure is the mean value of K for the aliphatic esters, calculated from the results of Schiff and J. C. Brown. As Brown's

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[*] Communicated by Prof. H. B. Dixon, F.R.S.

results are invariably higher than those of Schiff, the agreement between the calculated and observed values of the latent heat will not be so good in those cases where the results of only one of the above observers are known.

Liquid.	Molecular Volume V at the Boiling-Point.	Latent Heat (observed).	Authority.	Mean.	Latent Heat (calculated).
Propyl formate	107·0	85·25 90·36	Schiff Brown	87·80	85·41
Isobutyl formate	129·9	77·0 80·12	Schiff Brown	78·56	78·52
Isoamyl formate	151	71·65 73·75	Schiff Brown	72·70	72·60
Methyl acetate	83·7	98·26 97·0	Brown Ramsay & Marshall	97·63	93·57
Ethyl acetate	106·0	83·1 88·37	Schiff Brown	85·73	85·13
Propyl acetate	128·4	77·3 80·45	Schiff Brown	78·87	78·24
Butyl acetate	150·6	73·9	Brown	73·9	72·65
Isobutyl acetate	150·1	69·9 72·46	Schiff Brown	71·18	72·47
Isoamyl acetate	174	66·35 69·00	Schiff Brown	67·67	67·94
Methyl propionate	104·6	84·15 89·0	Schiff Brown	86·57	84·72
Propyl propionate	150·0	71·5 73·73	Schiff Brown	72·61	72·46
Ethyl propionate	127·8	77·1 80·3	Schiff Brown	78·7	78·72
Isobutyl propionate	174	66·0	Schiff	66·0	67·14
Isoamyl propionate	196	63·05 65·31	Schiff Brown	64·18	63·8
Methyl butyrate	126·7	77·25 79·75	Schiff Brown	78·50	78·07
Ethyl butyrate	150·4	71·5 73·65	Schiff Brown	72·57	72·52
Propyl butyrate	173·9	66·2 68·29	Schiff Brown	67·24	67·98
Propyl isovalerate	192·2	64·37	Brown	64·37	63·91
Isoamyl butyrate	221·5	59·4 61·59	Schiff Brown	60·50	60·58
Isobutyl butyrate	199·2	61·9 64·59	Schiff Brown	63·24	64·16
Methyl isobutyrate	126·5	75·5 79·07	Schiff Brown	77·28	77·9
Ethyl isobutyrate	150·7	69·2 71·75	Schiff Brown	70·47	72·56
Propyl isobutyrate	174	63·9	Schiff	63·9	67·94
Isobutyl isobutyrate	199·2	59·95 63·4	Schiff Brown	61·67	64·16
Isoamyl isobutyrate	223·0	57·65	Schiff	57·65	60·72
Methyl valerate	149·1	69·95	Schiff	69·95	72·31
Isoamyl valerate	245·5	56·2	Schiff	56·2	57·25

Liquid.	Molecular Volume V at the Boiling-Point.	Latent Heat (observed),	Authority.	Mean.	Latent Heat (calculated)
Methyl isovalerate	148·7	72·38	Brown	72·38	72·25
Ethyl isovalerate	173·3	67·84	Brown	67·84	67·85
Ethyl caprylate	197·7	60·46	Brown	60·46	63·99
Isobutyl isovalerate	222	60·41	Brown	60·41	60·63
Ethyl nonylate	270 (calculated)	58·08	Brown	58·08	56·0
Diethyl carbonate...............	138·8	72·85	Louginine	72·85	68·85
Chloral	108·9	54·1	Berthelot	54·1	51·10
Chloroform	84·5	58·49	Wirtz	58·49	58·09
Carbon tetrachloride	103·7	46·35	Wirtz	46·35	52·34
Ethyl iodide	86·1	46·87 46·0	Andrews Kahlenberg	46·43	44·54
Methylene chloride	65·12	75·3	Berthelot & Ogier	75·3	74·87
Ethyl bromide	77·7	60·37 61·65	Wirtz Berthelot	61·01	61·98
Methyl iodide	63·9	46·1	Andrews	46·1	44·54
Acetaldehyde.....................	56·9	136·4	Berthelot	136·4	138·3
Benzene............................	95·9	94·37 94·93 92·91	Griffiths & Marshall Brown Wirtz	94·07	92·85
Ethyl benzene	138·8	76·4	Schiff	76·4	77·27
Cymene	184·4	66·3 67·64	Schiff Brown	67·0	67·20
Mesitylene.........................	162·4	71·75 74·42	Schiff Brown	73·08	71·92
Propyl benzene..................	161·8	71·75	Schiff	71·75	71·83
Terpene	182·8	68·73 68·5	Favre & Silbermann Schall	68·61	66·01
Toluene.............................	117·9	83·55 86·8 87·43	Schiff Ramsay & Marshall Brown	85·92	84·34
o-Xylene	138·7	82·47	Brown	82·47	77·25
m-Xylene	139·7	81·34 78·25	Brown Schiff	79·77	77·44
p-Xylene	140·2	80·98	Brown	80·98	77·53
Piperidine........................	106·3	88·9	Louginine	88·9	88·8
Sulphur oxychloride (SO_2Cl_2)	86·3	52·4	Ogier	52·4	51·79
Tin tetrachloride	131·2	30·33	Andrews	30·33	30·91
Silicon tetrachloride	123·4	37·3	Ogier	37·3	46·3
Carbon disulphide	62·1	83·81	Wirtz	83·81	82·43
Phosphorus trichloride	93·4	51·4	Andrews	51·4	52·4
Ethylene oxide	51·8*	138·6	Berthelot	138·6	134·1
Ethyl propyl ketone	143·3*	82·96	Louginine	82·96	82·78
Dipropyl ketone	165·3*	75·94	Louginine	75·94	76·17
Methyl ethyl ketone............	99·3*	103·4	Louginine	103·4	101·7
Pseudocumene	176*	72·8	Schiff	72·8	72·67

* These values of V are calculated from the atomic volumes of Kopp, experimental values not being obtainable.

Liquid.	Molecular Volume V at the Boiling-Point.	Latent Heat (observed).	Authority.	Mean.	Latent Heat (calculated).
n. Heptane	162·54	74·0	Mabery & Goldstein	74·0	86·33
n. Hexane	139·8	79·4	Mabery & Goldstein	79·4	93·3
n. Octane	186·15	70·92 71·1	Louginine Mabery & Goldstein	71·01	79·23
Di-isoamyl	231·3	60·85	Mabery & Goldstein	60·85	68·35
Ethyl ether	106·1	84·74 90·45	Brown Andrews	87·59	101·3
Amyl ether	246	69·4	Favre & Silbermann	69·4	62·77

Liquids whose Molecules Dissociate on Vaporization.

Water	18·78	536·2 535·97 535·9	Berthelot Favre & Silbermann Andrews	536·0	233·5
Methyl alcohol	42·6	262·2 261·7 263·7	Brown Schall Andrews	262·5	172·7
Ethyl alcohol	62·2	202·4 206·4 205·07 216·4	Andrews Schall Wirtz Brown	207·3	136·2
n. Propyl alcohol	81·2	166·3 162·6	Brown Schlamp	164·4	114·1
Formic acid	41·1	120·7 120·37	Favre & Silbermann Brown	120·5	118·7
Acetic acid	63·6	84·9 89·79 97·05	Berthelot & Ogier Louginine Brown	90·6	105·2
Butyric acid	108	114·67 113·96	Favre & Silbermann Brown	114·3	85·6
Acetone	77·3	125·3	Wirtz	125·3	116·2
Amyl iodide	150·4	47·5	Berthelot	47·5	42·5
Diethyl oxalate	166·2	72·72	Andrews	72·72	59·8
Methyl formate	62·7	116·1 110·45	Andrews & Ogier Brown	113·2	104·7
Ethyl formate	84·7	100·1 100·4	Brown Berthelot & Ogier	100·2	93·9

It will be observed from the Table that there is a close agreement between the calculated and observed values of the latent heat. The only classes of substances which do not seem to conform to the relationship are the aliphatic hydrocarbons and ethers and of course associated liquids as the hydroxyl compounds. The validity of the relation is in general affected by the following factors :—

(1) Experimental errors in the values of the latent heats. These are rather considerable as a comparison of the results of different observers shows. The difference between the calculated and observed values of the latent heat does, as a general rule, come easily within the range of experimental errors except in the fews cases mentioned above.

(2) Association of the molecules and their dissociation on vaporization.

The Effect of Molecular Association on the Relation.

The last portion of the above Table deals with liquids which show molecular association, and it will be observed that in these cases there are very wide divergences between the calculated and observed values of the latent heats. The question may be divided into two cases, viz. :—

(*a*) Liquids whose molecules are associated but which do not dissociate on vaporization.

(*b*) Liquids whose molecules dissociate on vaporization.

Case (*a*).—In the first case the relation should obviously be written

$$LMn = K\sqrt[3]{Vn},$$

where n is the association factor.

The true latent heat then becomes

$$L = \frac{K\sqrt[3]{V}}{Mn^{\frac{2}{3}}}.$$

Whereas the latent heat L_1 calculated according to the equation without considering association is

$$L_1 = \frac{K\sqrt[3]{V}}{M}.$$

For this class of liquids, therefore, the calculated values of the latent heats will be greater than the observed values.

Case (*b*).—The second case includes liquids like water, whose molecules are associated in the liquid state, but are normal in the vapour state, and also liquids like amyl iodide, which on vaporization suffers a partial chemical dissociation into amylene and hydriodic acid.

Suppose that the process of vaporization takes place in two stages, viz.:—(1) The vaporization of the associated molecules without dissociation; (2) the dissociation of the associated molecules of vapour. Let the heat absorbed per associated molecule in the first stage be HMn, where H is the specific heat absorbed, M is the molecular weight, and n is the association factor. This will be equal to $K\sqrt[3]{Vn}$. For the second stage let the heat absorbed per associated molecule be XMn, where X is the specific heat absorbed. Therefore in the complete vaporization of one associated molecule the total heat absorbed (apart from heat required to do external work) may be written

$$HMn+XMn=K\sqrt[3]{Vn}+XMn.$$

And if λ represents the heat required to do external work during the second stage of the vaporization, the true latent heat L_1 of vaporization becomes

$$L_1=\frac{1}{Mn}\{K\sqrt[3]{Vn}+XMn\}-\lambda,$$

$$=\frac{K\sqrt[3]{V}}{Mn^{\frac{2}{3}}}+X-\lambda.$$

Whereas the calculated latent heat not considering molecular association is

$$L=\frac{K\sqrt[3]{V}}{M}.$$

Therefore we may say that for liquids where molecular dissociation occurs on vaporization, the latent heat calculated according to the equation $LM=1583\sqrt[3]{V}$ may be either greater or smaller than the observed latent heat according to the magnitude of the heat of dissociation.

It may therefore happen that an associated liquid might not show any deviation from the equation $LM=K\sqrt[3]{V}$. An example is formic acid for which, as it will be noticed from the Table, the calculated value of the latent heat is very close to the observed result. Water and the alcohols give calculated values lower than the observed, whilst some of the acids give higher and some lower calculated values.

On the whole it may be said that with the exception of the aliphatic hydrocarbons and ethers, the relation holds for normal liquids with an exactitude which quite corresponds to the exactitude of the latent heat determinations.

Indeed, by the aid of the equation $LM=K\sqrt[3]{V}$, the latent heat of a liquid (other than those excepted above) can be calculated merely from a knowledge of its formula with a very fair degree of accuracy. In the above table the values of the molecular volume for several liquids marked with an asterisk are calculated from Kopp's atomic volumes, and it will be noticed that in these cases there is a very fair agreement between the calculated and observed latent heats.

A Relation between the Molecular Volume and the Boiling-Point.

If the relation $LM=K\sqrt[3]{V}$ be combined with Trouton's equation $LM=20{\cdot}5\,T$ we get a very simple equation

$$T=K_1\sqrt[3]{V},$$

where T is the temperature of boiling, V is the molecular volume at the boiling-point, and K_1 is a constant.

The value of the constant in Trouton's equation varies for normal liquids from about 19·5 to 22·5. Taking the constant in the equation $LM=K\sqrt[3]{V}$ as equal to 1583 we should expect that the value of K_1 will vary roughly between 70 and 80, and will have a very small value for the aliphatic hydrocarbons and ethers.

The validity of the equation is tested in the following Table. The values of T and V are the mean results of Kopp, Pierre, Buff, Thorpe, Zander, Gartenmeister, Young, and others.

Liquid.	Temperature of Boiling T_{BP} (absolute).	Molecular Volume V at Boiling-Point.	$K_1=\frac{T_{BP}}{\sqrt[3]{V}}$.
Aliphatic Esters.			
Ethyl formate	327·3	84·7	74·53
Methyl acetate	330·1	83·7	75·47
Propyl formate	353·9	107·0	74·54
Ethyl acetate	350·1	106·0	73·98
Methyl propionate	352·7	104·6	74·95
Butyl formate	372	130·7	73·2
Isobutyl formate	370·9	129·9	73·2
Propyl acetate	374·5	128·4.	74·2
Ethyl propionate	372	127·8	73·8
Methyl butyrate	375·7	126·7	74·8
n. Amyl formate	403·4	150·5	75·8
Isoamyl formate	396·7	151·0	74·5
Ethyl butyrate	393	150·4	73·9
Methyl valerate	399·3	149·1	75·5
n. Amyl acetate	420·6	173·8	75·4

Liquid.	Temperature of Boiling T_{BP} (absolute).	Molecular Volume V at Boiling-Point.	$K_1=\frac{T_{BP}}{\sqrt[3]{V}}$.
Isoamyl acetate	409	174	73·2
Ethyl valerate	417·7	174·5	74·8
Isoamyl propionate	433·7	196·0	74·7
Butyl butyrate	438·7	197·8	75·3
Isobutyl butyrate	430·8	199·2	73·7
Propyl valerate	440·5	197·8	75·6
Isopropyl valerate	429	197·2	73·7
Amyl butyrate	457·8	222·3	75·6
Methyl nonylate	477·5	245·7	76·2
Methyl acrylate	353·3	98·4	76·5
Propyl acrylate	395·9	144·9	75·4
Acetaldehyde	294	56·9	76·4
Valeraldehyde	374	119·9	75·8
Paraldehyde	397·4	150·7	74·7
Aromatic Hydrocarbons.			
Benzene	353·2	95·9	77·3
Toluene	382·2	117·9	77·9
o-Xylene	414·7	138·7	80·1
m-Xylene	412	139·7	79·4
p-Xylene	411	140·2	79·2
Ethyl benzene	409·3	138·8	79·1
Cymene	448·3	184·4	78·8
Aliphatic Hydrocarbons.			
n. Hexane	341·9	139·8	65·8
n. Heptane	371·4	161·8	68·2
Diisopropyl	331	136·3	64·3
Diisobutyl	382·2	184·5	67·24
Diisoamyl	432·6	231·3	70·5
Valerylene	314	104	66·8
Aliphatic Ethers.			
Ethyl ether	307·6	106·1	64·9
Methyl propyl ether	311·9	105·1	66·1
Methyl butyl ether	343·3	127·2	68·3
Ethyl propyl ether	336·6	127·8	66·9
Ethyl butyl ether	364	150·1	68·6
Dibutyl ether	413·9	197·3	71·1
Aromatic Esters.			
Methyl benzoate	463	150·3	87·1
Ethyl benzoate	482	174·2	86·3
Methyl phenyl propionate	509·6	195·2	87·9
Ethyl phenyl propionate	521·1	221·5	86·3
n. Propyl phenyl propionate	535·1	245·9	85·4

Liquid.	Temperature of Boiling T_{BP} (absolute).	Molecular Volume V at Boiling-Point.	$K_1 = \frac{T_{BP}}{\sqrt[3]{V}}$.
Aromatic Ethers.			
Phenyl propyl ether	463·5	172·0	83·3
Phenyl butyl ether	483·3	195·3	83·3
Phenyl octyl ether	555·8	296·1	83·4
o-Tolyl ethyl ether	457·8	170·9	82·5
o-Tolyl butyl ether	495·0	218·4	82·2
m-Tolyl ethyl ether	465·0	172·0	83·6
m-Tolyl butyl ether	502·2	220·5	83·1
p-Tolyl ethyl ether	462·9	172·1	83·2
p-Tolyl propyl ether	483·4	196·0	83·2
Aliphatic Chlorides.			
Ethyl chloride	285·2	71·2	68·8
Propyl chloride	319·2	91·4	70·9
Isopropyl chloride	309·5	93·6	68·2
Isoamyl chloride	372·6	134·4	72·7
Amyl chloride	374·5	136·3	72·5
Allyl chloride	318·5	84·5	72·6
Aliphatic Bromides.			
Methyl bromide	286	58·2	73·8
Ethyl bromide	312·7	77·7	73·0
Propyl bromide	344	97·2	74·8
Isopropyl bromide	333	97·2	71·9
Aliphatic Iodides.			
Methyl iodide	315·8	84·1	78·1
Ethyl iodide	345·3	86·1	78·2
Propyl iodide	375·5	106·9	79·1
n. Amyl iodide	424·7	150·4	79·9
Butyl iodide	402·9	128·2	79·9
Amines.			
Diethylamine	329	109·1	68·8
Triethylamine	362	153·8	67·6
Tripropylamine	429·5	222·1	70·9
Isobutylamine	340·7	106·2	71·9
Chloroform	334·1	84·5	76·1
Carbon tetrachloride	349·7	103·7	74·3
Ethylene chloride	356·5	85·2	81·0
Ethylidene chloride	331·8	88·7	74·4
Chlorobenzene	405·0	114·3	83·5
Bromobenzene	429·0	119·8	85·0
Iodobenzene	461·4	130·6	90·9
Nitric peroxide N_2O_4	294·6	63·9	73·7
Sulphur dioxide	265	43·9	75·1
Carbon bisulphide	319	62·1	80·6
Tin tetrachloride	387·1	131·2	76·3

Liquids which show Molecular Association.

Liquid.	Temperature of Boiling T_{BP} (absolute).	Molecular Volume V at Boiling-Point.	$K_1 = \frac{T_{BP}}{\sqrt[3]{V}}$.
Water	373	18·78	140·3
Methyl alcohol	337·9	42·6	97·1
Ethyl alcohol	351·3	62·2	88·7
n. Propyl alcohol	370·4	81·2	85·1
n. Hexyl alcohol	429·6	146·3	81·5
Formic acid	373	41·1	108·1
Acetic acid	391·5	63·6	98·0
Propionic acid	413·8	85·5	93·9
Butyric acid	435	108	91·3
Methyl formate	304·7	60·10	76·65
Methyl oxalate	435·6	116·8	89·1
Ethyl oxalate	459·0	166·2	83·5
Propyl oxalate	486·5	215·4	81·2
Dimethyl succinate	468·2	159·7	86·3
Methyl ethyl succinate	481·2	184·6	84·6
Diethyl succinate	489·2	209·0	82·5
Acetonitrile	347	54·3	91·7
Propionitrile	370	78·3	80·1
Valeronitrile	402	119·7	81·6
Phenol	467	103·6	99·4

It will be observed from the Table that the relation gives an approximately constant value of K for all the homologous series, but the value varies considerably from one homologous series to another. In general the higher boiling liquids seem to give rather high values of K. The approximate values of the constant for the different homologous series are given below.

The aliphatic hydrocarbons and ethers give K = 68.
The aliphatic chlorides and amines give K = 70.
The aliphatic esters and bromides give K = 74.
The aliphatic iodides and aromatic hydrocarbons give K = 79.
The aromatic ethers give K = 83.

The validity of the relation is also considerably affected by molecular association, as the latter portion of the above Table indicates. For associated liquids the equation should obviously be written

$$T = K\sqrt[3]{V}n,$$

where n is the association factor.

Were it not for the uncertainty of the value of K for any particular liquid, the above equation would furnish a method of determining n the association factor.

There is one way of distinguishing between the effects of association and constitution. If the members of an homologous series give a gradually diminishing value of K as the series is ascended, then the members of that particular series show molecular association. If the value of K remains approximately constant then no molecular association occurs. For this reason the esters of the aliphatic dibasic acids, like oxalic and succinic, have been classed along with the alcohols and acids as associated liquids.

Mention must be made here of other relations between the molecular volume and the boiling-point. It has long been noticed in a general way that there is a certain parallelism between the molecular volume and the boiling-point, but no exact relation has yet been discovered. Masson (Phil. Mag. vol. xxx. p. 412, 1890) discovered empirically the relation $\frac{V}{T}$ = constant, where V and T are the molecular volume and temperature of boiling respectively, which he found to hold closely for the alkyl halides, but apparently only for these few classes of substances.

On the other hand, Young (Phil. Mag. vol. xxx. p. 423, 1890) showed that Masson's relation should only hold for substances which have the same critical pressures, and deduced the relation (from van der Waals' generalizations)

$$V = \text{const.} \times \frac{T_c}{P_c},$$

where V is the molecular volume at the boiling-point, T_c is the critical temperature, and P_c the critical pressure. Obviously for those liquids where P_c is constant, Masson's relation will hold.

Summary.

An empirical relation between the latent heat of a liquid and the molecular volume at the boiling-point is shown to hold for most classes of liquids, with the exception of the aliphatic hydrocarbons and ethers and liquids which show molecular association. The relation may be written

$$LM = K \sqrt[3]{V},$$

where L is the latent heat at the boiling-point, M the molecular weight, V the molecular volume at the boiling-point, and K is a constant equal to 1583. The effect of molecular

association on the validity of the relation is examined and it is shown that with associated liquids the calculated value of the latent heat may be either greater or smaller than the actual observed value.

The relation combined with Trouton's equation gives the simple relation

$$T = K\sqrt[3]{V},$$

where T is the boiling-point, V the molecular volume at the boiling-point, and K is a constant. This relation gives a fairly constant value of K for the members of an homologous series, but its value varies rather considerably from one homologous series to another. The relation is also greatly affected by molecular association, the value of K always being much greater for associated liquids than the average.

The Chemical Department,
The University, Manchester.

LIII. *The Energy Relations of Certain Detectors used in Wireless Telegraphy.* *By* W. H. Eccles, *D.Sc., A.R.C.S.*[*]

[Plate X.]

THE results of an experimental examination into the physical properties of four very different types of detector used in radio-telegraphy are set forth briefly in the following pages. The conditions of the experiments have been made generally identical with those arising in the ordinary employment of the detectors, and, in particular, the quantities of energy given to the instruments, in the form of electrical oscillations, have been of the same order in these experiments as in actual practice. The detectors investigated are the electrolytic, the carborundum rectifier, the zincite detector, and a thermoelectric detector. All these have before this been subjected to close scrutiny by various observers, who, however, used methods different from that of this paper; a summary of their work will be given alongside the results of the present experiments. These results, it will be seen, are expressed in the form of curves rather than as tables of figures; each curve may be regarded as typical of the detector concerned, and has been selected from a number of curves drawn from measurements accumulated during last year.

The method and apparatus used are the same as were described in a paper "On Coherers," read before the Physical

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[*] Communicated by the Physical Society: read July 8, 1910.

Society in March last (Phil. Mag. June 1910). The present experiments were for the most part carried out at an earlier date than those described in that paper. The properties of the detectors are examined in three distinct ways. The first way consists in applying to the detector an electromotive force which is gradually increased, and measuring the consequent current at each step. The second way is to fix the electromotive force at some particular value, to send trains of oscillations of various energy values through the instrument, and to measure the intensity of sound produced in the telephone on each occasion. The third way is to send trains of constant energy value through the instrument while the steady electromotive force applied to it is varied in steps, and to measure at each step the intensity of the sound produced in the telephone. These modes of experimenting give curves that may be called respectively the steady-current curve, the power curve, and the sensitiveness curve. It will be seen from the curves that the power supplied to the detector in the form of electrical oscillations and the power handed to the telephone in the form of intermittent current are both recorded in fractions of a watt. For this purpose, the circuit-calibrations described in the former paper were used. It must be mentioned here that the calibration of the telephone circuit is probably much less accurate than that of the detector circuit.

RESULTS OF THE MEASUREMENTS.

The Electrolytic Detector.

This detector consisted of two platinum electrodes in dilute sulphuric acid (one of acid to four of water). One electrode was a platinum wire of 0·0006 cm. diameter drawn by the Wollaston process, dipping a fraction of a millimetre into the electrolyte; the other was a piece of thick wire well immersed. When a potential difference less than one volt is established between the electrodes the current that passes is very small; but as the potential difference is increased the counter electromotive force of polarization is overcome, till finally a large current flows with evolution of gas. The stage of the process which is useful for detecting feeble electrical oscillations is that where the bubbles of gas do not yet form on and break away from the point freely. The steady current curves of fig. 1 (Pl. X.) indicate the difference between the two cases, point as anode and point as cathode. The power curves for various cases are collected in fig. 2, all from the same detector. Curve *a* shows the relation between the power w delivered by the detector to the telephone and the power W given in the form of electrical oscillations to the detector, when the potential difference between the platinum point and the large electrode has the value 2·9 volts—the voltage of highest sensitiveness. Curve *b* shows the large fall in sensitiveness caused by altering the applied electromotive force, the point still being anode.

In the same way, curves *c* show the efficiency of the energy transformation when the point is negative. Curve *c* is an attempt to reach the best possible sensitiveness with the point as cathode; but it is to be remarked that when the point is covered with hydrogen, the electrical conditions are somewhat unstable, and the best potential difference is an uncertain quantity. This is in strong contrast with the very definite conditions that rule when the platinum point is polarized with oxygen. This is clearly indicated by the curves of fig. 3, where the ordinates represent the proportion of energy delivered to the telephone when the applied voltage has various values.

This detector has received a very great deal of attention in the past, but the precise mode of operation of the instrument is still unknown. Reich*, after making experiments with superposed direct current and alternating current of low frequency, considered that the phenomena could only be accounted for by a dissolution of the small electrode used as anode and a simultaneous disappearance of oxygen—processes purely chemical. Rothmund and Lessing†, using a Blondlot oscillator and Lecher wires, and measuring the potential difference across the detector and the current through it when the oscillator was working and not working, concluded that the whole action of the instrument depended upon some unexplained "depolarization action" of the oscillations; and by using a variety of electrolytes, proved the incorrectness of the hypothesis, which was a mere surmise unsupported by scientific measurements, that the instrument operated by resistance alterations due to the heat generated in the liquid mass near the minute anode. Later Dieckmann‡ measured the current changes that followed upon the passage of strong oscillations of (unmeasured) intensity through a detector. Later still, Austin§, using alternating current of low frequency, showed that the detector was affected by

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* *Phys. Zeitschr.* v. p. 338 (1904).

† *Ann. d. Phys.* xv. 1, p. 193 (1904).

‡ *Phys. Zeitschr.* v. p. 529 (1904).

§ Bulletin, Bureau of Standards, i. 3, p. 435 (1905).

electromotive amplitudes of 1/10000 volt, and that oscillations produced by spark-discharges in the laboratory affected the detector equally whether the small electrode was anode or cathode. He concluded that in the action of the instrument heat had a share, and that chemical action, electrostatic attraction across the gas film, and also a property styled rectification, all took part.

Carborundum.—The detector was set up by clamping a crystal of carborundum between brass plates, so that a smooth crystalline edge or corner was in contact with one plate, and a blunt and more amorphous part of the crystal in contact with the other plate. The steady current curves of two crystals widely different in their electrical behaviour appear in fig. 4 (Pl. X.). Curves *a b* belong to one crystal, the dotted curves AB belong to another. The upper curve of each pair was obtained when the jagged blunt end of the crystal was positive.

The power curves are given in fig. 5. Lines *a b c* exhibit the energy relations for the crystal that gave *a b* in fig. 4. Line *a* was obtained while the blunt end was at a potential 2·62 volt higher than the smooth end; *b* was got when the potential difference was −0·44; curve *c* was got without electromotive force. Lines A, B, C refer to the other crystal. Line A was obtained while the blunt end was 2·9 volt above the smooth end; line B while the blunt end was 2·1 volt below; line C while no external electromotive force was applied. The curve of fig. 6 shows how sensitiveness altered with the electromotive force applied to the terminals of the detector.

The Carborundum detector has been examined very exhaustively by Pierce*. He has shown that crystals of this substance may be as much as 1000 times more conductive for current in one direction than in the opposite, and has concluded that the substance acts as a detector of high frequency oscillations solely because of this unilateral conductivity. Heat, he considered, played no part in the process. The curves given above show, however, that a crystal may be a good detector even though its unilateral conductivity be not very pronounced.

Zincite-chalcopyrite.—The detector made by arranging a corner of a fragment of brown zincite (native oxide of zinc) to press against a piece of chalcopyrite (iron copper sulphide) is one of the most sensitive known. It is used extensively in various navies. Fig. 7 gives the results of measurements of current under steady electromotive force. For this particular detector the most sensitive condition was attained

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* Phys. Review, xxv. p. 31 (1907).

when the zincite was maintained at a potential about 0·45 volt below that of the pyrite. The power curves are given in fig. 8; here *a* is the curve when no electromotive force was applied: *b* is the curve for an applied electromotive force of 0·45 volt, zincite negative, and *c* is the curve for an applied electromotive force of 0·45 volt, zincite positive. It will be seen from these that the combination forms a very sensitive detector, even when no external electromotive force is applied. The curves showing the change in sensitiveness with variation of the applied electromotive force are plotted in fig. 9.

Graphite-Galena.—A detector that is very widely used for every-day telegraphy is that consisting of a pointed piece of graphite touching the face of a crystal of galena. The curves connecting applied electromotive force and current flowing through the contact appear in fig. 10. The power curves are shown in fig. 11: curve *a* is obtained when the external electromotive force is not applied, and curves *b* and *c* when electromotive forces of 0·45 volt and −0·45 volt were applied. The connexion between the power given to the telephone and the electromotive force applied to the detector is given in fig. 12.

These two last detectors and others similar to them are sometimes called "rectifiers," sometimes "thermoelectric detectors." They are styled thermoelectric because it was originally supposed that they owed their power of detecting high frequency vibrations to the thermoelectromotive forces set up at the contact by the rise of temperature produced at that point—the point of highest resistance in the whole oscillation circuit—in obedience to Joule's law; but most observers have concluded from experiments with both direct and alternating currents, that these detectors derive their function from an unexplained and hitherto unknown power of rectifying rather than from a combination of the Joule and Peltier effects. Pierce[*] has examined the behaviour of contacts made with anastase, brookite, and molybdenite under alternating currents of ordinary frequency, and obtained oscillograms of the current through them. No evidence of thermoelectric or other integrative action was perceived in the photographs. Austin[†] has examined quantitatively, also by aid of slow alternating currents, the properties of detectors consisting of contacts of silicon and steel, carbon and steel, tellurium and aluminium. Brandes[‡] and Raetenkrantz[§]

[*] Phys. Review, p. 153 (1909).

[†] Bulletin, Bureau of Standards, v. p. 133 (1908).

[‡] *Elektro. Zeitschr.* xxvii. p. 1015 (1906).

[§] *Phys. Zeitschr.* ix. p. 911 (1908).

have also contributed greatly to our knowledge of the connexion between the steady current curve of a detector and its behaviour under electrical oscillations.

Conclusion.

The chief fact brought to light by the above experiments is that the energy passed to the telephone by a detector is connected linearly with the energy given to the detector in the form of electrical oscillations. This is true for all the detectors examined, even including the coherers discussed in the earlier paper. The curves connecting the input and output of energy though they are straight lines usually pass some distance away from the origin. This implies that for a particular detector under invariable conditions there is a fixed wastage of oscillation energy, amounting commonly to about 1/10 of an erg per second, however large or small the oscillation energy given to the detector may be. Another interpretation is, however, that a small quantity of energy, which is invariable while the detector is undisturbed, is delivered by the detector to the telephone circuit in a form that never makes any proportion of itself manifest as sound. The curves suggest, though they do not prove, that all detectors are fundamentally thermal in their action. That this deduction is opposed to the conclusions reached by previous experimenters is clear from the summary of their work given above. The principal cause of this difference between our conclusions appears to be that nearly all previous observers have used comparatively large quantities of oscillation energy, and have therefore probably brought into play phenomena that never arise in detectors as used in wireless telegraphy.

The above investigations were carried out by the aid of a grant from the Royal Society's Government Grant Committee.

LIV. *The Mechanical Pressure of Radiation effective on the smallest as well as on larger Particles.* *By* G. W. DE TUNZELMANN, *B.Sc.*[*]

It has been pointed out by Prof. Schuster in a letter to 'Nature'[†] that "there is a widespread impression that light pressure acts only on particles the linear dimensions of which include several wave-lengths of light, but this is not

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[*] Communicated by the Author.

[†] 'Nature,' vol. lxxxi. p. 97 (1909).

correct. The determining factor is the extinction of light, whether by scattering or by absorption, as indeed appears if we take the view adopted in Prof. Poynting's work on the subject, that a propagation of momentum accompanies the transmission of light. The momentum is destroyed equally whether the molecules act as scattering or absorbing centres."

This conclusion is in accordance with Tyndall's experiments[*] on the colours of precipitated clouds of small particles, and on the blue colour and polarization of the light from the sky, and Lord Rayleigh's theoretical investigations suggested by them[†]; and with the experimental evidence, adduced by Lord Rayleigh in the last paper referred to, tending to the conclusion that the molecules of air are responsible for nearly a third of the atmospheric scattering observed.

The cases of plane waves normally incident upon a perfectly black body and a perfect reflector are capable of simple treatment by elementary mathematical methods[‡], and since the work done across a small surface of a wave-front cannot depend on the question whether the wave is plane or not, the relation so arrived at must hold good for any simply periodic electromagnetic disturbance. The subject is treated on these lines in a recent work by the present writer[§], and a more general analytical investigation is given by Sir Joseph Larmor on p. 131 of 'Æther and Matter.' It is shown in chapters vii. and viii. of the latter work that Maxwell's equations of electric force are not applicable to the investigation of problems in which radiation is important. These equations are derived from an electrodynamic stress-formula in which the function of a uniform dielectric is regarded as merely to transmit the forces without adding anything to them. In the light of present knowledge, which is most completely formulated in terms of the electron theory, any material dielectric must be regarded as susceptible of polarization analogous to that of a magnet. Now, while in metallic conduction the current arising from this polarization is usually negligible in comparison with the total, in radiation it forms an important part of the total current.

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[*] Phil. Mag. vol. xxxvii. 1869, p. 384; and Phil. Trans. vol. clx. 1870, p. 383.

[†] Scientific Papers, vol. i. pp. 87, 104, 518; and vol. iv. pp. 305, 397.

[‡] See Drude's *Lehrbuch der Optik*, p. 447, or English edition, p. 488, and Sir Joseph Larmor's article "Radiation," Supplement to *Encyclopædia Britannica*.

[§] Treatise on Electrical Theory and the Problem of the Universe, pp. 270–274.

A detailed theory of radiation pressure was developed by K. Schwarzschild[*], and published in 1901, in which, by means of somewhat intricate mathematical analysis, he succeeded in arriving at numerical results, according to which the radiation pressure on a spherical particle vanishes when the radius is too small to include several wave-lengths of the incident radiation. The investigation is, however, based on Maxwell's equations of electric force, in which the existence of the polarization current is not recognized, and is therefore invalid.

Dr. J. W. Nicholson, in his recent paper "On the Size of the Tail-particles of Comets, and their Scattering Effect on Sunlight"[†], relies largely on Schwarzschild's results. The writer was also referred to these results in December 1909, by Prof. Svanté Arrhenius, when kindly reading some of the proofs of the work previously referred to, in which some modifications had been made in the theory proposed by Prof. Arrhenius to account for the constitution of the solar corona and the origin of the polar auroras. It therefore appeared advisable to draw attention to their unsoundness in a more prominent way than has already been done in a footnote to the writer's recent work[‡].

LV. *Notices respecting New Books.*

Mathematical and Physical Papers. Vol. IV. *Hydrodynamics and General Dynamics.* By the Right Honourable Sir WILLIAM THOMSON, Baron KELVIN. Arranged and Revised with brief annotations by Sir JOSEPH LARMOR, D.Sc., LL.D., Sec. R.S. Cambridge: at the University Press. 1910.

TWENTY years have elapsed since the Third Volume of Kelvin's collected papers was issued. During that period Kelvin himself edited and greatly expanded the Baltimore Lectures, and added many new papers to the already long list of original contributions to science. But the remarkable papers on Vortex Motion remained generally inaccessible save to students in command of a good scientific library; and many had to be content with the presentation of Kelvin's work as it was given in the Treatises of Lamb and Basset. Now, thanks to the care and energy of Sir Joseph Larmor, this has been changed. The present volume

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[*] *Münchener Berichte*, vol. xxxi. 1991, p. 293.

[†] Phil. Mag. vol. xix. 1910, p. 626.

[‡] *Op. cit.* p. 378.

opens with the short paper on Vortex Atoms, which was communicated to the Royal Society of Edinburgh in 1867, and was published both in the Proceedings of that Society and in the Philosophical Magazine. Then follows the great memoir "On Vortex Motion," published in the Transactions of the Royal Society of Edinburgh, vol. xxv., which has been for many years accessible only in the older scientific libraries of the world. Probably the vast majority of students of hydrodynamics have never had a good opportunity of reading this great paper. No doubt the outstanding features of Kelvin's mode of presentation—especially the conceptions of Flow and Circulation—are well given in our standard treatises on the motion of fluids; but Kelvin had a method all his own, full of suggestiveness to the thoughtful reader. It is of infinite value to the real student to have ready access to the original work of a man like Kelvin, especially when, as in the present instance, each series of papers forms a kind of continuity. The arrangement is broadly by subject matter; and in each section a chronological arrangement is made the basis. Thus the Hydrodynamic section includes the papers on vortex motion, on the motion of solids through fluids, and on capillary waves. Then come three papers on the Tides; and under the heading Waves on Water are grouped a number of connected investigations on stationary waves, ship waves, the front and rear of a free procession of waves, and so on. Several of these papers deal with difficult subjects, and constitute some of the latest of Kelvin's most characteristic contributions to the theory of certain types of water waves. The five papers communicated to the Royal Society of Edinburgh at intervals from 1904 to 1906 form a continuous series, the paragraphs being numbered consecutively. These portions occupy about four-fifths of the volume. The remaining fifth is concerned with General Dynamics and Elastic Propagation; but many of the papers enumerated in the Table of Contents are represented only by their titles, the papers having being already reprinted in the Baltimore Lectures, or in the earlier volumes of 'Mathematical and Physical Papers.' The last paper printed *in extenso* is on a new method for specifying stress and strain in an elastic solid. In place of the usual Cartesian specification, Kelvin uses a tetrahedron of reference, and is thus able to obtain a symmetrical specification of stress and strain for finite as well as for infinitesimal strains. It need hardly be said that the editorial work has been well and faithfully done, the annotations, brief though they are, being always to the point and full of instructive allusions. The final volume (V.), we are told, is almost ready for press, and will contain papers on Thermodynamics, Cosmical and Geological Physics, Electrodynamics and Electrolysis, Molecular and Crystalline Theory, Radioactivity and Electrionic Theory, and other miscellaneous matter.

An Elementary Treatment of the Theory of Spinning Tops and Gyroscope Motion. By H. Crabtree. Longmans, Green & Co. London: 1909.

The history of applied mathematics is full of illustrations of the truth that problems which tried the powers of the most powerful thinker of one age become the familiar possession of the average student in the succeeding generation. Usually the first presentation of the theory is crude and difficult; but with the flight of the years the combined attacks of many minds evolve a simpler and generally a more natural way of looking at the associated problems, which finally find their appropriate place in a so-called elementary textbook. Spinning tops and gyroscopic motion are a case in point. In this refreshing little book which Mr. Crabtree has prepared, the dynamical principles of the conservation of energy and the conservation of moment of momentum are applied with simplicity and power to many familiar phenomena of motion—spinning tops, mono-rail, precession, diabolo, torpedo, golf-ball, rifle-bullet, and so on. Simple diagrams help to elucidate the discussion—with the exception (if a fault must be noted) of the misleading diagram on page 53 of the flight of a rifle-bullet. Here also the attempt to explain the "drift" is not convincing—indeed, the hydrokinetics is not sound. The footnote on the same page referring to the golf-ball and Tait's investigations is so full of misstatement and the mythology of the Club-house that the author had better suppress it altogether in a second edition. These flaws apart, the book deals in an interesting way with great problems. There are many examples for the student to work at; the mathematics is kept well under control, and the dynamical ideas are never lost sight of. The book should be in the hands of all students who are beginning their higher studies in applied mathematics.

Funktionentafeln mit Formeln und Kurven. Von Dr. E. Jahnke und Ingenieur F. Emde. Teubner: Leipzig und Berlin. 1909.

These tables of functions of various kinds are a most valuable addition to the many books of tables which have recently been prepared. The mere enumeration of some of the functions which are here tabulated will suffice to show to all interested the real importance of the work: Exponential Functions, Hyperbolic Functions, Fresnel's Integrals, the Gamma Function, the Error Integral, Elliptic Integrals and Functions, Spherical Harmonics, Bessel's Functions, etc. Among the elliptic functions there are not only the familiar functions in their earliest form, but also Theta functions, and the Weierstrass functions; and a valuable addition gives the mutual induction and attraction between parallel co-axial circular circuits in terms of a quantity which depends on the radii of the circuits and their distance apart.

Here, as in other cases, the tables are supplemented by the corresponding curves or graphs. This graphical representation is indeed an extremely important feature throughout. Each Table is accompanied by an exposition of the theory sufficient to refresh the memory of the worker in applied mathematics who wishes to make use of it. In most cases the values are given to four or five significant figures. The names of the authors are a guarantee of the care that must have been taken in preparing this most timely publication.

LVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xix. p. 918.]

January 26th, 1910.—Prof. W. J. Sollas, LL.D., Sc.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'On a Skull of *Megalosaurus* from the Great Oolite of Minchinhampton.' By Arthur Smith Woodward, LL.D., F.R.S., F.L.S., Sec. G.S.

2. 'Problems of Ore-Dèposition in the Lead and Zinc Veins of Great Britain.' By Alexander Moncrieff Finlayson, M.Sc., F.G.S.

Chemical analyses show traces of lead and zinc in several of the rock-formations of Britain, but the ores of the veins are concluded to be derived, not from the country-rock, but from deeper sources, probably in the first place by magmatic segregation. They were transported in the deeper zones by 'juvenile' waters, in which fluorine was an important constituent, while in the upper zones, especially in limestone districts, underground waters of meteoric origin have played a large part. The vein-solutions carried (1) alkaline sulphides, which held the sulphides of the metals in solution, and (2) alkaline and earthy carbonates. The presence of the latter is indicated by the alteration of the wall-rock, which shows a concentration of potash, lime, and carbon dioxide, and a leeching of soda, magnesia, oxides of iron, and silica. In limestones, however, the chief effects of solution on wall-rock were concentration of silica and magnesia.

The filling of fissures rather than direct replacement of rocks by ores, has been the chief process, but the calcium of fluorspar has been very largely derived from the country-rock. Further, much local metasomatism is seen, such as replacement of limestone by fluorspar, galena, blende, and quartz; and replacement of fluorspar by galena.

The order of deposition, determined by microscopic examination of polished specimens of ores, has been: chalcopyrite, fluorspar, blende, galena. The galena carries its silver generally in molecular or isomorphous combinations, except in the case of rich ores, when native silver and argentite appear sometimes as threads along the cleavage-planes.

In the effect of the country-rock on ore-deposition, the chief factors have been: (1) the physical character of the rock and the consequent nature of the fissure, (2) its porosity, and (3) its chemical composition. The process of deposition involves interchange of constituents between rock and solutions, even with the least soluble rocks.

Ore-deposition has persisted over a vertical range of 5000 to 6000 feet, of which over one-half has been shorn off by denudation. The effects of secondary processes have been exerted to depths of over 600 feet. The main points in the work are supported by field-observations, and by the results of microscopic and chemical research.

3. 'The Vertebrate Fauna found in the Cave-Earth at Dog Holes, Warton Crag (Lancashire).' By John Wilfrid Jackson, F.G.S., Assistant Keeper in the Manchester Museum.

LVII. *Intelligence and Miscellaneous Articles.*

To the Editors of the Philosophical Magazine.

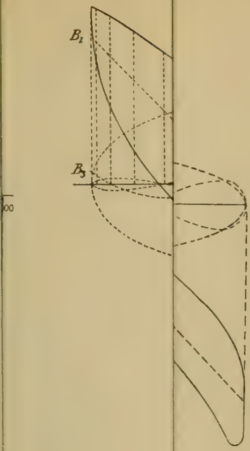
Cavendish Laboratory, Cambridge,
Aug. 9th, 1910.

GENTLEMEN,—

WITH reference to the paper in your last issue by Mr. Jeans on the motion of an electrified particle near an electrical doublet, and its bearing on the theory of radiation given by me in the June number, I should like to state that I was quite aware that the state of steady motion I considered would not be permanent. As a matter of fact I showed in the paper that if the particle suffered a radial displacement from its circular orbit, no force acted upon it tending to bring it back to its former position or to drive it still further away; thus if the particle were started with a radial velocity it would slowly drift from its state of steady motion. I did not then, nor do I now, consider this fact of any importance with respect to the theory of radiation I was discussing, for there is nothing in that theory which requires these systems to be permanent. All that is necessary is that, at any time, there should be a number (infinitesimal in comparison with the number of molecules) of such systems which remain in this state, or only depart slightly from it, in the time occupied by a few vibrations of ultra-violet light.

Yours very sincerely,
J. J. THOMSON.

Fig. 20.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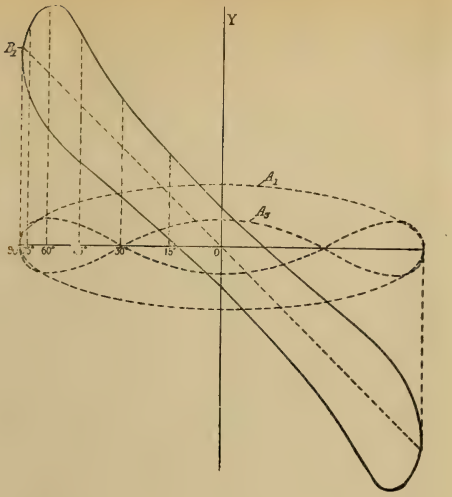
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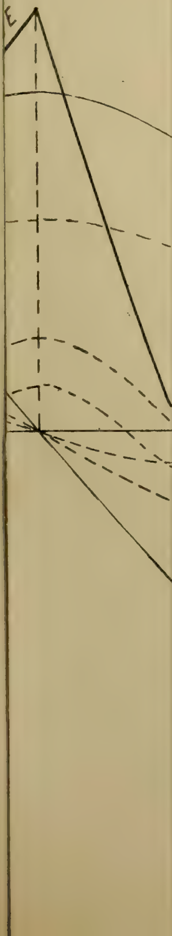
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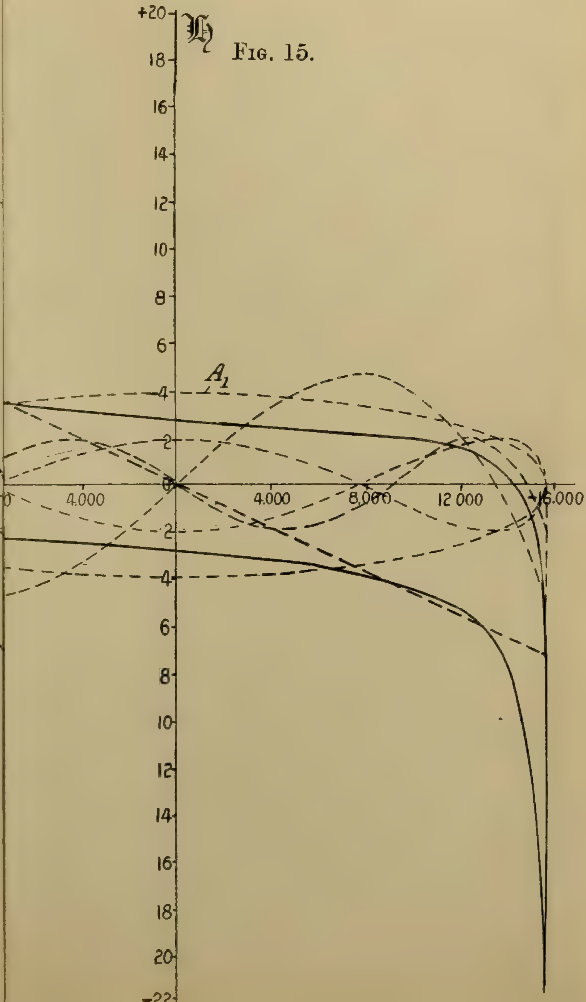
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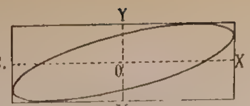
Fig. 15.

Phil. Mag. Ser. 6, Vol. 20, Pl. VI.

Fig. 2.



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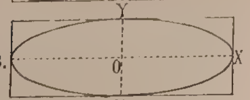

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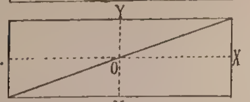

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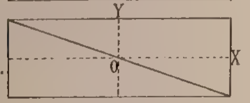

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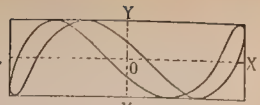

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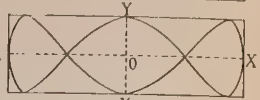

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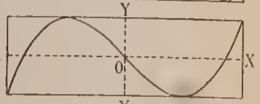

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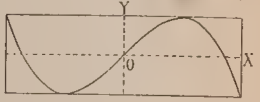

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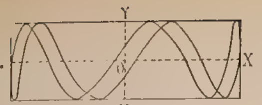

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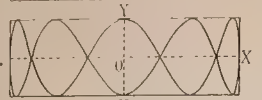

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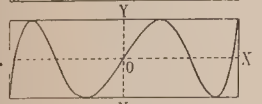

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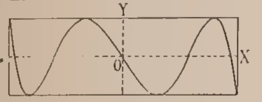

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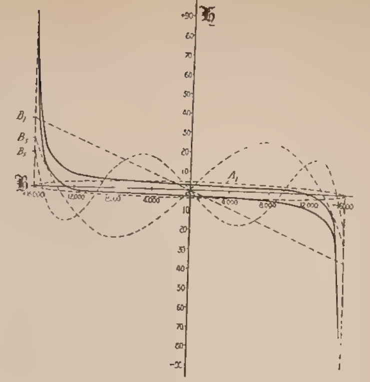

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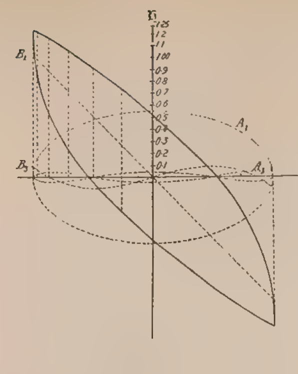

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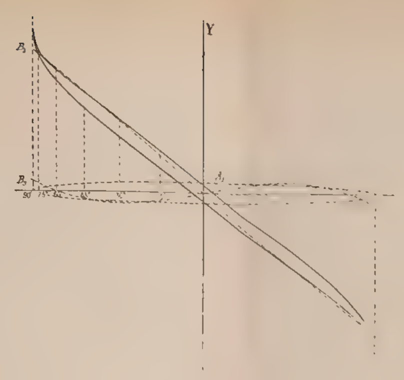

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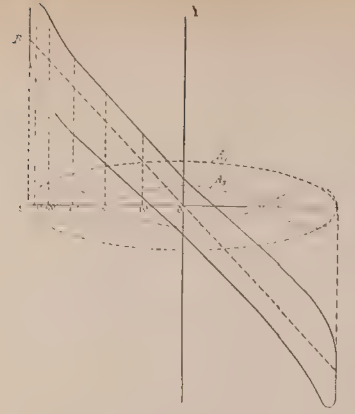

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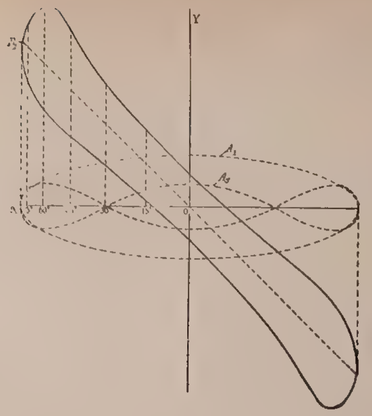

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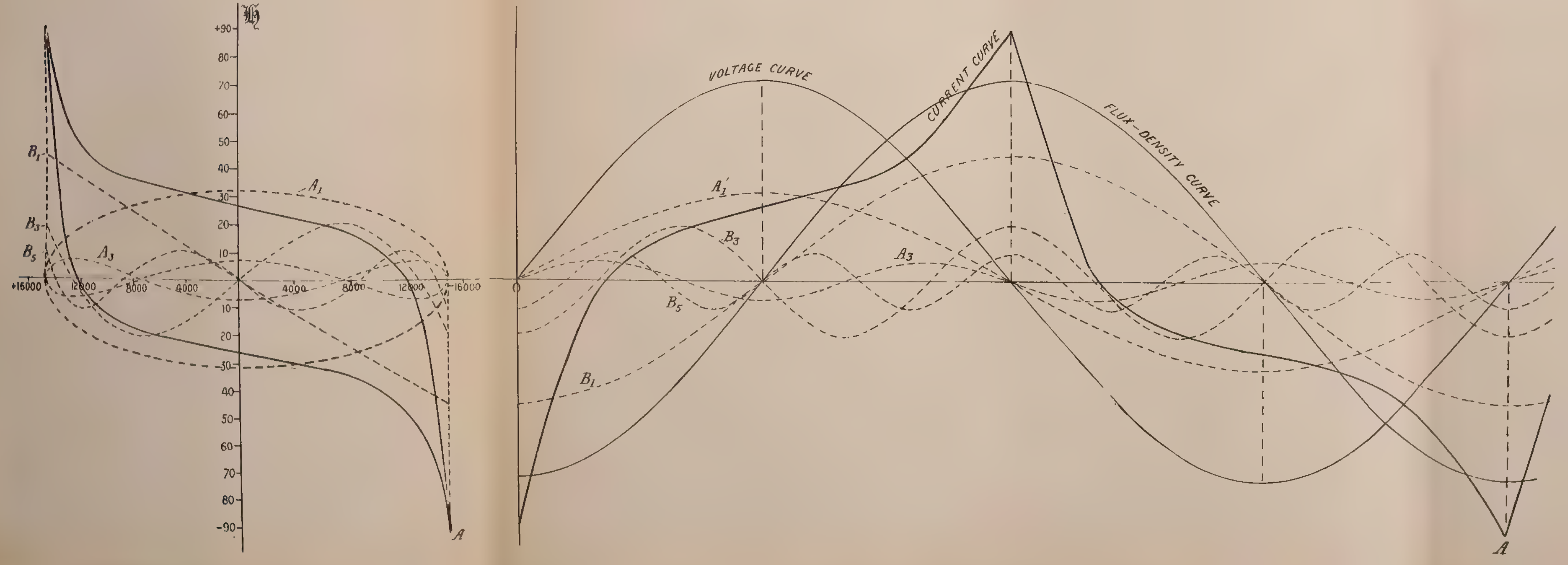

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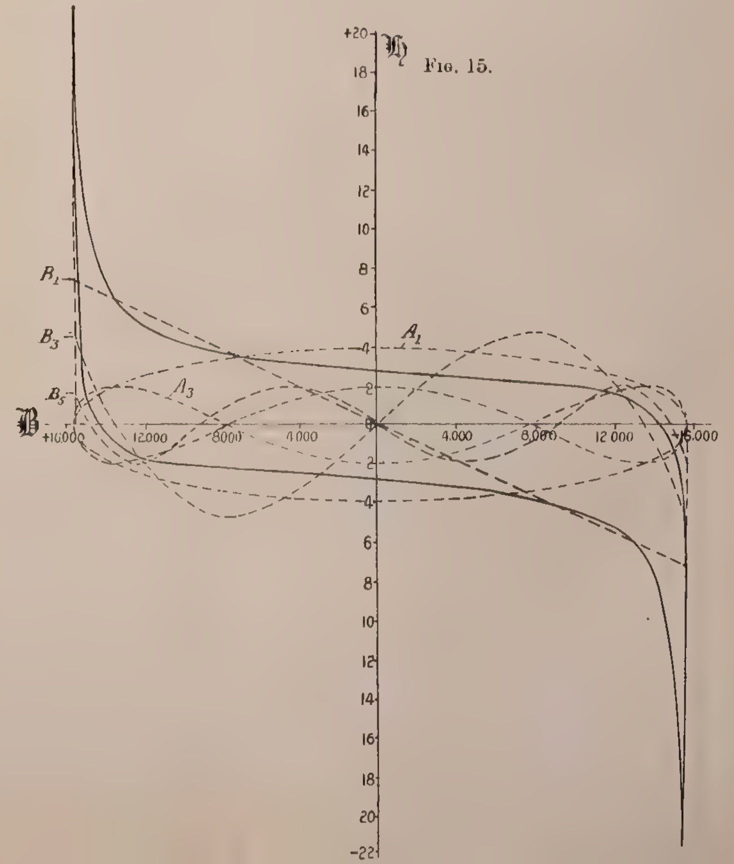


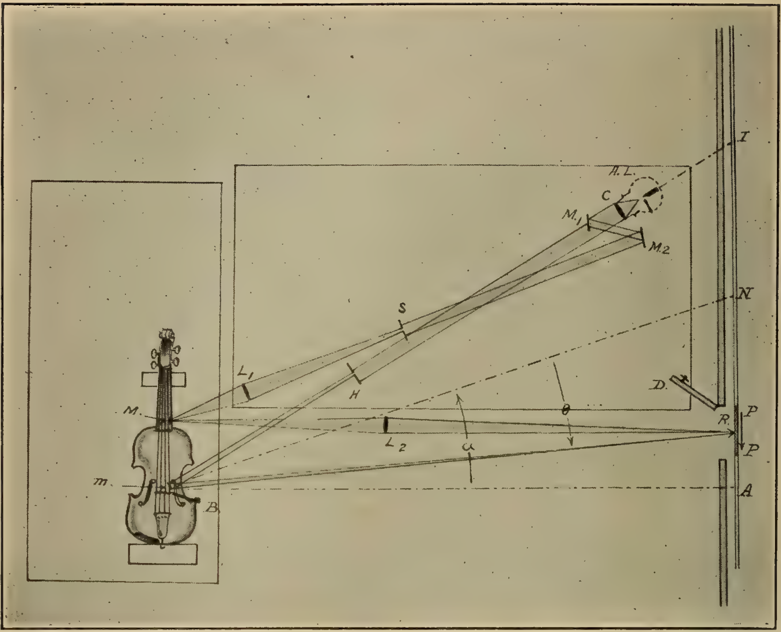


Fig. 1.—Optical Arrangements for Longitudinal Motions of Bridge.

Fig. 3.—Enlarged detail of Bridge and Optical Lever.

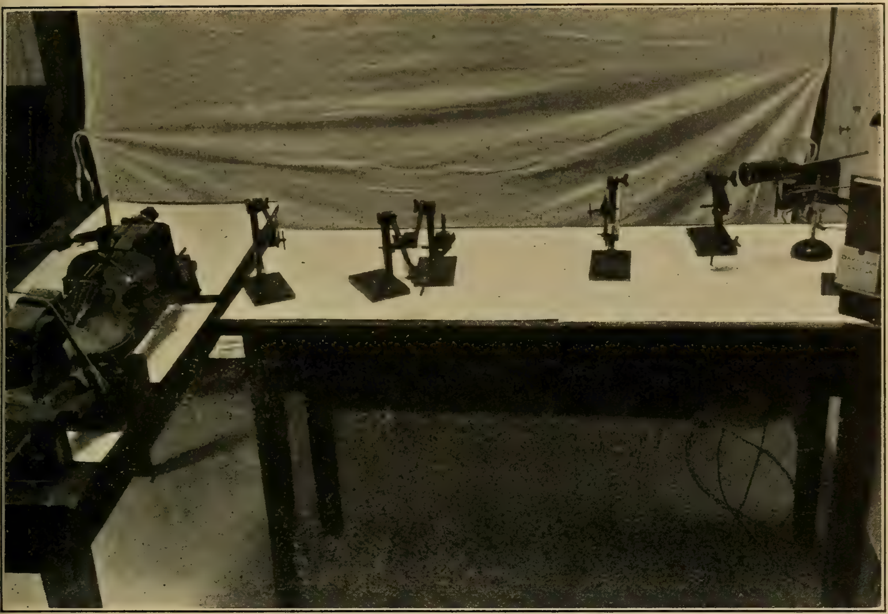
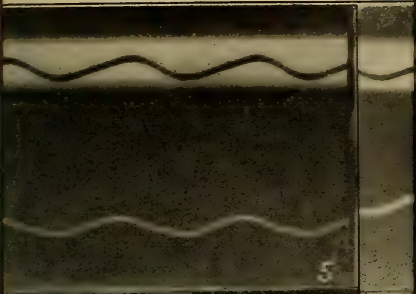


Fig. 2.—Perspective View of Experimental Arrangements.

Fig. 4.—Violin showing positions of Bass Bar
and Sound Post.

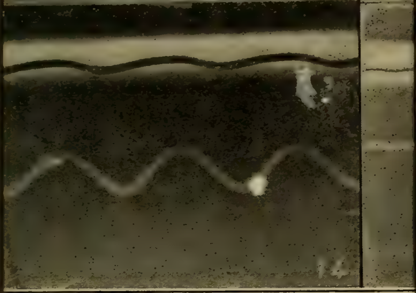
G-string plucked at $\frac{1}{6}$.

4



G-string struck by wooden hammer at $\frac{1}{7}$.

7



11

-string plucked by plectrum at $\frac{1}{4}$.

14

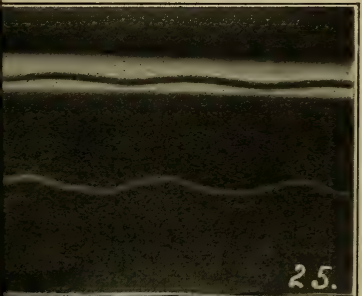
D-string struck at $\frac{1}{4}$.

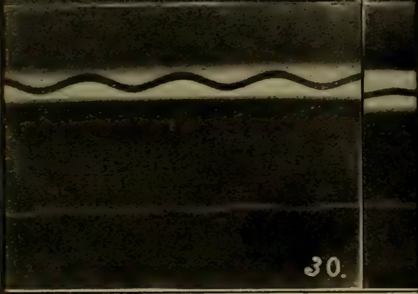
G-string struck at $\frac{1}{7}$.

18

G-string plucked at $\frac{1}{7}$.

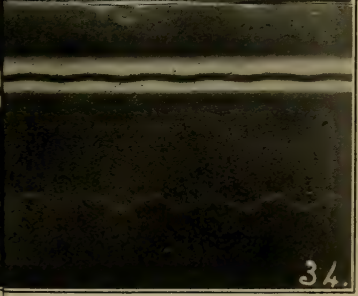
21





25

D-string struck at $\frac{1}{7}$.



28

A-string bowed at $\frac{1}{5}$.

VERTICAL MOTION OF BRIDGE.

E-STRING CORNER.

G-string bowed at $\frac{1}{7}$.
1

G-string bowed at $\frac{1}{6}$.
2

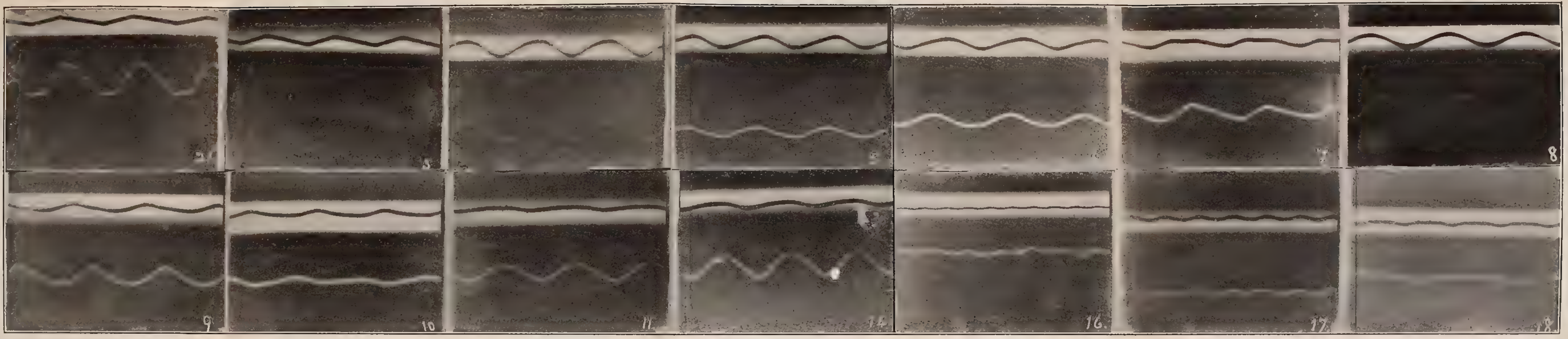
G-string plucked at $\frac{1}{4}$.
3

G-string plucked at $\frac{1}{6}$.
4

G-string plucked at $\frac{1}{7}$.
5

G-string struck by wooden hammer at $\frac{1}{4}$.
6

G-string struck by wooden hammer at $\frac{1}{7}$.
7



8
G-string struck at $\frac{1}{4}$.

9
G-string struck at $\frac{1}{7}$.

10
G-string plucked by plectrum at $\frac{1}{7}$.

11
G-string plucked by plectrum at $\frac{1}{4}$.

12
E-string struck at $\frac{1}{4}$.

13
A-string struck at $\frac{1}{4}$.

14
D-string struck at $\frac{1}{4}$.

G-STRING CORNER.

G-string bowed at $\frac{1}{7}$.
15

G-string bowed at $\frac{1}{6}$.
16

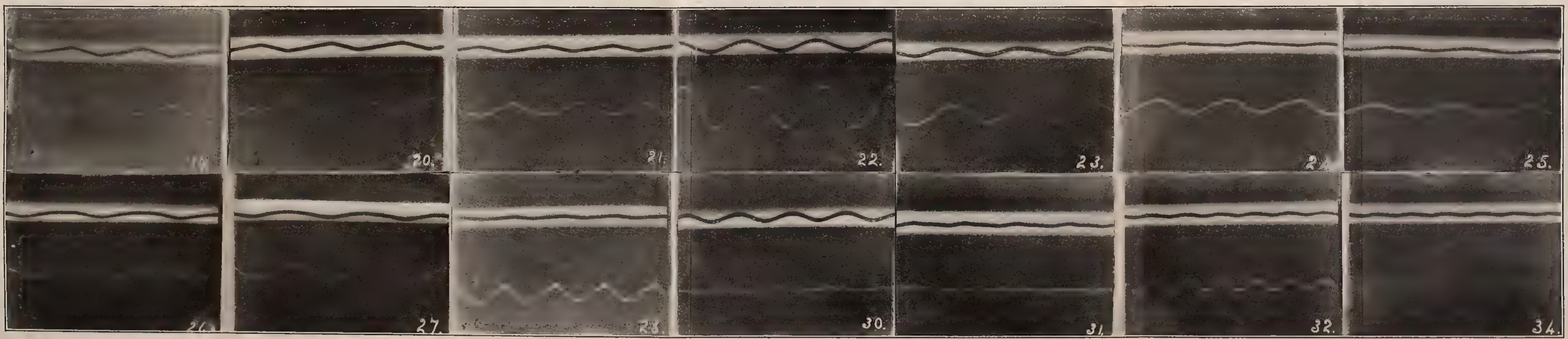
G-string bowed at $\frac{1}{5}$.
17

G-string struck at $\frac{1}{7}$.
18

G-string struck at $\frac{1}{4}$.
19

G-string plucked at $\frac{1}{4}$.
20

G-string plucked at $\frac{1}{7}$.
21



22
G-string plucked by plectrum at $\frac{1}{7}$.

23
G-string plucked by plectrum at $\frac{1}{4}$.

24
D-string bowed at $\frac{1}{7}$.

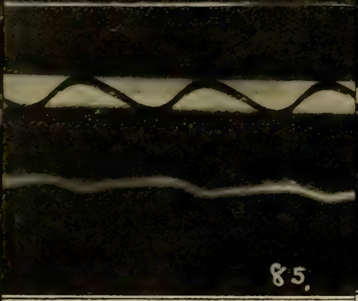
25
D-string struck at $\frac{1}{7}$.

26
D-string struck at $\frac{1}{4}$.

27
A-string bowed at $\frac{1}{7}$.

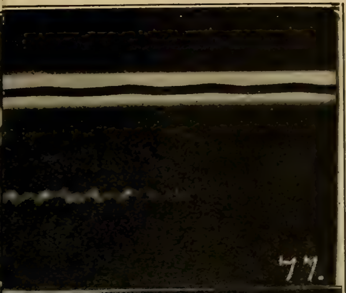
28
A-string bowed at $\frac{1}{5}$.

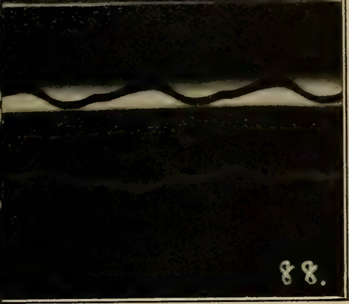
A-string plucked at $\frac{1}{7}$.
36



47
G-string plucked at $\frac{1}{4}$.

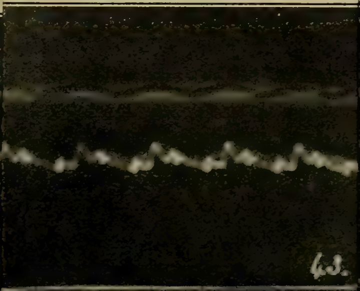
D-string bowed at $\frac{1}{5}$.
39

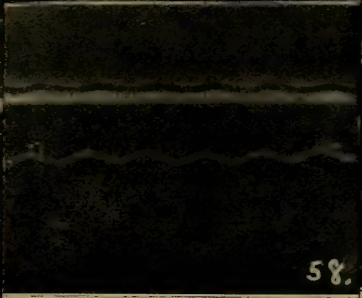




50
G-string struck at $\frac{1}{4}$.

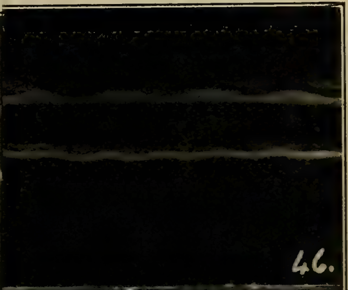
D-string bowed at $\frac{1}{7}$.
58

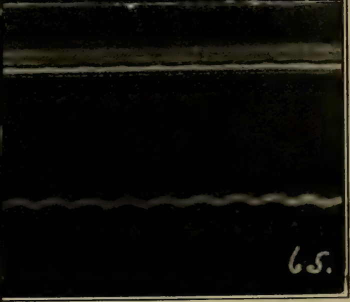




69
A-string plucked by plectrum at $\frac{1}{7}$.

D-string struck at $\frac{1}{4}$.
61





72
-string plucked by plectrum at $\frac{1}{4}$.

MOTION OF BRIDGE LENGTHWISE OF STRING.

E-STRING CORNER.

E-string bowed at $\frac{1}{7}$.
29

E-string bowed at $\frac{1}{5}$.
30

E-string plucked at $\frac{1}{7}$.
31

A-string bowed at $\frac{1}{7}$.
32

A-string bowed at $\frac{1}{5}$.
33

-ing plucked by plectrum at $\frac{1}{7}$.
34

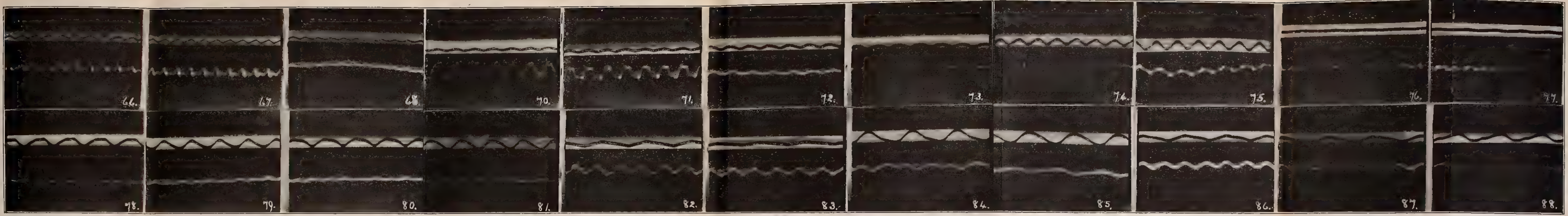
A-string plucked by plectrum at $\frac{1}{4}$.
35

A-string plucked at $\frac{1}{7}$.
36

A-string plucked at $\frac{1}{4}$.
37

D-string bowed at $\frac{1}{7}$.
38

D-string bowed at $\frac{1}{5}$.
39



40
D-string plucked at $\frac{1}{7}$.

41
D-string plucked at $\frac{1}{4}$.

42
D-string plucked by plectrum at $\frac{1}{7}$.

43
D-string plucked by plectrum at $\frac{1}{4}$.

44
G-string bowed at $\frac{1}{7}$.

45
G-string bowed at $\frac{1}{4}$.

46
G-string plucked at $\frac{1}{7}$.

47
G-string plucked at $\frac{1}{4}$.

48
G-string plucked by plectrum at $\frac{1}{7}$.

49
G-string plucked by plectrum at $\frac{1}{4}$.

50
G-string struck at $\frac{1}{4}$.

G-STRING CORNER.

G-string bowed at $\frac{1}{7}$.
51

G-string bowed at $\frac{1}{5}$.
52

G-string struck at $\frac{1}{7}$.
53

G-string plucked at $\frac{1}{7}$.
54

G-string plucked at $\frac{1}{4}$.
55

G-string plucked by plectrum at $\frac{1}{7}$.
56

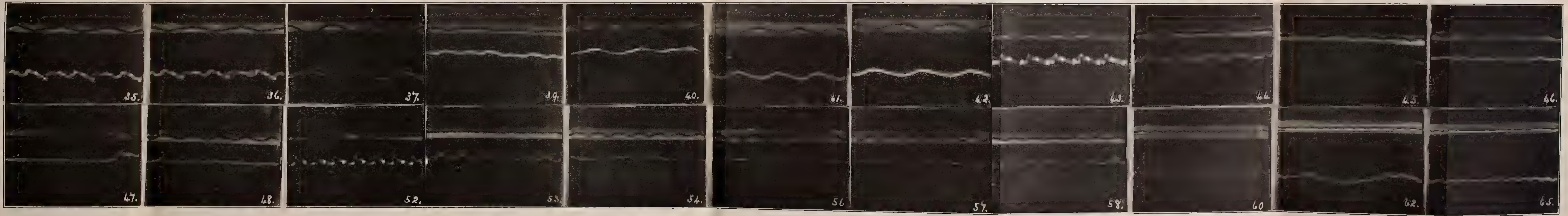
G-string plucked by plectrum at $\frac{1}{4}$.
57

D-string bowed at $\frac{1}{7}$.
58

D-string bowed at $\frac{1}{4}$.
59

D-string struck at $\frac{1}{7}$.
60

D-string struck at $\frac{1}{4}$.
61



62
D-string plucked at $\frac{1}{7}$.

63
D-string plucked at $\frac{1}{4}$.

64
A-string bowed at $\frac{1}{7}$.

65
A-string bowed at $\frac{1}{4}$.

66
A-string struck at $\frac{1}{7}$.

67
A-string plucked at $\frac{1}{7}$.

68
A-string plucked at $\frac{1}{4}$.

69
A-string plucked by plectrum at $\frac{1}{7}$.

70
E-string bowed at $\frac{1}{7}$.

71
E-string struck at $\frac{1}{7}$.

72
E-string plucked by plectrum at $\frac{1}{4}$.

ECCLES.

ELECTROLYTIC DETECTOR.

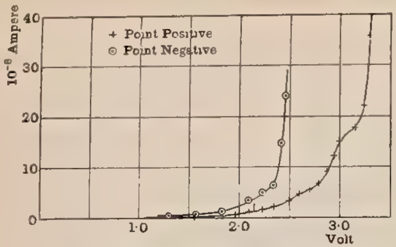


FIG. 1.—Steady Current Curves.

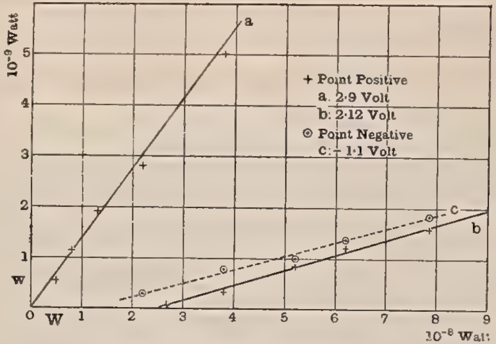


FIG. 2.—Power Curves.

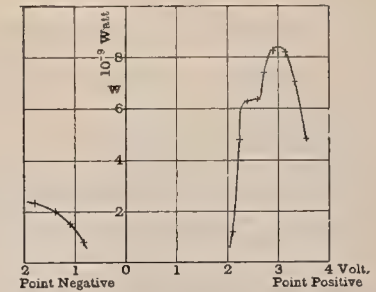


FIG. 3.—Sensitiveness Curve.
$W = 6{\cdot}2 \times 10^{-8}$ Watt.

CARBORUNDUM DETECTOR.

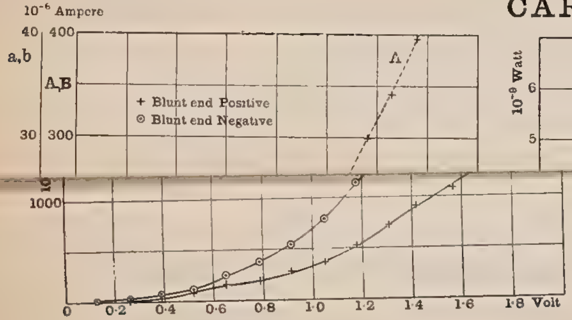


FIG. 10.—Steady Current Curves.

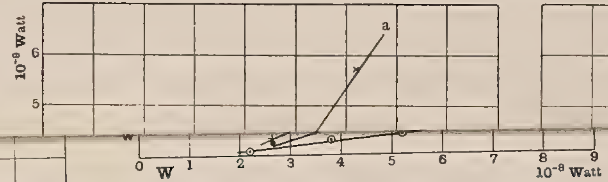


FIG. 11.—Power Curves.

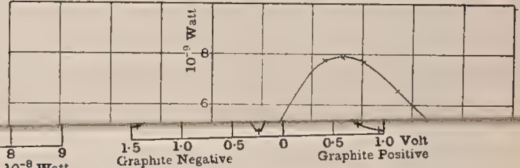


FIG. 12.—Sensitiveness Curve.
$W = 7{\cdot}85 \times 10^{-8}$ Watt.

ELECTROLYTIC DETECTOR.

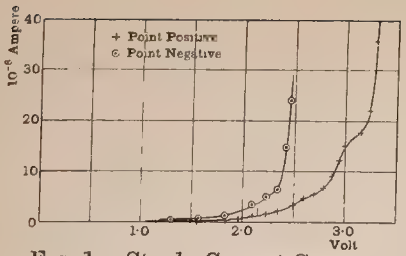


Fig. 1.—Steady Current Curves.

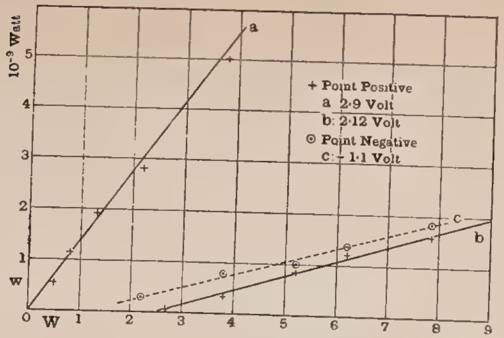


Fig. 2.—Power Curves.

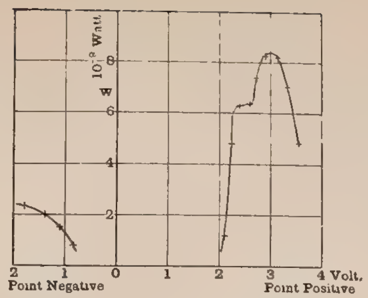


Fig. 3.—Sensitiveness Curve.
$W=6{\cdot}2\times10^{-8}$ Watt.

CARBORUNDUM DETECTOR.

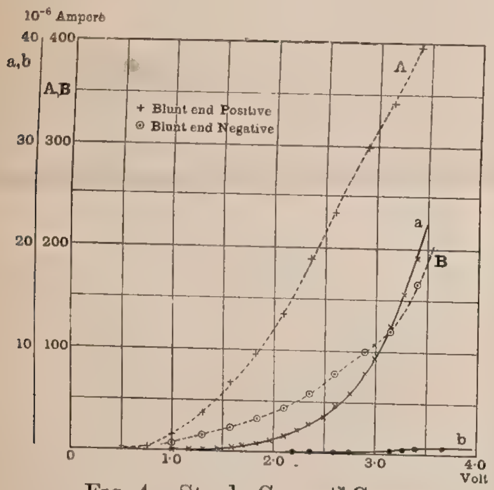


Fig. 4.—Steady Current Curves.

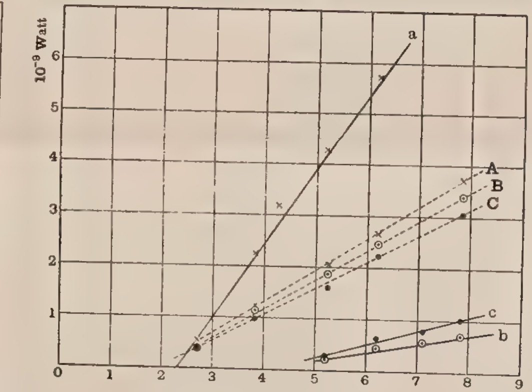


Fig. 5.—Power Curves.

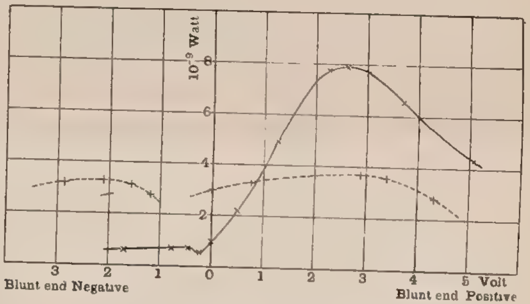


Fig. 6.—Sensitiveness Curves.
$W=7{\cdot}85\times10^{-8}$ Watt.

ZINCITE-CHALCOPYRITE DETECTOR.

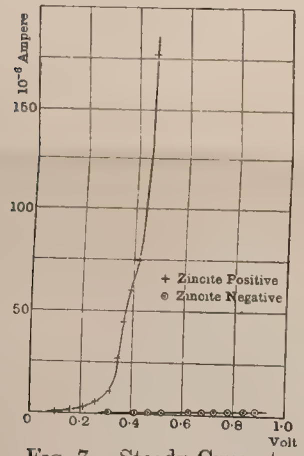


Fig. 7.—Steady Current Curves.

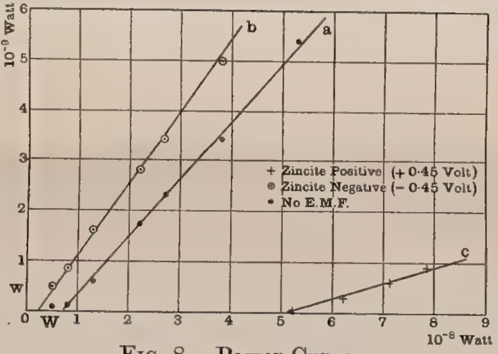


Fig. 8.—Power Curves.

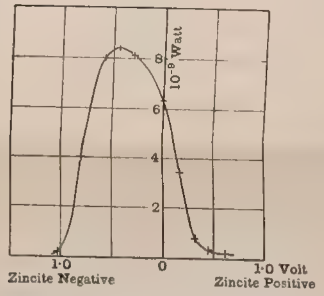


Fig. 9.—Sensitiveness Curve.
$W=6{\cdot}2\times10^{-8}$ Watt.

GRAPHITE-GALENA DETECTOR.

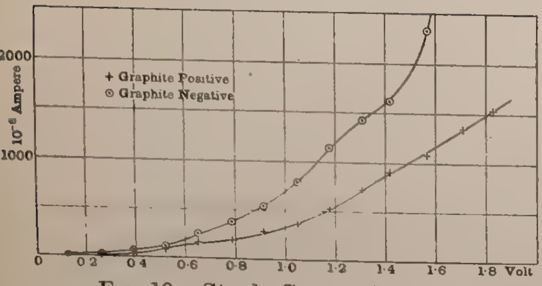


Fig. 10.—Steady Current Curves.

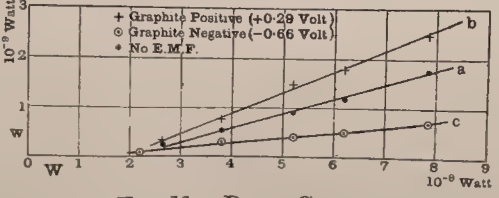


Fig. 11.—Power Curves.

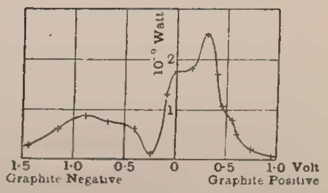


Fig. 12.—Sensitiveness Curve.
$W=7{\cdot}85\times10^{-8}$ Watt.

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PHILOSOPHICAL MAGAZINE
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[SIXTH SERIES.]

OCTOBER 1910.

LVIII. *The Specific Charge of the Ions emitted by Hot Bodies.* —II. *By* O. W. RICHARDSON, *M.A.*, *D.Sc.*, *Professor of Physics, and* E. R. HULBIRT, *A.M.*, *Princeton University*[*].

IN a previous communication[†] one of the authors developed a method of measuring the value of e/m for the ions emitted by hot bodies and applied it to the case of the ions of both signs from platinum and carbon. As was to be expected from the results of earlier investigations, the value of the specific charge for the negative ions was found to correspond to that for the negative electrons, whereas the number obtained for the positive ions pointed to bodies of atomic magnitude. Somewhat contrary to expectation, the value of e/m for the positive ions was found to be identical within the limits of experimental error for both platinum and carbon, despite their wide divergence of atomic weight as well as both chemical and physical properties. The values found were also very close to the value given by Sir J. J. Thomson for the corresponding quantity in the case of iron, which appears to have been the only substance for whose positive ions the value of e/m had been determined. The value of e/m in all these cases was about 380 E.M. units, and corresponds to an atomic weight of the carriers of about 26, assuming that they carry the same charge as the hydrogen atom in electrolysis.

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[*] Communicated by the Authors.

[†] O. W. Richardson, Phil. Mag. [6] vol. xvi. p. 740 (1908).

In view of the unexpected identity of the specific charge of the positive ions from these three very different elements, it seemed desirable that a greater variety of elements should be examined. The present investigation was undertaken with that object in view, and the materials which have been experimented upon include platinum, palladium, gold, silver, copper, nickel, iron, osmium, tantalum, tungsten, brass, nichrome, and steel. In addition, unsuccessful experiments were made upon aluminium, magnesium, and zinc. It was found that the strips of these metals which were used invariably melted before sufficient ionization could be obtained to carry out the necessary measurements.

The foil from which the strips were cut varied in thickness from ·002 to ·005 cm., depending on the material. Each strip was cut as narrow as possible, none being more than ·02 cm. wide.

The platinum, palladium, gold, and silver were cut from pure foil supplied by Messrs. Johnson, Matthey & Co. The copper was rolled from ordinary magnet wire, and the tantalum was rolled from a filament out of a tantalum lamp. The source of the other materials, where it is of interest or importance, is stated in the context.

Both the apparatus and the method of using it are precisely the same as before. No change was made, even in detail, so that for the description of the method it will be sufficient to refer to the previous paper. We shall, therefore, content ourselves with stating the results which have been obtained.

Platinum.

A number of new measurements of e/m have been made for the positive ions from platinum, partly to compare with the results obtained previously, and partly in order to test the working of the apparatus from time to time. Different values have been used both of the magnetic intensity and the electrostatic potential difference. The results of the measurements are given in the following table (p. 547).

The quantity m/H represents the value of the ratio of the mass of the positive ions to that of an atom of hydrogen on the assumption that the charge on these ions is the same as that carried by an atom of hydrogen in electrolysis. The value of e/m for the hydrogen atom has been taken to be $9{\cdot}66 \times 10^3$ E.M. units.

It was pointed out in the previous paper that the absolute values of e/m obtained by this method were subject to a possible uncertainty arising from the theoretical conditions not

Platinum, Positive Ions.

Distance between plates z (cms.).	Magnetic Intensity H (lines per cm.).	Volts V.	Deflexion of Ions x (1·0635 cm.).	e/m (E.M. units).
·452	4850	82	1·35	275
·452	4850	158	·95	262
·452	4850	320	·65	250
·452	4475	200	·75	244
·452	4200	82	1·00	202
·452	3175	83	·885	273
·473	4850	119	1·10	222
·473	4850	80	1·37	233
·473	4850	147	1·00	227

Average values ... $e/m=243$, $m/\mathrm{H}=39·8$.

being completely satisfied. It was pointed out that a check on this uncertainty could be obtained by determining the value of e/m for the negative electrons which are emitted at somewhat higher temperatures. The value of this quantity is known to be very near $1·88\times10^7$, so that a determination of the experimental value will enable us to determine the correction factor which has to be applied in order to get the true value for the positive ions. In making this correction we assume that the factor is the same for the positive as for the negative ions. There seems to be no reason why this should not be very nearly the case.

The results of the measurements for the negative electrons from hot platinum are given in the following table. The units in this and all succeeding tables are the same as in the preceding table except where the contrary is stated.

Platinum. Negative Ions.

z.	H.	V.	x.	e/m.
·443	28·75	74	1·65	$1·15\times10^7$
·443	28·75	164	1·10	1·13
·443	14·2	41	·95	·86
·443	14·2	41	1·00	·96
·473	14·2	41	1·225	1·11
·473	14·2	81	·975	1·38
·473	14·2	123	·775	1·33
·473	14·2	41	1·40	1·44
·473	14·2	41	1·33	1·30

Average value ... $e/m=1·18\times10^7$.

The average value of e/m for the negative ions thus comes out considerably lower than the standard value $1·88 \times 10^7$. The ratio of the two is 1·59. Assuming that the measurements for the positive ions are subject to the same proportional error, we get for the corrected values for the positive thermions from platinum: $e/m = 387$ and $m/\mathrm{H} = 25·0$.

In what follows we shall apply the correction factor 1·59 which has been obtained for platinum to the other metals investigated. This is legitimate, since the dimensions of the apparatus were the same in every case, and with most of the materials used it was not possible to push the temperatures high enough to obtain the negative ionization without melting them.

In the experiments on platinum the average temperature during the experiments on the positive ions was about 900° C. (and with the negative ions about 1100° C.). On account of the falling off of the positive emission with time, it was necessary to raise the temperature from time to time when the measurements on the positive ions were being made. This effect was not so noticeable with the other metals used, and in fact in the case of silver the ionization appeared to increase with lapse of time. This may be due to the strip used becoming thinner owing to sputtering, and so requiring a smaller current to heat it.

The platinum strips used were always boiled in nitric acid before testing. The method could not be used with most of the other materials as they were soluble in nitric acid. They were, however, cleaned with alcohol and distilled water instead.

Palladium, Copper, Silver, and Nickel.

The numbers given by the above metals are exhibited in the following tables, and do not appear to call for special discussion.

Palladium. Positive Ions.

z.	H.	V.	*x*.	*e*/*m*.
·433	4850	83	1·05	201
·443	4850	165	·71	182
·443	4850	329	·57	235
·443[1]	4850	41	1·60	230

Average values ... $e/m = 212$, Corrected ... $e/m = 337$.
$m/\mathrm{H} = 45·6$, $m/\mathrm{H} = 28·7$.

Copper. Positive Ions.

z.	H.	V.	*x*.	*e*/*m*.
·578	4850	153	1·50	238
·578	4850	196	1·275	221

Average values ... $e/m=230$, Corrected ... $e/m=366$.
$m/\mathrm{H}=42$, $m/\mathrm{H}=26{\cdot}4$.

Silver. Positive Ions.

z.	H.	V.	*x*.	*e*/*m*.
·562	4850	160	1·35	225
·622	4850	197	1·40	200
·622	4850	120	1·80	200
·622	4850	158	1·70	235

Average values ... $e/m=215$, Corrected ... $e/m=342$.
$m/\mathrm{H}=45$, $m/\mathrm{H}=28{\cdot}3$.

Nickel. Positive Ions.

z.	H.	V.	*x*.	*e*/*m*.
·586	4850	305	1·10	241
·586	4850	225	1·375	278
·586	4850	143	1·525	218
·586	4850	183	1·35	218

Average values ... $e/m=239$, Corrected ... $e/m=380$.
$m/\mathrm{H}=40{\cdot}4$, $m/\mathrm{H}=25{\cdot}4$.

Osmium.

This metal was not obtainable in the form of foil or strip, so that a filament such as is used in an osmium lamp was employed. The principal effect of using a narrow filament instead of a strip is to broaden out the pattern in the diagram showing the distribution of the ions, so that it is less easy to determine the position of the maximum point. The following gives the results of the only measurement which was made with the substance.

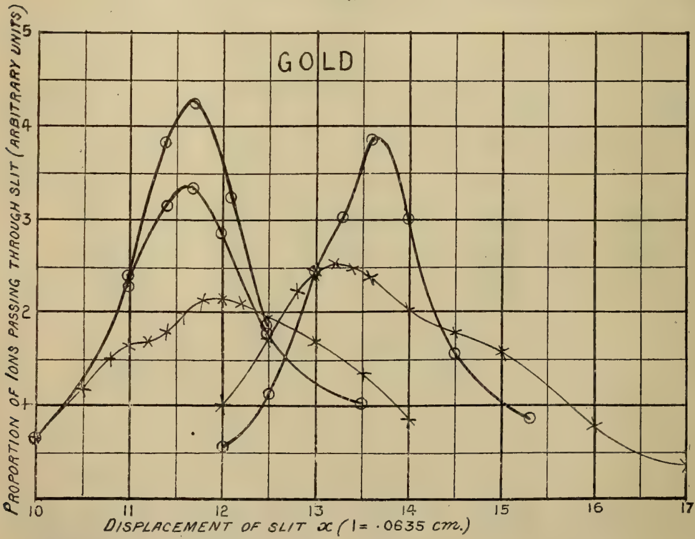
Osmium. Positive Ions.

z.	H.	V.	x.	e/m.
·587	4850	41	3·15	264
Values ... e/m=264, $m/$H= 36·6,		Corrected ... e/m=420. $m/$H= 23·0.		

Gold.

Gold was found to behave differently from any of the preceding metals in so far as the curves obtained when the metal was first heated were irregular in outline and very broad. The maxima were not as definite as in the preceding cases, and the displacement corresponded to a smaller value of e/m. The character of these curves is well shown by the curve with points thus :—× in fig. 1.

Fig. 1.



After the gold had been heated for some time the curves assumed a more normal shape and at the same time the distance between the maxima increased. The curves with the points marked thus :—⊙ in fig. 1, which were obtained after the gold had been heated for some time, show those characteristics.

The numbers which are given by two different gold strips when they were first heated are shown in the following table:—

Gold (freshly heated). Positive Ions.

z.	H.	V.	x.	e/m.
·583	4850	160	1·175	148
·583	4850	200	1·00	135
·583	4850	81	1·375	103
·487	4650	200	·75	168

Average values ... $e/m=139$, $m/\mathrm{H}=69{\cdot}5$, Corrected ... $e/m=221$. $m/\mathrm{H}=43{\cdot}7$.

The more definite values given by the more normal curves obtained after the metal had been heated for some time are shown in the next table. The numbers represent measurements made on three separate strips.

Gold (after heating for some time). Positive Ions.

z.	H.	V.	x.	e/m.
·563	4850	122	1·85	319
·563	4850	162	1·50	280
·563	4850	202	1·275	254
·583	4850	325	1·10	264
·487	4650	200	·97	280

Average values ... $e/m=280$, $m/\mathrm{H}=34{\cdot}5$, Corrected ... $e/m=445$. $m/\mathrm{H}=21{\cdot}7$.

The most natural interpretation of the peculiar behaviour of gold would seem to be that the low values of e/m obtained from a new wire are caused by the presence of impurities which are very readily volatilized. The values obtained after the metal had been heated for some time are not very different from those given by the metals which have already been examined. It is curious that the initial value of e/m is exactly one-half that found later.

Iron.

Very erratic results were obtained with this metal and the values of e/m obtained showed no tendency, so far as we have been able to observe, to become constant either with lapse of time or with any other conditions. This is probably to be attributed to irregularities in the emission itself, as it was very frequently noticed that during the experiments with iron the electrometer spot did not move uniformly, but was liable to jerks as though the thermionic emission was an intermittent phenomenon. Moreover, the value of the fraction of the total ionization which passed through the slit in any particular position was not constant, but kept varying, so that it was often impossible to get the same value twice at the same point. For these reasons the values obtained with iron do not possess the same definiteness as in the case of the preceding metals. A large number of experiments were made with iron in the hope of being able to make the conditions more definite. Two different kinds of iron were used: (*a*) strips of Norway iron rolled from wire, (*b*) strips of transformer iron rolled from sheet. The numbers for those experiments on Norway iron which led to an estimate of e/m are given in the following table:—

Norway Iron. Positive Ions.

z.	H.	V.	x.	e/m.
·550	4850	304	1·40	500
·550	4850	223	1·475	410
·455	4650	200	·90	317
Average values ... $e/m=409$, $m/\mathrm{H}=23{\cdot}6$,		Corrected ... $e/m=650$. $m/\mathrm{H}=14{\cdot}8$.		

In considering the above numbers it is important to observe that it was noted at the time that in the case of the experiment which gave the lowest value of e/m the conditions were exceptionally steady. If this number (317) were taken alone we should have for the corrected values of e/m and m/H the numbers

$$e/m \quad 503 \qquad \text{and} \qquad m/\mathrm{H} \quad 19{\cdot}2.$$

The experiments with the transformer iron led to the numbers in the following table:—

Transformer Iron. Positive Ions.

z.	H.	V.	x.	e/m.
·569	4850	314	1·525	535
·569	4850	231	1·70	490
·569	4850	147	2·02	441
·555	4850	195	1·50	356
·567	4850	122	1·85	322
·567	4850	194	1·50	337
·567	4850	232	1·35	327
·555	4850	159	1·50	290
·555	4850	308	1·00	250

Average values ... $e/m=372$, $m/\mathrm{H}=26{\cdot}0$, Corrected ... $e/m=592$. $m/\mathrm{H}=16{\cdot}4$.

The first three of the above values were given by the same specimen of iron. It will be noticed that they were much higher than any of the others, and we were unable to obtain such high values in any of the subsequent experiments. If these are excluded the mean of the rest gives e/m 305, corrected e/m 486, corrected m/H 19·9. The three high values obtained from the first specimen alone give e/m 487, corrected e/m 775, corrected m/H 12·5.

In several of the experiments with iron a black soot-like deposit was observed on the part adjacent to the hot strip after the apparatus had been taken down. This was especially noticeable in the experiments with both kinds of iron in which high values of e/m had been obtained.

It was thought at one time that the peculiar values of e/m obtained from iron might be due to the magnetic properties of the metal affecting the applied magnetic field. This does not seem to be possible however, since all the experiments were made above the critical temperature at which the ferromagnetic property disappears. Moreover, it does not seem as though the magnetic properties of the metal had anything to do with the phenomenon, since the value of e/m for nickel, nichrome, and steel (see below), all of which are magnetic, was the same as for the other metals investigated above.

In fact it seems pretty certain that in the case of iron we have to do with more than one source of positive ionization.

One of these might well be the same substance as that which gives rise to the emission of the positive ions by the other metals investigated, and the high values of e/m obtained would be due to the presence of some other substance which gave rise to ions of smaller mass. The fact that when the highest values of e/m were obtained a sooty deposit was observed, would lead one to suspect that this substance was carbon, which was dissolved in or chemically combined with the iron. On this view, it would be necessary to suppose that the dissolved or combined carbon was given off in the form of positive ions. This view is supported by the fact that the value of m/H corresponding to the cases which gave rise to the largest values of e/m is almost identical with the atomic weight of carbon. Against this we have to set the fact that in the former paper experiments were made on the positive ions emitted by carbon itself, and these were found to possess the same value of e/m as those emitted by platinum. This is not, however, of necessity conclusive. It may be necessary for the carbon to be dissolved in a metal before it can be given off in the ionized form. In fact there is now a good deal of evidence to support the general statement that when a substance is expelled by heat from a metal in which it has been dissolved, some of it is in the form of positive ions. One of the authors* has adduced a considerable amount of evidence in favour of the view that the permanent positive ionization produced by hot platinum in oxygen and hydrogen is caused by the emission of those gases from the metal, in which they have been either dissolved or absorbed.

The discussion of the nature of the substance which gives rise to the heavier ions from iron may be conveniently postponed until the various substances under investigation can be discussed together.

Tantalum.

Tantalum was found to resemble gold in so far as it gave small values of e/m when first heated and larger ones afterwards. It was not found possible to heat tantalum continuously for any length of time as it burnt away rapidly, even when the pressure was kept below ·001 mm. The numbers which were obtained are given in the following table:—

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* Phil. Trans. A. ccvii. p. 1 (1906).

Tantalum. Positive Ions.

z.	H.	V.	x.	e/m.
·449	4650	200	·59	145
·449	4650	400	·46	175
·551	4850	122	1·15	135
·551	4850	160	·925	115
·551	4850	200	1·225	257
·551	4850	122	1·55	245
·551	4850	160	1·375	253

Average value ... $e/m=189$, $m/\mathrm{H}=51$, Corrected ... $e/m=301$. $m/\mathrm{H}=32$.

The first two measurements were made on one strip and the succeeding five on another. The first measurements are probably not so reliable as the others on account of the smallness of the deflexions. If we take the last three together as representing the final steady value we find e/m (average) 252, corrected e/m 400, corrected m/H 24·2. Whereas for the initial values the third and fourth give :—average e/m 125, corrected e/m 199, corrected m/H 48·4. Here again the ratio of the initial and final values is 2 to 1 as in the case of gold.

Tungsten.

The tungsten used was in the form of filaments taken from a new tungsten lamp. On account of the fact that it was impossible to obtain the material in the form of strip we should expect, as in the case of osmium, that the curves would be very flat and the maxima not sharply defined. The case was, however, worse than this, because the curves were very irregular in outline and usually exhibited more than one maximum. These were not due to the simultaneous emission of more than one kind of ion, as they were present just the same in the absence of the magnetic field. The most plausible explanation seems to be that the positive ions are emitted by some impurity which is liable to be irregularly distributed about the filament. A number of attempts were made to estimate the value of e/m from the displacement of what appeared to be corresponding points in the patterns. There is a good deal of uncertainty in this procedure, so that it is perhaps not to be wondered at that the results obtained do not show a very satisfactory agreement. They are given in the following table :—

Tungsten. Positive Ions.

z.	H.	V.	x.	e/m.
·567	4850	122	1·30	159
·567	4850	194	·85	108
·567	4850	194	·85	108
·567	4850	307	·55	72
·567	4850	307	·45	48
·567	4850	122	·70	47
·467	4650	200	1·20	541

Average values ... $e/m=155$, $m/\text{H}=62·5$, Corrected ... $e/m=246$. $m/\text{H}=39·3$.

All that we can reasonably conclude from the above numbers is that the positive ions from tungsten are of the same order of magnitude as the other metals investigated so far as their specific charge is concerned.

Alloys.

Experiments were made on brass, nichrome, and steel. These were all found to give only one kind of ion for which the value of e/m was near that for platinum. Although both nichrome and steel contain iron, neither of them was found to give the high values of e/m which were obtained with that metal in the purer state. The numerical values are given in the following tables :—

Brass. Positive Ions.

z.	H.	V.	x.	e/m.
·583	4850	305	1·05	225

Values ... $e/m=225$, $m/\text{H}=43$, Corrected ... $e/m=358$. $m/\text{H}=27$.

Steel. Positive Ions.

z.	H.	V.	x.	e/m.
·567	4850	41	2·50	194
·567	4850	81	1·85	214
·567	4850	41	2·75	239

Average values ... $e/m=216$, $m/\text{H}=44·7$, Corrected ... $e/m=343$. $m/\text{H}=28·1$.

Nichrome. Positive Ions.

z.	H.	V.	*x*.	*e*/*m*.
·563	4850	122	1·575	233
·563	4850	160	1·475	268
·563	4850	200	1·30	273
·563	4850	122	1·725	280

Average values ... $e/m=264$, Corrected ... $e/m=420$.
$m/\mathrm{H}=36{\cdot}6$, $m/\mathrm{H}=23$.

Summary.

In order to see at a glance the results which have been obtained, the corrected values of e/m and of m/H are collected together in the following table. Where the substance gave more than one value of e/m and m/H the abnormal values are also shown in the first two columns marked "initial values." The term initial value seems strictly applicable in the case of gold, and probably also tantalum, but in the case of iron we are not sure that the high values of e/m were really initial values. With this metal, the values obtained seemed to depend more on the specimen used than any other factor that we could discover. In the case of tungsten the values are so erratic that we have made no attempt to distinguish between them, although there was some slight indication of an approach towards higher values of e/m with continued heating. The last two values for platinum and the carbon are taken from the previous paper.

Substance.	Initial value of *e*/*m*.	Initial value of *m*/H.	Permanent value of *e*/*m*.	Permanent value of *m*/H.
Platinum	......	......	387	25·0
Palladium	......	......	337	28·7
Copper	......	......	366	26·4
Silver	......	......	342	28·3
Nickel...............	......	......	380	25·4
Osmium	......	......	420	23·0
Gold	221	43·7	445	21·7
Iron	775	12·5	486	19·9
Tantalum	199	48·4	400	24·2
Tungsten	246	39·3	......	......
Brass	......	......	358	27·0
Steel	......	......	343	28·1
Nichrome	......	......	420	23·0
Platinum	......	......	384	25·7
Carbon	......	......	353	27·6

With one or two exceptions the numbers in the last column do not differ from one another by more than the error of observation. There is a considerable error in these measurements arising from the curvature of the strip when heated. Although the strips were very short (·5 cm. in length) the effect of this on z is important since the value of e/m involves the fourth power of z. An attempt was made to allow for this by direct observations of the displacement of the strips when heated, and they were always arranged so that they curved in towards the plates.

The mean value of all the numbers in the last column counting platinum only once and equal to 25·35 is 25·3. It is probable that the value for iron is affected by the presence of some of the substance which gives rise to the ionization with very high values of e/m. If we omit iron from the average we find the mean value of $m/\mathrm{H}=25{\cdot}7$. This number is very close to the values found for carbon and platinum in the previous paper, so that the greater part of the discussion there applies equally to the present results. The case against the view that this ionization is due to one or more of the gases whose molecular weights are about 30 (O_2, N_2, and CO) is strengthened by the present experiments. It is probable that traces of carbon monoxide are always present when a metal is heated in a vacuum in the kind of apparatus used in the present experiments, but it is difficult to see why practically all the ionization should be due to this gas in the case of all the substances investigated. It is known that when a great many metals are heated the bulk of the gas given off is hydrogen, and one of the authors* has shown that when this gas escapes from the platinum a considerable amount of it is in the form of positive ions; whereas in none of the present experiments were any ions detected for which the value of e/m approached that of hydrogen. Moreover, the metal most likely to emit carbon monoxide in quantity is iron, and this is the one metal for which the value of e/m deviated most widely from that corresponding to carbon monoxide.

It is perhaps of interest to remark that a great difference was observed in the amount of gas given off by the various substances used. Platinum and palladium gave off most, gold gave a much smaller quantity, whilst the amount given off by the other materials was inappreciable.

The mean value of m/H is very near to the atomic weight

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* O. W. Richardson, Phil. Trans. A. ccvii. p. 1 (1906).

of sodium (23·1), and it seems most probable that these positive ions which seem common to so many different substances are due to sodium or its compounds which are present as an impurity. It seems unlikely that they are due to a common constituent of the different substances carrying a fraction of the ionic charge, since Dr. F. C. Brown[*] has shown that the positive ions emitted by most of the substances examined have approximately the value of the kinetic energy proper to the temperature of the metal from which they are emitted, on the assumption that they carry the normal charge. The fact that the value of m/H tends to run a little higher than the atomic weight of sodium, may mean that in most cases there is a small amount of potassium or its compounds present.

Additional evidence in favour of the view that the positive ionization emitted by metals at low pressure is due to the presence of alkaline impurities will shortly be presented in a paper by one of the authors, dealing with the positive ions emitted by the various alkali sulphates.

Whatever the cause of the positive ionization may be, it is clear that it is very intimately associated with the metal. For a platinum wire which has been boiled in pure nitric acid for hours and afterwards had oxygen deposited on it by electrolysis in the same medium, when mounted and tested, after washing with distilled water, is found to give a large initial positive ionization which decays with time. In fact it behaves very like a wire which has not been specially treated. This shows that the "impurities" must be very deep-seated.

In conclusion we desire to thank Mr. Irving B. Crandall, A.B., graduate student in physics, and Mr. Cornelius Bol, research assistant, for their help during part of the investigation.

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[*] Phil. Mag. [6] vol. xviii. p. 649 (1909).

LIX. *The Eye as an Electrical Organ.* *By* W. M. THORNTON, *D.Sc., D.Eng., Professor of Electrical Engineering, Armstrong College, Newcastle-on-Tyne* [*].

1. ON the electromagnetic theory of light the amplitude of a progressive wave in a partially conducting medium is reduced by dissipation of energy as heat. The optical media of the eye are typical conducting dielectrics, and the following notes are a consideration of (1) the influence of absorption on vision, (2) the reticulation of the optic nerve on the inner surface of the retina, (3) the least electrical current which can be detected by the eye as light, from the point of view of the electromagnetic theory. Apart from the physiological question of the degree in which sensation is proportional to stimulus, and considering only the energy of the wave, the reduction of light in intensity between entering the cornea and reaching the retina can be found by the expressions given by Maxwell [†] and Heaviside [‡] for the decrease of amplitude of waves in a conducting dielectric.

In a distance r they are reduced in the ratio $e^{-\alpha r}$, where

$$\alpha = \frac{1{\cdot}41\,\pi}{\lambda}\left[\left\{1+\left(\frac{2v^2}{\rho n}\right)^2\right\}^{\frac{1}{2}}-1\right]^{\frac{1}{2}},$$

in which λ is the wave-length, n the frequency, and v the velocity of the wave in the medium of specific resistance ρ.

At high frequencies, such as those of light, this reduces to

$$\alpha = 2\pi v/\rho.$$

In the vitreous humour for example, with $\rho = 83 \times 10^9$ C.G.S. units, and with the velocity of the wave, calculated from the refractive index, equal to $2{\cdot}3 \times 10^{10}$ cm. a second, α is found to be 1·7, and the reduction of amplitude in 1·43 cm., the thickness of the vitreous humour in the human eye, is to ·088 of that of the incident wave. The energy of the wave, which is proportional to the square of the amplitude, is therefore ·0077 of the initial value.

The following table gives the thickness and resistivity of the various media, the former for the human eye, the latter for ox eyes, and the reduction of amplitude in each part.

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[*] Communicated by the Author.

[†] Electricity and Magnetism, vol. ii. § 798.

[‡] Electrical Papers, vol. ii. p. 422. See also Lodge, Phil. Mag. April 1899, "On Opacity."

The resistances were measured by the Kohlrausch bridge-telephone method on freshly killed, though cold, eyes.

The high conductivity of the humours, greater than that of blood, is remarkable.

Medium.	Thickness r.	ρ.	Mean.	a.	ar.	Reduction ratio.
Cornea	·115 cm.	455	455	0·3	·0345	·968
Aqueous humour.	·36	92–114	103	1·37	·495	·610
Crystalline lens...	·39	650–750	700	0·20	·078	·925
Vitreous humour.	1·43	80–87	83	1·7	2·43	·088

The total reduction of amplitude is the product of all the figures in the last column and is equal to ·048 ; the energy is therefore ·0023 of that of the incident light.

The reduction of intensity is independent of frequency, that is, of colour. The limitation of vision at the blue end of the spectrum is not then due to simple absorption of the kind considered, but either to selective absorption—probably in the cornea—or to photo-chemical inactivity of the visual yellow and purple in ultra-violet light.

The greater part of the incident energy is absorbed before reaching the vitreous humour, but the rate of diminution in the latter is so great, that in the case of exposure to very strong light, injury is lessened. The chief function of the vitreous humour, from this point of view, is to act as an absorbing screen protecting the retina from possible over-exposure.

Although absorption would appear to reduce the sensitiveness of the eye by its presence, the structure of the retina can by it be much more delicate without risk of injury.

2. Light falling on the retina encounters first the reticulated optic nerve. The reason for the fine subdivision of this is not fully known. The size of the fibres is, however, such that they are peculiarly well suited, as a bolometer, to receive the incident energy.

The distribution of alternating current in the cross-section of a cylindrical conductor is not uniform when the frequency exceeds a certain value, which depends upon the conductivity and diameter. Since the current density is then greater at the circumference, this is known as the "skin effect"; it reduces the effective current in the conductor.

The diameter of the nerve fibres of the retina is such (about 4 to 10 μ), that notwithstanding the frequency approaching 10^{15} a second, the skin effect does not occur. That is, the current density of the electrical current forming the light-wave, which being transverse traverses the fibres longitudinally, is uniform over their cross-section. In the calculation of this the resistivity of the fibres was taken to be, as a lower limit, 20 ohms per cm. cube. The value given by Waller[*] is 200 ohms per cm. cube for muscle and nerve; the previous value was chosen to cover any possible increase of conductivity in non-medullated fibres. If the inner layer of nerve fibre were continuous and of the same thickness as the fibres, it would not be opaque to electric radiation at the frequency of light, unless by selective absorption. The object of the reticulation cannot therefore be only to let the light through to the rods and cones.

From observations given later, it can be shown that the energy absorbed in the faintest visible light is not sufficient to account for a rise of temperature in the fibres of more than 10^{-8} degree C. a second; and since the eye is able to follow rapid flicker, it seems improbable that the visual stimulus can be in any way thermal in a medium maintained at blood-heat. It is more probable, and it is suggested here, that the stimulus caused by the electrical currents in the light-wave incident on the fibres may be contributory to vision by acting as a continuous "messenger" to the brain, or as the vibrator in a coherer system keeping sensitive the contact at the synapse between the retina and the rods and cones.

3. An approximate estimate of the least current which can be detected by the eye as light, may be made by considering the distance at which the sun would cease to be visible. The mean energy reaching the earth's surface in full sunlight was found by the late Prof. S. P. Langley to be $4{\cdot}3 \times 10^{-5}$ erg per cubic centimetre. In a letter from him, shortly before his death, he estimates the energy in the visible part of the spectrum from the curves of luminosity to be 21 per cent. of the whole. The stellar magnitude of the sun according to Pickering is $-25{\cdot}5$. The mean of Wollaston's, Zollner's, and Bond's values is $-26{\cdot}4$. Thus with the former value the sun has 4×10^{12} the intensity of a star of the 6th magnitude, the highest visible by the unaided eye, with the latter value $9{\cdot}1 \times 10^{12}$. Taking the former as probably the more accurate, the sun would cease to be visible at 2×10^{6} its present distance[†].

The energy reaching the earth would then be $0{\cdot}25 \times 10^{-12}$

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[*] A. D. Waller, 'Signs of Life.'

[†] I am indebted to Prof. R. A. Sampson for the astronomical data.

of Langley's value, that is $1{\cdot}07 \times 10^{-17}$ erg per cubic centimetre or 0·32 micro-erg per square centimetre per second. The ratio of the visible to total energy can scarcely be the same at the very low intensities. Retaining it in the absence of more reliable data, the energy in the visible light is ·067 micro-erg per square cm. per second. It is then reduced by absorption in the eye in the ratio ·0023, giving $1{\cdot}5 \times 10^{-4}$ erg, or with a velocity of $2{\cdot}3 \times 10^{10}$ centimetres a second, $6{\cdot}5 \times 10^{-15}$ erg per cubic centimetre of space at the retina.

The average energy in unit volume of light-wave in non-magnetic media is $4\pi i^2$, where i is the root-mean-square value of the current per square centimetre. The current corresponding to the energy in the visible part of the spectrum is then

$$i = (6{\cdot}5 \times 10^{-15}/4\pi)^{\frac{1}{2}},$$

that is 23 micro-amperes per square centimetre at right angles to the wave front.

Since there is no skin effect, this is also the current-density in the nerve fibres. The current in a fibre of ·0004 cm. diameter would be $2{\cdot}87 \times 10^{-14}$ ampere. This, then, appears to be about the least electrical current in a nerve fibre which can produce the sensation of light.

The current, when viewing white clouds in full sunlight, with one's back to the sun, is about $7{\cdot}0 \times 10^{-12}$ ampere in the fibres.

Taking the value of 200 ohms per centimetre cube as the resistivity of nerve, the energy absorbed per centimetre length corresponding to a current of $2{\cdot}87 \times 10^{-14}$ ampere is $1{\cdot}31 \times 10^{-18}$ watt, or $1{\cdot}31 \times 10^{-11}$ erg per centimetre of fibre per second. If each nerve fibre conveys a separate stimulus, this is what may be called the least specific stimulus required in the mental process of vision; the actual length of fibre in the retinal image is a small fraction of a centimetre.

Rayleigh * has suggested that the least power required for hearing is not very different from that of least vision. From Rayleigh's figures for sound, Lodge † finds this power to be 6 micro-ergs per second per square cm. Comparing this with the energy entering the eye at least visibility, obtained above from Langley's values, viz. 0·32 micro-erg per second per square cm., the eye would appear to be able to detect about one twentieth of the energy required for the least perception of sound.

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* 'Sound,' Article 384, footnote.

† Jour. Inst. Elec. Engineers, vol. xxvii. p. 931.

LX. *The Photoelectric Fatigue of Metals.* *By* H. Stanley Allen, *M.A., D.Sc., Senior Lecturer in Physics at University of London, King's College* *.

THE recorded facts relating to the diminution of the photoelectric activity of metal surfaces with time are somewhat confusing and contradictory. The difficulties have been in part removed by the researches of Hallwachs and his fellow workers †. Hallwachs maintains that the photoelectric "fatigue" is not primarily due to illumination, and that the size of the vessel in which the plate is kept affects to a marked degree the rate at which the fatigue takes place. Ignorance of the latter result goes far to explain the contradictions amongst the earlier experiments.

My investigations, which have been in progress for some years past, have led me to the same conclusions; and in view of the importance of these conclusions in explaining the changes involved in fatigue, it seems desirable to put on record a short account of my results.

In the following paragraphs it is shown that in the case of zinc, (1) light is not the primary cause of fatigue, (2) the fatigue is practically independent of the electric field, (3) the fatigue takes place in an atmosphere of hydrogen as in ordinary air, (4) the fatigue proceeds more slowly when the plate is kept in a small vessel.

To explain the last result we are forced to the conclusion that the fatigue must be due to some substance (ozone, Hallwachs; in the case of zinc, ozone, water vapour, Ullman) present in small quantity in the atmosphere surrounding the plate. The fatigue must be associated with the condition of the gaseous films on the surface of the plate or with the gas occluded in the metal.

The foregoing remarks apply to fatigue in gases at ordinary pressures ; in a vacuum other sources of fatigue may possibly be present ‡, though recent results tend to show that with a perfectly clean metal surface in a very high vacuum there would be no fatigue §.

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* Communicated by the Author.

† W. Hallwachs, *Phys. Zeit.* v. p. 489 (1904); *Ber. d. math.-phys. Klasse d. Kgl. Sächs. Gesellsch. d. Wissensch. zu Leipzig*, lviii. p. 341 (1906); *Ann. d. Phys.* xxiii. p. 459 (1907); *Abh. d. naturwissensch. Gesellsch. Isis in Dresden*, i. p. 65 (1909). H. Beil, *Ann. d. Phys.* xxxi. p. 849 (1910). E. Ullmann, *Ann. d. Phys.* xxxii. p. 1 (1910).

‡ As, for example, changes in pressure due to absorption of gas by the metal (Dember, *Phys. Zeit.* ix. p. 188, 1908). A change in pressure due to gradual absorption of gas by charcoal at the temperature of liquid air may have been the cause of the apparent fatigue of zinc in a vacuum recorded in my first paper (§ 12).

§ Millikan and Winchester, Phys. Rev. xxix. p. 85 (1909).

Method of experimenting.—The apparatus used in the present research was identical with that described in my earlier papers referred to below. I desire again to express my thanks to the Government Grant Committee of the Royal Society and to the Council of King's College for defraying the cost of the greater part of this apparatus. The mercury-vapour lamp of fused quartz supplied with current from a special set of accumulators was used as a source of ultra-violet light throughout this investigation. Provided sufficient time (from 20 to 30 minutes) is allowed for it to assume a steady state, this gives a sufficiently constant stream of radiation.

The photoelectric current between the positively charged wire gauze and the metal plate was measured by means of a Dolezalek electrometer in connexion with a suitable condenser. Readings of the rate of leak were usually taken at intervals of two minutes. Most of the results recorded were obtained with a zinc plate polished with fine emery-paper; both the initial activity and the rate of fatigue showed considerable variations from day to day, probably in consequence of the atmospheric conditions, but the results obtained on any particular day were usually concordant. In most cases the figures given represent the mean of two or three concordant determinations.

(1) *Light is not the primary cause of fatigue.*

In my earlier investigations I found that the rate at which fatigue takes place is not much affected by the intensity of the illumination * or by the character of the source of light (mercury-vapour lamp or Nernst lamp †). Later experiments carried out to determine the influence of light on fatigue confirm the conclusions of Hallwachs. The photoelectric fatigue of zinc proceeds in darkness almost at the same rate as when the metal is continuously exposed to light.

The results of these experiments are embodied in the following tables (I., II., and III.). The tests in Table I. were made with a zinc plate polished with fine emery and rouge, tested in the air of the room, readings of the activity being taken at intervals of two minutes. The plate was exposed continuously to the mercury-vapour lamp except where an asterisk appears in the table. In the latter case the plate was shielded from ultra-violet light but not from the dim light of the room. The activity is expressed as a

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* H. S. Allen, Proc. Roy. Soc. (A) lxxviii. § 7, p. 489 (1907).
† H. S. Allen, Proc. Roy. Soc. (A) lxxxii. § 5, p. 164 (1909).

percentage of the initial activity, measured immediately after polishing.

Table I.

Zinc plate in air of room. Fatigue period, 16 minutes.

I.	100	100	100	100	100
II.	75	*	77	76	77
III.	66	*	*	67	64
IV.	57	58	*	*	58
V.	54	55	55	*	*
VI.	49	51	51	48	*
VII.	47	49	47	44	48
VIII.	46	46	45	43	44
IX.	43	45	42	42	43

The fatigue is not affected by shielding the zinc from ultra-violet light for a period of about five minutes, no matter at what stage in the process the shielding takes place.

In the tests recorded in Table II. the zinc plate was polished with fine emery-paper only. The initial activity is given in arbitrary units in the first row of the table, and below is given the activity at the end of a fatigue period of 16 minutes, expressed as a percentage of the initial activity.

Table II.

Zinc plate in air of room. Fatigue period, 16 minutes.

		a.	*b.*	*c.*	*d.*	*e.*
Initial activity	Arbitrary units ...	318	290	288	237	211
	Percentage	100	100	100	100	100
Final activity.	Percentage	47	44	43	44	46

In test *a* the plate was exposed to ultra-violet light continuously. In test *b* it was shielded from ultra-violet light for 5 minutes, while in tests *c*, *d*, and *e* it was shielded from ultra-violet light for 15 minutes.

Experiments were also carried out in a closed testing-vessel of brass fitted with a quartz window. The zinc plate was polished with fine emery, placed in position as quickly as possible, and the first reading was taken two minutes after polishing. The initial activity was found by extrapolation, and in the table has been taken as 100. In experiments *a*, *d*, and *e* the plate was illuminated continuously by the mercury-vapour lamp. In *b* and *c* it was in complete darkness for 9 minutes, as indicated by the asterisks in the table. During this period the testing vessel was closed with a light-tight wooden cover.

TABLE III.

Zinc plate in testing vessel. Fatigue period, 16 minutes.

	a.	*b.*	*c.*	*d.*	*e.*
I.	100	100	100	100	100
II.	91	93	92	92	89
III.	85	88	87	83	80
IV.	79	*	*	79	78
V.	78	*	*	78	75
VI.	75	*	*	77	71
VII.	73	*	*	72	70
VIII.	71	73	75	71	69
IX.	67	73	74	71	68

It appears from the results in the table that the fatigue takes place in complete darkness, though there is evidence of a small increase in the rate of fatigue under the influence of the ultra-violet light.

We conclude that light cannot be the primary cause of fatigue, though it may play a secondary part in accelerating or retarding fatigue. These secondary actions are illustrated in my earlier experiments on amalgamated zinc [*], or on polished zinc at different distances from the mercury-vapour lamp [†].

Ullmann [‡] arrives at similar conclusions, attributing the secondary actions of light to the formation of ozone and to the heating of the plate.

I have also examined the action of Röntgen rays on the plate and could detect no decisive change in the rate of fatigue, at any rate for an exposure of one or two minutes to the rays from a focus-tube at a distance of about 50 cms. Hallwachs [§] records a similar result.

[*] H. S. Allen, Proc. Roy. Soc. (A) lxxviii. § 11, p. 492 (1907).

[†] H. S. Allen, Proc. Roy. Soc. (A) lxxxii. § 2, p. 163 (1909).

[‡] Ullmann, *Ann. d. Phys.* (4) xxxii. § 5, pp. 15-20 (1910).

[§] Hallwachs, *Ann. d. Phys.* (4) xxiii. p. 467 (1907).

2. *Fatigue independent of the Electric Field.*

The rate at which fatigue takes place does not depend on the strength of the electric field applied. This is illustrated in Table IV., which contains results of experiments made in the air of the room and of others made in the brass testing vessel. The zinc plate used was polished with fine emery-paper.

Table IV.

Zinc plate. Fatigue period, 16 minutes.

	In air of room.		In testing vessel.	
	110 volts.	480 volts.	110 volts.	480 volts.
I.	100	100	100	100
II.	85	89	95	93
III.	80	83	91	88
IV.	75	79	88	85
V.	71	75	83	83
VI.	68	70	81	80
VII.	65	66	79	78
VIII.	62	60	77	77
IX.	59	58	76	76

Again the percentage fatigue was the same whether the gauze was charged (to 100 volts) positively (as of course it must be when a measurement of the photoelectric current is being made) or negatively. This is shown in Table V.

Table V.

Zinc plate in air of room. Fatigue period, 16 minutes.

I.	100	100
II. to VII....	Gauze positive	Gauze negative.
VIII.	63	62
IX.	60	60

It was thought that possibly more effect would be produced by keeping the zinc plate at a high (positive or negative) potential with the rest of the apparatus earthed. The results in Table VI. show no effect of this kind when the potential of the zinc plate is ± 100 volts.

TABLE VI.

Zinc plate in air of room. Fatigue period, 16 minutes.

I.	100	100	100	100
II. to VII....	Gauze +ve	Zinc +ve	Gauze +ve	Zinc −ve
VIII.	50	49	51	51
IX.	45	46	47	47

When the zinc plate was under examination in the brass testing vessel and was charged positively, a small effect was sometimes observed on reversing the direction of the field for the purpose of taking a reading of the photoelectric current. The effect in question corresponded to a small increase in the observed current, the increase amounting to about ten per cent. of the anticipated value of the current. The increase only persisted for a few minutes after the direction of the field was reversed. This effect is comparable with that observed by Campbell * in the case of the leak from hot bodies, the reading taken immediately after reversal being greater than the normal.

3. *Fatigue of various Metals in Air and in Hydrogen.*

Zinc.—In my earlier papers (*loc. cit.*) I have shown that the fatigue of zinc proceeds in such a way that the activity for some hours after polishing can be represented as the sum of two exponential terms. This would indicate that after a prolonged period the activity would approach asymptotically a zero value. It has been found, however, that the zinc plate retains a small sensibility after several days (in one case after 26 days); a result which points to the existence of a state in which the zinc plate would show a small residual activity. This would mean, provided the atmospheric conditions remained invariable, the addition of a small constant term to the two exponential terms.

Experiments were made with the zinc plate when the testing vessel was filled with hydrogen, prepared by the action of pure hydrochloric acid on pure zinc and dried by

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* N. R. Campbell, Phil. Mag. ix. p. 549 (1905).

passing over solid caustic potash*. The fatigue in hydrogen was found to be very similar to that in air.

Some results as to the fatigue of other metals are here briefly summarized.

Silver.—One of the most interesting cases examined was a plate of pure silver supplied by Messrs. Johnson, Matthey & Co. The plate was polished with rouge paper and put in position in the brass testing vessel. After two hours' continuous exposure to the light of the mercury-vapour lamp the activity remained unaltered.

It is remarkable that Ladenburg †, who carried out fatigue experiments in a vacuum, mentions silver as one of the metals showing marked fatigue, but it must be remembered that his surfaces were "polished once with emery and oil."

When the air in the testing vessel was replaced by hydrogen, the same result was obtained as in air; that is, no fatigue could be detected after two hours' exposure to the source of light.

The same plate tested later in the air of the room showed fatigue effects, the activity falling to half its initial value in two hours. We have here an example of the influence of the size of the vessel to be discussed later.

Aluminium.—This metal was found to behave in much the same way as zinc. Its activity can be represented by the sum of two exponential terms. When examined in air in the closed testing vessel, using the mercury-vapour lamp as the source of light, the first term fell to half value in 6 minutes, the second in 190 minutes. In hydrogen the values were not very different, being 7 minutes and 165 minutes, respectively.

Copper.—When a copper plate was examined in the testing vessel, the fatigue proceeded slowly from the outset; about 3 hours would be required for the activity to fall to one-half of the initial value. In hydrogen the fatigue took place at about the same rate as in air. In the air of the room more rapid fatigue was observed.

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* It should be noted that the metal plate was polished and put in position in the testing vessel, the air was displaced by a current of hydrogen, and readings of the activity were commenced a few minutes after polishing. It is not probable that the gas was entirely free from water-vapour, nor is it likely that the air-film on the surface of the plate was immediately changed. It is to be wished that experiments could be carried out in which the plate should be polished *after* being placed in a good vacuum or in an atmosphere of the gas to be employed in the investigation.

† E. Ladenburg, *Ann. d. Physik*, xii. p. 558 (1903).

4. *Fatigue depends on the size of the containing vessel.*

The influence of the size of the containing vessel on the rate at which fatigue takes place was verified during the present investigation. Examples of this influence have already been recorded in the earlier parts of the paper. If we compare the results of Tables I. and II. with those of Table III., we find that the fatigue is more rapid in the air of the room than in the testing vessel. The same difference is also shown in Table IV. Similar effects are mentioned in § 3 with regard to silver and copper.

Inasmuch as the rate of fatigue varied somewhat from day to day, probably being dependent on the state of the atmosphere at the time, it seemed desirable to have a direct comparison between the fatigue in the room and that in the testing vessel when the air was in the same condition. The results of experiments made on the same day are recorded in Table VII.

Table VII.

Zinc plate. Fatigue period, 16 minutes.

In air of room.		In testing vessel.
Emery.	Rouge.	Emery.
100	100	100
86	89	90
79	79	82
72	73	79
67	67	77
64	64	75
59	58	72
57	55	71
53	52	69

The fatigue is diminished by putting the plate in the smaller receptacle. Incidentally we notice that the fatigue proceeds at the same rate when the plate is rubbed with emery-paper only as when this is followed by the application of rouge paper.

Conclusion.

There has been much discussion as to the nature of the change associated with photoelectric fatigue. The principal views of the character of the change may be summarized as follows:—

1. A chemical change such as oxidation of the surface.
2. A physical change of the metal itself, as for example a roughening of the surface.
3. An electrical change in the formation of an electrical double layer (Lenard [*]).
4. A disintegration of the metal due to the expulsion of electrons by light (Ramsay and Spencer [†]).
5. A change in the surface film of gas or in the gas occluded in the metal (Hallwachs).

Hallwachs has shown from the behaviour of copper and its oxides that oxidation cannot be the cause of fatigue, and the results of the present paper confirming those of other observers are inconsistent with the second, third, and fourth views. We must therefore conclude with Hallwachs that the main cause of photoelectric fatigue is to be found in the condition of the gaseous layer at the surface of the plate. This does not exclude the existence of secondary causes of fatigue in particular cases.

The fact that the activity at any instant can be expressed by means of exponential terms is not inconsistent with the theory put forward. It is sometimes assumed that equations of the type here indicated necessarily refer to unimolecular changes. But in certain cases reactions are met with which, though really polymolecular, behave like unimolecular reactions [‡]. Thus certain gaseous reactions take place on the surface of the walls of the containing vessel, and the velocity of the reaction is proportional to the pressure of the gas. The chemical change then appears as a reaction of the first order. Thus a purely surface action may simulate the character of a unimolecular reaction.

In conclusion I may be allowed a few words of personal explanation. I have been represented as a supporter of the theory that photoelectric fatigue is due to a kind of radioactive change induced by light. Although when my first paper was written I was prepared to recognise the *possibility* of this explanation, I was careful to state that the nature of the modifications [§] of the surface suggested was left an open question. The view which I favoured for a long time was that these modifications of the surface corresponded with the

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[*] P. Lenard, *Ann. d. Phys.* viii. p. 196 (1902).

[†] Sir W. Ramsay and J. F. Spencer, Phil. Mag. [6] xii. p. 397 (1906).

[‡] H. M. Dawson, Nature, lxxi. p. 532 (1905).

[§] "Whether physical or chemical modifications of zinc."

amorphous and crystalline phases described by Beilby*, photoelectric fatigue being a gradual change from the amorphous to the crystalline form through an intermediate (labile) phase.

The experiments described in this paper show that such a view is untenable, at least in this simple form, and that we must look to the gaseous films on the surface of the metal for the explanation of the chief effects of photoelectric fatigue.

Wheatstone Laboratory,
University of London, King's College.
June, 1910.

LXI. *Positive Electrification due to Heating Aluminium Phosphate.* *By* A. E. Garrett, *B.Sc.*†

[Plate XI.]

I. *Introduction and Experimental Arrangements.*

In a paper published in the 'Philosophical Magazine' for October, 1904, by Dr. R. S. Willows and myself, it was found that the halogen compounds of zinc when heated are able to discharge both positively and negatively electrified bodies. A more detailed examination of this phenomenon was subsequently carried out by one of us ‡.

In those experiments the temperature to which the salts were raised was in no case higher than 360° C., and no series of observations at pressures lower than a few mm. were undertaken.

Sir J. J. Thomson § made some experiments to determine whether the base or the acid is instrumental in producing the ionization, and came to the conclusion that the nature of the ionic charge is determined by the acid. Thus he found that phosphates when heated produce a very large excess of positive ions, halogen compounds produce an excess of positive ions, and nitrates an excess of positive at first, but when heated sufficiently to be converted into oxides they produce an excess of negative. Incidentally he found that aluminium phosphate gives off a very large excess of positive ions.

Now the halogen and other compounds used in the previous

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* G. T. Beilby, Phil. Mag. viii. p. 258 (1904); Proc. Roy. Soc. (A) lxxii. p. 227 (1905); lxxix. p. 463 (1907).

† Communicated by the Physical Society: read June 10, 1910.

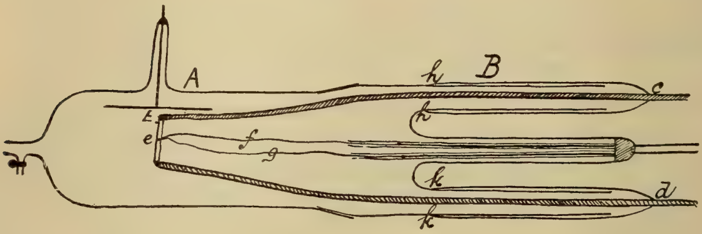
‡ Garrett, Phil. Mag., June 1907.

§ Cambridge Phil. Soc. Proc., p. 105, 1907.

experiments are known to be bodies which undergo decomposition when strongly heated, and the ionization in this case may be due to chemical action. Aluminium phosphate, on the other hand, is an extremely stable substance, and it is of interest to investigate the source of ionization in this instance. This salt was therefore chosen for detailed examination.

The apparatus used is shown in the following diagram.

Fig. 1.



The glass tube consists of two parts connected by a ground-glass joint. The part A is shown in vertical section, the part B in horizontal section. *e* is the strip of thin platinum foil, ¼ sq. cm. in area, on which the salt is placed to be heated; the temperature of the platinum *e* is raised by a current, the leads for which are the thick copper wires *c*, *d*. The electrode E, which is connected through a galvanometer to earth, is an oblong aluminium disk about 3 sq. cm. in area; the distance between the heated salt and this electrode was in most cases 0·5 cm. *f*, *g* are wires of the thermo-electric couple used for ascertaining the temperature of the platinum foil with which they are fused. To obtain the temperature from the thermo-electric current, the deflexion of the galvanometer to which leads from the junction pass was noted when a tiny particle of K_2SO_4 just melted on the foil. In this way the deflexion for two temperatures differing by about 1000° C. was obtained, and the temperature in degrees centigrade corresponding to any other deflexion could be got by aid of the correction curves given by Callendar [*]. The reliability of this method was checked by observing the melting-point of Na_2SO_4. The observations of the behaviour of aluminium phosphate were taken over a range of temperature from 900° C. to 1300° C.

Before commencing work with aluminium phosphate it was ascertained that only a small current due to ions of either sign could be detected when the platinum foil was used alone.

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[*] Phil. Mag. [5] xlviii. pp. 519 *et seq.*

The sensitivity of the galvanometer was such that a deflexion of one scale division represented a current of 2×10^{-9} ampere.

When taking readings a saturation voltage, obtained from a battery of small accumulators the negative terminal of which was earthed, was put on *e* (fig. 1) as soon as the heating of the salt was commenced, and the deflexion of the galvanometer noted from time to time. When the voltage was taken off *e* in order to read the thermo-current, time was allowed, when the voltage was again put on, for the current to become steady before readings were taken.

When the heating-current had been continued for some time, such a large amount of heat had been conducted along the copper leads as to cause the melting of the wax which was used to render the tube air-tight. This was remedied by soldering a small metal tube over each lead as shown in fig. 1, and making air-tight wax joints at *h* and *k*.

During the course of the experiments in which the galvanometer was used many attempts under varying conditions were made to detect the presence of negative ions, but with no success. That such ions are present was afterwards proved, but from the results obtained they must be less than $\frac{1}{2}$ per cent. of the positive.

Now if the positive ions are produced by chemical change brought about by the heat, then one would expect that a decay in the current would take place with the time. It was found that the current does decrease when heating is continued, so it was decided to obtain the curve of decay for this substance.

II. *Decay of Positive Ionization.*

The aluminium phosphate was made into a paste with distilled water and then placed on the foil *e*; the foil was heated slightly by the current before putting it in the tube, this causes the phosphate to adhere to the platinum, and also gets rid of the excess of water. To lessen the effect of the contained gas the tube was evacuated, and the temperature of the foil quickly raised to the degree desired. Varying conditions of temperature and pressure were tested, and it was found that the most expedient method was to reduce the pressure to about 0·05 cm., and to use a temperature of about 1200° C. Under such circumstances it was possible to obtain a record of the decay in 5 or 6 hours.

The method of procedure was as follows:—+60 volts were put on *e* (fig. 1), and as soon as the temperature became steady readings were taken; the pressure and temperature were kept constant throughout.

Experiments of this kind were carried out with air, hydrogen, and CO_2, as the gas in the tube. It was found in every case when air or hydrogen was used that the manner in which the current varied with the time for the first 20 minutes was peculiar.

A typical curve to illustrate this is given (Pl. XI. fig. 2). In this curve the currents are plotted as ordinates and the times as abscissæ.

This shows a rapid fall from A to B, then a rise to a maximum at C, and lastly a decay C to D, in which the current decreases roughly exponentially with the time. The part of the curve near B sometimes showed still further irregularities.

With CO_2 as the gas in the tube a typical decay curve is represented by ECD. The initial changes observed in air, and hydrogen, are apparently due to water, since a preliminary heating of the phosphate at a lower temperature sufficient to expel the water, gets rid of them altogether.

Further, in the case of CO_2, that gas may possibly assist in the removal of hygroscopic moisture, and so prevent its action on the salt.

After some hours' heating a more or less steady state was reached. This state persisted for some months, nor did it regain any activity if dry or moist air was admitted, even if left for 2 or 3 days. Only on one occasion was a slight temporary regain noted, and in this case the interval was 16 days.

If after the steady state was reached the salt was moistened with distilled water there was a large increase in the current which quickly died away, and in about 10 minutes the steady state was again reached. The decay of this, AF (Pl. XI. fig. 2), being taken in conjunction with a typical decay curve ECD, a curve of the form ABCD is obtained.

This is further evidence that the initial changes are due to water. These changes will not be further considered.

A typical decay-curve over a longer period omitting these changes is shown in Pl. XI. fig. 3.

The part of the curve near C is exponential; the portion EDC is very similar to the curve given by Rutherford in the 2nd edition of 'Radioactivity,' p. 342, for the variation in activity of the active deposit of Th due to a very short exposure to the emanation. In the case of Rutherford's curve this is known to be due to the decay of two substances Th A and Th B, the former of which does not produce any rays, and the equation of the curve is of the form $A(e^{-\lambda_1 t}-e^{-\lambda_2 t})$. The curve of decay of aluminium phosphate can be represented by an equation of the same form up to the point C, beyond this the exponential curve lies below the experimental. Neglecting this latter point for the moment, if the physical analogy as well as the algebraical one holds, we can suppose the first effect of the high temperature is to produce from the phosphate and the surrounding gas a substance A which does not emit ions, that this next produces a substance B which is the agent producing the conductivity. As in Rutherford's case the curve alone does not allow one to say to which substance the different λ's refer.

If the analogy holds further and the salt also independently produces C, the latter supplying ions but decaying so slowly that its decay can be neglected, the activity due to C is represented by a curve having an equation of the form $B(1-e^{-\lambda_3 t})$, and the whole curve EDCAB should be capable of being fitted by an equation

$$A(e^{-\lambda_1 t}-e^{-\lambda_2 t})+B(1-e^{-\lambda_3 t}).$$

This is actually found to be the case. The values of the λ's depend of course upon the temperature of the salt.

In Pl. XI. fig. 3 the dots represent experimental points, the ⊙'s points calculated from the above formula.

It can be seen from the curve that immediately after the very rapid decay there is a somewhat steady state which is in turn succeeded by a gradual rise in the current to a final steady state. Owing to the small scale used, this is not well shown in the curve at AB, although in the experiment there illustrated the actual rise amounted to about 20 per cent. of the previous steady values. The upper curve AB represents this section on a larger scale and makes this point more distinct.

The relatively large current at the beginning of the heating appears to depend very largely upon the nature of the gas in the tube, while the final steady current is due entirely to the heated salt.

The results obtained with hydrogen were always of a most irregular nature. The rate of decay was also much slower in that gas than in air or CO_2. It was quicker in CO_2 than in air.

No alteration of the gas contained makes any difference to the current when in the steady condition if the pressure and temperature are kept constant. Further, although an increased current is obtained with higher temperatures, and an alteration in the pressure produces also an alteration in the current, yet on bringing both temperature and pressure to their former values, the same steady current is obtained.

III. *Attempts to increase the Activity.*

Richardson * found that a platinum wire which is heated to such a temperature that an excess of positive ions are given off, gradually becomes less and less active in this respect until a more or less steady state is reached. When the wire reaches this state he found that it could be rendered much more active by passing, for about a minute, an electric discharge through the tube containing the wire, and he further showed that this regained activity persisted for a considerable time after the discharge had ceased.

It was thought that a discharge might have a similar effect upon the heated phosphate when it had reached the steady state. The heating-current was therefore cut off and a discharge from a Ruhmkorff coil sent through the tube. This increased the current temporarily. If the coil was again applied less effect was produced until, after several repetitions, the coil produced no effect.

The actual period during which the discharge lasted was gradually increased, and it was found that the maximum effect was attained when the discharge continued for ½ minute. On no occasion did it require more than 20 minutes again to reach the original steady state after discontinuing the discharge. In order to ascertain whether the temporary increase in current was due to the effect which the discharge produced upon the salt itself, or upon the residual gas, a fresh supply of CO_2 was admitted when the state at which the coil discharge produced no effect was reached, and the tube pumped down to 0·12 cm. pressure. The coil discharge again caused a temporary increase. The direction of the coil discharge did not influence the result.

The extra current therefore appears to be due to an effect produced by the action of the discharge upon the surrounding gas.

IV. *Action of Heat in the absence of Electrostatic Field.*

When the electrode e was insulated while the heating was continued an abnormally large current was obtained so soon as the field was put on between e and E (fig. 1). This current gradually decayed, but it was some 2 or 3 minutes before it

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* Phil. Mag. [6] pp. 93 *et seq.*, 1903.

reached its normal value. The magnitude of the increased current was found to depend upon the time during which *e* was insulated. It gradually increased with the time, and reached a maximum when the insulation had lasted ten minutes. Any longer period of insulation was found to have no further increasing effect upon the current.

It is possible that during the time of insulation positive ions are being freed in the salt on '*e*,' these accumulate in the substance and are prevented from escaping by a discontinuity of the potential at the surface. This continues until, at the end of 10 minutes, the field due to the accumulated charges is sufficient to take them over as they are formed, when of course no further increase in the number accumulated takes place.

When the field is again put on these ions are of course dragged out, and the initial value of the increased current will depend upon the number of ions which have accumulated.

This effect greatly increased the labour of taking readings under varying conditions, as considerable time had to be allowed after a change had been made for the current to become steady. These experiments were carried out after the steady state had been reached.

This effect was more apparent in some gases than in others, of those tried it was most marked in the case of CO_2.

V. *Effect of Pressure upon Current.*

When the salt is in the steady state it is most convenient for investigating the changes due to alterations of pressure and temperature.

The changes in the current when the temperature was kept constant while the pressure was varied were first undertaken. The contained gases used were air and CO_2. The results obtained were of a similar nature for both these gases.

Some typical curves are shown in the accompanying diagram (Pl. XI. fig. 4) in which the pressures are plotted as abscissæ, and the currents as ordinates.

From these it can be seen that starting from zero pressure there is a very rapid rise in the current in all cases, the higher the temperature the more rapid being the rise. For each temperature the current reaches a well-marked maximum value. This, again, is more pronounced at the higher temperatures. When the maximum current has been obtained, any further increase in the pressure produces an immediate and rapid decrease in the current. For the temperatures investigated, this decrease continues until the pressure attains the value 5 or 6 cms., after this the decrease which takes place in the current for any further increase in the pressure is always smaller but is still quite marked. The rate of decrease is always more rapid at the higher temperatures.

When the pressures for which the currents have maximum values are plotted against the temperatures, it appears as if the pressure and temperature are connected by a straight-line law, and that if the temperature could be pushed to a sufficiently high degree the largest current would be obtained in the highest attainable vacuum.

The fact that the maximum currents obtained at the higher temperatures and lower pressures were always greater than those obtained with the lower temperatures and higher pressures is further evidence in support of this view.

It is quite possible, however, that the slope of the temperature-pressure line may gradually become less and less, and that it never actually reaches the zero pressure line.

The peculiar manner in which the current varies with the pressure under these conditions cannot be explained by the collision of moving ions, as in all cases the voltage used was that corresponding to the flat part of the saturation curve. Evidence given later suggests that neutral doublets, such as Righi suggested compose the magneto-cathode rays, and Sir J. J. Thomson [*] found indications of in his experiments on positive electricity, are driven off when the salt is heated, and the current may be due to the break up of these doublets by collision with the gas molecules.

These doublets would be shot off with relatively large velocities at the lower pressures, but would have small chances of colliding with gas molecules or other doublets, and so relatively few free ions are produced. At higher pressures the doublets would have much slower speeds but greater chances of collision. Somewhere between these extremes the most favourable conditions for obtaining a maximum current may be looked for at each temperature.

At the higher temperatures the velocity of ejection is greater, and a less number of collisions will be required in order to split up the doublet, hence the maximum current is obtained under such conditions at a lower pressure.

With an increase of pressure more collisions are possible, but less doublets escape from the heated salt since the temperature is lower, hence the current obtained is smaller.

The great drawback in the way of this explanation is the

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[*] Phil. Mag. xviii. pp. 828 *et seq.*, Dec. 1909.

very small current due to negative ions, as compared with that carried by positive ions, which can be obtained under these conditions.

VI. *Effect of Temperature at Constant Pressure.—Phosphate in Steady State.*

Richardson[*] has proved that the formula $I=a\theta^{\frac{1}{2}}e^{-Q\ 2\theta}$, where I=saturation current, and θ=the temperature in degrees absolute, while Q=a measure of the energy associated with the liberation of an ion, represents the connexion between the saturation current and the temperature, for positive as well as for negative ions given off by heated platinum wires.

The same law holds for various chemical compounds which have been tested up to a temperature of 360° C. about[†].

The following results have been obtained by heating aluminium phosphate in CO_2 at 0·05 mm. pressure. Different quantities of the salt having been used in these experiments the absolute values of the currents are not comparable.

I.

Temperature, ° C.	Current, 2×10^{-9} amp. as Unit.
880	1
950	4
970	7
995	15
1030	35
1055	49
1095	103
1110	126

II.

Temperature, ° C.	Current, 2×10^{-9} amp. as Unit.
1036	1
1088	3
1135	5
1160	8
1195	15
1230	34
1245	35
1295	74
1330	168

The diagram (Pl. XI. fig. 5) shows the results obtained when $1/\theta$ is plotted against $\frac{1}{2}\log_e\theta-\log_e I$. The points are fairly evenly distributed about straight lines, and these lines are

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[*] Roy. Soc. Phil. Trans. A. 207, pp. 22 *et seq.*

[†] Garrett, Phil. Mag. June 1907, pp. 732 *et seq.*

parallel to one another. Thus the two sets of readings are in accord with one another, and the law may be looked upon as true for positive ions given off by heated aluminium phosphate in an atmosphere of CO_2, up to a temperature of 1300° C.

When the tube was filled with hydrogen gas at a pressure of 0·05 mm., and the results obtained were plotted in a similar manner, the same law was found to hold for that gas up to 1300° C. (see Pl. XI. fig. 5, curve iii.).

The value of Q may be obtained direct from the diagrams by multiplying the tangent of the angle which the line makes with the $1/\theta$ axis by 2.

By this means it is found that for the temperatures ranging from 900° C. to 1300° C. when the surrounding gas is CO_2 at a pressure of 0·05 mm., the value of Q is $7 \cdot 1 \times 10^4$, while with the hydrogen gas under similar conditions of pressure the value of Q is only $5 \cdot 3 \times 10^4$ for temperatures ranging from 1095° C. to 1300° C.

VII. *Determination of e/m.*

Sir J. J. Thomson's cycloid method* was used for this purpose. In this method the ions move in a gas at very low pressures under the influence of a magnetic and electrostatic field acting at right angles to one another. For a given electrostatic field the magnetic field was altered until it caused an appreciable diminution of the current passing to the electrode E (fig. 1). These experiments could not be pushed far because a magnetic field of sufficient strength could not be created. The magnet used produced a field of 800 gausses. The distance between the electrodes was 0·45 cm., and the air pressure in the tube was less than 0·01 mm. When the lower electrode was at a positive potential of 6·3 volts the magnetic field produced a decrease of about 10 per cent. in the current.

Thomson has shown that in the case of ions starting from a given plane the value of e/m for these ions may be found from the formula $e/m = 2V/H^2d^2$, in which V is the voltage to which the electrode from which the ions start is raised, H the value of the magnetic field, and "d" the distance between the electrodes in cms.

Substituting the above experimental values in this equation we find that $e/m = 9700$ about. Similar values were obtained from other experiments.

This value of e/m refers, of course, to the lightest positive ions present.

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* 'Conduction of Electricity through Gases,' 1st edition, pp. 107 *et seq.*

Thomson found for the positive ions from hot platinum values ranging from 60 to 720.

The value of e/m for the hydrogen atom in electrolysis is taken as 10^4. From this it is seen that these positive ions are comparable in size with the hydrogen atom, if we assume the same value for "e" in both cases.

A quite appreciable though smaller diminution of the current was also obtained under such conditions that e/m when calculated was found to be some 3 or 4 times as large as given above. Either the ions affected in this case have a mass smaller than that of the hydrogen atom, or else their velocity is much less than that due to the electrostatic field applied ; in the latter case we might assume that they started as free ions at some point between the two electrodes and not as such from the surface of the heated salt.

VIII. *Velocity with which ions are shot off from the Salt.*

Earlier in the paper it has been suggested that some of the ions escape from the salt on account of their kinetic energy without the application of an electrostatic field.

To put this in evidence a Dolezalek electrometer was substituted for the galvanometer, since the ions so escaping could not be detected with the latter. The sensitivity of the electrometer was such that 1 volt produces a deflexion of 180 scale-divisions. The pressure was reduced to 0·01 mm. and the temperature varied as required.

A weak magnetic field was imposed so as to remove any effect which negative ions might produce, and both E and the lower heated electrode are earthed initially.

E was then found to receive a positive charge on disconnecting it with earth.

If the lower electrode was now given a negative potential, this had to be raised to 1·2 volts to stop altogether the charging up of E.

If V = the negative potential to which the electrode e is raised to prevent positive ions leaving it, e = the charge on an ion, m = its mass, and v = its velocity ; then, from $Ve = \frac{1}{2}mv^2$ we can calculate the velocity "v" with which these ions are ejected from the heated salt.

Taking the value of e/m obtained earlier, we find that $v = 1 \cdot 4 \times 10^6$ cm. per sec., a velocity comparable with that (10^7) of the positively charged particles which constitute the anode rays.

With weak magnetic field of too low a value to affect the positive ions, the charging up effect was in every case increased, the final deflexion of the electrometer being always greater when the field was on.

When, however, a field of 800, which had previously been found to produce a measurable decrease in the current due to positive ions, was used, it was found that with temperatures below 1050° C. about, the rate of charging up of the quadrants was diminished when the field was on. As the temperature was reduced below this limit, the effect of the field became more marked. This was tested to temperatures about 950° C.

Above 1050° C. the magnetic field caused an increase in the rate at which the electrometer was charged up by the positive ions, and when the temperature had reached 1200° C. about, the rate with the field on was twice as rapid as when the field did not act.

These increases in the rate of charging up can be explained by the fact that negative as well as positive ions are produced under these conditions. These ions would cause the rate at which E charged up to be smaller than if positive ions alone were present, so when they are prevented by the magnetic field from reaching the electrode the rate at which it charges up increases. This, however, does not occur until the number of negative ions which are deflected is in excess of the number of deflected positive ions, and this state is apparently not reached until the temperature is above 1050° C.

It must be understood that the actual number of ions present under these conditions was very much less than in those cases in which the galvanometer was used, since no indication of ions of either sign was then obtained in the absence of an electrostatic field.

From 1050° C. to 1200° C. the rate at which E was charged up in the absence of the magnetic field was practically constant, while the rate with the field on gradually increased.

This would occur if the actual excess of positives which reached E per second remained constant, and for this to be the case, since more ions are now present, negative and positive ions must be formed in equal quantities, such as might happen when neutral doublets split up.

It may be that salts which give off an excess of positive ions when heated, at first eject positive ions only. Next, it would appear that doublets are ejected also, and when the salt is raised to a positive potential, or is at zero potential, the quickly moving positive ions may by collision with the doublets cause them to break up, hence causing a large positive current to pass between the electrodes. The initial positive ions appear to increase in the number given off per second as the temperature is raised until about 1050° C., after which the output appears to remain constant.

If, on the other hand, the salt is raised to a negative potential, the initial positive ions are prevented from leaving it, and so at reduced pressures, with electrodes a very small distance apart, the doublets have smaller chances of breaking up ; thus the current when the salt is negatively charged is relatively small compared with that due to positive ions.

That the potential to which the salt is raised has an important bearing upon the relative number of positive and negative ions present is clearly shown by the fact that the current due to negative ions is not so small compared with that due to positive ions when the salt is at zero potential and the gas pressure is low.

Also, at atmospheric pressure when the products due to heating the salt were removed by an air blast, there was always quite a large current produced by the negative ions.

IX. *Nature of the Ions at Atmospheric Pressure.*

For this purpose the apparatus used was two brass tubes of 1·7 cm. internal diameter, insulated from each other, and each having an insulated wire 0·33 cm. diameter and 28 cm. in length along the axis. These wires could be in turn connected with a Dolezalek electrometer of such sensitivity that one volt caused a deflexion of 820 scale-divisions.

The method adopted was to heat the phosphate on platinum foil through which a current was passed, and to suck air past the heated salt, and then through the two brass tubes placed one behind the other.

In order to avoid great fluctuations in the temperature, the platinum and its leads were enclosed in a wide glass tube, one end of which was connected air-tight to the testing apparatus, and the other closed loosely with cotton-wool.

Readings were taken after the salt had been heated for a sufficiently long time to bring it to the steady condition.

The electrometer showed no initial leak even when one of the electrodes was connected with its quadrants, and the tube containing the electrode was raised to a positive potential of 650 volts. A saturation current was obtained when the electrode nearer the heated salt was connected with the electrometer and a potential difference of 314 volts was used. This is shown by the following Table :—

Volts.	Current due to positive ions in Arbitrary Units.	Volts.	Current due to positive ions in Arbitrary Units.
42	46	390	130
84	58	432	130
126	75	474	128
168	85	516	130
210	95	558	126
236	111	608	130
275	123	656	130
314	130		
348	130		

Under the conditions of experiment (velocity of air through the tube being 40 cms. per sec.) it can easily be calculated from the formula

$$v = \frac{(b^2 - a^2) \log_e b/a}{2\mathrm{V}t},$$

in which

v = velocity of ions in cms. per sec.,
b = radius of the tube,
a = radius of wire electrode,
V = potential-difference in volts between wire and tube,
t = time taken by air to pass from one end of the electrode to the other,

that all ions with velocity greater than 0·0027 cm. per sec. are withdrawn when the saturation voltage of 314 volts is put on. When the voltage is raised to 656, ions must have a velocity less than 0·001 cm. per sec. to be able to escape from the first tube.

If the front electrode (*i. e.* one nearer the heated salt) is earthed and the front tube kept at any positive potential greater than 320 volts, no current should be found near the back electrode when this is connected with the electrometer, and the back tube raised to any positive potential ; a current could, however, be detected.

Even when both tubes were raised to a positive potential of 656 volts there was a current of 8 or 9 arbitrary units. The total current on the back electrode when the front tube was earthed was found to be 118 units. Thus about 8 per cent. of the total current here appears to be due to ions which are too slow moving to be extracted even with the very high voltage used, or which have been formed after passing the front electrode.

It may be mentioned that it was necessary to raise the back tube to a high potential before any indication of these extra ions was forthcoming. Thus with 432 volts on the front tube a current could be just detected when 190 volts was put on the back tube.

If the current of 8 units on the back electrode is due to ions which are too slow to be stopped by the field on the front electrode, then some indication of these would be expected on the saturation current curve, *i. e.* after passing 314 volts the curve should still gradually ascend.

Nothing of the kind, however, takes place, and, as is seen from the table of observations given, a small increase could easily have been detected.

If we assume that neutral doublets are present which break up into ions after passing the first electrode, then the results are readily explained.

Should the extra ions be in reality due to the splitting up of neutral doublets rather than to the presence of ions of extremely low velocity, one would expect to find an equal number of negative and positive ions formed after passing the first electrode, and this should occur although the saturation currents on the front electrode due to positive and negative ions may differ widely. For aluminium phosphate these saturation currents on the front electrode are in fact very different. It was found that a negative voltage of 220 on the front tube was sufficient to obtain a saturation current with negative ions. When both tubes were brought to a negative potential of 656 volts, the front electrode being earthed, and the back electrode connected with the electrometer, there was a current of 8 units—*i. e.*, precisely the same as that obtained with positive ions under exactly similar conditions.

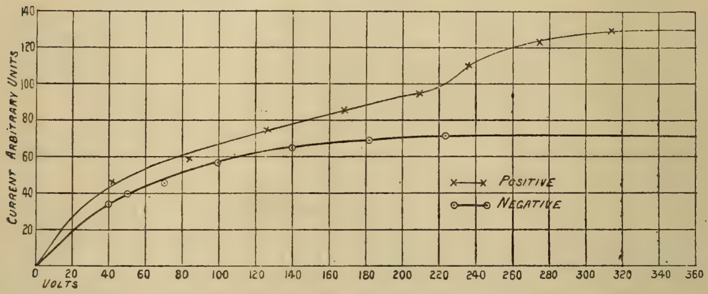
This appears strong evidence in favour of the view that the extra ions are due to the splitting up of neutral doublets and not to ions of very low velocity.

When a current voltage curve for the positive ions is plotted using the values given above, it is seen that the curve formed by joining the points obtained is not of the usual type.

At about 200 volts there are indications that the current is nearly saturated, yet on slightly increasing the voltage, it again rises very rapidly and does not actually reach its saturation value until over 300 volts are put on.

On the other hand, the curve obtained with negative ions is quite a smooth one and does not show any indication of saturation at a voltage lower than 220, nor does any further increase in current take place if the voltage is raised from 220 to 656. This is shown in fig. 6, in which the upper curve represents the current due to positive ions, the lower curve that due to negative ions at different voltages.

Fig. 6.



This, taken in conjunction with the fact that a current is obtained at the second electrode when 656 volts are put on the first, suggests that either two classes of positive ions are present, or else neutral doublets. The former is rendered unlikely on account of the constancy of the current which passes between the electrodes after 320 volts is reached.

X. *Further Evidence of Doublets.*

In order to test whether neutral pairs as well as ions are shot off from the heated salt when surrounded by gas at a low pressure, the apparatus shown in the next diagram was used.

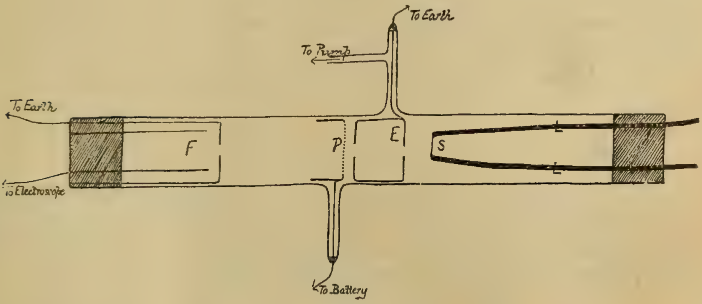
The essential part of this apparatus consists of a long glass tube, in one end of which is a Faraday cylinder F, and in the other end the heated salt on the platinum foil S.

During the experiment the foil was kept at a positive potential sufficiently high to prevent negative ions from leaving the salt. The wire gauze P was also kept at such a positive potential as to drive back any positive ions which have passed through the earthed metal tube E.

The apparatus was evacuated to an air-pressure of about

0·01 mm. The outer Faraday cylinder was earthed and the inner one connected to the leaf of an electroscope which was charged to a definite potential, positive or negative, as required.

Fig. 7.



The insulation was such that the rate of leak of electricity from the leaf when the salt was not heated was imperceptibly small when the charge was of either sign.

As soon as heating was commenced quite a distinct leak was noticed, and the rate of leak was the same whether the leaf was charged positively or negatively.

On the other hand, after the inner cylinder had been reduced to zero potential, no charging up could be detected, thus showing that there was no excess of free ions of either sign in the neighbourhood of the inner cylinder.

No positive ions could pass through the field between P and E, and it is highly improbable that any free negative ions leave the salt when the latter is charged positively, as in the experiment. Again, the field between P and the outer cylinder is a further preventive against any stray negative ions passing through the small hole into the space between the cylinders. Hence it seems that any ionization produced in the Faraday cylinder when the salt is heated, can only be brought about by the split up of doublets which have passed through the various electrostatic fields and diffused into the space between the two cylinders.

An effect of a similar nature has been noted by Sir J. J. Thomson [*] when working with a hot lime cathode.

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[*] Phil. Mag. Dec. 1909, pp. 829 *et seq.*

XI. *Rectifying Effect of the Heated Salt.*

Owing to the great velocity with which the positive ions are shot off from the heated salt when the pressure is very low, it was thought that such a tube as shown in fig. 1 could be used for rectifying alternating currents providing the temperature of the salt was kept within certain limits. It has been found by various experiments that it can be so used.

Further work on this point is in progress.

XII. *Summary.*

(i.) The decay of the current due to positive ions obtained by heating aluminium phosphate has been investigated, and it is found that the curve connecting current and time can be represented by a formula of the type

$$A(e^{-\lambda_1 t}-e^{-\lambda_2 t})+B(1-e^{-\lambda_3 t}).$$

(ii.) During the first part of the decay, the nature of the surrounding gas and the water contained by the salt have an important influence. When the steady state is reached the gas has no apparent influence, but water still temporarily increases the activity.

(iii.) The discharge produced by an induction-coil temporarily increases the current which is carried by the positive ions.

(iv.) When the temperature is kept constant, it is found that for each temperature there is a definite pressure at which the current is a maximum. This pressure being lower, the higher the temperature.

(v.) The Richardson formula $I=a\theta^{\frac{1}{2}}e^{-Q/2\theta}$ can be used to express the relationship between the current and absolute temperature when the pressure is kept constant.

(vi.) A value is obtained for e/m which indicates that the smallest positive ions present at the lowest pressures must be of a magnitude comparable with that of the hydrogen atom.

(vii.) The high velocity of the ions at low pressures, and also the fact that some escape with great velocity even when no external field is applied, leads one to expect that a tube in which some aluminium phosphate is heated might be of use as a rectifier for alternating currents. It can be so used.

(viii.) The experiments (*a*) with varying pressures at constant temperature, (*b*) at atmospheric pressure in which a current is produced after all the ions are apparently removed, and (*c*) in which the charge on a Faraday cylinder leaks away when care is taken to prevent free ions reaching it, seem to indicate that neutral doublets as well as free ions are ejected from the salt.

In conclusion, I should like to thank Dr. R. S. Willows, in whose laboratory these experiments have been carried out, for the interest he has taken throughout the course of this research, and Mr. F. C. G. Bratt for help in the construction of the apparatus used.

Cass Technical Institute,
Jewry Street, E.C.
May 1910.

LXII. *The Convection of Heat from a Body cooled by a Stream of Fluid. By* ALEXANDER RUSSELL, *M.A., D.Sc., M.I.E.E., Principal of Faraday House* [*].

TABLE OF CONTENTS.

1. *Introduction.*

THE phenomenon of the convection of heat at the surface of a body immersed in a cooling fluid is one which does not lend itself readily to mathematical calculation. If the fluid be a gas the variations of the pressure, density, and velocity at different points of the gas so complicate the problem that little progress towards a complete solution has yet been made. In the case of liquids flowing past a body with appreciable but not excessive velocity, Boussinesq [†] has

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[*] Communicated by the Physical Society: read July 8, 1910.

[†] *Théorie Analytique de la Chaleur*, t. ii. 1903, and *Journal de Mathématiques*, 6^e Série, t. i. (1905).

found some approximate solutions which deserve to be more widely known. The author has therefore thought that it would be useful to give the proofs in full of the more practical of Boussinesq's formulæ, laying stress on their limitations, and pointing out some of their applications. The author also discusses the important problem of the heating, due to streamline convection, of a liquid flowing through a cylindrical tube, and gives a table by means of which approximate solutions can be found without much difficulty.

2. *Historical.*

The differential equations the solutions of which would give the flow of heat through a fluid were first given by Fourier [*]. The fundamental equation was put into a more manageable form by Poisson [†], but neither he nor Fourier gave any solution of it.

Poisson writes the equation as follows:—

$$c\frac{\mathrm{D}\theta}{\mathrm{D}t}=\frac{\partial}{\partial x}\left(k\frac{\partial\theta}{\partial x}\right)+\frac{\partial}{\partial y}\left(k\frac{\partial\theta}{\partial y}\right)+\frac{\partial}{\partial z}\left(k\frac{\partial\theta}{\partial z}\right), \quad . \quad (1)$$

where θ is the temperature of the fluid at the point (x, y, z), c the capacity for heat per unit volume, k the conductivity, and $\mathrm{D}\theta/\mathrm{D}t$ the rate at which the temperature of a particle of fluid passing through the point (x, y, z) is increasing in the direction of the motion of the fluid at the point. When written in this form it is interesting to notice how similar this equation is to the equation of the flow of heat through a solid body. We may also write

$$\frac{\mathrm{D}\theta}{\mathrm{D}t}=\frac{\partial\theta}{\partial t}+u\frac{\partial\theta}{\partial x}+v\frac{\partial\theta}{\partial y}+w\frac{\partial\theta}{\partial z}, \quad . \quad . \quad . \quad (2)$$

where u, v, and w are the component velocities of the current at the point (x, y, z) parallel to the three axes respectively.

In addition to equation (1) we have the ordinary hydrodynamical equations [‡], namely, the equation of continuity and the three equations of Euler.

A. Oberbeck [§] discusses the general equations, and gives a solution for a special case. In a valuable paper [||] L. Lorenz

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[*] *Mémoires de l'Académie*, t. xii. p. 507 (1820), or *Œuvres de Fourier* (Darboux's Edition), t. ii. p. 275.

[†] *Théorie Mathématique de la Chaleur*, chapter iv. (1835).

[‡] Lamb's 'Hydrodynamics,' chap. i.

[§] *Ann. der Physik*, vii. p. 271 (1879).

[||] *Ann. der Physik*, xiii. p. 582 (1881).

obtains an approximate solution for the case of a heated strip cooling in air. When the strip is protected from draughts he proves that the heat convected from it varies as $\theta^{5/4}$ where θ is the difference of temperature between the strip and the air before it is heated by the strip. L. Graetz [*] finds the mathematical equation for thermal conduction in a liquid flowing through a cylindrical tube, and obtains a solution in terms of Bessel's functions. Harold Wilson [†] gives a solution of this problem, taking the viscosity of the liquid into account; but unfortunately his solution is only applicable to a very special case.

Boussinesq was the first to state clearly the laws for the cooling of a heated body by a stream of liquid when the flow is not turbulent. In 1901 [‡] he published the formula for the cooling of a strip by a liquid flowing past it in a direction at right angles to its length and parallel to its breadth. Four years afterwards (*l. c. ante*) the same author published the solution of the problem of the convection of heat from a horizontal cylindrical rod of elliptical cross-section immersed in a liquid flowing in a direction at right angles to the axis of the rod. He also gave the solution for the similar problem of the convection of heat from an ellipsoidal shaped body.

3. *The Assumptions made.*

In order to simplify the mathematical work the following assumptions are made. The liquid is supposed to be athermanous, that is, opaque to heat rays. It is also supposed to have no viscosity. The liquid therefore slips past the surface of the solid. In addition it is supposed to be incompressible. Hence we should only expect the solutions to give roughly approximate values when applied to the problem of spheres and cylinders being cooled by currents of air. It is instructive to notice, however, that Boussinesq's result, that the convection of heat by a stream of liquid from a sphere or a cylinder maintained at a constant temperature varies as the difference of temperature between the solid and the liquid and as the square root of the velocity of the current, is in good agreement with the results obtained by P. Compan [§] from experiments with spheres in draughts of air, and also with Kennelly's [||] results for the cooling of cylindrical wires. Boussinesq's theoretical results also would lead us to

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[*] *Ann. der Physik,* xviii. p. 79 (1883).

[†] Camb. Phil. Soc. Proceedings, xii. p. 406 (1904).

[‡] *Comptes Rendus,* cxxxiii. p. 257.

[§] *Ann. de Chim. et Phys.* xxvi. p. 488 (1902).

[||] Amer. Inst. Elect. Engin. Proc. July 1909.

expect that the loss of heat per square centimetre of the surface of a wire would be greater the smaller the diameter of the wire. This is in agreement with the experiments of Cardani [*], Ayrton and Kilgour [†], Sala [‡], and Kennelly [§].

We also show later on that in certain cases the fusing-current of wires when immersed in a stream of liquid varies as the 1·25th power of the radius of the wire. This agrees with experimental results obtained by Schwartz and James [||] for wires in air.

The further assumptions are made that the thermal conductivity of the liquid is very small and that the variation in its density does not appreciably alter the shape of the trajectories of the liquid particles in the immediate neighbourhood of the solid from the shape they have during isothermal flow. The former assumption is true in most practical cases, and the latter is permissible when the velocity of the current is appreciable and no eddies are formed.

It is interesting to remember that in Hele-Shaw's[¶] method of reproducing the stream-lines of a perfect fluid flowing past an obstacle in two dimensions, a thin film of viscous liquid, glycerine for example, is employed, and results of high accuracy are obtained. Even for a thick film, the shape of the lines does not alter much from the ideal case, and hence the assumption that the stream-lines coincide with the stream-lines of a perfect fluid is not a serious one.

The surface of the solid being cooled by the current is supposed to be isothermal, and the liquid in immediate contact with it at any instant is supposed to have the same temperature as the solid. These two assumptions are quite legitimate.

4. *Flow in Two Dimensions.*

Making the above assumptions we shall now obtain the differential equation which determines the temperature at any point of the liquid, once the steady state has been established.

Let us suppose that the velocity of the liquid at a great distance from the solid being cooled is V. In our problem

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[*] *Nuov. Cim.* xxx. p. 33 (1891).

[†] Phil. Trans. clxxxiii. part i. p. 371 (1892).

[‡] *Nuov. Cim.* iv. p. 81 (1896).

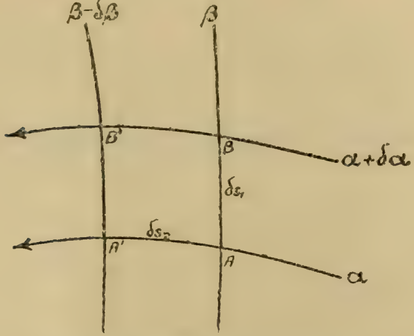
[§] *L. c. ante.*

[||] Journ. Inst. Elect. Engin. xxxv. p. 364 (1905).

[¶] Brit. Assoc. Report, 1898. In this report Sir G. G. Stokes gives a theoretical proof of the method.

it is convenient to denote the hydrodynamical stream-function by $V\alpha$, and the velocity-potential by $V\beta$. In fig. 1,

Fig. 1.



AA′ and BB′ denote adjacent stream-lines, and A′B′ and AB denote adjacent equipotential curves. Let

$$AA' = \partial s_2,$$

and let

$$AB = \partial s_1.$$

Then, by hydrodynamics,

$$\frac{\partial V\alpha}{\partial s_1} = \frac{\partial V\beta}{\partial s_2} = q, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where q is the velocity of the flow of the liquid at the point (s_1, s_2).

Consider the flow of heat in the time Dt into a prism having unit length, and having ABB′A′ for its cross-section (fig. 1). We suppose that this prism is moving with the liquid, and its velocity is therefore q. Let θ be the initial temperature of the liquid inside this prism, and let $\theta + D\theta$ be the temperature at the time Dt. The gain by the flow of heat from AA′ to BB′ during this interval is

$$\frac{\partial}{\partial s_1}\left(k\frac{\partial \theta}{\partial s_1}\right)\partial s_1 \, \partial s_2 \, Dt,$$

and the gain by the flow from AB to A′B′ is

$$\frac{\partial}{\partial s_2}\left(k\frac{\partial \theta}{\partial s_2}\right)\partial s_1 \, \partial s_2 \, Dt,$$

where k is the conductivity of the liquid. Hence, if c denote the capacity for heat of the liquid per unit volume, the gain of heat by the element contained by the prism is $c\,\partial s_1 \partial s_2 \, D\theta$.

We have, therefore,

$$c\,\partial s_1\,\partial s_2\,\mathrm{D}\theta=\left\{\frac{\partial}{\partial s_1}\left(k\frac{\partial\theta}{\partial s_1}\right)+\frac{\partial}{\partial s_2}\left(k\frac{\partial\theta}{\partial s_2}\right)\right\}\partial s_1\,\partial s_2\,\mathrm{D}t,$$

and thus

$$c\frac{\mathrm{D}\theta}{\mathrm{D}t}=\frac{\partial}{\partial s_1}\left(k\frac{\partial\theta}{\partial s_1}\right)+\frac{\partial}{\partial s_2}\left(k\frac{\partial\theta}{\partial s_2}\right). \quad . \quad . \quad . \quad (4)$$

Since we suppose that the liquid is flowing in the direction AA′, we have, when the steady state is reached,

$$c\frac{\mathrm{D}\theta}{\mathrm{D}t}=c\frac{\partial\theta}{\partial s_2}\cdot\frac{\partial s_2}{\partial t}=-cq\frac{\partial\theta}{\partial s_2},$$

and hence, assuming k constant, we get

$$-\frac{\partial\theta}{\partial s_2}=\frac{k}{cq}\left\{\frac{\partial^2\theta}{\partial s_1^{\,2}}+\frac{\partial^2\theta}{\partial s_2^{\,2}}\right\}. \quad . \quad . \quad . \quad . \quad (5)$$

As q varies with both s_1 and s_2, it appears at first sight as if it would be very difficult to obtain a solution of this equation. If, however, we alter the variables from s_1 and s_2 to α and β, the equation simplifies in a remarkable way.

We have

$$\frac{\partial\theta}{\partial s_1}=\frac{\partial\theta}{\partial\alpha}\frac{\partial\alpha}{\partial s_1}+\frac{\partial\theta}{\partial\beta}\frac{\partial\beta}{\partial s_1},$$

and thus

$$\frac{\partial^2\theta}{\partial s_1^{\,2}}=\frac{\partial^2\theta}{\partial\alpha^2}\left(\frac{\partial\alpha}{\partial s_1}\right)^2+2\frac{\partial^2\theta}{\partial\alpha\partial\beta}\frac{\partial\alpha}{\partial s_1}\frac{\partial\beta}{\partial s_1}+\frac{\partial^2\theta}{\partial\beta^2}\left(\frac{\partial\beta}{\partial s_1}\right)^2$$
$$+\frac{\partial\theta}{\partial\alpha}\frac{\partial^2\alpha}{\partial s_1^{\,2}}+\frac{\partial\theta}{\partial\beta}\frac{\partial^2\beta}{\partial s_1^{\,2}}.$$

A similar equation holds for $\frac{\partial^2\theta}{\partial s_2^{\,2}}$.

Noticing that

$$\frac{\partial\alpha}{\partial s_1}=\frac{\partial\beta}{\partial s_2}=\frac{q}{\mathrm{V}},\quad \frac{\partial\alpha}{\partial s_2}=-\frac{\partial\beta}{\partial s_1}=0,$$

$$\nabla^2\alpha=0,\quad \text{and}\quad \nabla^2\beta=0,$$

we get

$$\frac{\partial^2\theta}{\partial s_1^{\,2}}+\frac{\partial^2\theta}{\partial s_2^{\,2}}=\frac{q^2}{\mathrm{V}^2}\left(\frac{\partial^2\theta}{\partial\alpha^2}+\frac{\partial^2\theta}{\partial\beta^2}\right).$$

We also have

$$\frac{\partial\theta}{\partial s_2}=\frac{\partial\theta}{\partial\beta}\frac{q}{\mathrm{V}}.$$

Hence, substituting these values in (5), we get

$$-\frac{\partial\theta}{\partial\beta}=\frac{k}{c\mathrm{V}}\left(\frac{\partial^2\theta}{\partial\alpha^2}+\frac{\partial^2\theta}{\partial\beta^2}\right), \quad . \quad . \quad . \quad . \quad (6)$$

which is a much simpler equation than (5) as the coefficient of the right-hand side is a constant quantity.

Our assumptions allow us to simplify this equation still further. Since the liquid is a very bad conductor of heat, θ alters very rapidly with α but very slowly with β. The term $\partial^2\theta/\partial\beta^2$ is also negligibly small compared with $\partial^2\theta/\partial\alpha^2$. We thus obtain the equation

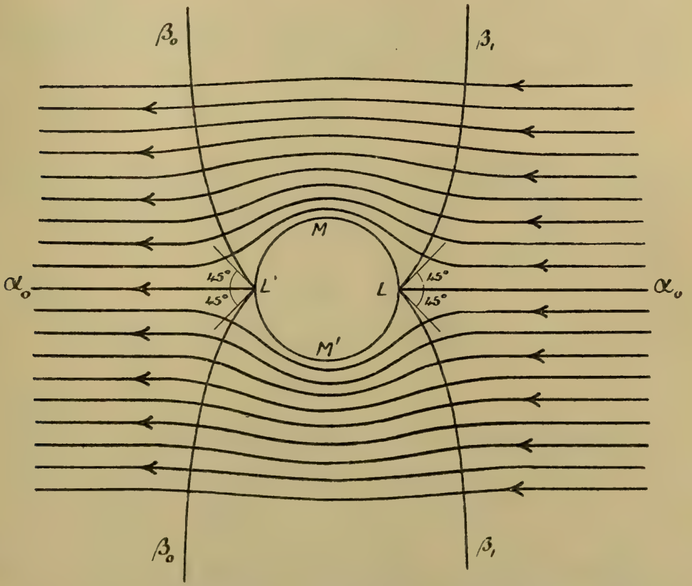
$$-\frac{\partial\theta}{\partial\beta}=\frac{k}{c\mathrm{V}}\frac{\partial^2\theta}{\partial\alpha^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

the solution of which has been put into various forms by Fourier and others.

5. *Circular Cylinder.*

We shall now consider the problem of the cooling of a circular cylinder immersed in a stream of liquid with its axis horizontal and at right angles to the direction of flow.

Fig. 2



Stream lines of Fluid flowing past cylinder.
β_0 & β_1 are the two singular equipotential curves.

Let us take the origin of co-ordinates on the axis of the cylinder, and let us suppose that the liquid is flowing with velocity V in the direction XO, and that its temperature is zero before it meets the cylinder.

In this case we know * that

$$\left.\begin{aligned}\alpha &= y - \frac{a^2 y}{r^2}\\ \text{and}\qquad \beta &= x + \frac{a^2 x}{r^2}\end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

where a is the radius of the cylinder and

$$r^2 = x^2 + y^2.$$

The equation to the stream-line α_0, which flows on the surface of the cylinder (fig. 2), is $\alpha = 0$, and the equations to the two equipotential lines, β_0 and β_1, are

$$x\left(1+\frac{a^2}{r^2}\right) = -2a \quad \text{and} \quad x\left(1+\frac{a^2}{r^2}\right) = 2a$$

respectively. These curves cut the cylinder and the stream-line α_0 at angles of 45°. We see therefore that the velocity of the liquid at L and L′ must be zero. The velocity at M and M′ is 2V. At a great distance away from the cylinder β_0 and β_1 practically coincide with the lines

$$x = -2a \quad \text{and} \quad x = 2a.$$

Let us suppose that the temperature flow has become steady and that the temperature of all points on the stream-line α_0 is $f(\beta)$. On this stream-line (fig. 2), from $\beta = \infty$ to $\beta = \beta_1$, we have

$$\theta = f(\beta) = 0,$$

and on the same stream-line from β_1 to β_0 we have

$$\theta = f(\beta).$$

It is easy to verify † by differentiation that

$$\theta = \sqrt{\frac{2}{\pi}}\int_0^\infty f\left(\beta + \frac{cV}{k}\frac{\alpha^2}{2\xi^2}\right)\epsilon^{-\frac{\xi^2}{2}}\partial\xi \quad . \quad . \quad (9)$$

is a solution of (7). Also, when α is zero, $\theta = f(\beta)$. This solution, therefore, is applicable to our problem.

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* Lamb's 'Hydrodynamics,' Third Edition, p. 74.

† *Cf.* Boussinesq, *Application des Potentials*, p. 360 (1885).

The flux of heat emitted per unit length of the cylinder per second is $\Sigma - k\left(\frac{\partial\theta}{\partial s_1}\right)_0 \partial s_2$, where $\left(\frac{\partial\theta}{\partial s_1}\right)_0$ is the thermal gradient at the surface of the cylinder where $\alpha = 0$. By means of (3) this may be written in the form $\Sigma - k\left(\frac{\partial\theta}{\partial\alpha}\right)_0 \partial\beta$. But from (9) we have

$$\left(\frac{\partial\theta}{\partial\alpha}\right)_0 = 2\sqrt{\frac{c\mathrm{V}}{\pi k}}\int_0^\infty f'(\beta + \eta^2)\,\partial\eta,$$

where we have written η^2 for $c\mathrm{V}\alpha^2/(2k\xi^2)$.

Hence the total flux H of heat per second from unit length of the cylinder is given by

$$\begin{aligned}\mathrm{H} &= -4\sqrt{\frac{ck\mathrm{V}}{\pi}}\int_{\beta_0}^{\beta_1}\int_0^\infty f'(\beta+\eta^2)\,\partial\beta\,\partial\eta \\ &= 4\sqrt{\frac{ck\mathrm{V}}{\pi}}\int_0^\infty \{f(\beta_0+\eta^2) - f(\beta_1+\eta^2)\}\partial\eta. \qquad (10)\end{aligned}$$

Now $f(\beta_1+\eta^2)$ is zero from η almost equal to nothing up to η equal to infinity; and $f(\beta_0+\eta^2)$ is θ_0 from η equal to zero up to η equal to $\sqrt{\beta_1-\beta_0}$, and practically vanishes for all greater values of η. Hence

$$\begin{aligned}\mathrm{H} &= 4\sqrt{\frac{ck\mathrm{V}}{\pi}}\int_0^{\sqrt{\beta_1-\beta_0}} f(\beta_0+\eta^2)\,\partial\eta \\ &= 4\sqrt{\frac{ck\mathrm{V}}{\pi}}\sqrt{\beta_1-\beta_0}\,\theta_0 \\ &= 4\sqrt{\frac{s\sigma k\mathrm{V}}{\pi}}\sqrt{\beta_1-\beta_0}\,\theta_0, \quad . \quad . \quad . \quad . \quad (11)\end{aligned}$$

where s is the specific heat, and σ is the density of the liquid.

This result, which is true for two-dimensional flow round a solid of any shape immersed in a stream of liquid, agrees with that given by Boussinesq. It shows that the loss of heat from the solid is proportional to the difference of temperature between the solid and the liquid. Newton's law is thus verified when the cooling fluid is a liquid. It will be remembered that Newton enunciated his law with reference to the convection and not the radiation of heat. He considered the case of a block of iron being cooled in a current of air flowing uniformly. He states * "*aeris partes aequales aequalibus temporibus calefactae sunt & calorem conceperunt calori ferri proportionalem.*"

A. C. Mitchell † has shown that Newton's law is very approximately true up to a difference of temperature between the solid and the air of 200° C., and P. Compan ‡ has proved it true for temperatures up to 300° C.

In several practical applications the assumption of Newton's law for the convection of heat by fluids leads to results which are found to be in close accordance with experiment. For instance, in the theory of the Irwin § hot-wire oscillograph, the assumption is made that the convection of heat from the heated metal strips which are immersed in convection-currents of oil is proportional to the difference of temperature between the metal and the oil. The very satisfactory results obtained in practice prove that the assumption is approximately correct. It will be seen from § 11 below that, even in the case of the turbulent motion of water through a pipe, Newton's law is very approximately true. It is not applicable, however, to natural free convection from a heated body in a gas or a liquid. In this case ‖ Lorenz's law (see above) is applicable.

In the case of the circular cylinder we find, from the values of β_1 and β_0 given above, that

$$\beta_1 - \beta_0 = 4a,$$

and hence

$$\mathrm{H} = 8\sqrt{\frac{s\sigma k\mathrm{V}a}{\pi}}\,\theta_0. \quad . \quad . \quad . \quad . \quad (12)$$

If we denote the surface of unit length of the cylinder by S, so that $\mathrm{S} = 2\pi a$, the expression for the rate at which heat is lost by the cylinder per unit length is generally assumed by engineers to be equal to $h\mathrm{S}\theta$, where h is independent of the radius of the cylinder. We see from (12) that the value of h for the perfect liquid is given by

$$h = \frac{4}{\pi}\sqrt{\frac{s\sigma k\mathrm{V}}{\pi a}}. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Thus h varies inversely as the square root of the radius of

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[*] "Scala Graduum Caloris," Phil. Trans. p. 828, April 1701. The paper is not signed. In *Newtoni Opera Horsleii*, vol. iv. p. 403 (1782), the title is given as "Tabula Quantitatum et Graduum Caloris."

[†] Roy. Soc. Edin. Trans. xl. 1, p. 39 (1899).

[‡] *L. c. ante.*

[§] Journ. Inst. of Elect. Engin. vol. xxxix. p. 617 (1907).

[‖] P. Compan, *l. c. ante*; H. Ebeling, *Ann. der Physik*, xxvii. 2, p. 391 (1908).

the cylinder, and therefore the assumption that it is constant is not permissible. For example, if the radius of one wire is a hundred times that of another, the average heat per square centimetre of surface which is carried off per second by the liquid from the small wire is ten times greater than from the large wire. We also see that if we quadruple the velocity of the flow of the liquid, the temperature of the wire being maintained constant, the convection of heat is doubled, and if the convection of heat is constant the difference of temperature between the wire and the liquid is halved.

6. *Cylinder with Elliptic Section.*

Let the direction of the current be at right angles to the axis of the cylinder, and let it make an angle α with the major axis of the elliptic section which we take as the axis of X. If

$$l=\cos\alpha \text{ and } m=\sin\alpha,$$

we easily find from the formulæ given in Lamb's 'Hydrodynamics' (p. 70, 3rd ed.) that

$$\beta=lb\sqrt{\frac{a+b}{a-b}}\,\epsilon^{-\eta}\sin\xi+lx$$

$$+ma\sqrt{\frac{a+b}{a-b}}\,\epsilon^{-\eta}\cos\xi+my,$$

where

$$x=c\sin\xi\cosh\eta,\quad y=c\cos\xi\sinh\eta,\quad\text{and}\quad c=\sqrt{a^2-b^2}.$$

On the surface of the cylinder we have

$$a=c\cosh\eta,\quad b=c\sinh\eta,$$

and thus at these points

$$x=a\sin\xi,\quad\text{and}\quad y=b\cos\xi.$$

At points, therefore, on the surface of the cylinder,

$$\beta=l\frac{b}{a}x+lx+m\frac{a}{b}y+my,$$

$$=\left(l\frac{x}{a}+m\frac{y}{b}\right)(a+b),$$

$$=(a+b)\left\{(l^2+m^2)\left(\frac{x^2}{a^2}+\frac{y^2}{b^2}\right)-\left(\frac{ly}{b}-\frac{mx}{a}\right)^2\right\}^{\frac{1}{2}}$$

$$=(a+b)\left\{1-\left(\frac{ly}{b}-\frac{mx}{a}\right)^2\right\}^{\frac{1}{2}}.$$

Thus β has extreme values when

$$x=la, \quad y=mb,$$

and when

$$x=-la \quad \text{and} \quad y=-mb,$$

Hence we find that

$$\beta_1-\beta_0=2(a+b).$$

Substituting this value in (11) we get

$$\mathrm{H}=4\sqrt{\frac{s\sigma k\mathrm{V}}{\pi}}\sqrt{2(a+b)}\,\theta_0. \quad . \quad . \quad . \quad . \quad (14)$$

Hence the cooling of the cylinder by the stream of liquid is independent of the direction in which the stream impinges on it. For a given area of cross-section and a given temperature the cooling power increases with the eccentricity of the ellipse, being a minimum for a cylinder having a circular cross-section. It is not permissible to apply (14) when the liquid is flowing parallel to the minor axis and b/a is a very small quantity. In this case, the velocity of the liquid round the pointed ends of the ellipse would be very high and eddy currents would be formed.

7. *Flat Strip.*

If the solid be a thin strip of metal placed so that its length is perpendicular and its surface parallel to the direction of flow, we have by (11)

$$\mathrm{H}=4\sqrt{\frac{s\sigma k\mathrm{V}b}{\pi}}\,\theta_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where b is the breadth of the strip. This also follows from (14). The convection of heat h per square centimetre of the surface of the strip per degree of temperature per second is given by

$$h=2\sqrt{\frac{s\sigma k\mathrm{V}}{\pi b}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

If the strip be bent so as to form a hollow cylinder of circumference b, we have, by (13)

$$h=4\sqrt{\frac{2}{\pi}}\sqrt{\frac{s\sigma k\mathrm{V}}{\pi b}}$$

$$=3{\cdot}19\sqrt{\frac{s\sigma k\mathrm{V}}{b\pi}} \text{ approximately.}$$

Hence the average convection per square centimetre of effective surface is considerably increased.

8. *Cylindrical Tube.*

Let the length of the tube be b, its temperature θ_0 and the velocity of the liquid flowing through it V.

In this case, when the steady state is attained, Poisson's equation (1) gives us

$$\frac{\partial^2\theta}{\partial r^2}+\frac{1}{r}\frac{\partial\theta}{\partial r}+\frac{\partial^2\theta}{\partial x^2}=\frac{s\sigma \mathrm{V}}{k}\frac{\partial\theta}{\partial x}.$$

As the mathematical formulæ are complex we shall simplify the work by neglecting the conduction of heat in the direction of the flow, in which case

$$\frac{\partial^2\theta}{\partial r^2}+\frac{1}{r}\frac{\partial\theta}{\partial r}=\frac{s\sigma \mathrm{V}}{k}\frac{\partial\theta}{\partial x}\quad.\quad.\quad.\quad.\quad.\quad(16)$$

It is easy to show that the equation [*]

$$y=\frac{4\theta_0}{\pi}\sum_0^\infty\frac{1}{2n+1}\sin\frac{(2n+1)\pi l}{2a}\cos\frac{(2n+1)\pi x}{a}\quad.\quad(17)$$

makes y, θ_0 from $x=-l/2$ to $+l/2$, 0 from $l/2$ to $a-l/2$, $-\theta_0$ from $a-l/2$ to $a+l/2$, 0 from $a+l/2$ to $a+3l/2$, and so on periodically.

Let us now consider an infinitely long tube. Take the origin at the centre of a portion of it of length l which is maintained at temperature θ_0. Let the contiguous portions be of length $a-l$ and be kept at zero temperature, and let the portions beyond these be of length l and be at temperature $-\theta_0$, and so on. Then by taking a/l sufficiently great we can ensure that the liquid entering the hot portion of the tube is practically at zero temperature.

Writing equation (16) in the form

$$\frac{\partial^2\theta}{\partial r^2}+\frac{1}{r}\frac{\partial\theta}{\partial r}=\frac{(2n+1)m^2}{(2n+1)(\pi/a)}\frac{\partial\theta}{\partial x},\quad.\quad.\quad.\quad(18)$$

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[*] Russell, 'Alternating Currents,' vol. ii. p. 388.

where $m^2 = \pi s \sigma \mathrm{V}/ak$, we deduce that *

$$\begin{aligned}
\theta = \frac{4\theta_0}{\pi} \Bigg\{ & \frac{\mathrm{ber}\, m\mathrm{R}\, \mathrm{ber}\, mr + \mathrm{bei}\, m\mathrm{R}\, \mathrm{bei}\, mr}{\mathrm{ber}^2 m\mathrm{R} + \mathrm{bei}^2 m\mathrm{R}} \sin\frac{\pi l}{2a} \cos\frac{\pi x}{a}, \\
& + \frac{1}{3} \frac{\mathrm{ber}\, m\sqrt{3}\mathrm{R}\, \mathrm{ber}\, m\sqrt{3}r + \mathrm{bei}\, m\sqrt{3}\mathrm{R}\, \mathrm{bei}\, m\sqrt{3}r}{\mathrm{ber}^2 m\sqrt{3}\mathrm{R} + \mathrm{bei}^2 m\sqrt{3}\mathrm{R}} \sin\frac{3\pi l}{2a} \cos\frac{3\pi x}{a}, \\
& + \ldots\ldots \\
& - \frac{\mathrm{ber}\, m\mathrm{R}\, \mathrm{bei}\, mr - \mathrm{bei}\, m\mathrm{R}\, \mathrm{ber}\, mr}{\mathrm{ber}^2 m\mathrm{R} + \mathrm{bei}^2 m\mathrm{R}} \sin\frac{\pi l}{2a} \sin\frac{\pi x}{a}, \\
& - \frac{1}{3} \frac{\mathrm{ber}\, m\sqrt{3}\mathrm{R}\, \mathrm{bei}\, m\sqrt{3}r - \mathrm{bei}\, m\sqrt{3}\mathrm{R}\, \mathrm{ber}\, m\sqrt{3}r}{\mathrm{ber}^2 m\sqrt{3}\mathrm{R} + \mathrm{bei}^2 m\sqrt{3}\mathrm{R}} \sin\frac{3\pi l}{2a} \sin\frac{3\pi x}{a}, \\
& - \ldots\ldots \Bigg\}
\end{aligned}$$

where R is the radius of the tube.

This value of θ satisfies (18), and when $r = \mathrm{R}$, $\theta = \theta_0$ from $-l/2$ to $+l/2$, &c., and thus the boundary conditions are satisfied.

Hence the loss of heat H per second from the portion of the tube from $-l/2$ to $+l/2$ is given by

$$\begin{aligned}
\mathrm{H} &= \int_{-l/2}^{+l/2} 2\pi \mathrm{R} k \frac{\partial \theta}{\partial r}\, dx, \text{ when } r = \mathrm{R}, \\
&= 16\mathrm{R}\sqrt{\frac{s\sigma k \mathrm{V} a}{\pi}}\, \theta_0 \Bigg\{ f(m\mathrm{R}) \sin^2\frac{\pi l}{2a}, \\
&\qquad + \frac{1}{3\sqrt{3}} f(m\sqrt{3}\mathrm{R}) \sin^2\frac{3\pi l}{2a}, \\
&\qquad + \ldots\ldots \Bigg\} \quad \ldots\ldots (19)
\end{aligned}$$

$$\begin{aligned}
\text{where } f(\xi) &= \frac{\mathrm{Z}}{\mathrm{X}}, \\
&= \frac{\mathrm{ber}\, \xi\, \mathrm{ber}' \xi + \mathrm{bei}\, \xi\, \mathrm{bei}' \xi}{\mathrm{ber}^2 \xi + \mathrm{bei}^2 \xi}.
\end{aligned}$$

It will be seen that H is proportional to θ_0, but except in the case when $m\mathrm{R}$ is great it is not proportional to

$$\mathrm{R}\sqrt{s\sigma k \mathrm{V} l}.$$

I have to thank Mr. H. Savidge for permission to publish the table of the values of Z/X given below. This, in addition

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* Russell, Phil. Mag. April 1909, p. 535.

to the table * and formulæ † for Z/X previously published, makes (19) a practical formula.

9. *Tables of the Values of the Function* Z/X.

ξ.	Z/X.	ξ.	Z/X.	ξ.	Z/X.
3·0	0·5399	4·4	0·5925	5·8	0·6180
3·2	0·5550	4·6	0·5964	6·0	0·6211
3·4	0·5656	4·8	0·6002	6·2	0·6240
3·6	0·5734	5·0	0·6040	6·4	0·6267
3·8	0·5793	5·2	0·6077	6·6	0·6293
4·0	0·5842	5·4	0·6113	6·8	0·6317
4·2	0·5885	5·6	0·6147	7·0	0·6339

10. *Simplified Formulæ for Cylindrical Tube.*

In many practical cases m^2R^2, which equals $\pi s\sigma VR^2/ak$, is a large number, and thus we may write

$$f(\xi)=\frac{1}{\sqrt{2}}-\frac{1}{2\xi}.$$

When we do this (19) becomes

$$H=8\sqrt{2}R\sqrt{\frac{s\sigma kVa}{\pi}}\,\theta_0\left\{\sin^2\frac{\pi l}{2a}+\frac{1}{3\sqrt{3}}\sin^2\frac{3\pi l}{2a}+\frac{1}{5\sqrt{5}}\sin^2\frac{5\pi l}{2a}+\dots\right\}$$

$$-\frac{8ak}{\pi}\theta_0\left\{\sin^2\frac{\pi l}{2a}+\frac{1}{3^2}\sin^2\frac{3\pi l}{2a}+\dots\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

If $a=2l$, so that we have lengths of the tube l, at temperatures θ_0 and $-\theta_0$, separated by lengths l at temperature zero, we have

$$H=4\sqrt{2}R\sqrt{\frac{s\sigma kVa}{\pi}}\,\theta_0\left(1+\frac{1}{3\sqrt{3}}+\frac{1}{5\sqrt{5}}+\dots\right)-\frac{\pi}{2}ak\theta_0,$$

and noticing that $\sum\limits_0^\infty\frac{1}{(2n+1)^{3/2}}=1{\cdot}6888$ approximately,

we get

$$H=13{\cdot}51R\sqrt{\frac{s\sigma kVl}{\pi}}\,\theta_0-\pi lk\theta_0. \quad . \quad . \quad . \quad (21)$$

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* Savidge, Phil. Mag. Jan. 1910, p. 56.

† Russell, Phil. Mag. April 1909, pp. 529 & 532.

When the last term can be neglected this becomes

$$H = 13{\cdot}51 R \sqrt{\frac{s\sigma k V l}{\pi}}\, \theta_0 . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Similarly when $a = 3l$ we get

$$H = 2\sqrt{6} R \sqrt{\frac{s\sigma k V l}{\pi}} \left(1 + \frac{1}{\sqrt{3}}\right) \sum_0^\infty \frac{1}{(2n+1)^{3/2}}$$

$$= 13{\cdot}05 R \sqrt{\frac{s\sigma k V l}{\pi}}\, \theta_0 , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and when $a = 6l$,

$$H = 12{\cdot}86 R \sqrt{\frac{s\sigma k V l}{\pi}}\, \theta_0 . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

If the temperature of the liquid entering the tube be zero and the temperature of the liquid leaving it be practically zero, except at points very close to the tube, we may deduce a formula from Boussinesq's formula (15) for a strip as follows:

$$H = \int_0^{2\pi R} 2 \sqrt{\frac{s\sigma k V l}{\pi}}\, \theta_0 \partial s,$$

$$= 4\pi R \sqrt{\frac{s\sigma k V l}{\pi}}\, \theta_0,$$

$$= 12{\cdot}57 R \sqrt{\frac{s\sigma k V l}{\pi}}\, \theta_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

This result is in good agreement with the preceding three formulæ.

11. *Turbulent Flow.*

It must be carefully noticed that in the above problem we have supposed that the particles of water flow in straight lines parallel to the axis of the tube. It is known, however, that in practice, when the velocity exceeds a certain critical value, the flow becomes turbulent and the eddy currents cause the particles of liquid to flow in sinuous paths. The theory of the convection of heat in this case has been studied by Osborne Reynolds *. He states that it is due to two causes. 1. The natural internal diffusion when at rest. 2. The eddies caused by visible motion which mix the fluid

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* Proc. of the Lit. and Phil. Soc. of Manchester, vol. xiv. p. 9 (1874).

up and continually bring fresh particles into contact with the surface. In our notation, the formula deduced is

$$H = A\theta + B\sigma V\theta,$$

where A and B are constants.

As the first term is small, H is approximately proportional to V. T. E. Stanton *, who has given an experimental verification of Reynolds's theory, finds that H varies as V^n where the value of n is a little less than unity.

E. G. Coker † and S. B. Clement have proved that the critical velocity at which stream-line motion changes to eddy motion varies directly as the viscosity of the liquid and inversely as the radius of the tube.

12. *Electric Current required to fuse a Wire.*

Let us suppose that the wire is horizontal with its axis at right angles to the direction of the flow of the liquid in which it is immersed, and let us suppose that the electric current through it is increased very slowly until the wire fuses. Let a be the radius in centimetres of the wire which we suppose to be cylindrical, C the current in amperes, θ the steady temperature corresponding to this current, and ρ_t the volume resistivity of the metal at t° C. When the steady state is attained the heat generated by the current per unit length of the wire per second must equal the heat convected. Hence, by (12),

$$0{\cdot}239 C^2 \frac{\rho_\theta}{\pi a^2} = 8\sqrt{\frac{s\sigma k V a}{\pi}}\,\theta \quad . \quad . \quad . \quad . \quad (26)$$

and thus,

$$C = 7{\cdot}70\,(\theta/\rho_\theta)^{1/2}(s\sigma k V)^{1/4} a^{1{\cdot}25} \quad . \quad . \quad . \quad . \quad (27)$$

If θ be the melting temperature of the metal, we see that the fusing current varies as $(s\sigma k V)^{1/4}$, and also as the 1·25th power of the radius of the wire. This latter result is in good agreement with experimental results obtained by Professor Schwartz (*l. c. ante*). In his experiments the wire was stretched horizontally in air. The current through it was then increased very slowly until the wire melted, the reading on the ammeter in the circuit at this instant giving the fusing current. Before it melted a vertical stream of air was flowing past the wire, the heating of the air by the wire causing this convection current. For wires of small diameter this current would be approximately constant, and so making

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* Phil. Trans. vol. 190, p. 67 (1897).

† Phil. Trans. vol. 201, p. 45 (1903).

the assumption that the formulæ given above for cooling by incompressible fluids may be applied for gases, we see that the fusing current varies as the 1·25th power of the radius.

13. *Schwartz's Experimental Results.*

Expressing the fusing current by λa^n where λ and n are constants for a given metal, the following results were obtained for λ and n.

Metal.	Length of fuse.	S.W.G.	Fusing Currents.	λ.	n.
Copper (tinned) .	5 cms. and upwards ...	47 to 33	1 to 10	358	1·20
,, ...	3·8 cms....	,,	,,	491	1·26
Tin	7·6 cms. and upwards.	43 to 20	,,	147	1·13
,, ...	15 cms. ,,	20 to 7	10 to 80	239	1·32
Silver...............	12·7 cms. ,,	35 to 18	7 to 70	967	1·29
Aluminium	10 cms. ,,	42 to 20	2 to 30	640	1·27

In the case of most of the wires placing them vertically did not affect the value of n. Before this paper was published electricians, making the assumption that the heat emitted per unit surface of the wire was independent of its radius, deduced that n should be 1·5.

14. *Steady Temperature of a Wire carrying an Electric Current.*

If we assume that the volume resistivity of a wire varies with temperature according to the law

$$\rho_\theta = \rho_0 (1 + \alpha\theta),$$

we get by (26),

$$\theta \left\{ 8\sqrt{\frac{s\sigma k V a}{\pi}} - 0{\cdot}239 C^2 \frac{\rho_0 \alpha}{\pi a^2} \right\} = 0{\cdot}239 C^2 \frac{\rho_0}{\pi a^2} \quad . \ (28)$$

and thus θ can be easily computed. The value of C must of course be less than the fusing current.

Suppose, for example, that the wire is being cooled by a stream of ice-cold water. We shall take

$$s = \sigma = 1 \quad \text{and} \quad k = 0{\cdot}0016.$$

Hence

$$\theta = 1 \Big/ \left\{ 2{\cdot}37 \frac{\sqrt{V a^5}}{C^2 \rho_0} - \alpha \right\}. \quad . \quad . \quad . \quad . \ (29)$$

If the rod were of pure copper

$$\rho_0 = 1{\cdot}56 \times 10^{-6}, \quad \text{and} \quad \alpha = 0{\cdot}004.$$

If, in addition,

$a = 0{\cdot}25$ cm. $V = 25$ cm./sec. and $C = 1600$ amperes,

we readily find from (29) that θ is 11°·3 C.

15. *The Effect on the Convection of Heat from a Cylinder of putting a Covering round it* *.

Let a be the radius of the cylinder which we suppose to be maintained at a constant temperature θ_1, and let b be the outer radius of the insulating covering. We shall suppose that k_1, the thermal conductivity of the insulating covering, is large compared with the conductivity k of the cooling liquid, so that we can suppose the outer surface of this covering to be isothermal.

The equation to the steady flow of heat across the insulating covering is

$$-k_1 2\pi r \frac{\partial \theta}{\partial r} = \text{constant} = \mathrm{H},$$

and hence,

$$\theta_1 - \theta_0 = \frac{\mathrm{H}}{2\pi k_1} \log_\epsilon \frac{b}{a} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where θ_0 is the temperature of the outer surface of the covering. By (12), we find that

$$\theta_1 = \frac{\mathrm{H}\sqrt{\pi}}{8\sqrt{s\sigma k \mathrm{V} b}} + \frac{\mathrm{H}}{2\pi k_1} \log_\epsilon \frac{b}{a} \quad . \quad . \quad . \quad . \quad (31)$$

Let us now consider how the temperature θ_1 of the wire varies with the thickness $b-a$ of the insulating covering when H remains constant. We have

$$\frac{\partial \theta_1}{\partial b} = \frac{\mathrm{H}}{2\pi k_1 b^{3/2}} \left\{ b^{1/2} - \frac{\pi\sqrt{\pi k_1}}{8\sqrt{s\sigma k \mathrm{V}}} \right\}.$$

Hence if a be less than $\pi^3 k_1^2/(64 s\sigma k \mathrm{V})$, we see that when the thickness of the covering is very small $\partial\theta_1/\partial b$ is negative, and thus putting on a thin layer of insulating material will have the effect of lowering the temperature of the wire. When $b = \pi^3 k_1^2/(64 s\sigma k \mathrm{V})$ the temperature of the wire has its minimum value $\theta_{\min}$ which is given by

$$\theta_{\min} = \frac{\mathrm{H}}{\pi k_1} \left\{ 1 + \log_\epsilon \frac{\pi^{3/2} k_1}{8\sqrt{s\sigma k \mathrm{V} a}} \right\} \quad . \quad . \quad . \quad (32)$$

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* *Cf.* L. Roy, *Soc. Int. Elect. Bull.* p. 69 (1910).

The following simple experiment illustrates this effect. Portions of a piece of thin manganin wire are insulated with glass, the rest being left bare. When placed in a current of air and heated electrically the bare pieces of wire glow brilliantly, but the portions covered by the glass are quite dark and are therefore at a much lower temperature.

In very high tension systems for the electric transmission of power the overhead wires are sometimes surrounded with coronæ which appreciably increase the transmission losses. The author has previously suggested that the losses would be diminished by insulating the overhead wires with a suitable material of high electric strength. The above analysis indicates that this procedure instead of diminishing the permissible current in the wires would actually, in many cases, allow an appreciably greater current to be transmitted for the same rise of temperature of the wire.

In conclusion, I have to thank Professor Charles Lees, F.R.S., for his kind help in giving me a long list of references to papers on this subject.

LXIII. *The Accelerated Motion of an Electrified Sphere.*

By J. W. Nicholson, *M.A.*, *D.Sc.*[*]

When a sphere carrying a surface charge is placed in a uniform field of electric force at any instant of time, it is set into motion under the mechanical action on its electrification during the adjustment necessary for the satisfaction of the new conditions at its surface. A direct solution of the appropriate electromagnetic relations, with a determination of the motion of the sphere, has been given by Mr. G. W. Walker[†] for the general case in which the sphere is assumed to possess a Newtonian mass in addition to its inertia of electrical origin, and in which the applied field of force is small.

The application of the quasi-stationary principle to accelerated motions has never received formal justification, and in addition to certain general considerations tending to throw doubt upon its validity for such problems, Walker has obtained, in a later paper[‡], a formula for the transverse inertia of a moving sphere which is not in accord with that derived by Abraham with the aid of this principle. The

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[*] Communicated by the Author.

[†] Proc. Roy. Soc. 1906, p. 260.

[‡] Phil. Trans. 1910, vol. 210. p. 145.

method employed is to obtain solutions of the primary electromagnetic relations which satisfy definite surface conditions, and neither the relations nor the conditions are dispensed with at any stage. After a calculation of the mechanical reaction on the sphere has been made, the motion of the sphere is worked out by the principles of Newtonian dynamics, and Walker contends that this method, by its direct nature, is the one most fitted to yield correct results. With this view it seems necessary to agree, and as the method does lead to a different formula for the electrical inertia, and, moreover, indicates a redistribution of the charge in certain cases of motion which is again contrary to the results of the quasi-stationary principle, this principle has perhaps been pushed too far. Its use is therefore not to be regarded as definitely justified in cases of accelerated motion, until its exact limits of validity have been examined in a more formal manner, and the more direct method seems preferable in every way for the solution of special problems. But on the other hand, the conditions holding inside a conductor in a state of accelerated motion are at present quite unknown, and there is no certainty that the evanescence of either the tangential electric force or electromagnetic force, conditions hitherto used for a perfect conductor, at all represent the facts. It is difficult to believe that there could be no electrical effect inside a conductor with an acceleration, and all that can be done at present apparently is to work out the consequences of various possible assumptions. Thus Walker's results do not necessarily disprove the quasi-stationary principle for small accelerations, and the results of the present paper will be found to cast some doubt upon the theory that the usual treatment of the perfect conductor is still valid when its motion is accelerated.

The object of the paper is a brief discussion of the initial motion under a small field of electric force, or a small force of a purely mechanical nature, of a sphere whose charge is initially uniform, and whose mass is purely of electric origin. Walker states in his first paper that when the Newtonian inertia is zero, the damped harmonic vibration present at the beginning of the motion becomes evanescent, and it is impossible to satisfy all the initial conditions, so that his solution fails in this case. The formal deduction of this solution as a limiting case from Walker's formulæ is attempted in the present paper.

Prof. A. W. Conway, in a recent paper *, has concluded that when a charged sphere without Newtonian mass is

* Proc. Royal Irish Academy, xxviii. p. 1.

placed in a uniform field, it moves in such a way that its charge remains uniform. But his investigation does not take account of the initial conditions of the motion, and it is by no means obvious that the effect of these conditions would vanish in the same way as for a sphere with both electrical and Newtonian inertia.

Let ζ denote the displacement, at time t, of the centre of a sphere of radius a initially placed in a uniform field of electric force F of small magnitude, so that F^2 can be neglected. F and ζ are both measured along the axis of z. The uniform charge initially present on the sphere is e, and (x, y, z) denote the coordinates of a point referred to an origin instantaneously coinciding with the centre of the sphere, r being the distance of this point from the origin. Then, within the region defined by $r=ct+a$, Walker shows that the components of the electric and magnetic forces are given by

$$(\mathrm{X}, \mathrm{Y}, \mathrm{Z})=\frac{e}{r^3}(x, y, z)+(0, 0, 1)\left\{\mathrm{F}-\frac{c}{r^3}\left(r^2\chi''+r\chi'+\chi-\frac{e\zeta}{c}\right)\right.$$

$$\left.+\frac{cz}{r^5}(x, y, z)\left\{r^2\chi''+3r\chi'+3\left(\chi-\frac{e\zeta}{c}\right)\right\}\right\},$$

$$(a, \beta, \gamma)=\frac{c}{r^3}(y, -x, 0)(r\chi''+\chi') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where χ denotes $\chi(ct-r)$, and c is the velocity of radiation. χ and $\frac{e\zeta}{c}$ are small after the manner of F.

The surface condition is taken to be the continuity of (X, Y, Z). Whether this or the more probable (X′, Y′, Z′), the electromagnetic force, is to be continuous does not matter in the present case, as they only differ by an order F^2. The surface condition yields, if $\xi=ct-a$, and if the tangential component is zero inside,

$$\frac{d^2\chi}{d\xi^2}+\frac{1}{a}\frac{d\chi}{d\xi}+\frac{1}{a^2}\left(\chi-\frac{e\zeta}{c}\right)=\frac{a\mathrm{F}}{c} \quad . \quad . \quad . \quad . \quad (2)$$

and the surface density is found to be given by

$$4\pi\sigma=\frac{e}{a^2}+\frac{c\mathrm{P}_1}{a^2}\left(\frac{3a^3\mathrm{F}}{c}-2a^2\chi''\right) \quad . \quad . \quad . \quad (3)$$

leading to a mechanical force on the sphere of magnitude

$$e\mathrm{F}-\frac{2}{3}\frac{ec}{a}\chi''(ct-a) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

along the axis of z, so that if m be the Newtonian mass,

$$m\ddot{\zeta}+\frac{2}{3}\frac{ec}{a}\chi''(ct-a)=e\mathrm{F}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

with initial conditions

$$\zeta=\dot{\zeta}=0 \quad \text{at } t=0 . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

the sphere being initially at rest with ζ vanishing.

Other conditions may be deduced from the consideration that the undisturbed portion of the external medium commences where $r=ct+a$, so that $\chi(ct-r)=\chi'(ct-r)=0$ when $r=ct+a$, or

$$\chi(-a)=\chi'(-a)=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The solution of these equations and conditions is, so far as ζ is concerned,

$$\zeta=-\frac{2}{3}\frac{e\mathrm{A}}{mac}e^{-ct/2a}\sin\left\{\left(3+\frac{4m'}{m}\right)^{\frac{1}{2}}\frac{ct}{2a}+\epsilon\right\}$$

$$+\frac{1}{2}\frac{e\mathrm{F}}{m+m'}t^2-\frac{e\mathrm{F}m'}{(m+m')^2}\frac{at}{c}-\frac{1}{3}\cdot e\mathrm{F}\frac{(2m^2+4mm'-m'^2)}{(m+m')^2}\cdot\frac{a^2}{c^2},$$

where

$$m'=\frac{2}{3}\cdot\frac{e^2}{ac^2}, \quad \mathrm{A}\sin\epsilon=-\mathrm{D}', \quad \left(3+\frac{4m'}{m}\right)^{\frac{1}{2}}\mathrm{A}\cos\epsilon=-(\mathrm{D}'+2a\mathrm{B}')$$

$$\mathrm{D}'=\frac{m(2m^2+4mm'-m'^2)}{2(m+m')^3}\frac{a^3\mathrm{F}}{c}, \quad \mathrm{B}'=\frac{3}{2}\cdot\frac{mm'}{(m+m')^2}\frac{a^2\mathrm{F}}{c} \quad . \quad . \quad (8)$$

An error of sign has crept into one of the terms as given by Walker, and continues in some of the later analysis, though not interfering with the general conclusions. The value given above has been corrected in this respect.

The corresponding value of χ becomes

$$\chi(ct-r)=\mathrm{A}e^{-(ct-r+a)/2a}\sin\left\{\left(3+\frac{4m'}{m}\right)^{\frac{1}{2}}\frac{ct-r+a}{2a}+\epsilon\right\}$$

$$+\mathrm{A}'(ct-r+a)^2+\mathrm{B}'(ct-r+a)+\mathrm{D}'$$

where

$$\mathrm{A}'=\frac{3}{4}\cdot\frac{m'}{m+m'}\cdot\frac{a\mathrm{F}}{c} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In Walker's formula (17), p. 264, for the value of χ after the vibrations have subsided, there is an incorrect sign in the second term.

We proceed to an examination of the case in which m is very small. It may be shown without difficulty that the various constants take the forms

$$A' = \frac{3}{4}\frac{aF,}{c} \quad B' = \frac{3}{2} \cdot \frac{m}{m'} \cdot \frac{a^2F}{c}, \quad D' = -\frac{m}{2m'} \cdot \frac{a^3F}{c},$$

$$A \sin \epsilon = \frac{m}{2m'} \cdot \frac{a^3F}{c}, \quad A \cos \epsilon = -\frac{5}{4} \cdot \left(\frac{m}{m'}\right)^{\frac{3}{2}} \frac{a^3F}{c},$$

so that on reduction,

$$\zeta = -\frac{ea^2F}{c^2m'} e^{-ct/2a} \left\{ \cos . \frac{ct}{a}\left(\frac{m'}{m}\right)^{\frac{1}{2}} - \frac{5}{2}\left(\frac{m}{m'}\right)^{\frac{1}{2}} \sin . \frac{ct}{a}\left(\frac{m'}{m}\right)^{\frac{1}{2}} \right\}$$

$$+\frac{1}{2}\frac{eF}{m'}t^2 - \frac{eF}{m'}\frac{at}{c} + \frac{1}{3}\frac{eF}{m'}\frac{a^2}{c^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and, except at $t=0$, ζ tends to involve the sine and cosine of an infinite angle as the Newtonian mass decreases to zero. But even in the immediate neighbourhood of the limit $m=0$, it may be shown that this expression continues, like the corresponding value of χ, to satisfy all the conditions of the problem, and moreover, that no other forms can do so. Whatever the interpretation to be put upon the sine and cosine when m is zero, they cannot exceed unity, so that the vibrational term of ζ will very rapidly disappear on account of the damping. A slight departure from the usual condition of perfect conductivity in the sphere may perhaps remove the indeterminate character of the limit, by preventing the argument of the sine and cosine from becoming infinite, so that when $t=0$, this argument vanishes, and the initial conditions continue to be satisfied with no Newtonian mass present. On this supposition, ζ and $\dot{\zeta}$ vanish with t, and the initial conditions are satisfied, although the initial *acceleration* of the sphere would be practically infinite.

The displacement of the sphere may be regarded as a superposition of a periodic part upon a part corresponding to uniformly accelerated motion, and the damping factor is such that the periodic portion is evanescent after an extremely small time. The displacement thus tends to the form

$$\zeta = \frac{1}{2}\frac{eF}{m'}t^2 - \frac{eF}{m'}\frac{at}{c} + \frac{1}{3}\frac{eF}{m'}\frac{a^2}{c^2} \quad . \quad . \quad . \quad . \quad (11)$$

In the formula as given by Walker (p. 268) the sign of the second term is positive, and the factor $\frac{1}{3}$ has been dropped in the last term.

We proceed to a determination of the surface density on the sphere. The coefficient of the zonal harmonic term in $4\pi\sigma$ becomes from (3)

$$3F - \frac{2c}{a}\chi'',$$

and, with a little reduction, it may be shown that the part of $\ddot{\zeta}$ not evanescent on account of m is

$$\frac{eF}{m'} + \frac{1}{3}\frac{eF}{m} e^{-ct/2a} \cos . \frac{ct}{a}\left(\frac{m'}{m}\right)^{\frac{1}{2}}$$

and thus by (5)

$$\begin{aligned}\chi'' &= \frac{3a}{2ec}(eF - m\ddot{\zeta}) \\ &= \frac{3Fa}{2c} - \frac{aF}{2c}e^{-ct/2a} \cos . \frac{ct}{a}\left(\frac{m'}{m}\right)^{\frac{1}{2}}; \quad . \quad . \quad . \quad (12)\end{aligned}$$

so that the surface density is finally given by

$$4\pi\sigma = \frac{e}{a^2} + F\cos\theta \,.\, e^{-ct/2a} \cos . \frac{ct}{a}\left(\frac{m'}{m}\right)^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad (13)$$

and tends very rapidly to the uniform value belonging to a sphere at rest with no applied field, whatever the meaning given to the cosine. This conclusion is in accord with that of Conway. Thus a sphere with no Newtonian mass must move, when placed in an electric field of small intensity, without a change in its electrical distribution, if the usual conditions for a perfect conductor can continue to be valid. The value of σ at $t=0$, before the field has influenced the distribution by setting up vibrations, is of course

$$\sigma = \frac{1}{4\pi}\left(\frac{e}{a^2} + F\cos\theta\right). \quad . \quad . \quad . \quad . \quad (14)$$

When Newtonian mass is present, the surface density soon settles down to the steady value

$$\sigma = \frac{1}{4\pi}\left(\frac{e}{a^2} + \frac{3m}{m+m'}F\cos\theta\right) \quad . \quad . \quad (15)$$

(Walker's first result for this case, given in (19) p. 265, is corrected in a footnote in the second paper), and for a large value of m, gives the ordinary electrostatic formula, as it should.

Effect of a small Mechanical Force.

The corresponding solution for a small applied force of purely mechanical nature, which we may call G, has been given in Walker's second paper. With the previous notation, the primary equations, of which the first expresses the vanishing of the tangential electric or electromagnetic force (these only differ to the second order) at the surface, become

$$a^2\chi''(ct-a)+a\chi'(ct-a)+\chi(ct-a)-\frac{e\zeta}{c}=0$$

$$m\ddot{\zeta}+\frac{2}{3}\frac{ec}{a}\chi''(ct-a)=\mathrm{G} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

with the conditions

(1) $\chi=\chi'=0$ when the functions have argument $-a$,

(2) $\zeta=\dot{\zeta}=0$ at $t=0$; . . . . (17)

and the solutions are

$$\chi(ct-r)=\mathrm{A}e^{-(ct-r+a)/2a}\sin\left\{\left(3+\frac{4m'}{m}\right)^{\frac{1}{2}}\frac{ct-r+a}{2a}+\epsilon\right\}$$
$$+\frac{1}{2}\cdot\frac{e\mathrm{F}}{c^3(m+m')}\left\{(ct-r+a)^2-\frac{2am'}{m+m'}(ct-r+a)-\frac{2a^2mm'}{(m+m')^2}\right\}$$

$$\zeta=-\frac{2}{3}\frac{e\mathrm{A}}{mac}e^{-ct/2a}\sin\left\{\left(3+\frac{4m'}{m}\right)^{\frac{1}{2}}\frac{ct}{2a}+\epsilon\right\}$$
$$+\frac{1}{2}\frac{\mathrm{F}}{m+m'}\left\{t^2+\frac{2m'}{m+m'}\cdot\frac{at}{c}+\frac{2m'^2}{(m+m')^2}\frac{a^2}{c^2}\right\}, \quad . \quad . \quad . \quad . \quad (18)$$

where

$$\mathrm{A}\sin\epsilon=\frac{e\mathrm{F}a^2mm'}{c^3(m+m')^3},\quad \left(3+\frac{4m'}{m}\right)^{\frac{1}{2}}\mathrm{A}\cos\epsilon=\frac{e\mathrm{F}a^2m(2m+3m')}{c^3(m+m')^3}.$$

When the Newtonian mass becomes small,

$$\mathrm{A}\sin\epsilon=\frac{e\mathrm{F}a^2m}{c^3m'^2},\quad \mathrm{A}\cos\epsilon=\frac{3}{2}\cdot\frac{e\mathrm{F}a^2}{c^3m'}\left(\frac{m}{m'}\right)^{\frac{3}{2}},$$

and on reduction,

$$\zeta=-\frac{\mathrm{G}a^2}{c^2m'}e^{-ct/2a}\left\{\cos.\frac{ct}{a}\left(\frac{m'}{m}\right)^{\frac{1}{2}}+\frac{3}{2}\left(\frac{m}{m'}\right)^{\frac{1}{2}}\sin\frac{ct}{a}\left(\frac{m'}{m}\right)^{\frac{1}{2}}\right\}$$
$$+\frac{\mathrm{G}}{2m'}\left(t^2+\frac{2at}{c}+\frac{2a^2}{c^2}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

satisfying all necessary conditions for values of m tending to zero. The formula for the surface density of electrification at any time is

$$4\pi\sigma = \frac{e}{a^2} - \frac{2c}{a}\chi'' \cos\theta. \quad . \quad . \quad . \quad . \quad . \quad (20)$$

But

$$\chi''(ct-a) = \frac{3a}{2ec}(\mathrm{G} - m\ddot{\xi}),$$

and finally, when m is nearly zero,

$$4\pi\sigma = \frac{e}{a^2} - \frac{3\mathrm{G}}{e}\cos\theta\left(1 - e^{-ct/2a}\cos\frac{ct}{a}\left(\frac{m'}{m}\right)^{\frac{1}{2}}\right). \quad . \quad (21)$$

A constant surface density (as regards time) is therefore speedily established, with a term involving the first zonal harmonic. Initially, the value is

$$\sigma = e/4\pi a^2,$$

as it should be.

But the infinite acceleration with $m=0$ again appears, although it may be formally shown that these are the only expressions capable of satisfying all the hypothetical conditions. The motion does not seem, therefore, to be physically likely to occur, and the results serve to indicate that an assumption of perfect conductivity with the ordinary condition cannot readily be justified in an accelerated system, and is of a very artificial character. That the electrical motions of the conductor should be confined to the surface in this case is very unlikely, and in the case of a single electron, it is difficult to find a physical meaning for the assumption.

In the more difficult case in which the sphere has a steady motion on which a longitudinal or transverse acceleration is superposed, a calculation of the electrical inertia on the basis of the two usually adopted surface conditions only leads to two values which must be regarded as somewhat arbitrary, and although one formula may be more supported by, for example, the experiments of Kaufmann, than the other, it still remains as but one of many perhaps equally likely results. The agreement with experiment may indicate that the proper vector has been made continuous, but not that it is zero inside the conductor. Yet in the present state of the theory, it seems necessary to emphasise Walker's contention that the Newtonian type of analysis affords the safest mode of attack on the problems of accelerated motion.

The contracted electron is rejected by Walker as having no apparent dynamical foundation, but this may be only apparent, and certainly it does not seem possible to dispense with the Principle of Relativity and its consequences. Moreover, Bucherer's contracted electron gives a very good agreement with Kaufmann's experiments, and it is desirable that a direct mode of analytical treatment of an electron which changes its shape, not associated with the quasi-stationary principle, should be found, but none has been suggested as yet.

There is one combination of a small mechanical force with a weak electric field which would give a finite initial acceleration to a sphere whose inertia is electrical only, no electrical effect being maintained inside. This combination satisfies the condition

$$\mathrm{G}=-\tfrac{1}{3}e\mathrm{F}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and the corresponding value of ζ is the limit of

$$\zeta=\frac{4}{3}\frac{ea^2\mathrm{F}}{c^2m'}\left(\frac{m}{m'}\right)^{\frac{1}{2}}e^{-ct/2a}\sin.\frac{ct}{a}\left(\frac{m'}{m}\right)^{\frac{1}{2}}+\frac{1}{3}\frac{e\mathrm{F}}{m'}t^2-\frac{4}{3}\frac{e\mathrm{F}}{m'}\frac{at}{c}. \quad (23)$$

so that the acceleration at $t=0$ is $\frac{2}{3}\frac{e\mathrm{F}}{m'}$. But it becomes infinite afterwards. The surface density remains permanently equal to

$$\frac{1}{4\pi}\left(\frac{e}{a^2}+\mathrm{F}\cos\theta\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

so long at least as ζ is small.

In connexion with the question of electrical inertia, the investigations of Conway and Walker, starting from the same differential equations and surface conditions, lead to different values of the transverse inertia, that of Conway being identical with Abraham's expression. A comparison of the two methods will be made in a later note, for it seems that the formula given by Walker in this case is the only possible result of a rigorous analysis applied with the vanishing of the tangential electromagnetic force as its surface condition.

Trinity College, Cambridge,
1910, May 28th.

LXIV. *On Threefold Emission-Spectra of Solid Aromatic Compounds.* *By* Professor E. GOLDSTEIN [*].

SOME years ago I observed [†] that bright, fluorescent, and phosphorescent light is emitted by a number of aromatic solid compounds—for example, naphthalene, xanthone, anthracene, &c.—if cathode rays strike on these substances, cooled by liquid air to prevent their evaporation and decomposition. In this way I was also able to obtain bright-light emission from a great many substances, which at an ordinary temperature are liquid bodies—for example, benzene, the three xylenes, benzonitrile, the chinolines, acetophenone, &c. The light emitted by these substances gave bright *discontinuous* spectra of a great variety, all consisting of bands of various width and intensity.

Since that time I have extended this research on nearly all aromatic substances which I could obtain in any way, and have thus obtained about two thousand emission-spectra of aromatic substances and of mixtures of such substances with other bodies.

Of course, time does not allow me to give a complete report of this work. Here I just want to speak about *one* result of my experiments.

In the beginning I was satisfied to observe just a single spectrum for each substance, because it was thought that every substance could emit only one single spectrum. But soon I found that the complexity of phenomena is much greater than it seemed at first sight. For each substance does not show only *one* spectrum, but, according to the conditions of the experiment, there may appear *three* spectra, which are quite different from each other, and have no coincident maximum. I call these three kinds of spectra respectively the *initial-spectrum*, the *chief-spectrum*, and the *solution-spectrum* of the substance.

At the first moment, when cathode-rays fall upon the substances, there appears quite alone and bright the spectrum which I call the *initial-spectrum*. Then the brightness of the initial-spectrum diminishes and gets fainter and fainter till its density becomes very small; but it never *entirely* disappears. When the initial-spectrum gets fainter, the *chief-spectrum* at the same time appears and grows brighter and brighter.

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[*] Communicated by the Author. Read at the Winnipeg Meeting of the British Association, August 1909.

[†] *Verhandl. d. Deutsch. Physik. Ges.*, vi. p. 156, and vi. p. 185 (1904).

The chief-spectrum is for a great number of substances so characteristic that it is possible to recognize the substance in this way at a glance and without measuring the wave-lengths, just as you can recognize nitrogen by its well-known bands, or hydrogen, mercury and helium by their line-spectra. This is even the case with isomeric substances; for one is able to distinguish at a glance, for instance, the three isomeric xylenes or other isomeric aromatic hydrocarbons. The third kind of spectra, which is quite different from the two others, appears if an aromatic substance is dissolved in any other liquid or melted compound and the solidified solution is exposed to cathode-rays.

Now let me just say a few words on the properties of each of the three kinds of spectra.

The *chief-spectra* always begin from the infra-red, never reach the violet end of the visible spectrum, but end about the middle part of it in the green or in the blue, sometimes even in the yellow. I never observed that a chief-spectrum passes the wave-length of λ 460. The chief-spectra consist of narrow channelled bands, which nearly always have their sharper boundary toward the violet end of the spectrum. The number of the bands varies within a wide range for the different substances between a few strips and several dozen. The distances between them appear generally irregular. The substances, when they send out their chief-spectrum, look red or yellow or green, or of any other tint which occurs with fluorescent minerals or inorganic salts. On the other hand, the light which is emitted during the first moments of radiation and belongs to the initial-spectrum is —at least, for colourless substances—always *blue*. The discontinuous *initial-spectra* of two substances are, like their chief-spectra, never quite the same; but as in their general appearance they are rather similar to each other, so one cannot recognize a substance at a glance by its initial-spectrum as one can by the chief-spectrum, but measures of its wave-lengths are necessary. The initial-spectra begin always like the chief-spectra in the red; but not only reach into the green or blue, but go on into the ultra-violet. One type of initial-spectra occurring especially frequently invariably consists of *six groups* of bands. Each of the six groups is formed by the same number of strips at the same relative distance and intensity; and as the relative distance of the groups themselves is also not very different—at least in the prismatic spectrum—the whole spectrum gives the impression of having a *very high regularity*. Such spectra, consisting of six groups, with different wave-lengths for each individual substance, are, for example, the initial spectra of mesitylenic acid, of metatoluic acid, of the anhydride of benzoic acid, of toluene and of its halogen substituted derivates—and of many other substances, especially of those aromatic bodies whose molecules contain a single-ring group.

In the groups which contain two or even more benzene rings, and especially in condensed substances, one finds also other types of initial-spectra, all extending from red into the ultra-violet, which I will not speak of in this short report.

The *third* spectrum of aromatic compounds is shown in very characteristic forms especially by dissolved compounds of the condensed type; for instance, by naphthalene and most of its derivates. The chief-spectrum of naphthalene shows the wave-lengths

539 (very bright)
555
560
573
589 (very bright)
615 (probably a doublet)
630
648

λ 539 and 589 mark sharp boundaries on the violet side, the other wave-lengths belong to the middle of narrow strips.

The spectrum of the same naphthalene, if dissolved in monochlorobenzene (which itself gives only a faint and almost continuous spectrum) shows the following wave-lengths (all for the middle of the narrow strips):—

$$\left.\begin{matrix}473\\483\end{matrix}\right\}\text{bright}\quad\left.\begin{matrix}505\\510\end{matrix}\right\}\begin{matrix}\text{rather}\\\text{bright}\end{matrix}\quad\left.\begin{matrix}517\\523\end{matrix}\right\}\begin{matrix}\text{rather}\\\text{faint}\end{matrix}\quad\left.\begin{matrix}540\\545\end{matrix}\right\}\left.\begin{matrix}557\\565\end{matrix}\right\}\begin{matrix}\text{rather}\\\text{faint}\end{matrix}$$

582 faint.

Beyond this last strip the illuminated ground cannot be separated distinctly into strips.

One cannot, however, speak of a *single* solution-spectrum of a body, as the solution-spectrum of the same substance varies greatly with the solvent.

The solution-spectrum of naphthalene, for example, shows differences, if the naphthalene has been dissolved in metaxylene or in orthoxylene or in paraxylene. Therefore, if one substance shows remarkable differences in *isomeric* solvents, one cannot wonder that the solution-spectra of the same substance show even much greater differences if more different solvents are used; for instance, if we compare the solution-spectra of the same substance when dissolved either in a xylene or in aniline, pyridine, ethyl-alcohol, and ethyl-ether.

On the other hand, each condensed compound and its derivates, *even in the case of isomers*, shows an individual solution-spectrum. The chief-spectrum of the β-bromonaphthalene presents a similar aspect to the chief-spectrum of the α-bromonaphthalene. But the solution-spectra of the two substances, for example, in monochlorobenzene, are *very* different. The solution-spectrum of the α-substance is of a similar type to the solution-spectrum of naphthalene itself, presenting only an appearance of a certain regularity by the occurrence of some doublets, while the solution-spectrum of the β-form is of a quite different type, and shows a most regular structure. It consists of four bands, of quite equal aspect, extending from the red into the blue. Each of the four bands is formed by five narrow strips, the relative distance and intensity of which is quite corresponding in all bands.

The light of the *chief-spectra* is *fluorescent*, and disappears at the moment when the cathode-rays stop.

The light of the solution-spectra is *phosphorescent*, and very often one can see it for some minutes after the discharge which produces the cathode-rays is interrupted.

Only *very small quantities* of a substance are necessary to produce a solution-spectrum bright enough to be remarked and to be measured. For example, one can detect in this way less than the hundred thousandth part of naphthalene dissolved in monochlorobenzene or in methylbenzoicester.

Of course these phosphorescent solution-spectra are, on the other hand, a very sensitive test for the purity of aromatic substances, or, what is the same, a very sensitive means of detecting very small quantities of admixed foreign aromatic substances. And I am sorry to say that, among many hundreds of preparations of the best obtainable "purity," the specimens which did not show very marked signs of impurities could be counted on the fingers of one hand, if there are any at all.

I spent much time and money in getting even only very small quantities of certain substances really pure, for example, diphenyl, indene, carbazol, fluorene, and other condensed compounds, and some of the most famous chemists helped me kindly by the best known methods ; but at last I had to give up the hope of getting any of these substances in pure condition. Until now they have never been produced in a really pure state, and I fear that the same holds true for all other aromatic bodies.

LXV. *The Relation between Electromagnetism and Geometry.*

By H. Bateman, *Fellow of Trinity College, Cambridge, and Reader in Mathematical Physics at the University of Manchester*[*].

1. RECENT theoretical researches in electromagnetism indicate that the science of electromagnetism is closely connected with the geometry of a system of spheres. According to the generalized form of the principle of Huyghens, an electromagnetic disturbance at any point in space can be regarded as the resultant of a large number of elementary disturbances which are propagated in the form of spherical waves. It should be profitable then to study the geometrical properties of an aggregate of spherical waves travelling inwards or outwards with the velocity of light.

Two distinct sets of properties must be dealt with. First of all we must regard the spheres simply as geometrical figures and study the geometrical properties in the usual way, and secondly we must consider the relations between the different spheres when various numbers are attached to each.

If ct denote the radius of a sphere which is contracting with the velocity c, it will have contracted to a point at a time t subsequent to the moment at which it was first contemplated. Similarly, if it is expanding with the velocity of light its radius must have been zero at a time t previous to the moment when it was first contemplated. We shall say in either case that the sphere is the representative sphere of a particle which is at its centre at time $\pm t$.

For some purposes it is convenient to study the kinematics of a particle when different times are associated with its different positions, and for other purposes it is convenient to study the geometry of the system of representative spheres. The advantage of using the second method is that we may study the whole history of a particle by considering its chain of representative spheres at a given moment of contemplation[†].

A complex of ∞^3 representative spheres which are related to one another in some way will be called a *view* of the universe. It may be replaced by the corresponding system of particles if each particle is considered at an appropriate time determined by the radius of the representative sphere.

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[*] Communicated by the Author.

[†] It should be noticed that if a particle is moving with a velocity less than that of light, no two of its representative spheres with positive radii intersect.

It has been shown that the fundamental equations of the theory of electrons simply describe the properties of an arbitrary view of the universe[*].

We may pass from one view of the universe to another by means of a transformation which transforms a representative sphere into a corresponding representative sphere[†]. It has been shown that the fundamental equations of the theory of electrons are covariant for all transformations of this kind.

This group of transformations possesses the remarkable property that the lines of curvature on the wave surface enveloped by a system of representative spheres are transformed into the lines of curvature on the corresponding wave surface. The group of transformations is in fact identical with that studied by Sophus Lie[‡]. A particular transformation due to Ribaucour[§] which has been called by Laguerre[||] "la transformation par directions réciproques" is easily seen to be identical with the transformation used by Lorentz[¶], Larmor[**], and Einstein[††], to pass from the views obtained by one observer to the views obtained by another observer moving with uniform velocity relative to the first.

2. The late Russian mathematician Minkowski of Göttingen has made considerable use of a representation in which a particle which is at the point (x, y, z) at time t is represented by a point whose coordinates are (x, y, z, ict) in a space of four dimensions[‡‡].

The group of *Lorentzian transformations* for which the electron equations are covariant is then represented by the group of transformations of rectangular axes in the space of four dimensions. The more extensive group of *spherical wave transformations* for which the electron equations are

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[*] See a paper by the author "On the Transformation of the Electrodynamical Equations," Proc. Lond. Math. Soc. (1910).

[†] A simple transformation may be obtained by increasing or decreasing the radii of the spheres by the same amount. Other typical transformations are displacements, magnifications, and inversions.

[‡] *Mathematische Annalen*, vol. v. *Göttinger Nachrichten* (1871).

[§] *Comptes Rendus*, t. lxx. p. 332 (1870).

[||] *Ibid.* t. xcii. p. 71 (1881). See also Darboux's *Théorie des Surfaces*, t. i. p. 253.

[¶] Amsterdam Proceedings (1904). The covariance of Maxwell's equations was established by Voigt, *Göttinger Nachr.* 1887, p. 41.

[**] Æther and Matter, 1900.

[††] *Annalen der Physik*, Bd. xvii. (1905).

[‡‡] *Göttinger Nachrichten*, 1908. *Physikalische Zeitschrift*, 1909, pp. 104, 216. The transition from Minkowski's representation to our representation gives rise to a very interesting correspondence between the spheres in space and the points of a space of four dimensions. This correspondence has been studied by Darboux, *Annales de l'Ecole Normale*, 1872.

covariant is represented by the group of conformal transformations of the space of four dimensions *.

Minkowski, Born †, and Herglotz ‡ endeavour to represent the paths of a system of connected particles by means of the orthogonal trajectories of a system of ∞' hyperplanes in the space of four dimensions. The sections cut out on the different hyperplanes by a tube of orthogonal trajectories may be derived from one another by means of displacements (*i.e.* transformations of rectangular axes) in the space of four dimensions, and so the corresponding views of the system of particles are derived from one another by means of transformations for which the electron equations are covariant.

This result may be generalized by considering the orthogonal trajectories of a system of hyperspheres (or spheres) in the space of four dimensions. It has been proved that the sections of these hyperspheres (or spheres) by a tube of orthogonal trajectories, may be derived from one another by *conformal transformations* of the space of four dimensions §. The corresponding views of the connected system of particles are consequently derived from one another by means of transformations for which the electron equations are covariant.

3. The *space-time vectors* introduced by Minkowski ‖ admit of simple representations by means of our representative spheres (or spherical waves).

If we take a particular sphere A as the *sphere of observation*, its relation to a second sphere B may be specified by a space-time vector (AB) of the first kind which has the effect of displacing the sphere A so that it becomes concentric with B and at the same time of increasing or diminishing its radius so that it becomes equal to that of B ¶. The vector, in fact, is exactly analogous to a displacement vector from one point to another.

Now just as there are different physical quantities which may be represented by vectors, so there are different physical vectors which may be specified by means of space-time vectors of the first kind.

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* See papers by E. Cunningham and the author, Proc. London Math. Soc. 1910.

† *Ann. d. Physik*, vol. xxx. (1909). *Physik. Zeitschr.* vol. x. p. 814 (1909).

‡ *Ann. d. Physik*, vol. xxxi. Heft ? (1910).

§ This is practically done by Darboux, *Leçons sur les Systèmes orthogonaux*, Paris, 1898, Ch. II.

‖ *Göttinger Nachr.* 1908. *Physik. Zeitschr.* 1909, p. 104.

¶ The components of the displacement of the centre and the change in radius may be taken as the four components of the space-time vector.

In order to specify a space-time vector of the first kind through a given sphere of observation A when the above representation is used, it is sufficient to know the position of the centre of similitude of the spheres A, B (attention being paid to the signs of their radii in determining the choice of one out of the two centres of similitude), and a number indicating the magnitude of the vector *. If the centre of similitude lies within the sphere of observation, the vector is said to be *temporal,* if it lies outside, the vector is said to be *spacial* †. Two vectors are said to be orthogonal ‡ when the corresponding centres of similitude are conjugate points with regard to the sphere of observation. A vector orthogonal to a temporal vector is necessarily spacial, but the converse does not hold.

The relations which two spheres B and C (or a space-time vector of the first kind not passing through A) bear to the sphere of observation determine a species of space-time vector of the second kind containing A. A space-time vector of the second kind is specified by six components

$$(E_x, E_y, E_z, H_x, H_y, H_z),$$

and the special type at present under consideration is characterized by the existence of the relation

$$E_xH_x+E_yH_y+E_zH_z\,.$$

A more general space-time vector of the second kind may be obtained by adding the components of two *special* space-time vectors of the second kind.

A *special* space-time vector of the second kind may be specified by means of a line, viz. the axis of similitude of the spheres A, B, C and a number to indicate the magnitude of the vector. The magnitude of the vector may be taken to be equal to this number multiplied by the area of the triangle PQR, where P, Q, R are the points of contact of a common tangent plane of the three spheres A, B, C.

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* The magnitude of the vector may be taken to be equal to this number multiplied by the length of a common tangent of the two spheres. The magnitude of a vector may vanish although its components do not.

† These terms were introduced by Minkowski, but are defined analytically. If (X, Y, Z, cT) are the four components of a space-time vector of the first kind, it is said to be temporal or spacial according as

$$c^2T^2 \gtrless X^2+Y^2+Z^2.$$

‡ Minkowski uses the word *normal.* Two vectors whose components are (X, Y, Z, cT) (X_1, Y_1, Z_1, cT_1) are normal to one another if

$$XX_1+YY_1+ZZ_1=c^2TT_1.$$

Two special space-time vectors of the second kind are said to be orthogonal when their corresponding lines are polar lines with regard to the sphere of observation *.

A space-time vector of the third kind may be regarded as representing the relation of three spheres B, C, D to the sphere of observation A. It may be represented by the plane of similitude of the four spheres A, B, C, D, and may be classified as spacial or temporal according as the plane does or does not intersect the sphere. Two space-time vectors of the third kind are said to be orthogonal when their representative planes are conjugate with regard to the sphere of observation.

The application of these ideas to electromagnetism depends upon the fact that the components of the magnetic induction together with the components of the electric force must be regarded as the six components of a space-time vector of the second kind. In the case of the simplified equation of the theory of electrons, the components of the convection current together with the volume density of the electricity form the four components of a space-time vector of the first kind †.

The components of the electromagnetic vector potential together with the electromagnetic scalar potential form the four components of a space-time vector of the third kind ‡.

The study of the properties of these vectors is facilitated by considering integral forms of the type

$$\begin{gathered}\mathrm{H}_x d(y, z) + \mathrm{H}_y d(z, x) + \mathrm{H}_z d(x, y) \\ + \mathrm{E}_x d(x, t) + \mathrm{E}_y d(y, t) + \mathrm{E}_z d(z, t),\end{gathered}$$

$$\rho\omega_x d(y, z, t) + \rho\omega_y d(z, x, t) + \rho\omega_z d(x, y, t) - \rho d(x, y, z),$$

$$\mathrm{A}_x d(y, z, t) + \mathrm{A}_y d(z, x, t) + \mathrm{A}_z d(x, y, t) - \Phi d(x, y, z),$$

as in my paper on the transformation of the electrodynamical equations.

It should be remarked that the transformations which can be used to transform a *particular* electromagnetic field into another are not confined to the group of spherical wave

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* A vector of the second kind may be regarded as temporal when its representative line meets the sphere of observation in real points, and as spacial when the line does not meet the sphere in real points.

† The principle of the conservation of energy is expressed by the fact that the space-time vectors, whose four components are the three component forces and the rate at which work is being done, is normal to the space-time vector of the first kind mentioned above.

‡ There is a reciprocal relation between vectors of the first and third kind.

transformations. If we denote the velocity of light by unity, it may be shown, for instance, that a transformation which is such that

$$\lambda\left[dx^2+dy^2+dz^2-dt^2\right]+\mu\left[v_z dx+v_y dy+v_z dz-dt\right]^2$$
$$=dx'^2+dy'^2+dz'^2-dt'^2.$$

is suitable for the purpose provided the vector $\boldsymbol{v}$ whose components are (v_x, v_y, v_z) is connected with the components (E_x, E_y, E_z) (H_x, H_y, H_z) of the electric and magnetic force by the relations

$$E_x+v_y H_z-v_z H_y=v_x(E_x v_x+E_y v_y+E_z v_z),$$
$$H_x-v_y E_z+v_z E_y=v_x(H_x v_x+H_y v_y+H_z v_z),$$
$$v_x^2+v_y^2+v_z^2=1.$$

It can be shown that an expression of the form

$$\nu\left[v_x dx+v_y dy+v_z dz-dt\right]$$

is an invariant for transformations of this kind and for the whole group of spherical wave transformations. I have been trying to find a physical interpretation of this vector.

The University, Manchester,
June 16th, 1910.

[*Note added Aug. 6th*, 1910.] Since the electromagnetic equations specify the properties of a *view* of a set of particles and a view is represented by a hypersurface in the four-dimensional space, it appears that a transformation from one view to another for which the electromagnetic equations are covariant need only give a conformal representation of one hypersurface on the other, and not necessarily a conformal transformation of the whole hyperspace.

It is possible then that the motion of a connected system of particles may be represented by a continuous conformal transformation of a hypersurface or, in particular, by a continuous deformation without stretching. The path of a particle is represented by the successive positions of a point on the hypersurface in the successive deformations. The case in which the hypersurface becomes torn during the deformation is probably irrelevant for physics since a particle corresponding to a point at which the tear originates would divide into two. This case may, however, be of some biological interest.

LXVI. *Molecular Attraction.* *By* J. E. MILLS [*].

IN a recent article [†] on "The Electric Origin of Molecular Attraction," Mr. W. Sutherland called attention to a relation discovered by the author. Mr. Sutherland's criticisms of the author's point of view were largely justified, so far as the papers cited by Mr. Sutherland were concerned. In later papers by the author, overlooked by Mr. Sutherland, the meaning and derivation of the relation were more particularly discussed, and the criticisms made could not, I think, apply to the views there expressed. The author would like therefore to restate the facts and give his own interpretation of them.

I. *Statement and Experimental Proof of the Fundamental Equation.*

The relation under discussion can be expressed in the form

$$\frac{L-E_e}{\sqrt[3]{d}-\sqrt[3]{D}}=\text{constant}, \quad \text{or} \quad \lambda=\mu'(\sqrt[3]{d}-\sqrt[3]{D}) \quad . \quad (1)$$

Here L is the heat of vaporization of one gram of liquid. E_e is the energy spent in overcoming the external pressure as the liquid vaporizes and expands from the density of the liquid d, to the density of the vapour D. $L-E_e$ is, therefore, equal to the internal heat of vaporization and is designated λ. The constant given by the equation is called μ'. It is a characteristic constant for any liquid and is not affected by changes in temperature.

The above equation has been tested for thirty-eight substances [‡], and a summary of the results obtained is given in the last two papers referred to above.

I think that *the evidence there presented is sufficient to justify the conclusion that the equation*

$$\frac{L-E_e}{\sqrt[3]{d}-\sqrt[3]{D}}=\text{constant}$$

represents a new and most exact law, holding true at all temperatures for all normal non-associated liquids.

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[*] Communicated by the Author.

[†] Phil. Mag. [6] vol. xvii. p. 664 (1909).

[‡] Journ. Phys. Chem. Part I. vol. vi. p. 209 (1902); Part II. vol. viii. p. 383 (1904); Part III. vol. viii. p. 593 (1904); Part IV. vol. ix. p. 402 (1905); Part V. vol. x. p. 1 (1906); Part VI. vol. xi. p. 132 (1907); Part VII. vol. xi. p. 594 (1907); Part VIII. vol. xiii. p. 512 (1909). Journ. Amer. Chem. Soc. vol. xxxi. p. 1099 (1909).

II. *Theoretical Derivation of the Fundamental Equation.*

The equation was deduced theoretically (see sixth paper above cited) from certain assumptions which may be stated as follows :—

1. The total energy *per se* of a molecule must be the same in the liquid as in the gaseous state, the temperature being the same. If at a given temperature a given weight of gas represents more energy than the same weight of the substance as a liquid, the extra energy of the gas must be energy of position only (assuming no intramolecular change).

Expressing the above belief in a different form, it may be said that the energy necessary to change a liquid into a gas must be spent solely in overcoming the external pressure and in altering the distance apart of the molecules. (Unless the molecule breaks apart also or nears the point of disruption.) Hence the internal heat of vaporization must be spent solely in overcoming the molecular attraction as the molecules move further apart.

2. The molecular attraction between two molecules varies inversely as the square of the distance apart of the molecules.

3. The molecular attraction does not vary with the temperature.

4. The molecules in the liquid and in the gaseous condition are evenly distributed throughout the volume occupied by them and the number of molecules does not change.

5. The molecular attractive forces are definite in amount. If this attraction is exerted upon another particle, the amount of the attraction remaining to be exerted upon other particles is diminished by an exactly equivalent amount.

The above assumptions are, none of them, purely gratuitous assumptions made to fit the case in hand. The evidence in their favour cannot be given and discussed fully in the present paper, but a few comments are warranted by the general importance of the assumptions.

The first assumption followed from a study of the kinetic theory of gases, the specific heat of gases, and the application of the gas law, $PV=RT$, to solutions. If the gaseous pressure was produced by the motion of the molecules and a similar pressure (as osmotic pressure) was produced in solution, it seemed reasonable to suppose that the osmotic pressure was in some way due to an equal molecular motion. The molecules of the dissolved substance could not have an average kinetic energy of translational motion different from the molecules of the solvent. Hence the conclusion that the *average translational energy of gaseous and liquid molecules of the same temperature must be equal.*

Now a study of the specific heat of gases showed that the total energy of a gaseous molecule, exclusive of the energy which holds the molecule together and of extraneous forces, is proportional to the translational energy. When the causes for this relation were considered, it seemed a reasonable inference that *the corresponding portion of the energy of a molecule of a liquid would similarly be found to be proportional to its translational energy.* Therefore the first assumption follows *.

The second assumption was made because all of the attractive forces, whose law of variation with the distance is known, obey the inverse square law. This is true of electrical, magnetic, and gravitational forces. Also the intensity of sound, of light, and of heat, vary inversely as the square of the distance from the origin. It seemed to the author, whatever the nature of the molecular attractive force—be it wave-motion or emanation—that the intensity of the force must decrease directly in proportion to the increase in the surface of the wave or emanation front, and since and because this surface increases as the square of its distance from the origin, the attractive force must decrease proportionately, and therefore obey the inverse square law †.

The third assumption that the molecular attractive force did not vary with the temperature seemed the most natural assumption, for none of the other attractive forces, chemical, magnetic, electrical, or gravitational, are affected by temperature changes so far as is known.

The fourth assumption that the molecules in the liquid and in the gaseous condition are evenly distributed throughout the space occupied by them is probably always more or less untrue. But if the molecules are shifted from their ideal position by reason of the attractive force, the particles would gain in kinetic energy exactly so much as they would lose in potential energy. It is possible therefore, without error,

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* The liquid molecules may conceivably possess a "concealed" energy not possessed by the gaseous molecules. If such energy exists it is surrendered in proportion to the internal heat of vaporization, and its effect is cancelled so far as the conclusions here drawn are concerned. The evidence upon this point will be discussed in a subsequent paper.

† I do not intend, however, by this statement to be understood as implying that the reason given is the sole reason for the inverse square law. The neutralization of the attraction may be another factor tending to produce the law. And yet other factors may exist. I am not now trying to explain the mechanism of the attraction or of its neutralization.

to consider them to be shifted back into their position of even distribution; and the fundamental supposition upon which the mathematical work is based is, that the molecules of a liquid and the molecules of its vapour have *per se* the same * energy when they are in this ideal position of even distribution throughout the space occupied by them.

Except for associated substances or substances undergoing decomposition, it is generally believed, and the belief rests upon considerable experimental evidence, that the number of molecules in the liquid and in the gaseous condition are the same. The equation is not true where this condition is violated.

The fifth assumption warrants the closest study. In the first paper, when equation 1 was originally deduced, this assumption was not expressly made. The deduction of that equation contained an error which was later corrected in the sixth paper. Attention was called in that paper to the following facts:—

1. The equation, $\lambda=\mu'(\sqrt[3]{d}-\sqrt[3]{D})$, was true experimentally.

2. The above equation followed if *a constant mass of liquid was taken* and the law of the force acting between the particles of the liquid was, force $=\frac{\mu^2 m^2}{s^2}$, where μ was the constant of molecular attraction and was equal to a constant times μ', m was the mass of the attracting particles, and s was their distance apart.

3. If the *mass of liquid taken was varied* then the same law of force between the particles showed that the heat required for vaporization should vary as the 5/3 power of the mass.

4. We know experimentally that the heat required to vaporize a liquid varies directly as the mass of the liquid taken.

The question to be determined therefore is, in what way to modify the assumed law of the force, namely, force $=\frac{\mu^2 m^2}{s^2}$, in order to obtain the experimentally true equation

$$M\lambda=M\mu'(\sqrt[3]{d}-\sqrt[3]{D}),$$

with either a constant or a variable mass, M. An inspection of the factors involved makes it very probable that the

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* See footnote (*), p. 631.

trouble is caused by the numerator factor of the force as defined in statement 2 above, and not by the denominator. Now undoubtedly the molecular attraction is a mutual property of the molecules, but it is not necessary to suppose that the attraction of one molecule can be indefinitely multiplied by the introduction of new molecules into the surrounding space. If we assume that the amount of the molecular attraction is a constant, and does not vary with the total mass of the surrounding molecules, all of the above facts can be reconciled at once. From this point of view the total attractive force of each molecule is independent of the number of molecules and we can write for the law of the force as exerted between two molecules, force $=\frac{\text{constant}}{s^2}$. But in order to deduce the experimentally true equation (and for other reasons) it is convenient to consider the force as being a function of the mass of the individual molecule and to write for the law governing the attractive force of any molecule, force $=\frac{\mu m}{s^2}$, where μ is a constant and m is the mass of the molecule. Now if all of the attractive force is utilized by being concentrated upon another molecule we would have for the energy necessary to pull the molecules apart from distance s_1 to s_2,

$$E=\int_{s_2}^{s_1}\mu m\frac{ds}{s^2}=\mu m\left(\frac{1}{s_1}-\frac{1}{s_2}\right) \quad . \quad . \quad . \quad . \quad (2)$$

For a mass of liquid M containing n molecules, and of molecular weight m, we have, if v is the volume of the liquid and V the volume of the vapour,

$$nm=M,\quad s_1=\sqrt[3]{\frac{v}{n}},\quad s_2=\sqrt[3]{\frac{V}{n}},\quad v=\frac{nm}{d},\quad V=\frac{nm}{D},$$

and equation 2 becomes

$$E=\int_{\sqrt[3]{\frac{V}{n}}}^{\sqrt[3]{\frac{v}{n}}}\mu m\frac{ds}{s^2}=\mu m\left(\frac{1}{\sqrt[3]{\frac{v}{n}}}-\frac{1}{\sqrt[3]{\frac{V}{n}}}\right)=\frac{\mu m}{\sqrt[3]{m}}\left(\sqrt[3]{d}-\sqrt[3]{D}\right). \quad (3)$$

This equation gives the energy necessary to pull two molecules from each other during the given expansion if all of the attractive force of one molecule be regarded as concentrated upon the other. The energy necessary to pull n

molecules from each other is simply n times as great, or probably with more exactness $n/2$ times as great, and we have

$$nE=\frac{\mu nm}{\sqrt[3]{m}}(\sqrt[3]{d}-\sqrt[3]{D})=\frac{M\mu}{\sqrt[3]{m}}(\sqrt[3]{d}-\sqrt[3]{D}). \quad . \quad (4)$$

If $\mu=\sqrt[3]{m\mu'}$ (or $2\sqrt[3]{m\mu'}$), this equation reduces very simply to

$$M\lambda=M\mu'(\sqrt[3]{d}-\sqrt[3]{D}), \quad . \quad . \quad . \quad . \quad (5)$$

which is the law that we have above shown to be experimentally true.

III. *Statement of the Fundamental Equation in a Simpler Form.*

While it seems to the author that all of the above assumptions are conditions that are probably fulfilled if the equation

$$M\lambda=M\mu'(\sqrt[3]{d}-\sqrt[3]{D})$$

is true, and I have shown that it is true, I do not mean at all to say that the equation as stated really represents all of those conditions. The equation rests upon those conditions and was derived logically from them, but the meaning of the equation itself is more restricted. Taking into consideration the theory by which the equation was derived, it is certainly probable that the equation will represent under all circumstances, the temperature remaining constant during the expansion, the work done against the force of molecular attraction in moving molecules further apart. Now, the further the molecules are moved apart the less becomes the value of D, and D will finally become zero when the molecules have been moved an infinite distance apart. Making, therefore, D equal to zero, and remembering that the distance apart of the molecules, s, is proportional to $\frac{1}{\sqrt[3]{nd}}$, where n is the number of molecules and is therefore a constant, we can write

$$\lambda_{\infty}s=\text{constant}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

as the very simple form for the law under discussion. This statement means simply this :—

In any normal substance the internal heat given out as the molecules approach each other, multiplied by the distance apart of the molecules, is equal to a constant.

The equation

$$\frac{L-E_e}{\sqrt[3]{d}-\sqrt[3]{D}}=\text{constant},$$

and the above statement, are true, because the molecular attraction varies inversely as the square of the distance apart of the attracting particles and because the total amount of attractive force possessed by a molecule is a constant.

The author believes that the above statement and italicized sentences express the physical reality represented by the equation under discussion,

$$\lambda=\mu'(\sqrt[3]{d}-\sqrt[3]{D}).$$

The true nature of the attractive forces is a subject which I will not attempt to discuss in the present paper.

Regarding the errors cited by Mr. Sutherland contained in the earlier papers, I would say that I have never supposed the molecular cohesive force and the attraction of gravitation to be identical in the sense attributed to me by Mr. Sutherland. In the first paper, p. 230, I state in italics, "*the molecular attraction appears to resemble the attraction of gravitation in that it varies inversely as the square of the distance apart of the attracting molecules and does not vary with the temperature. It differs from the attraction of gravity in being determined primarily by the construction of the molecule and not by its mass.*" I have never receded from the above view, and by the statements made in the second and fifth papers, that the molecular force obeyed the law of gravitation, I did not intend to imply that the constant factor of the force was identical in the two cases. I still believe that *all* attractive forces may be identical in origin and character and obey the same general law, but of course the constant factors of the forces, in the usual sense of that term, are totally different. The statements as I made them were misleading, I admit.

I did not at first understand the fact that the law of gravitation extended to the molecular attractive force, made the heat of vaporization vary, not as the mass, but as the 5/3 power of the mass. A realization of this fact and its consequences caused me to publish, in the sixth paper already cited (1907), a full discussion of the derivation of the equation under discussion, and to express a belief which I had long held, namely, that the numerator factor of Newton's law of gravitation needed modification. A further statement of my views upon this subject will shortly be published.

Camden, S. C.
June 7th, 1910.

LXVII. *The Series Spectrum of Mercury.* *By* S. R. Milner, *D.Sc., Lecturer in Physics, University of Sheffield* *.

As we pass up from group to group of the elements in the periodic table, the lines in their spectra connected by series relations become in general less and less marked. Thus, while the spectra of the alkalies show on the average some seven or eight of the lines in each series, those of the alkaline earths show only the first three or four of the lines. In mercury, Kayser and Runge have observed only three complete members of the triplets of which the sharp and the diffuse series of this element are composed, and the principal series was entirely unknown until last year, when Paschen discovered the first three members of it in the ultra-red.

In taking some photographs of the spectrum of the mercury arc *in vacuo* recently, I was struck by the almost complete absence of a visible background to the spectrum which it showed. In the spectrum of the arc in air a limit is set to the faintness of lines which can be observed by the brightness of the continuous spectrum which is always present, but trial showed that with the arc *in vacuo* it was possible to give exposures over 50 times the normal without any background making itself evident. Photographs taken with these long exposures showed a great many lines which have not been previously observed, but the chief interest about them was that the lines which form the continuation of the various series of mercury were very strikingly developed.

The mercury arc used was a very simple home-made apparatus similar to that described by Pfund †; the arc was about 5 cm. long, and was worked at 4 amp., 15 volts. With a Hilger single-prism quartz spectrograph, with which the normal exposure was about 30 seconds, an exposure of half an hour showed the lines of the diffuse series up to $m=16$, and those of the sharp to $m=14$. Traces of still higher lines could be seen, but they did not come out any better with a longer exposure of two hours, as a continuous background then appeared sufficiently strong to mask the continuation of the series. With a suitable instrument of higher dispersion (which would diminish the continuous spectrum) it would doubtless be possible to extend the series further, but attempts with a two-prism calcite spectrograph were not very successful through the much greater

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* Communicated by the Author.

† Astrophys. Journ. xxvii. p. 299 (1908).

absorption than quartz which calcite exerts in this region (λ 2500). An exposure of eight hours through the calcite prisms gave no greater effect than half an hour through the quartz.

The following are the wave-lengths and frequencies of the lines of the series obtained by comparison with the iron arc (Kayser, B. A. Report, 1891). The first components only of the triplets are given: the series formed by the two other components are also well developed, but the higher lines in them lie beyond the region in which quartz is fairly transparent, and require very long exposures to bring them out:

	Diffuse Series.		*Sharp Series.*	
m.	λ (air).	*n* (vac.).	λ (air).	*n* (vac.).
2* ...	3663·46 63·05 55·00 50·31	27289·0 292·1 352·1 387·3	5460·97	18306·8
3* ...	3027 66 25·79 23·64 21·68	33019·4 039·8 063·3 084·8	3341·70	29916·5
4* ...	2803·69	35657·0	2925·51	34172·3
5* ...	2699·74	37029·9	2759·83	36223·6
6......	2639·92	37868·9	2675·20*	37369·5
7......	2603·10	38404 5	2625·37	38078·7
8......	2578·34	38773·2	2593·43	38547·7
9......	2561·15	39033·5	2571·85	38871·0
10	2548·51	39227·1	2556·36	39106·6
11......	...... †	......	2545·09	39279·8
12......	2531·74	39487·0	...... †	......
13......	2525·90	39578·2	2529·47	39522·3
14......	2521·27	39650 9	2524·48‡	39600·5
15......	2517·57	39709 2		
16......	2514·48	39758·0		

* Kayser, *Spectroscopie*, vol. ii. p. 545.

† Hidden by the over-exposed strong line, λ 2536·7.

‡ Kayser and Runge give a weak line 2524·80 (B. A. Rep. 1892).

An exposure of two hours with the quartz prism gave also a series of converging lines which was evidently a continuation of the principal series which starts in the ultra-red.

Their wave-lengths were measured on the calcite spectrograph. With four hours' exposure the series down to $m=16$ was well developed, traces of several further lines may be seen, and on some of the negatives a faint indication of what may possibly be the limit. There is a slight diminution in density just beyond the point where the limit should theoretically be, but it is too faint to speak with certainty of it.

Principal Series.

m.	λ (air).	*n* (vac.).
5......	5354·3	18671·5
	5316·0	18806·0
6......	5120·93	19522·4
	5102·85	19591·5
7......	4981·28	20069·7
	?	
8......	4890·0	20444·3
	4884·0	20469·4
9......	4826·36	20713·9
10......	4781·07	20910·1
11......	4747·72	21057·0
12......	4722·09	21171·2
13......	4701·96	21261·9
14......	4684·86	21339·5
15......	4672·38	21396·5
16......	4661·29	21447·4

The principal series should theoretically consist of triplets converging to a common limit; the higher lines are all very diffuse, they show distinct evidence of broadening from $m=12$ to $m=9$, $m=8$, 6, 5 are double, $m=7$ is possibly double also, as the smaller wave-length component may be swamped by the spreading out of the over-exposed strong line λ 4959·7 close to it. λ 5354 ($m=5$) shows a considerable broadening towards the red, which may be due to the partial separation of a third line of the triplet ; on the other hand, Kayser and Runge give a faint nebulous line 5365·25 which may be the cause of it. Beyond this point it is difficult to identify the series lines. Paschen from his observations in the ultra-red gave the following as probably forming the series [*] :—

m.	(air).	*n* (vac.).
2	12071·32	8281·937
	11288·16	8856·527
3	7082·72	14115·05
	6907·93	14472·20
4	5890·05	16973·17
	5859·59	17061·38
	5804·18	17224·28

Another peculiar feature which is brought out by these photographs with long exposures may also be remarked on. It is the extraordinary complexity of the strong lines which form the earlier members of the diffuse series. Kayser and Runge observed these to be composite and to consist of several components, but with these long exposures in some cases over a score of faint satellites show on each side of the main line. Thus in λ 3132 a space of 50 Å. units on each side of the main line is closely filled with them.

This development of the series spectrum makes the series of mercury in one respect more complete than those of other elements. In other elements, single series may be more extensively developed it is true: thus in hydrogen the diffuse series has been observed down to $m=31$, but the principal series is unknown except for the first line. In sodium, Wood has recently observed in the absorption spectrum the principal series down to practically the theoretical limit, but only seven terms of the sharp and diffuse series are known[†].

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[*] *Ann. d. Physik*, xxix. p. 662 (1909). The choice for $m=4$ does not fit in well with the higher lines of the series, as judged by the frequency differences of their components. Below are given the wave-lengths of all the lines observed in this region of the photographs which are not given by Kayser and Runge :—

Wave-length.	Intensity.	Wave-length.	Intensity.
6907·9	3	5872·24	1
6705·0	2	5859·63	2
6234·55	6	5676·14	2
6123·62	2	5025·80	3
6072·71	1	4995·91	1

[†] Zickendraht has, however, recently extended the number to 12. *Ann. d. Phys.* xxxi. p. 249 (1910).

In mercury all three series are equally well developed and extensively so.

This fact is of special interest because it allows an accurate test to be made of one of Rydberg's empirical laws connecting the different series with each other. The law in question runs as follows:—"The difference of the frequency of the convergence limit of the principal series and that of the common limit of the sharp and diffuse series is equal to the frequency of the first line of the sharp series." This law is known to be very approximately true, but there must always remain a certain amount of doubt about its absolute truth so long as any one of the series is represented by only a few terms all of them remote from the limit. The limit in such a case can only be determined from an empirical equation designed to represent these terms; at the best this can be but an imperfect representation of them, and the value of the limit will to a certain extent depend on the particular form of the equation adopted. But this difficulty does not arise when so many lines of the series have been measured that the last members of them are quite close to the limit. The extrapolation to the limit itself is then a small one, and any approximate equation will determine it accurately.

Thus if we apply to the principal series Rydberg's equation in the form

$$P(m) = P(\infty) - N/(m + \cdot 90845)^2$$

we obtain the following values of the limit, $P(\infty)$, for each line of the series :—

m.	$P(\infty) - P(m)$.	$P(\infty)$.
3*	7179·5	21651·7
4†	4552·1	21776·4
5‡	3141·7	21813·2
6‡	2298·0	20·4
7	1753·6	23·3
8‡	1382·0	26·3
9	1117·1	31·0
10	921·8	31·9
11	773·4	30·4
12	658·3	29·5
13	567·0	28·9
14	493·3	32·8
15	433·2	29·7
16	383·4	30·8

* $P(m) = 14472 \cdot 2$. † $P(m) = 17224 \cdot 3$.

‡ Lower frequency component.

These values are not constant, they undergo on the whole a regular progression with *m*, but if each value be plotted against its distance $P(\infty)-P(m)$ from the limit, the extrapolation of this curve to the axis of zero $P(\infty)-P(m)$ will give an accurate value for the limit, even when the formula itself is quite out in the representation of the lower lines. The extrapolation by a curve is too great unless the lines have been measured close up to the limit, but with the sixteenth line given it is both easy and accurate, and gives

$$P(\infty) = 21832{\cdot}5.$$

The diffuse series was worked out in a similar way except that a modified formula * which gives a closer representation of the lines was used :

$$D(m) = D(\infty) - N \Big/ \left(m + {\cdot}981485 - \frac{{\cdot}178601}{m + {\cdot}981485}\right)^2.$$

The limit $D(\infty)$ calculated for each line of the series from the above formula is shown below :—

m.	$D(\infty)$.	*m.*	$D(\infty)$.
4......	40141·0	11	......
5......	126·2	12......	40139·2
6......	35·7	13......	40·3
7......	35·8	14......	40·3
8......	38·8	15......	39·2
9......	38·3	16......	38·8
10......	39·3		

Extrapolation is here almost unnecessary, and the value of the limit is

$$D(\infty) = 40139{\cdot}6.$$

This, as may be judged from the table, is probably accurate to less than a unit. The principal limit is not quite so accurately determined owing to the smaller dispersion of the prisms in this region of the spectrum.

The difference between these limits is 18307·1. The frequency of the first line of the sharp series (λ 5460·97) is 18306·8. The agreement is unmistakable. Thus the case

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* This is one of the variations of that used by Hicks, Phil. Trans. vol. ccx. p. 57 (1910).

of mercury with its extensive number of series lines forms strong evidence in favour of the absolute accuracy of Rydberg's law.

Note *added July* 1910 :—Since the above was in press I have remeasured the first few lines of the Principal Series, using a small plane grating on the spectrograph in place of the calcite prisms, with the following results :—

m.	λ (air).	*m.*	λ (air).
5	5366·03 5353·96 5316·95	7	4980·78
6	5120·84 5102·49	8	4889·79
		9	4826·82

15 hours exposure was required ; the lines given were quite sharp, and their values are I think now correct to about ·1 unit ; the remaining lines were not sufficiently developed to distinguish.

The new lines in the footnote on p. 639 were also (except the first two) remeasured with the grating, and the values there given are the corrected ones. Most of these lines have been observed by Stiles, Astrophys. Journal, vol. xxx. p. 48 (1909).

LXVIII. *On the Analysis of the Radiation from Electron Orbits.* *By* J. H. Jeans, *M.A., F.R.S.*[*]

1. In the present paper an attempt is made to examine the nature of the radiation which would be emitted by electrons describing orbits about various centres of force and in fields of force of various kinds, with a view to collecting evidence as to whether black-body radiation can be interpreted as radiation emitted in this way.

In a previous paper[†] a proof has been given that if radiation can be explained in this way, the orbits must be described about centres of force varying as the inverse cube of the distance. The present investigation confirms this result in an independent manner, and tests how far such radiation would be in agreement with that observed experimentally.

If $\int E_\lambda d\lambda$ is the partition of radiant energy in matter, the

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[*] Communicated by the Author.

[†] "On the Motion of Electrons in Solids," Phil. Mag. [6] xvii. p. 773 and xviii. p. 209 (1909).

rate of absorption per unit volume is, as Sir J. J. Thomson * has shown

$$\int 4\pi c_\lambda V^2 E_\lambda d\lambda,$$

where c_λ is the conductivity for waves of frequency equal to that of light of wave-length λ. For this to be equal to the emission, say $\int F_\lambda d\lambda$ per unit volume, we must have :—

$$F_\lambda = 4\pi c_\lambda V^2 E_\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Since E_λ is the same for all kinds of matter, it follows that the ratio of c_λ to F_λ must be the same—the conductivity stands in a constant ratio to the emission in the interior of a solid, in spite of the fact that c_λ varies greatly from one substance to another. It seems legitimate to draw the inference (at any rate as a working hypothesis) that the mechanism of emission must be the same as that of absorption.

For long waves, the mechanism of absorption is almost certainly to be found in the motion of free electrons, and the supposition that this is also the mechanism of emission is known to lead to results which are in agreement with experiment.

For short waves, there is less certainty as to the mechanism of absorption. It seems probable that other agencies, such for instance as various types of resonance, contribute something to the absorption of light of short wave-length, and it may be that at the wave-lengths with which we are primarily concerned this contribution may greatly preponderate over the original contribution from the motion of free electrons. If so, we should have to look for the origin of emission as well as of absorption in a motion subject to resonance, such for instance as the motion of electrons in small closed orbits.

It follows that we have to analyse the radiation from both closed and open types of orbits, although naturally only those closed orbits need be considered in which the motion is stable for all possible displacements.

General law μr^{-n}.

2. Consider first the motion of an electron in a single orbit described under a law of force μr^{-n}. The equations of motion are :

$$\frac{d^2r}{dt^2} - r\dot{\theta}^2 = \mu r^{-n}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$r^2\dot{\theta} = H, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where H, the moment of momentum, is a constant of the

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* Phil. Mag. [6] xiv. p. 223 (1907).

orbit. Eliminating the time, the equation of the orbit is

$$\frac{d^2u}{d\theta^2}+u=-\frac{\mu}{\text{H}^2}u^{n-2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where u as usual is $1/r$. If u_0 is the value of u at the apse nearest the origin, integration with respect to u gives:

$$\left(\frac{du}{d\theta}\right)^2=u_0^2-u^2+\frac{2\mu}{\text{H}^2(n-1)}(u_0^{n-1}-u^{n-1}). \quad . \quad (5)$$

If we now put $u=u_0\cos\chi$ and

$$\alpha=\frac{2\mu u_0^{n-3}}{\text{H}^2(n-1)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

this has the integral:

$$\theta=\int\frac{\sin\chi\,d\chi}{\{\sin^2\chi+\alpha(1-\cos^{n-1}\chi)\}^{\frac{1}{2}}}. \quad . \quad . \quad . \quad (7)$$

From (3), the time is given by

$$t=\int\frac{d\theta}{\text{H}u^2}=\frac{1}{\text{H}u_0^2}\int\frac{\sin\chi\,d\chi}{\cos^2\chi\{\sin^2\chi+\alpha(1-\cos^{n-1}\chi)\}^{\frac{1}{2}}}. \quad (8)$$

The components of acceleration are

$$\mu r^{-n}\cos\theta, \qquad \mu r^{-n}\sin\theta,$$

from which the radiation can be written down.

Resolved into its constituents by Fourier's Theorem, the radiation from the complete orbit is

$$\frac{2e^2}{3\pi\text{V}}\int_0^\infty(\text{I}^2+\text{J}^2)\,dp, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where

$$\text{I}=\int\mu r^{-n}\cos\theta\cos pt\,dt. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\text{J}=\int\mu r^{-n}\sin\theta\sin pt\,dt, \quad . \quad . \quad . \quad . \quad (11)$$

in which the limits are $t=-\infty$ to $t=+\infty$ for an open orbit, and are taken through a complete revolution if the orbit is closed. On substituting the values of θ and t from equations (7) and (8), and effecting the integrations with respect to χ, we obtain:

$$\text{I}=\mu u_0^{n-2}\text{H}^{-1}\Phi(\alpha,\ p/\text{H}u_0^2),$$

$$\text{J}=\mu u_0^{n-2}\text{H}^{-1}\Phi'(\alpha,\ p/\text{H}u_0^2),$$

in which Φ, Φ' are functions of which the form is not at present required. If $\Phi^2+\Phi'^2$ be denoted by Ψ, the integrand of expression (9) for the complete radiation becomes:

$$\mu^2 u_0^{2n-4} \mathrm{H}^{-2}\Psi(\alpha,\ p/\mathrm{H}u_0^2). \quad . \quad . \quad . \quad . \quad (12)$$

Let c_0 be the velocity at the apse, so that $\mathrm{H}u_0 = c_0$. The value of α becomes (*cf.* equation (6))

$$\alpha = \frac{2\mu u_0^{n-1}}{c_0^2(n-1)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

so that α is the ratio of potential to kinetic energy at the apse, and expression (12) becomes

$$\tfrac{1}{4}(n-1)^2\alpha^2 c_0^2 \Psi(\alpha,\ p/c_0u_0). \quad . \quad . \quad . \quad . \quad (14)$$

At this stage the treatments appropriate to open and closed orbits diverge.

Open Orbits.

3. Open orbits will be described by electrons which are free except when in encounters with the centres of forces, and the law of distribution of these electrons is known. We require first to investigate how many orbits of any specified kind are described per unit of time. The orbit may be specified in time by the instant at which the apse is passed, this instant being specified analytically by the condition $\dot{r}=0$.

The probability at any instant of finding an electron within a given element $dx\,dy\,dz$ of volume, having its velocity components within a range $d\dot{x}\,d\dot{y}\,d\dot{z}$ is

$$\mathrm{NA}e^{-hm\mathrm{G}}d\dot{x}\,d\dot{y}\,d\dot{z}\,dx\,dy\,dz, \quad . \quad . \quad . \quad . \quad (15)$$

where N is the number of electrons per unit volume, and A is a constant determined by the condition that expression (15) integrated through unit volume shall be equal to N; h has its usual meaning in kinetic theory, being given by $1/2h=\mathrm{RT}$, and G is twice the total energy of the electron per unit mass, given by

$$\mathrm{G} = \dot{x}^2+\dot{y}^2+\dot{z}^2+\frac{2\mu}{(n-1)r^{n-1}}.$$

In polar coordinates expression (15) becomes

$$\mathrm{NA}e^{-hm\mathrm{G}}r^4\sin^2\theta\,dr\,d\theta\,d\phi\,d\dot{r}\,d\dot{\theta}\,d\dot{\phi}. \quad . \quad . \quad (16)$$

At the apse, from equations (2) and (3),

$$\frac{d}{dt}(\dot{r}) = r\dot{\theta}^2 + \mu r^{-n} = c_0^2 u_0 + \mu u_0^n,$$

so that for the electron to come to its apse within an interval dt, the value of $\dot{r}$ at the beginning of the interval must lie within a range $(c_0^2 u_0 + \mu u_0^n)\,dt$ of zero. Giving this value to $d\dot{r}$ in expression (16) we find

$$\mathrm{NA}e^{-hm\mathrm{G}}r^4 \sin^2\theta\, dr\, d\theta\, d\phi\, d\dot{\theta}\, d\dot{\phi}(c_0^2 u_0 + \mu u_0^n)\,dt$$

for the number of orbits of a certain type described per interval dt. On integrating with respect to θ and ϕ, and with respect to all values of $\dot{\theta}$ and $\dot{\phi}$ which give a range dc_0 to c_0, we obtain

$$8\pi^2 \mathrm{NA}e^{-hm\mathrm{G}} r_0^2 dr_0 c_0 dc_0 (c_0^2 u_0 + \mu u_0^n)\,dt, \qquad . \quad . \quad (17)$$

as the number of electrons which, per time dt, describe orbits having r_0 and c_0 within ranges dr_0 and dc_0.

The orbit may be more conveniently specified by the constants G and H, given by

$$\mathrm{G} = c_0^2 + \frac{2\mu}{(n-1)r_0^{n-1}}, \qquad \mathrm{H} = r_0 c_0.$$

We find, in the usual way, that

$$d\mathrm{G}\, d\mathrm{H} = 2dr\, dc(c_0^2 + \mu u_0^{n-1}),$$

so that expression (17) becomes, omitting the factor dt,

$$4\pi^2 \mathrm{NA}e^{-hm\mathrm{G}} \mathrm{H}\, d\mathrm{G}\, d\mathrm{H}, \qquad . \quad . \quad . \quad . \quad (18)$$

giving the number of orbits per unit time for which G and H lie within ranges $d\mathrm{G}\, d\mathrm{H}$.

4. On multiplying expressions (18) and (14) we obtain the total radiation per unit time. Transformed to the variables G and α, the new expression becomes

$$\frac{(n-1)^2 e^2}{12\pi \mathrm{V}^2} \int dp \frac{\mathrm{G}\alpha^2}{1+\alpha} \Psi \left\{ \alpha,\ p\big((n-1)\alpha/2\mu\big)^{-\frac{1}{n-1}} \big(\mathrm{G}/(1+\alpha)\big)^{-\frac{n+1}{2n-2}} \right\}$$
$$\times\, 2\pi^2 \mathrm{NA}e^{-hm\mathrm{G}} \mathrm{G}^{\frac{n-3}{n-1}} (2\mu/n-1)^{\frac{2}{n-1}} \frac{\partial}{\partial\alpha}\left(\alpha^{-\frac{2}{n-1}} (1+\alpha)^{-\frac{n-3}{n-1}}\right) d\mathrm{G}\, d\alpha.$$

We obtain the radiation from all possible open orbits on integrating this expression from $\alpha = 0$ to $\alpha = +1$, and from

$G=0$ to $G=\infty$. The result is of the form

$$F_p = (hm)^{-\frac{3n-5}{n-1}} f\left\{p(hm)^{-\frac{n+1}{2n-2}}(n-1/2\mu)^{-\frac{1}{n-1}}\right\}, \quad (19)$$

in which f is a new function of form unknown.

Since p is proportional to λ^{-1} and h to T^{-1} it is clear that the emitted radiation would satisfy a "displacement-law" of the form

$$\lambda T^{(n+1)/(2n-2)} = \text{cons.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

For natural radiation we must have $(n+1)/(2n-2) = 1$, or $n=3$, confirming the result previously obtained.

5. The existence of the displacement-law (20) is, in a sense, inconsistent with the displacement-law $\lambda T=\text{cons.}$, predicted by the second law of Thermodynamics. The law $\lambda T=\text{cons.}$, however, refers only to a steady state, while the law (20) has been derived for the natural state, which (at least in the view of the present writer) is not a steady state, as the æther has not the amount of vibratory energy required for the steady-state condition of equi-partition of energy.

Law of inverse square : μr^{-2}.

6. The electrons must attract and repel according to the law of the inverse square, when at sufficient distance apart. There must therefore be some radiation emitted under this law.

In formula (19) put $n=2$, and we obtain

$$F_p = (hm)^{-1} f\{2\mu p(hm)^{\frac{3}{2}}\}, \quad . \quad . \quad . \quad (21)$$

so that p enters, not through the factor p/T but through the factor $p/T^{\frac{3}{2}}$. This radiation accordingly does not obey Stefan and Wien's law.

If we replace μ by e^2/m, and h by $1/2RT$, equation (21) becomes

$$F_p = \frac{2RT}{m} f\{2e^2pm^{-1}(2RT)^{-\frac{3}{2}}\},$$

showing that the emitted radiation is of frequency comparable with $\frac{1}{2}(2RT)^{3/2}m/e^2$. At 300° abs. the value of this expression is about 2×10^{12}; at 600° it is 5×10^{12}. Thus radiation under the law of the inverse square may exist, but is necessarily so far in the infra-red as to elude observation.

This might in itself suggest that we must look for the source of natural radiation in collisions of a sharper nature than those which occur under the law μr^{-2}. It is not, therefore, surprising that our previous analysis has shown that the law must be μr^{-3}.

Law of inverse cube: μr^{-3}.

7. We now put $n=3$ throughout the foregoing analysis. Equations (7) and (8) at once become integrable, and we have

$$\theta = (1+\alpha)^{-\frac{1}{2}}\chi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$t = \frac{1}{\mathrm{H}u_0^2}(1+\alpha)^{-\frac{1}{2}}\tan\chi, \quad . \quad . \quad . \quad . \quad (23)$$

in which the value of α is now μ/H^2. If we put $\alpha = \tan^2\beta$, the value of I becomes (*cf.* equation (10))

$$\mathrm{I} = \mathrm{G}^{\frac{1}{2}}\sin^2\beta\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\cos\chi\cos(\chi\cos\beta)\cos(p\mu^{\frac{1}{2}}\mathrm{G}^{-1}\operatorname{cosec}\beta\tan\chi)d\chi,$$

and J is similar except that the last two cosines are replaced by sines.

It is not possible to integrate either I or J or $\mathrm{I}^2+\mathrm{J}^2$ in finite terms; each integral can be shown to satisfy a differential equation of a known insoluble type. On substituting for I and J in the total radiation we obtain F_p as a quintuple integral. One integration (with respect to G) can be effected, but the remaining four integrations cannot be carried out in finite terms. Various attempts to evaluate the integral have persuaded me that it will not agree with experiment for large values of p.

8. We shall accordingly discuss the form assumed by the integrals I and J when p is large.

Let us put

$$\mathrm{K} = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\cos(a\chi + b\tan\chi)\,d\chi, \quad . \quad . \quad . \quad . \quad (24)$$

$$\mathrm{K}' = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\cos(-a\chi + b\tan\chi)\,d\chi, \quad . \quad . \quad . \quad (25)$$

then clearly I and J are the sums of integrals of types K and K′. But from equation (24), K is readily seen to be a solution of the equation

$$\frac{\partial^2\mathrm{K}}{\partial b^2} = \mathrm{K}\left(1 + \frac{a}{b}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

and K′ is a solution of the same equation with $-a$ replacing a.

To examine the case of p large, we need only examine the case of a/b very small. The equation becomes

$$\frac{\partial^2 K}{\partial b^2} = K, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

and its solution is $K = Ae^{-b}$ where A is a function of a only. Similarly $K' = A'e^{-b}$, where A' is the same function of $-a$. Hence we have

$$\int_{-\frac{1}{2}\pi}^{\frac{1}{2}\pi} \cos a\chi \cos (b \tan \chi)\, d\chi = \tfrac{1}{2}(A + A')e^{-b},$$

$$\int_{-\frac{1}{2}\pi}^{\frac{1}{2}\pi} \sin a\chi \sin (b \tan \chi)\, d\chi = \tfrac{1}{2}(A' - A)e^{-b}.$$

It follows that I and J are each of the form

$$G^{\frac{1}{2}} f(\beta) e^{-p\mu^{\frac{1}{2}} G^{-1} \operatorname{cosec} \beta}, \quad . \quad . \quad . \quad . \quad (28)$$

and that $I^2 + J^2$ is of the form

$$I^2 + J^2 = GF(\beta) e^{-2p\mu^{\frac{1}{2}} G^{-1} \operatorname{cosec} \beta}. \quad . \quad . \quad . \quad (29)$$

9. The value of H^2 is now $\mu \cot^2 \beta$, so that

$$H\,dH = \mu \cot \beta \operatorname{cosec}^2 \beta,$$

and expression (18), which gives the number of orbits per unit time of given class, becomes

$$4\pi^2 NAe^{-hG} \mu \cot \beta \operatorname{cosec}^2 \beta \, dG \, d\beta.$$

Hence

$$F_p = \frac{8\pi e^2 NA\mu}{3V} \int_0^{\frac{1}{2}\pi} \int_0 G e^{-hG - 2p\mu^{\frac{1}{2}} G^{-1} \operatorname{cosec} \beta} \phi(\beta) \, d\beta \, dG.$$

Integration with respect to G requires the evaluation of an integral of the type

$$y = \int_0^\infty e^{-aG - bG^{-1}} dG, \quad . \quad . \quad . \quad . \quad (30)$$

the required integral being $-dy/da$.

It is easily found that y satisfies the differential equation

$$\frac{\partial^2 y}{\partial b^2} = \frac{a}{b} y,$$

of which the solution is $y = Ax^{\frac{1}{2}} K_1(ix^{\frac{1}{2}})$, in which $x = 4ab$, and A is a function of a only. Also from equation (30) it is clear that ay must be a function of ab only, and therefore a function of x.

Hence $A = A_0/a$, where A_0 is a constant. On differentiating (30) with respect to a, we have

$$\int_0^\infty e^{-aG-bG^{-1}} G\, dG = -\frac{\partial y}{\partial a} = 2A_0 \frac{b}{a} K_2(ix^{\frac{1}{2}}).$$

When p is large x is large, so that this integral vanishes with p large in the same way as $e^{-\sqrt{x}}$ or $e^{-2\sqrt{(ab)}}$. Hence on integrating with respect to β it is found that F_p vanishes when p is large, through the exponential

$$e^{-2\sqrt{(2ph\mu^{\frac{1}{2}})}} \quad \text{or} \quad e^{-2\sqrt{(p\mu^{\frac{1}{2}}/RT)}}. \quad . \quad . \quad . \quad (31)$$

As in equation (1) we have

$$F_p = 4\pi c_p V^2 E_p, \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

and it is known from experiment that when p is large E_p vanishes through the exponential

$$e^{-\kappa p/RT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

These results could only be reconciled if we were at liberty to suppose that c_p could increase, when p became large, in the same way as the exponential $e^{\kappa p/RT}$. But all evidence, both theoretical and experimental, indicates that c_p must decrease when p becomes large.

10. It can be seen that the difficulty which has been disclosed by the foregoing analysis is inherent in any theory which refers the origin of radiation to orbits in which Maxwell's law of distribution of energy is obeyed. For the radiation from a single orbit when p is large must, by a general law *, be of the form $e^{-pf(G)}$ in the limit, so that on integrating over all orbits we obtain an integral of the type (*cf.* expression (18))

$$\int e^{-pf(G)-hmG}\, dG.$$

For large values of p the whole value of this integral comes from contributions from that value G_0 of G which makes the index of the exponential a minimum; this is given by

$$pf'(G_0) = hm = \frac{m}{2RT},$$

so that G_0 is of the form $\phi(pT)$, and the integral becomes proportional to

$$e^{-p[f(G_0)-G_0 f'(G_0)]} \quad \text{or} \quad e^{-pF(pT)}.$$

For this to be of the form $e^{-cp/T}$ required by experiment, $F(pT)$ would have to be of the form c/T, which is of course impossible.

* Phil. Mag. [6] xvii. p. 250.

11. An alternative is found by assuming that some physical agencies are at work which prevent Maxwell's law from becoming established. An approximation to such a state of things, which will be seen *a posteriori* to be sufficiently good for our present purpose, will be obtained by supposing all the electrons to have exactly the same value of G, this being now given by $\mathrm{G}=3\mathrm{RT}/m$. The number of orbits of given type described per unit time will now be proportional simply to $\mathrm{H}\,d\mathrm{H}$, or (§ 9) to $\mu\cot\beta\,\mathrm{cosec}^2\beta$, so that when p is large the whole radiation F_p will be of the limiting form

$$\int f(\beta)e^{-2p\mu^{\frac{1}{2}}m/3\mathrm{RT}\sin\beta}\,d\beta,$$

and this will clearly vanish in the same way as the exponential

$$e^{-2p\mu^{\frac{1}{2}}m/3\mathrm{RT}}.$$

12. The limiting form just obtained will agree with Planck's law if

$$h=\frac{4\pi}{3}\mu^{\frac{1}{2}}m,$$

where h is Planck's constant of which the value is $6\cdot5\times10^{-27}$. Since the value of m is 8×10^{-28}, it follows that μ must be $3\cdot8$ in C.G.S. units. The force exerted on an electron at distance r is $m\mu/r^3$ or $3\times10^{-27}/r^3$. Thus if the force $m\mu/r^3$ is accompanied by an ordinary electrostatic force $\pm e^2/r^2$, then the latter force will predominate over the former at all distances greater than $1\cdot5\times10^{-8}$ cm.

The distance of closest approach of an electron to the centre of force $m\mu/r^3$ is given by

$$\frac{\mu}{r^2}=\mathrm{G}=\frac{3\mathrm{RT}}{m},$$

so that $r^2=7\times10^{-12}/\mathrm{T}$. At 700° abs. the closest approach is 10^{-7} cm.

This distance is greater than molecular distances and so is much too large to reconcile with the hypothesis that the orbit is described entirely under the law μr^{-3} from a single centre of force. Since this is known to be the only type of open orbit which can give radiation similar to that observed, it appears that the hypothesis that the radiation proceeds from electrons describing open orbits is one which must be abandoned. The consideration of closed orbits may be reserved for a separate paper.

Cambridge,
July 23, 1910.

LXIX. *The Pianoforte Sounding-Board.*
By G. H. Berry *.

[Plate XII.]

In a recent number of this Magazine † it was shown that a section of the sounding-board of a pianoforte had a natural period of vibration of its own, independent of the pitch of the strings upon it, and this natural vibration was apparent in all the photographs there reproduced.

With the particular section used the pitch of the sounding-board was roughly 50 and that of the string 261.

If the pitch of the sounding-board was the same as that of the string, it seemed reasonable to expect the sound to be considerably re-inforced, and the sounding-board to act as the air-column acts, in the usual resonator fixed to the stem of a suitable tuning-fork.

As will be shown, this did not prove to be the case, or at least a very important modification is necessary.

Apparatus.

The apparatus used was similar to that described in the article mentioned, but several improvements have been made. The photographic shutter was changed from 1/4 plate size to 1/1 plate to give a larger aperture. Instead of this shutter being opened direct, the tube from the releasing bulb was connected to the small shutter. The large shutter, giving the actual exposure, was released by means of a small electro-magnet. Two dry cells gave the necessary current and the circuit was completed by the small shutter, at any desired instant up to about 2 seconds, after the hammer had struck the strings.

To determine the speed of the film at the time of exposure, a large tuning-fork was used as an interrupter. A wire from one prong of the fork touched the surface of mercury in a small cup, when the fork was at rest. When the fork was vibrating it "made and broke" an electric circuit consisting of the fork, mercury cup, two accumulators, the primary of an induction-coil, and two contacts, one on either side of the shutter.

The two contacts pressed very lightly on the wings of the shutter, and when the wings flew back, on the shutter being released, the contacts came together and the current passed through the induction-coil, etc., while the shutter was open,

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* Communicated by Prof. Edwin H. Barton, D.Sc., F.R.S.E.

† April 1910, p. 648.

the contacts being insulated again when the wings flew back into position. The spark from the secondary of the coil marked the film 3·5 cm. behind the exposure line.

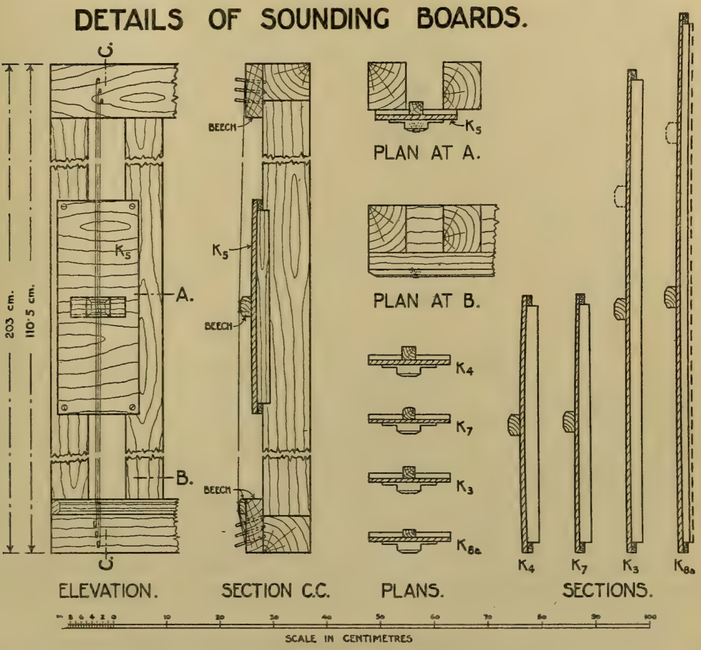
The frequency of the fork was determined by a stroboscopic method. The mean of several results gave 21·50 vibrations a second. Thus the distance between the centres of two time marks on the film represents $\frac{1}{21 \cdot 5}$ sec.

The speed of the phonograph drum carrying the film was kept as closely as possible the same for all the exposures, and was about 69 cm./sec. Thus the whole length of the film passed the exposure line in 0·25 sec.

The magnification on the films in every case is of the order 500.

In the course of the investigation several different sections of sounding-board were used. They varied in length and thickness and therefore had different natural frequencies. A drawing of these sections and the way in which they were supported is shown in fig. 1. The wood used for the sounding-board was that known commercially as "Swiss Pine." The bar at the back of sounding-board was of Spruce

Fig. 1.



and was slightly curved as is the practice of pianoforte-makers. The bridges are of English Beech. The steel strings used were of No. 18 gauge and weigh 0·062 grm. per cm.

The straw forming the connexion between the sounding-board and optical lever was in all cases about 5 cm. below the bridge.

Results.

On Plate XII. are shown 25 photographs.

Nos. 1–6 give the natural frequency of the different sections of sounding-board used. They were struck with a pianoforte hammer.

In the following table column A gives the distance of the point struck from the bottom of the section, column B the distance from the right-hand edge, and column C the pitch of the strings on the section.

Films.	A. cm.	B. cm.	C.	
1	24·0	4·4	A♯	116
2	13·5	3·0	*c′*	261
3	9·0	2·5	*c′*	261
4	11·0	2·5	*c′*	261
5	35·0	5·0	A♯	116
6	35·0	5·0	A♯	116

In every case the wave passes immediately from the right-hand edge of the print to the left-hand edge, and in most of the prints the waves somewhat overlap.

In the first six prints the shutter was set to open at the instant the hammer struck the board.

With the exception of No. 6 the amplitude falls off very rapidly and the upper partials become more marked as the vibration dies away. In practice, no part of the sounding-board of a pianoforte has so low a frequency as that shown on No. 6.

In No. 7 the three steel strings were 66·5 cm. long between the bridges and were struck at $\frac{1}{11}$ from the fixed or lower bridge. All the films Nos. 7–25 inclusive were exposed about one second after the hammer had struck the strings.

The opinion as to the tone is that of a pianoforte tuner who has an exceptionally good musical ear. He did not know for what purpose his opinion was asked, and it may therefore be regarded as being without prejudice.

In No. 8 the frequency of the strings was nearer to the natural frequency of the sounding-board than in No. 7. The length of strings and point struck were the same.

It will be noticed that while the 2nd partial was not apparent in No. 7 it was very strong in No. 8. This was not expected, and it was suggested that the end of the straw, where it was gripped by the nut on the optical lever, was weak and in some way influenced the result. Accordingly the nut was moved along the straw until it gripped as thick a part of the tapered end of the straw as was possible. The connexion was then quite stiff, but as will be seen from No. 9 the only effect was to reduce the amplitude of the vibration.

In No. 10 the strings were of the same length and struck at the same point. The pitch of the strings was nearly twice that of the sounding-board. The amplitude of the 1st partial was greater than in No. 7, and the tone of Nos. 7 and 10 was much better than that of Nos. 8 and 9. It is clear that an increased resonance is not to be obtained by making the frequency of the sounding-board the same as that of the strings. The bridge was in all these cases at or near the middle of the sounding-board, and the only explanation seems to be that the sounding-board divides in half with the bridge as a node and when each half has a frequency near the pitch of the strings a good note results. This is confirmed by the marked resonance of the octave of the strings in Nos. 8 and 9. In No. 11 we see that when the frequency of the sounding-board is much below half that of the strings, a bad note is also the result. The strings were 37 cm. long and struck at $\frac{1}{9}$.

Nos. 12 and 13 were both described as being good. In Nos. 14–16 the strings were 48 cm. long and struck at $\frac{1}{9}$. No. 15 gave an excellent result, the tone was the best of the series. The amplitude is very large, the wave regular and free from pronounced upper partials. The pitch of the strings was very nearly an octave above that of the sounding-board.

In No. 16 the amplitude becomes rapidly smaller on the print. This was due to the strings being slightly out of unison. Beats were audible to the ear and also apparent on watching the spot of light. If the exposure had been continued the amplitude would again have increased.

Nos. 17–25 were all taken with longer sounding-board sections and two copper-covered steel wires taken from the corresponding note on a pianoforte.

To get the distance between the bridges long enough to take these strings, another frame was made similar in construction to the previous one but to take only two sections at once, and is 187 cm. between the top and bottom beech planks. The strings were all 84·7 cm. between the bridges except in No. 25 where they were 89·4 cm. All were struck at $\frac{1}{9}$.

On section K_3 the bridge, instead of being near the middle, was 22 cm. from the top or very nearly $\frac{1}{4}$ the length of the section from that end.

In No. 17 the 2nd partial is very strong, as would be expected from the position of the bridge.

In No. 18 the two strings had been pulled up three semitones, which was as much as they would stand. The 2nd partial is not quite so strong.

In No. 19 a longer section K_8 was used, but owing to a stronger bar there was little difference in the pitch from that of K_3. The bridge was 21 cm. from the top, which is less than $\frac{1}{4}$ of the whole length 102 cm.

In No. 20 the bar at back of section K_8 had been planed down about 5 mm., reducing the natural frequency. The tone was worse than in No. 19. The 3rd partial is prominent in this case as well as the 2nd. Three times the natural pitch of the section is nearly the pitch of the strings.

In No. 21 the bridge has been moved to the middle of the sounding-board. The 2nd partial is not nearly so marked but is still easily seen and the tone was much better than that of Nos. 17 and 18.

The increased length of the sounding-board without a corresponding increase in the thickness probably tends to encourage the production of the upper partials.

In Nos. 22–24 the strings had a heavier copper covering in order to produce a lower note with the same length of string.

No. 22 shows a strong 2nd and marked 3rd partial, and very little difference in the wave or tone occurred when the strings were pulled up a tone.

In No. 24 the bridge was moved down to the middle of the sounding-board. The 2nd and other partials were very marked and the tone was not good.

No. 25 shows the last bass note. The long and weak section K_{8a} did not give any good results.

Conclusions.

The results of this investigation seem to indicate :—

(1) The vibrations of the sounding-board, when the bridge is near the middle, divide in half with a node at or near the middle.

(2) For the middle octaves of the pianoforte, when these two halves have a natural pitch near the pitch of the strings exciting them, a resonance takes place and a good musical tone results.

(3) For the two lower octaves the statement in (2) does not apply.

(4) Strong 2nd and 3rd partials are detrimental to good musical tone.

14 City Road, London, E.C.
June 17, 1910.

LXX. *The Mechanical Vibration of Atoms.*

By William Sutherland[*].

On account of the electric origin of rigidity and of cohesion, both within and without the atom, there is no real distinction between the mechanical and the electrical vibrations of atoms, but it is convenient to distinguish as mechanical vibrations those which can be calculated without directly considering the electrical properties of an atom.

The experimental researches of Rubens and his collaborators, Aschkinass, Nichols, and Ladenburg, have carried the measurements of wave-lengths into extreme regions of the infra-red spectrum, where the period of vibration is getting quite close to the order of magnitude to be expected from the mechanical vibrations of atoms and molecules. The recent measurements of wave-lengths by Rubens and Hollnagel for NaCl, KCl, KBr, and KI down to the seventh octave below the visible spectrum (Phil. Mag. [6] xix. May 1910, p. 761) invite the following brief theoretical investigation. Suppose an atom to be replaced by the least cube of the same mass and of uniform density that could circumscribe it. Let N be the rigidity of the material of this cube, ρ its density, m its mass, $m/h=\mathrm{M}$ its ordinary atomic weight or mass, and R the length of the edge of the cube, being equal to the atomic diameter. Here h is the mass of an atom of hydrogen, 1617×10^{-27} gramme. The velocity of propagation of a shear or simple distortion without change of volume through the cube is $(\mathrm{N}/\rho)^{\frac{1}{2}}$. The simplest type of vibration of the cube would have two opposite faces as middles of internodes so that within the atom the fundamental wave-length $=2\mathrm{R}$ and outside the atom it is $\lambda=c\tau$, where c is the

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[*] Communicated by the Author.

velocity of light through vacuum, or through air nearly, and τ is the period of vibration of the cube. But $\tau=2\mathrm{R}/(\mathrm{N}/\rho)^{\frac{1}{2}}$, so that $\lambda=2c\mathrm{R}/(\mathrm{N}/\rho)^{\frac{1}{2}}$.

It is convenient for the mathematical analysis to bring in the electric properties of the atom, though we shall not finally use them, as will appear immediately. Let the electric moment of the atom be denoted by *es* to be taken as a single symbol, and let K be its dielectric capacity. Then in "The Electric Origin of Rigidity and Consequences" (Phil. Mag. [6] vii. 1904, p. 417) it is shown that $\mathrm{N}=2\pi e^2s^2/3\mathrm{K}\mathrm{R}^6$, K being introduced to preserve generality. But in "The Nature of Dielectric Capacity" (Phil. Mag. [6] xix. 1910, p. 1) it was found that as regards the relations of the pairs of electrons forming the atom $\mathrm{K}=1$. It has also been found in my papers on the electric origin of cohesion that between atom and atom $\mathrm{K}=1$. I have taken this to be evidence that cohesion is due to electric attraction between the electrised molecule and its immediate neighbours, the attraction acting entirely through the æther in which $\mathrm{K}=1$. Within the atom it appears that the constitutive pairs of electrons act only upon their immediate neighbours through the æther with $\mathrm{K}=1$. It further appears that when we have taken account of the pairs of electrons forming matter as a cause of dielectric capacity different from 1, we have not to consider any other similar agency in the æther. In the formula given above for N then we put $\mathrm{K}=1$. In a recent Phil. Mag. article on Molecular and Electronic Potential Energy I have shown that the cohesional potential energy of unit mass of a substance may be written $l\rho^2$ (the $\mathrm{K}\rho^2$ of Laplace or the a/v^2 of van der Waals) where $l=4e^2s^2/m^2$, the values and laws of l having been investigated under M^2l and $\mathrm{M}l^{\frac{1}{2}}$ in various papers of mine on molecular attraction. If then in the formula for N we put $m^2l/4$ in place of e^2s^2, we get N expressed in terms of purely mechanical properties of the atom, the electrical moment *es* having been eliminated and K reduced to 1. Thus for the velocity of propagation of a shear through the atom we obtain the expression $(\pi l\rho/6)^{\frac{1}{2}}$ and

$$\lambda=2c\mathrm{R}/(\pi l\rho/6)^{\frac{1}{2}}=6\times10^{10}\times(1617\times10^{-27})^{\frac{1}{3}}(\mathrm{M}/\rho)^{\frac{1}{3}}/(\pi l\rho/6)^{\frac{1}{2}}$$

$$=973\cdot6(\mathrm{M}/\rho)^{\frac{1}{3}}/(l\rho)^{\frac{1}{2}}.$$

In the following table are gathered all the requisite data for computing the wave-lengths of the fundamental mechanical vibrations electrically communicated to the æther by the atoms of the combined alkali metals and the combined halogens, the wave-lengths being given in the last row in terms of $\mu = 10^{-4}$ cm. as unit.

	Li.	Na.	K.	Rb.	Cs.	F.	Cl.	Br.	I.
$10^{-6} M l^{\frac{1}{2}}$...	2·4	3·5	4·6	6·0	7·3	0·9	2·1	2·7	3·6
M/ρ.........	2·0	7·4	18·6	34·4	56·0	9	19	26	36
M	7	23	39	85·5	133	19	35·4	80	127
ρ	3·50	3·11	2·10	2·485	2·375	2·11	1·86	3·08	3·53
λ	19·12	70·69	151·0	286·2	440·3	294·2	351·6	505·9	603·9

To use these results for comparison with the experimental ones of Rubens and Hollnagel, I shall form the wave-length for NaCl by adding those in the table for Na and Cl, thus $70{\cdot}69 + 354{\cdot}6 = 425{\cdot}3$. The next table contains in the first row the wave-lengths thus calculated, in the second the experimental wave-lengths, and in the third the ratio of the calculated to the experimental wave-length.

	NaCl.	KCl.	KBr.	KI.
λ calcul.	425·3	505·6	656·9	754·9
λ exper.	51·7	63·4	82·3	96·4
Ratio............	8·23	7·97	7·98	7·83

The mean value of the ratio is 8·00. It is rather by chance that this ratio comes so exactly to 8, since the separate experimental determinations of these large wave-lengths, and the data and approximations used in the theoretical calculations, do not lead us to expect such exactness at the present. But it is sufficiently remarkable that we have found the calculated mechanical period of vibration and wave-length to be nearly three octaves below the lowest experimental period and length yet measured in each case. The theoretical fundamental wave-length for LiF is $313{\cdot}3\,\mu$, which is only between one and two octaves below the longest wave measured by Rubens and Hollnagel for KI.

It is necessary to comment on the process of adding the wave-length for combined Na to that for combined Cl to obtain the wave-length for NaCl. Let us consider an analogous case in acoustics. Suppose a length of tube l_1 is filled with gas 1, say hydrogen, and with both ends open is caused to sound, its period of vibration τ_1 is $2l_1/v_1$, where v_1 is the velocity of propagation of sound through gas 1. For a length l_2 filled with gas 2, for instance carbon dioxide, we have $\tau_2 = 2l_2/v_2$. If now the two tubes were placed so as to form a single one of length $l_1 + l_2$ open at both ends, but the part l_1 still filled with gas 1 and l_2 with 2, and the combined system were sounded, would the period of vibration be $\tau_1+\tau_2$? In the case where the gases 1 and 2 become identical we know that the period of the combined system is obtained correctly by adding together the corresponding values of τ_1 and τ_2. I do not know of the general case with two unlike gases having been tried. In the radiational case of NaCl, KCl, KBr and KI just considered, we have found that the periods of the two atoms in each compound have to be added together to give the period for the molecule. Now an exactly similar result was brought out in my paper on "A New Periodic Property of the Elements" (Phil. Mag. [5] xxx.) with a correction in "A Kinetic Theory of Solids" (*ibid.* xxxii.), and further consideration in "The Cause of the Structure of Spectra" (*ibid.* [6] ii.). It was shown that the atoms of the metallic elements and the molecules of their compounds at their melting-points have characteristic oscillations. The period of oscillation for a compound molecule like NaCl is shown to be obtainable as the sum of a period for Na and a period for Cl. This fact supports the assumption made above that in calculating the mechanical period of vibration and wave-length of NaCl we are to add the periods and lengths for Na and Cl. Moreover it is interesting to recall that the kinematical explanation which I have offered for the origin of Balmer's formula leads to the consideration of the period of each spectral line as the sum of two periods. From the calculations given above it appears that ordinary harmonic relations are to be expected amongst the wave-lengths of a substance in the extreme infra-red.

Melbourne, June 1910.

LXXI. *Musical Arc Oscillations in Coupled Circuits.* By E. Taylor Jones, *D.Sc., Professor of Physics in the University College of North Wales, and* David E. Roberts, *B.Sc., Isaac Roberts Student of the University College of North Wales, Bangor*[*].

[Plate XIII.]

In a former communication[†] a number of photographs were reproduced showing the variation of potential at the terminals of the secondary of a pair of coupled circuits when the two oscillations of the system are simultaneously maintained by a musical arc connected to the primary. In

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[*] Communicated by the Authors.

[†] E. T. Jones and Morris Owen, Phil. Mag. November 1909, p. 713.

the experiments there described the circuits were so adjusted that the frequency of one of the oscillations corresponded either to one of the harmonics of the other, or to the perfect fifth above it. It was pointed out that in the latter case it was necessary that the two notes of the system should be equally stable in order that the double oscillation curve might be produced, and that the note then heard was an octave below the lower of the two primaries, being in fact their difference tone.

It was thought desirable to continue these experiments, using some of the smaller intervals, in order to find out whether the same conditions hold, whether the difference tone is produced, and whether the same method of calculating the frequencies of the two oscillations also applies to these cases.

The smaller ratios are obtained by diminishing the coefficient of coupling of the two coils, and if we assume as the approximate condition of equal stability of the two notes $L_1C_1 = L_2C_2$*, the value of this coefficient may be calculated for any given ratio of the two frequencies.

If, with the usual notation for the constants of the two circuits, we put

$$1/L_1C_1 = N_1^2, \quad 1/L_2C_2 = N_2^2, \quad M^2/L_1L_2 = k^2,$$

the equation for the two frequencies, n_1, n_2, becomes

$$8\pi^2 n^2 = \frac{1}{1-k^2}\left[N_1^2 + N_2^2 \pm \sqrt{\{(N_1^2 - N_2^2)^2 + 4k^2 N_1^2 N_2^2\}}\right].$$

Assuming the condition $N_1 = N_2$, and writing m for the ratio of the frequencies, this leads to

$$k = \frac{m^2 - 1}{m^2 + 1}.$$

Taking as an example $m = 3/2$, as in the former experiments, this gives $k^2 = \cdot 1479$. The experimentally determined value of k^2 for the two coils was ·1483. During the singing-arc experiments the value of k^2 would be rather less than this, owing to the existence of self-inductance in the arc. In order to obtain the ratio $m = 4/3$ the value of k^2 should be, according to the above formula, ·0784.

There is no doubt, however, that the above condition for equal stability, $N_1 = N_2$, is only approximate; the value of the secondary capacity which makes the two notes equally stable depends also to some extent upon the mutual inductance of the coils.

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* *Cf.* E. T. Jones, Phil. Mag. January 1909, p. 41.

The apparatus used in the present experiments was the same as that previously described; the mutual inductance of the coils was varied by moving the primary along the axis of the secondary, and for each position of the primary coil the secondary capacity (a variable condenser with oil dielectric) was adjusted so that the two notes were equally stable. In a certain position of the primary coil the interval between the notes, as judged by ear, was a fourth, and if then the lower note is sounding, and the arc-length is gradually reduced, at a certain point the note suddenly falls by an interval which can be recognized as a twelfth, although the deep note thus produced generally dies away rapidly.

The terminals of the secondary condenser were connected to the electrostatic oscillograph, and after a considerable number of attempts a photograph was obtained showing the wave of potential* in the secondary circuit when this difference tone was sounding. The curve in the photograph (Pl. XIII. fig. 1) shows the grouping of the waves characteristic of simultaneous oscillations of different frequencies. The damping is strong in this case, but it was often much less than is shown in the photograph. The curve somewhat resembles those which may be produced by simply breaking a current in the primary circuit†.

The frequency of the groups determined from the photograph, by comparison with the curve given by the 768 tuning-fork, was 200·6.

The constants of the circuits were determined by methods which have been fully described by one of us in previous papers. In the paper above referred to it was shown that in order to calculate correctly the frequencies of singing-arc oscillations, it is necessary to assume that the arc possesses self-inductance which must be added to that of the primary circuit, the value of the apparent self-inductance of the arc depending upon the distance between the carbons.

In the present case it was found that there was no value of L_1 which made $n_2/n_1=4/3$, if the resistances of the circuits were neglected. After a number of trials the following results were calculated. Assuming the value ·0005 henry for the self-inductance of the arc, then $N_1^2=1{\cdot}693.10^7$, $N_2^2=1{\cdot}823.10^7$ C.G.S., $k^2={\cdot}08656$. Hence, neglecting the resistances, $n^2=794{\cdot}7$, $n_1=585{\cdot}7$, $n_2-n_1=209$, $n_2/n_1=1{\cdot}357$.

Taking the resistances into account, however, and assuming about 4 ohms for the arc, then $R_1=5$ ohms, $R_2=14000$ ohms;

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* As explained in previous papers the ordinate of the curve is proportional to the square of the difference of potential at the terminals of the instrument.

† *Cf.* E. T. Jones, Phil. Mag. January 1909, Plate, figs. 5, 6, 7, 8.

hence, by Drude's equations*, $n_2=791\cdot49$, $n_1=591\cdot03$, $n_2-n_1=200\cdot46$, $n_2/n_1=1\cdot339$.

It is therefore clear that if the arc be assumed to have a self-inductance rather less than ·0005 henry, and a resistance slightly greater than 4 ohms, the ratio of the frequencies of the two oscillations will be exactly 4/3, and their difference will agree with the observed value of the group-frequency.

Pl. XIII. fig. 2 shows the curve obtained with the coils in the same relative position but with larger capacities in the circuits. This photograph covers the period of change from the lower primary note to the difference tone. In this case, again assuming ·0005 henry for the self-inductance of the arc, we find $N_1{}^2=1\cdot3468.10^7$, $N_2{}^2=1\cdot3329.10^7$, $k^2=\cdot08636$. Hence, neglecting the resistances, $n_2=693\cdot28$, $n_1=512\cdot14$, $n_2-n_1=181\cdot14$, $n_2/n_1=1\cdot3538$. Again taking $R_1=5$ ohms, $R_2=14000$ ohms, we find by Drude's equations $n_2=690\cdot6$, $n_1=517\cdot4$, $n_2-n_1=173\cdot2$, $n_2/n_1=1\cdot3348$.

The frequency of the groups determined from the photograph is 174·8. In this case also the effect of taking the resistances into account is to diminish the ratio of the frequencies, and possible values can be found for the self-inductance and resistance of the arc which will make the ratio of the frequencies exactly 4/3, and make their difference agree with the observed frequency of the groups.

By withdrawing the primary coil to greater distances along the axis of the secondary, some of the smaller musical intervals, the major third and minor third, may be obtained, and deep difference tones sometimes heard; these are, however, very unstable and no photographs were obtained for these cases.

By increasing the coupling coefficient to a certain value, the two notes may be brought to an interval of an augmented fourth, and with a certain value of the secondary capacity the two notes may be produced simultaneously. The difference tone was not prominent in this case; the impression was rather that of the two primary notes sounding together. The photograph was easily obtained and is shown in Pl. XIII. fig. 3. This photograph was obtained with a new oscillograph which was at the time arranged for measuring much higher potentials, the phosphor-bronze strip being replaced by one of steel, and this being under very great tension. This accounts for the smallness of the amplitude of the curve. The curve was not measured, but it probably represents the case $n_2/n_1=7/5$.

Bangor, July 1910.

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* Drude, *Ann. der Physik*, xiii. p. 534 (1904).

LXXII. *Note on Mr. Bateman's Paper on Earthquake-Waves.* *By* Robert E. Baynes [*].

TOWARDS the end of his interesting paper on Earthquake-waves in the April number of the Phil. Mag. (p. 585), Mr. Bateman connects the times of transit T of the first-phase waves to stations at angular distance θ from the source, as given by Prof. Milne, by a formula of the type $T=C+A\theta-B\theta^2$, and, by assumption of the relation $dT/d\theta=(R/U)\cos\epsilon$, where R is the earth's radius, U the speed at the surface, and ϵ the angle of emergence, shows that $U=R/A$ if θ is measured in radians, and, by further application of Abel's transformation to the equation of the path, that the speed v at distance Rx from the centre is given by [†]

$$(1-U^2x^2/v^2)^{\frac{1}{2}}-\operatorname{sech}^{-1}(Ux/v)=(2\pi B/A)\log x. \quad . \quad (1)$$

The same procedure is of course equally applicable to the equation for the time along the path which is given on p. 583 and which takes the form

$$T=-\frac{2R}{U}\int_0^s\frac{\phi(t)dt}{(s-t)^{\frac{1}{2}}}$$

on putting $t=1-U^2x^2/v^2$, $(U^2x/v^2)dx\equiv\phi(t)dt$, $s\equiv\sin^2\epsilon$; the relation assumed above then gives

$$T=(\pi R/2U)(Es+2F),$$

where

$$E\equiv R/2\pi BU \text{ and } F\equiv CU/\pi R+(A^2U^2-R^2)/4\pi BRU,$$

and the transformation gives

$$\phi(t)=\frac{1}{\pi}\frac{d}{dt}\int_0^t\frac{Tds}{(t-s)^{\frac{1}{2}}}=-\frac{d}{dt}\cdot(\tfrac{1}{3}Et+F)t^{\frac{1}{2}},$$

whence

$$\begin{aligned}\log x&=Et^{\frac{1}{2}}-(E+F)\tanh^{-1}t^{\frac{1}{2}}\\&=E(1-U^2x^2/v^2)^{\frac{1}{2}}-(E+F)\operatorname{sech}^{-1}(Ux/v). \quad . \quad (2)\end{aligned}$$

Comparison of (2) with (1) requires $E=A/2\pi B$ and $F=0$, *i. e.* $U=R/A$ as before and $C=0$. The latter result is doubly obvious; for T must vanish with θ, and the assumed relation is not true except with this condition.

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[*] Communicated by the Author.

[†] In three places the factor R has dropped out by a slip and in the Table η/β should be substituted for η.

As a matter of fact Milne's numbers are better represented by Bateman's formula if 0, 5·69, ·45 are substituted for his constants ·4, 6·1, ·5; and these give 9·77 km. per sec. for the speed at the surface.

But, as Bateman's Table indicates, there is a depth at which v has a maximum value: this occurs when $U^2x^2/v^2=1-E^{-\frac{2}{3}}$, in which case $\log(v/U)=E(\tanh^{-1}E^{-\frac{1}{3}}-E^{-\frac{1}{3}})$, corresponding to $\sin\epsilon=E^{-\frac{1}{3}}$ with $\theta=(A/B)\sin^2\frac{1}{2}\epsilon$, *i. e.* with the above constants to $\epsilon=79\frac{1}{3}°$, $\theta=154°$; and for higher values of ϵ the solution will not apply, as there will be no total reflexion of the wave.

For the solution to be applicable throughout the earth and with perfect symmetry we must have for the maximum speed $\epsilon=\frac{1}{2}\pi$, or $E=1$ (*i. e.* $B=A/2\pi$) with a formula of the type $T=A\theta-B\theta^2$. The value 11·12 for A with θ expressed in radians gives Milne's results with very fair exactness, and thus 9·55 km. per sec. for the speed at the surface, the limiting speed at the centre being $\frac{1}{2}e$ times greater*, where e is the base of Naperian logarithms.

Christ Church, Oxford.
26 July, 1910.

LXXIII. *On the Equation of Continuity of the Liquid and Gaseous States of Matter.* By R. D. KLEEMAN, *D.Sc., B.A., Mackinnon Student of the Royal Society* †.

THE writer ‡ has shown that the attraction between two molecules besides that due to gravitation separated by a distance z is

$$\frac{1}{z^5}\phi_2\left(\frac{z}{x_c}, \beta\right)(\Sigma\sqrt{m_1})^2,$$

where x_c is the distance of separation of the molecules in the critical state, T is the temperature and T_c the critical temperature, and $\beta=\frac{T}{T_c}$, and $\Sigma\sqrt{m_1}$ is the sum of the square roots of the atomic weights of the atoms of a molecule;

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* In a problem suggested by Benndorf's and Herglotz's important papers ('Science Abstracts' for 1907, Nos. 383 and 985), and set in Jan. 1908 for the Senior Mathematical Scholarship Examination of the University, I asked for the deduction of the relation $\theta=2\epsilon-\sin 2\epsilon$ from the fancy law $T=\frac{4}{3}(R/U)\sin^3\epsilon$, and also, Abel's transformation being cited, for the proof that the ratio of the speeds at the centre and surface is $\sqrt{e}$.

† Communicated by the Author.

‡ Phil. Mag. May 1910, p. 783: in subsequent references to this paper it will be called (*a*).

$\phi_2\left(\frac{z}{x_c}, \beta\right)$ is a function whose exact theoretical form is not indicated by the investigation except that it has the same value for all substances at corresponding states. It was found that this function does not vary much with the temperature and as a first approximation may be taken as constant. Supposing it constant, its value was determined and found to be of the order of the magnitude of 2×10^{-46} (grm.)(cm.)(sec.)$^{-2}$. The above law of attraction is in this paper made the basis of some equations of continuity of the different states of matter.

Let us suppose that a molecule in the liquid state has the same amount of kinetic energy or energy of translation as in the gaseous. And let us suppose that the molecules in a liquid are in equilibrium between the gas or Boyle pressure of the molecules acting in one direction and the attraction between the molecules and the external pressure acting in the opposite direction. Then, if P_n denotes the negative pressure due to the attraction of the molecules, and p the external pressure and p_1 the Boyle pressure, we have

$$P_n + p = p_1 = \frac{RT}{mv}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where m denotes the molecular weight of the substance. This view of the equilibrium of the molecules in the liquid or any other state is now usually adopted by physicists, principally owing to the work of van der Waals. P_n has been called the intrinsic pressure of the liquid.

The law of molecular attraction given at the beginning of the paper enables us to obtain a more definite and fundamental expression for the intrinsic pressure than that obtained from van der Waals' equation of state. It is first of all necessary to make some supposition as to the relative distribution of the molecules in a liquid. Let us suppose, as we did in a previous paper, the liquid cut into equal squares by three sets of imaginary planes, one set of which is parallel to the surface, and that the molecules are situated at the points of intersection of these planes. The attraction of a slab of liquid whose thickness is greater than the radius of the sphere of action of a molecule on a molecule at a distance nx_a from the surface is

$$(\Sigma_{c_a})^2 \sum_{u=-\infty}^{u=\infty} \sum_{v=-\infty}^{v=\infty} \sum_{w=-\infty}^{w=\infty} \phi(z) \frac{x_a}{z}(n+w),$$

where $\Sigma_{c_a} = \Sigma\sqrt{m_1},$

and $\phi(z)(\Sigma\sqrt{m_1})^2$ is the attraction between two molecules, and

$$z = x_a\{(n+w)^2+u^2+v^2\},$$

x_a being the distance between two molecules situated on the same edge of one of the squares. For a proof of this expression see paper (*a*) p. 791. The attraction of the slab of liquid on a cylinder of the liquid of infinite length and unit cross-section, standing with one of its bases on the surface of the liquid, is therefore

$$\frac{1}{x_a^2}(\Sigma\sqrt{m_1})^2\sum_{n=1}^{n=\infty}\sum_{v=-\infty}^{v=\infty}\sum_{u=-\infty}^{u=\infty}\sum_{w=0}^{w=\infty}\phi_2\left(\frac{z}{x_c},\beta\right)\frac{x_a}{z^6}(n+w),$$

where for $\phi(z)$ we have now put $\frac{1}{z^5}\phi_2\left(\frac{z}{x_c},\beta\right)$, the factor $\frac{1}{x_a^2}$ giving the number of molecules lying on a plane cutting the cylinder of liquid parallel to the surface of the slab. This expression gives the intrinsic pressure of the liquid. On bringing $\frac{1}{x_a^4}$ a factor of $\frac{x_a}{z^5}$ outside the summation sign it may be written

$$K_2\left(\frac{\rho}{m}\right)^{7/3}(\Sigma\sqrt{m_1})^2,$$

where

$$\left(\frac{\rho}{m}\right)^{1/3}=\frac{1}{x_a},$$

and K_2 is a constant which is the same for all liquids at corresponding states. Since $\phi_2\left(\frac{z}{x_c},\beta\right)$ in the expression for the attraction between two molecules varies only slightly with the temperature, the value of K_2 will also vary only slightly with the temperature.

On the assumption that $\phi_2\left(\frac{z}{x_c},\beta\right)$ or K is constant, the intrinsic pressure in any given liquid can be calculated. The value of K_2 then becomes equal to

$$1\cdot66\times10^{-46}\sum_{n=1}^{n=\infty}\sum_{v=-\infty}^{v=\infty}\sum_{u=-\infty}^{u=\infty}\sum_{u=0}^{w=\infty}\frac{n+w}{\{(n+w)^2+v^2+u^2\}^3},$$

where $1\cdot66\times10^{-46}$* is the mean value of K obtained from ether and carbon tetrachloride at $T_c\frac{2}{3}$. The value of the

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* (*a*) p. 802.

summation quantity is approximately equal to 2·06; and the equation for the intrinsic pressure thus becomes

$$P_n = \left(\frac{\rho}{m}\right)^{7/3} (\Sigma \sqrt{m_1})^2 \, 1{\cdot}66 \times 2{\cdot}06 \times 10^{-46}.$$

If K is a function of the temperature only, the equation will give the correct value of the intrinsic pressure on substituting for $1{\cdot}66 \times 10^{-46}$ the value of K corresponding to the temperature for which the intrinsic pressure is calculated.

Let us, for example, calculate the intrinsic pressure in ether at $\frac{2T_c}{3}$, corresponding to which K has been determined. The values of m, $\Sigma\sqrt{m_1}$, and ρ are $74 \times 7{\cdot}1 \times 10^{-25}$, 27·8, and ·6907 respectively, taking the mass of an atom of hydrogen as $7{\cdot}1 \times 10^{-25}$ grm.* We thus obtain

$$P_n = 1992 \text{ atmos. per cm.}^2$$

Later we will compare this value with that found by a different method.

The intrinsic pressure, we have seen, is in general given by

$$P_n = K_2 \left(\frac{\rho}{m}\right)^{7/3} (\Sigma \sqrt{m_1})^2, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where K_2 is a constant which is the same for all liquids at corresponding states. Now the writer has shown in a previous paper † that

$$p_c = M^2 \left(\frac{\rho_c}{m}\right)^{7/3} (\Sigma \sqrt{m_1})^2,$$

p_c, ρ_c denoting the critical pressure and density and M a numerical constant. A comparison of these two equations shows that the intrinsic pressures in liquids at corresponding states are the same multiple of their critical pressures. Since ρ varies only slightly with the temperature when it is low and K_2 is approximately constant, this multiple will be at low temperatures roughly a constant whose value is $\frac{P_n}{p_c}$ or $\frac{1992}{36{\cdot}28} = 54{\cdot}9$, using for this calculation the value of P_n found for ether at $\frac{2T_c}{3}$, and 36·28 the critical pressure of ether in atmospheres.

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* It should be noticed that from the way K was determined it follows that P_n is independent of the value taken for m.

† Phil. Mag. Dec. 1909, p. 903; and (*a*) p. 788.

In a previous paper * it was shown that the internal latent heat of evaporation L of a liquid is given by

$$L = \frac{1}{m}\left\{A_1\left(\frac{\rho_1}{m}\right)^{4/3} - A_2\left(\frac{\rho_2}{m}\right)^{4/3}\right\}(\Sigma\sqrt{m_1})^2, \quad . \quad (3)$$

where ρ_1 and ρ_2 denote the densities of the liquid and saturated vapour respectively, and A_1 and A_2 are constants each of which is the same for all liquids at corresponding temperatures. This equation is based on the law of attraction between molecules, given at the beginning of the paper. The equation may be written

$$L = L' - L'',$$

where

$$L' = \frac{A_1}{m}\left(\frac{\rho_1}{m}\right)^{4/3}(\Sigma\sqrt{m_1})^2$$

and

$$L'' = \frac{A_2}{m}\left(\frac{\rho_2}{m}\right)^{4/3}(\Sigma\sqrt{m_1})^2.$$

From the way the above equation has been obtained, it follows that L′ denotes the internal latent heat of evaporation of a liquid into a vacuum, and L″ the internal latent heat of evaporation of the saturated vapour into a vacuum. The equation (2) for the intrinsic pressure may now be written

$$P_n = \rho L/K_3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where

$$K_3 = \frac{K_2}{A_1},$$

and is therefore a constant which is the same for all liquids at corresponding states. At low temperatures L″ is small in comparison with L′, and the above equation may then be written

$$P_n = \rho L K_3.$$

An equation similar to equation (4) may be very simply obtained if we make the supposition that matter does not consist of molecules but is evenly distributed in space. Let the attraction of a large mass of liquid, making this supposition, on a slab of liquid of unit area and thickness dz at a distance z from the surface of the liquid, be $\psi(z)dz$, in a direction at right angles to the surface of the liquid. The attraction on a cylinder of unit cross-section and infinite length standing with one of its bases on the surface of the liquid will therefore be $\int_0^\infty \psi(z) \, . \, dz$; and this is equal to the intrinsic pressure.

* (*a*) pp. 794–795.

Let us next obtain the internal heat of evaporation on this supposition, making use of the same notation. Suppose a thin layer of liquid of unit area and thickness dx is removed from the surface of the liquid and distributed in a space of infinite extent, the layer being taken so thin that the work done in distributing the matter in space is small in comparison with the work done in removing the layer. If L_v denote the internal latent heat per unit volume,

$$L_v dx = \int_0^\infty dx \, . \, \psi(z) \, . \, dz = dx \int_0^\infty \psi(z) \, dz,$$

or

$$L'\rho = \int_0^\infty \psi(z) \, dz \, ^*.$$

Comparing this equation with the above expression for the intrinsic pressure, we see that

$$P_n = L'\rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This equation, obtained on the supposition that matter is evenly distributed in space, gives on comparing it with equation (4) that $K_3 = 1$. Whether this supposition is admissible in the above investigation can be tested by calculating P_n by equation (5) and comparing it with that obtained by equation (2). Thus, in the case of ether at a temperature of $\frac{2T_c}{3}$ equation (5) gives

$$P_n = \frac{75{\cdot}4 \times 4{\cdot}2 \times 10^7 \times {\cdot}6907}{10^6} = 2187 \text{ atmos. per cm.}^2,$$

where 75·4 is the internal latent heat of evaporation[†] in

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[*] Stefan has shown (Wied. *Ann.* xxix. p. 665) that the internal heat of evaporation of a molecule is equal to the work done in moving it from the interior of the liquid to the surface and then to an infinite distance from the liquid. This is true, however, only when matter is not evenly distributed in space, *i. e.* consists of molecules, in which case a molecule must be brought from the interior of the liquid to fill up the gap made by removing one from the surface. When matter is evenly distributed in space, however, we may suppose that during evaporation infinitely thin layers of liquid are successively removed from the *whole surface* of the liquid. The radii of the spheres of action of a set of different molecules calculated by the writer, Phil. Mag. pp. 840-846, June 1910, on the supposition that matter is evenly distributed in space and using Stefan's result, therefore really denote their diameters.

[†] The internal latent heat of evaporation and density data used in this paper are taken from a paper by Mills, Journ. of Phys. Chem. vol. viii. p. 405 (1904), who has calculated the internal latent heat at different temperatures for a number of substances, using the density and pressure data of Ramsay and Young.

calories per gram at $\frac{2T_c}{3}$, which at that temperature may be taken equal to L′. The above value for P_n is practically the same as that obtained previously by equation (6), viz. 1992.

Thus we see that K_3 or $\frac{K_2}{A_1}$ is independent of the temperature and equal to unity, or at least approximately so. This result throws some light on a very important point. So far we have not yet obtained any information as to whether the function $\phi_2\left(\frac{z}{x_c}, \beta\right)$ in the expression for the attraction between two molecules is a function of the temperature or of the distance between the molecules, or of both. Referring back to the demonstrations of the equations (2) and (3), containing K_2 and A_1 respectively, it will be seen that if $\phi_2\left(\frac{z}{x_c}, \beta\right)$ is a function of the temperature only, it can at once be taken outside the summation and integral signs, and then appears as a factor of K_2 and A_1, which disappears in $\frac{K_2}{A_1}$ or K_3. The expression thus appears to be a temperature function only. This point will be discussed at length in a separate paper.

A general equation of the different states of matter will now be developed and some special cases of this general equation considered.

Substituting for the intrinsic pressure in equation (1) from equation (2), we have

$$p+K_2\left(\frac{1}{vm}\right)^{7/3}(\Sigma\sqrt{m_1})^2=\frac{RT}{mv}.$$

There is one point which has not been taken account of in formulating this equation, to which attention was first drawn by van der Waals. When the density of a gas is so great that the diameter of the molecules is comparable with their distance of separation, the diminution of the mean free path of a molecule on collision owing to its finite size is appreciable. The pressure is therefore greater than that given by Boyle's law, and according to van der Waals is such as if the volume of the gas were smaller than it actually is by four times the space actually occupied by the molecules. For v we must therefore write $(v-b)$, where b is the space occupied by the molecules. The effect produced by the molecules having finite size is quite large. Thus, consider a liquid at a low temperature: the pressure of its saturated vapour or external pressure is then small in comparison with the intrinsic pressure, and equation (1) becomes

$$P_n = \frac{RT}{mv};$$

or the intrinsic pressure would also be given by $\frac{RT}{mv}$ if the matter obeyed Boyle's law. For ether this equation gives

$$P_n = 240 \cdot 3 \text{ atmos. per cm.}^2$$

This is a much smaller value for the intrinsic pressure than that obtained from equation (2) or (5), viz. 1992 and 2187 atmos. per cm.^{2} respectively, and the effect in question is therefore quite large in liquids.

But b is strictly not a constant; the apparent volume of two colliding molecules will be influenced by their forces of attraction and those of the surrounding molecules, and consequently depends to a certain extent on the density of the matter. We must therefore write b a function of v and T. Equation (1) may then be written

$$p+\psi_2\left(\frac{z}{x_c}, \beta\right)\left(\frac{1}{vm}\right)^{7/3}(\Sigma\sqrt{m_1})^2=\frac{RT}{m(v-\psi_3(v_1T_1))}. \quad . \quad (6)$$

This is a general equation for any state of matter liquid or gaseous, for the same conditions of equilibrium apply to the gaseous as to the liquid state.

We have obtained some evidence that $\psi_2\left(\frac{z}{x_c}, \beta\right)$ or K_2 is a function of the temperature only, which must be such that its value is the same for all liquids at corresponding states. Let us first consider the equation taking $\psi_3(v, T)$ a constant b and K_2 a function of the temperature only. Substituting $\frac{1}{\rho}$ for v the equation may be written

$$\rho^{10/3}-\frac{1}{b}\rho^{7/3}+\left(\frac{bp+\frac{RT}{m}}{bA_3}\right)\rho-\frac{p}{bA_3}=0,$$

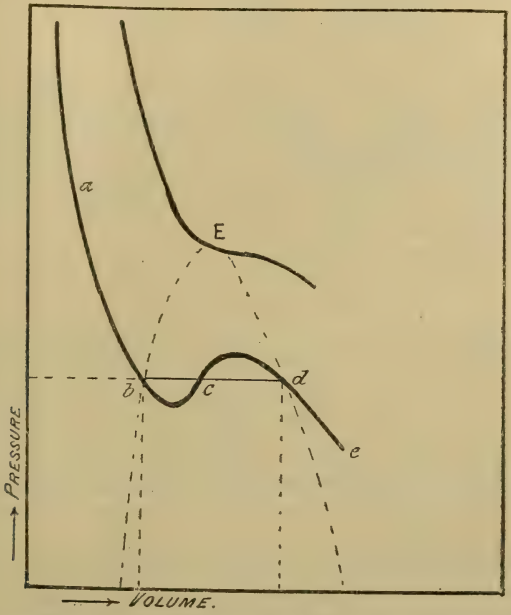
or

$$\sigma^{10}-\frac{1}{b}\sigma^{7}+\left(\frac{bp+\frac{RT}{m}}{bA_3}\right)\sigma^{3}-\frac{p}{bA_3}=0, \quad . \quad . \quad . \quad (7)$$

where

$$\sigma=\rho^{1/3} \quad \text{and} \quad A_3=K_2\left(\frac{\Sigma\sqrt{m_1}}{m^{7/3}}\right)^2.$$

According to Descartes's Rule of Signs the maximum number of positive roots that σ in equation (7) can have is three, and the maximum number v in the original equation can have is therefore also equal to three. Since the conditions of equilibrium of the molecules in matter are independent of its state of aggregation, there should be continuity as we pass from the liquid to the gaseous state. The isothermal for a given temperature would therefore in certain cases be a curve of the well-known form a, b, c, d, e, shown in the figure; the points b, c, d correspond to the three values of v at a given pressure. The points d and b correspond to the saturated vapour and liquid respectively at the same temperature. The part of the curve between b and d is, however, not realizable in practice. Why this is the case will be discussed later.



At the critical point, denoted by E in the figure, the three values of v become equal to one another. The equations giving the value of σ when it has three equal positive roots in equation (7) are, according to the Theory of Equations,

$$f=\sigma^{10}+a_1\sigma^7+a_2\sigma^3+a_3=0, \quad . \quad . \quad . \quad . \quad (a)$$

$$\frac{df}{d\sigma}=10\sigma^9+7a_1\sigma^6+3a_2\sigma^2=0, \quad . \quad . \quad . \quad . \quad (b)$$

$$\frac{d^2f}{{}^2d\sigma}=90\sigma^8+42a_1\sigma^5+9a_2\sigma=0, \quad . \quad . \quad . \quad . \quad (c)$$

where a_1, a_2, a_3 are the coefficients of σ^7, σ^3, σ^0 in equation (7). From equations (*b*) and (*c*) we obtain

$$70\sigma^9+28a_1\sigma^6=0,$$

which, on making the necessary substitutions, reduces to

$$b=\frac{1}{p_c 2\cdot 5}.$$

Equations (*a*) and (*b*) give the equation

$$7\sigma^{10}+4a_1\sigma^7-3a_3=0,$$

which becomes

$$p_c=\frac{p_c^7 A_1}{2\cdot 5}=\frac{K_2^c}{2\cdot 5}\left(\frac{\rho_c}{m}\right)^{7/3}(\Sigma\sqrt{m_1})^2,$$

where K_2^c is the value of K_2 at the critical state and is the same for all liquids. We have already found a relation of this nature connecting the critical constants *. It is therefore one of the conditions for the correctness of the equation of state that it should lead to this equation or to equations from which it can be deduced.

From equations (*b*) and (*c*) we also have

$$30\sigma^9-12a_1\sigma^2=0,$$

which, with the help of the results just obtained, reduces to

$$p_c=\frac{RT\rho_c}{m 2\cdot 1}.$$

This is the well-known law of Young and Thomas. The constant 2·1 is, however, too small, the mean value according to the facts is 3·7.

The proposed equation of state thus leads to two known relations between the critical constants, but the numerical constants involved do not agree with the facts. It will therefore be necessary to introduce some modifications into the equation. These should first of all take into account that *b* is not a constant. Since we know nothing as to the exact nature of the variation of *b*, let us assume

$$b=(n_1-n_2\rho).$$

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* *Loc. cit.*

Equation (7) may then be written

$$\rho^{13/3} - \frac{n_1}{n_2}\rho^{10/3} + \frac{1}{n_2}\rho^{7/3} + \frac{p}{\mathrm{A}_3}\rho^2 - \left(\frac{pn_1 + \dfrac{\mathrm{RT}}{m}}{\mathrm{A}_3 n_2}\right)\rho + \frac{p}{\mathrm{A}_3 n_2} = 0.$$

Now, if we form the equations of condition for equal roots, it will be found that if we put

$$n_1 = \frac{u_1}{p_c}, \quad n_2 = \frac{u_2}{\rho_c^2},$$

where u_1 and u_2 are numerical constants, we obtain two equations of the form

$$p_c = \mathrm{M}_1\left(\frac{\rho_c}{m}\right)^{7/3}(\Sigma\sqrt{m_1})^2, \quad p_c = \frac{\mathrm{RT}\rho_c}{m\mathrm{M}_2},$$

where M_1 and M_2 are functions of u_1, u_2, and K_2^c. We have seen that we must arrive at equations of this form, and the numerical constants u_1 and u_2 must be so chosen that they agree with the facts. It is necessary first to obtain the value of K_2^c. We have seen that

$$\mathrm{P}_n = \mathrm{L}'\rho = \mathrm{A}\left(\frac{\rho}{m}\right)^{7/3}(\Sigma\sqrt{m_1})^2\,^*,$$

and K_2^c is therefore the value of A at the critical point. Without finding the exact nature of the variation of A with temperature, it will be seen from an inspection of the values of A of methyl formate in Table V.,† which have been calculated up to the critical point, that the value of K_2^c is about 2800. If the pressure in the equation of state is expressed in atmospheres

$$\mathrm{K}_2^c = \frac{2800 \times 4{\cdot}2 \times 10^7}{10^6} = 117{,}600.$$

The mean value of M_1 can be deduced from the fifth column of Table IV.‡, this giving $\mathrm{M}_1 = (136{\cdot}8)^2$. (Through an oversight it was not mentioned in the paper that the values in this column are only relatively correct, the absolute values being obtained by dividing each value by 4·54.) We have

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* (*a*) pp. 794–795.

† (*a*), p. 797.

‡ (*a*) p. 788.

also $M_2=3{\cdot}7$. These two equations, substituting for K_2^c its numerical value, give $u_1={\cdot}734$ and $u_2={\cdot}176$.

It is necessary next to discover a function which will express the variation of K_2 with temperature. This variation is small: thus in the case of methyl formate the value of K_2 or A decreases from 4400 to 2865 when the temperature increases from 273 to 486. If the values of A given in Table V. quoted above are plotted against the temperature, it is at once apparent that they suffer from an accumulation of errors of data which affects them irregularly, but on the whole the values may be said to vary approximately linearly with the temperature. Bearing in mind that K_2 must be the same for all liquids at corresponding states, we may therefore write

$$K_2 = A - \frac{BT}{T_c}.$$

It was found that we may put $A=7222$ and $B=4422$; at the critical state we have then $K_2^c=2800$. The general equation of state is then

$$p+42\left(7222-4422\frac{T}{T_c}\right)\left(\frac{\rho}{m}\right)^{7/3}(\Sigma\sqrt{m_1})^2 = \frac{RT\rho}{m\left\{1-\frac{\rho}{\rho_c}\left({\cdot}734-{\cdot}176\frac{\rho}{\rho_c}\right)\right\}} \quad . \quad . \quad (8)$$

But this equation, on account of its generality, cannot be expected to agree very well with the facts in all cases. A better agreement would be obtained by determining the numerical quantities separately for each liquid under consideration. These quantities would obviously, however, vary only slightly from one substance to another.

It will be of interest now to compare the above equation of state with that given by van der Waals. Van der Waals' equation is

$$\left(p+\frac{a}{v^2}\right)=\frac{RT}{m(v-b)},$$

where a and b are constants which are supposed to be independent of temperature, &c., but which vary with the nature of the liquid. The term $\frac{a}{v^2}$ or $a\rho_1^2$ corresponds to the intrinsic pressure of the liquid. Now we have seen that this term must be equal to $\rho_1 L'$, or $a\rho_1^2 = L'\rho_1$, and therefore $L' = a\rho_1$. Since the internal latent heat of evaporation L is given by $L = L' - L''$ we have $L = a(\rho_1 - \rho_2)$, where a is constant. But this equation for the latent heat does not agree with the facts, and a is therefore not a constant. This is shown by Table I., which contains the values of $\dfrac{L}{\rho_1 - \rho_2}$ at different temperatures for a number of liquids; the values of this quantity or a, it will be seen, decrease considerably with increase of temperature.

TABLE I.

Ethyl oxide.				Carbon tetrachloride.				Methyl formate.			
T.	$\dfrac{L}{\rho_1 - \rho_2}$.	T.	$\dfrac{L}{\rho_1 - \rho_2}$.	T.	$\dfrac{L}{\rho_1 - \rho_2}$.	T.	$\dfrac{L}{\rho_1 - \rho_2}$.	T.	$\dfrac{L}{\rho_1 - \rho_2}$.	T.	$\dfrac{L}{\rho_1 - \rho_2}$.
273	117·1	393	100·2	273	29·6	473	25·3	273	112·9	443	89·5
313	109·9	433	93·4	393	27·4	513	24·4	323	107·6	483	73·4
353	104·7	460	88·7	433	26·4	553	22·1	403	95·6	486·5	68·1

From the equations of condition for equal roots of v we obtain

$$p_c v_c = \frac{RT}{m 2{\cdot}66}.$$

But the constant 2·66 is too small, its value we have seen ought to be 3·7. Van der Waals' equation thus satisfies only imperfectly two important conditions. The equation of state given in this paper satisfies these two conditions besides one other, and should therefore be in better agreement with the facts than van der Waals'. Moreover, it is more general in form and has a definite theoretical basis.

The equation of state given in this paper was developed taking $\phi_2\left(\dfrac{z}{x_c}, \beta\right)$ or K in the expression for the attraction between two molecules as a function of the temperature only, in support of which we obtained some evidence. It will be of interest to develop an equation of state taking K a function of ρ and thus independent of the temperature. It should be observed that when the equation of state is applied to a liquid and its saturated vapour, it does not matter whether we consider K a function of the temperature or of the density, as the density is thus a function of the temperature. Since $P_n = L'\rho$ it will be most convenient to develop first a formula for the latent heat along the same lines. We have seen * that in general, according to the law of attraction between molecules,

$$L = \left\{ \left(\frac{\rho_1}{m}\right)^{4/3} \cdot \phi_3\left(\frac{x_a}{x_c}, \beta\right) - \left(\frac{\rho_2}{m}\right)^{4/3} \cdot \phi_3\left(\frac{x_b}{x_c}, \beta\right) \right\} \frac{(\Sigma \sqrt{m_1})^2}{m},$$

where

$$\phi_3\left(\frac{x_a}{x_c}, \beta\right) \quad \text{and} \quad \phi_3\left(\frac{x_b}{x_c}, \beta\right)$$

have each the same values for all liquids at corresponding states. If K is to be independent of the temperature,

$$\phi_3\left(\frac{x_a}{x_c}, \beta\right) \quad \text{and} \quad \phi_3\left(\frac{x_b}{x_c}, \beta\right)$$

must be functions of ρ_1 and ρ_2 respectively, or rather of $\frac{\rho_1}{\rho_c}$ and $\frac{\rho_2}{\rho_c}$, since they must have the same values at corresponding states. A fairly good agreement with the facts is obtained by writing for these functions

$$U\left(\frac{\rho_1}{\rho_c}\right)^{2/3} \quad \text{and} \quad U\left(\frac{\rho_2}{\rho_c}\right)^{2/3}$$

respectively, where U is a numerical constant. The equation for the latent heat then becomes

$$L = U(\rho_1^2 - \rho_2^2)\frac{(\Sigma \sqrt{m_1})^2}{m^{7/3}\rho_c^{2/3}}. \quad . \quad . \quad . \quad . \quad (9)$$

This is the same equation as was obtained in a previous paper from surface-tension considerations † ; it was there applied only to liquids considerably below their critical temperatures, and therefore written

$$L = U\rho_1^2 \frac{(\Sigma \sqrt{m_1})^2}{m^{7/3}\rho_c^{2/3}}.$$

The above equation is tested for a number of liquids over considerable ranges of temperature in Table II. The values of $\frac{L}{\rho_1^2 - \rho_2^2}$ contained in the fifth and twelfth columns of the

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* (*a*) p. 746.

† Phil. Mag. Oct. 1909, pp. 499–505.

table are fairly constant for each liquid, as should be the case according to the equation. The constancy is more perfect in some cases than in others; and it would therefore seem difficult to discover a simple formula involving ρ_1 and ρ_2 that would be in perfect agreement with the facts in the case of each liquid.

TABLE II.

Ethyl oxide, C_4H_{10}. M. wt. 74.							Pentane, C_5H_{12}. M. wt. 72.						
T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.	T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	·7362	$\cdot 0_3 8270$	86·16	159·0	1486	1·73	273	·6454	$\cdot 0_3 7756$	85·85	206·5	1914	1·70
293	·7135	·001870	80·40	158·0	1486	1·72	313	·6062	·00339	75·55	205·6	1918	1·69
313	·6894	·003731	75·36	158·2	1489	1·72	333	·5850	·006024	71·66	209·3	1933	1·71
333	·6658	·006771	70·79	159·7	1497	1·73	353	·5624	·01013	66·84	211·3	1947	1·71
353	·6402	·01155	65·85	160·7	1502	1·73	373	·5378	·01627	61·51	212·7	1959	1·71
373	·6105	·01867	60·33	161·9	1537	1·75	393	·5107	·02503	56·33	215·9	1973	1·73
393	·5764	·02934	54·91	165·3	1530	1·75	413	·4787	·03861	49·08	215·6	1984	1·72
413	·5385	·04488	48·31	167·8	1547	1·76	433	·4394	·05910	40·89	215·6	1988	1·71
433	·4947	·06911	39·74	165·6	1496	1·79	453	·3867	·09354	30·02	213·4	1986	1·70
453	·4268	·1135	27·09	160·0	1539	1·68	463	·3445	·1269	21·11	205·8	1957	1·66
460	·3663	·1620	18·11	167·7	1510	1·90	468	·3065	·1609	13·38	196·8	1931	1·61
466	·3300	·2012	12·03	175·9	1464		469	·2915	·1745	10·55	193·5	1918	1·59
Stannic chloride, $SnCl_4$. M. wt. 260·8.							Octane, C_8H_{18}. M. wt. 114.						
373	2·0186	·005764	28·68	70·37	233·9	1·73	273	·7185	$\cdot 0_4 1942$	84·71	181·3	2415	1·70
393	1·9639	·00994	27·22	70·50	235·3	1·72	393	·6168	·0033	64·03	183·6	2347	1·79
413	1·9073	·01616	25·67	70·57	236·9	1·71	413	·5973	·005464	61·13	182·1	2360	1·81
433	1·8481	·02506	24·00	70·28	237·9	1·70	433	·5772	·008584	58·24	181·0	2375	1·84
453	1·7873	·03759	22·08	69·13	239·3	1·66	453	·5556	·01314	54·43	178·3	2385	1·85
473	1·7224	·05450	20·23	68·23	240·9	1·63	473	·5317	·01957	50·44	176·3	2390	1·86
493	1·6488	·07728	18·28	67·23	243·7	1·59	493	·5053	·02874	45·90	175·1	2419	1·87
513	1·5667	·1083	16·18	66·19	242·2	1·55	513	·4732	·04237	40·37	171·4	2424	1·88
533	1·4747	·1520	13·88	64·59	238·7	1·52	533	·4364	·06223	34·25	168·5	2418	1·90
553	1·3628	·2160	11·27	60·80	221·2	1·45	553	·3818	·09833	24·67	164·2	2395	1·89
Ethyl propionate, $C_5H_{10}O_2$. M. wt. 102.							Sulphur dioxide, SO_2. M. wt. 64.						
273	·9142	$\cdot 0_4 4850$	91·03	108·9	1396	1·74	263	1·460	·002964	86·56	44·19	359·1	1·73
383	·7823	·004739	70·17	114·7	1391	1·84	283	1·410	·0068	78·46	39·47	329·8	1·68
403	·7548	·008000	65·58	115·0	1396	1·84	303	1·353	·0134	73·32	40·05	333·3	1·69
433	·7115	·01615	58·09	114·8	1406	1·82	323	1·296	·0250	65·12	38·76	329·6	1·65
453	·6795	·02469	53·10	115·0	1413	1·82	343	1·233	·0396	62·75	41·29	337·0	1·72
473	·6443	·03676	48·24	116·5	1422	1·83	363	1·158	·0608	58·38	43·66	347·4	1·76
493	·6027	·05435	42·63	118·3	1430	1·85	383	1·070	·0995	48·43	42·67	348·1	1·74
513	·5501	·08230	35·17	118·9	1431	1·86	403	·960	·191	39·46	44·06	348·9	1·82
533	·4744	·1337	24·19	116·3	1415	1·84	418	·827	·254	28·57	46·19	346·5	1·87
541	·4227	·1751	16·83	113·8	1401	1·81	428	·650	·420	11·26	45·72	329·9	1·94

Table II. (*continued*).

Benzene; C_6H_6. M. wt. 78.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	·9041	$\cdot 0_3 1215$	100·1	123·6	1305	1·63
353	·8145	·002722	85·62	129·0	1317	1·68
373	·7927	·004690	81·98	133·6	1322	1·69
393	·7692	·007634	78·12	132·0	1330	1·70
413	·7440	·01174	74·09	133·9	1345	1·71
433	·7185	·01734	69·74	135·1	1356	1·71
453	·6906	·02487	65·12	136·6	1372	1·71
473	·6605	·03546	59·95	137·5	1377	1·71
493	·6255	·05015	53·84	138·8	1393	1·71
513	·5851	·07138	46·63	138·2	1390	1·71
533	·5328	·1038	37·49	137·3	1387	1·70
553	·4514	·1660	23·45	135·6	1392	1·67

Heptane, C_6H_{16}. M. wt. 100.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	·7005	$\cdot 0_4 6725$	84·44	172·1	2236	1·69
353	·6311	·001996	72·74	186·0	2216	1·81
373	·6124	·003584	68 95	183·8	2220	1·81
393	·5926	·006068	64·67	184 2	2228	1·81
413	·5711	·009775	60·07	184·2	2238	1·80
433	·5481	·01508	55·69	185·4	2250	1·81
453	·5232	·02242	51·62	188·6	2271	1·82
473	·4952	·03304	46·63	190·1	2269	1·84
493	·4616	·04892	40·57	192·6	2281	1·85
513	·4177	·07446	32·60	193·0	2279	1·86
533	·3457	·1287	19·02	184·9	2223	1 82
539	·2907	·1778	9·25	175·2	2177	1·76

N. Hexane, C_6H_{18}. M. wt. 86.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	·6770	$\cdot 0_3 2268$	84·68	184·8	2069	1·68
343	·6122	·00337	71·81	191·6	2067	1·75
363	·5918	·00585	67 91	193·9	2078	1·76
383	·5703	·00952	64·01	196·8	2094	1·77
403	·5467	·01502	59·10	197·7	2104	1·77
423	·5207	·02299	53·61	197·7	2114	1·76
443	·4913	·03472	47·41	197·3	2122	1·75
463	·4570	·05155	40·91	198·5	2128	1·76
483	·4124	·07900	32·20	196·6	2116	1·75
499	·3557	·1203	21·33	190·2	2095	1·71
506	·3040	·1658	11·76	180·9	2050	1·66

Carbon tetrachloride, CCl_4. M. wt. 154.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	1·6327	$\cdot 0_3 2984$	48·35	18·12	436·5	1·40
373	1·4343	·01026	39·68	19·31	389·1	1·67
393	1·3902	·01634	37·63	19 47	392·6	1·67
413	1·3450	·02481	35·56	19·65	395·9	1·67
433	1·2982	·03650	33·28	19·73	398 4	1·67
453	1·2470	·05249	30·83	20 00	400·2	1·66
473	1·1888	·07418	28·22	20·01	404·2	1·67
493	1·1227	·1040	25·35	20·28	407·1	1·68
513	1·0444	·1464	21·91	20·54	410·3	1 69
533	·9409	·2146	17·15	20·44	407·8	1 69
553	·7634	·3597	8 90	19·63	398·6	1·66

Iodobenzene, C_6H_5I. M. wt. 203·9.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
403	1·8149	$\cdot 0_4 1595$	53·75	16·31	464·9	1·57
503	1·7079	$\cdot 0_3 4400$	50 06	17·19	459·7	1·66
563	1·5627	·006020	40·97	16·78	457·6	1·64
583	1·5316	·008889	40·72	17·35	460·3	1·68
603	1·4941	·01296	39·72	17·79	464·6	1·71
623	1·4581	·01849	38·59	18·15	466·8	1·74
643	1·4172	·02605	37·29	18·58	469·6	1·73

Bromobenzene, C_6H_5Br. M. wt. 157.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
403	1·4815	$\cdot 0_4 4702$	64 84	29·51	620·4	1·64
533	1·2994	·005255	49·62	29·40	613·9	1·65
553	1·2697	·008071	48·51	30·07	617·0	1·67
573	1·2385	·01205	46·85	30·53	620·1	1·69
593	1·2037	·01750	44·93	30·99	625·2	1·70
613	1·1689	·02482	42·80	31·30	627·7	1·72
633	1·1310	·03427	40·82	31·91	622·7	1·73

Di-isobutyl, C_8H_{18}. M. wt. 114.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	·7102	$\cdot 0_4 4762$	76·24	151·1	2259	1·67
373	·6236	·002967	63·05	162·1	2227	1·82
393	·6046	·005236	57·63	157·7	2220	1·78
413	·5841	·008532	53·65	157·2	2222	1 77
433	·5620	·01319	50·11	158·4	2236	1·77
453	·5383	·01957	46·90	161·9	2250	1·80
473	·5117	·02874	42·91	163·9	2260	1·81
493	·4810	·04202	38·32	166·9	2275	1·83
513	·4434	·06223	32·59	169·0	2270	1·86
533	·3912	·09699	24·31	169·2	2247	1·88
547	·3187	·1572	12·39	161·7	2183	1·85

Ethyl acetate, $C_4H_8O_2$. M. wt. 88.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	·9244	$\cdot 0_3 1255$	94·45	110·5	1235	1·72
363	·8112	·004673	76·47	119·0	1234	1·81
383	·7831	·008000	72·19	117·7	1243	1·82
403	·7533	·01312	66 93	118·0	1248	1·82
423	·7210	·02062	61 66	118·7	1256	1·82
443	·6848	·03165	55·71	118·8	1261	1·82
463	·6441	·04751	49·48	119·9	1270	1·82
483	·5944	·07128	42 08	120·8	1277	1·82
503	·5281	·1131	31·32	117·7	1265	1·80
518	·4401	·1802	18·00	111·7	1233	1·75
522	·3893	·2288	10·41	95·3	1104	1·66

Table II. (*continued*).

Fluor-benzene, C_6H_5Fl. M. wt 96·1.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	1·0465	·0$_3$1179	81·74	74·57	983·5	1·60
353	·9496	·002885	72 96	80·89	985·1	1·73
373	·9233	·005040	69·71	81·79	990·4	1·74
393	·8955	·008333	65·68	81·96	995·6	1·73
413	·8665	·01321	60·97	81·19	999·3	1·71
433	·8363	·01992	56·86	81·28	1·005	1·70
453	·8037	·02911	52·69	81·56	1·010	1·70
473	·7671	·04184	48·13	82·02	1·017	1·70
493	·7265	·05907	43·57	83·02	1·024	1·71
513	·6789	·08403	38·00	83·71	1·025	1·72
533	·6163	·1226	30·75	84·28	1·024	1·73
553	·5133	·2034	18·00	81·04	1·001	1·70

Hexamethylene, C_6H_{12}. M. wt. 84·1.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	·7967	·0$_3$1374	89·77	141·5	1618	1·61
363	·7106	·003759	77·81	154·0	1636	1·74
383	·6898	·006289	72·75	152·9	1642	1·71
403	·6680	·01000	67·52	151·3	1649	1·69
423	·6448	·01508	63·03	151·6	1660	1·68
443	·6200	·02183	59·12	153·8	1674	1·69
463	·5926	·03140	53·98	153·6	1683	1·68
483	·5626	·04437	48·80	154·2	1699	1·69
503	·5271	·06250	42·97	156·9	1700	1·70
523	·4820	·09058	35·15	156·9	1690	1·70
543	·4125	·1433	22·85	152·7	1670	1·68
552	·3393	·2105	10·07	142 0	1614	1·62

Methyl formate, $C_2H_4O_2$. M. wt. 60.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	1·0032	·0$_3$6821	113·2	112·6	860·0	1·72
303	·9598	·002225	107·5	116·7	866·6	1·77
323	·9294	·004396	99·51	115·2	869·4	1·74
343	·8968	·007968	92·16	114·7	874·8	1·72
363	·8634	·01352	85·10	114·1	879·0	1·71
383	·8264	·02153	79·21	116·0	888·4	1·71
403	·7860	·03344	71·95	116·6	895·2	1·71
423	·7403	·05063	64·03	117·4	903·6	1·71
443	·6844	·07634	54·41	117·6	912·0	1·70
463	·6148	·1178	41·93	115·2	912·4	1·66
483	·4857	·2188	19·58	104·2	890·0	1·71

Carbon dioxide, CO_2. M. wt. 44.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
243	1·045	·0340	65·34	50·95	335·0	1·74
263	·956	·0725	54·45	58·15	323·8	1·78
283	·846	·135	40·56	59·84	323·4	1·73
298	·705	·253	22·07	60·56	308·5	1·65

Chlorobenzene, C_6H_5Cl. M. wt. 157.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	1·1278	·0$_4$1689	82·90	65·19	1036	1·55
413	·9723	·004316	66·48	70·33	1028	1·68
433	·9480	·006761	64·12	71·36	1035	1·70
453	·9224	·01020	61·46	72·24	1041	1·71
473	·8955	·01500	58·31	72·74	1048	1·71
493	·8672	·02145	55·29	73·52	1053	1·72
513	·8356	·03000	52·43	75·08	1062	1·74
533	·8016	·0417	49·09	76·42	1090	1·75

Chloroform, $CHCl_3$. M. wt. 119·5.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	1·5264	·0$_3$4027	62·45	26·93	415·5	1·35
293	1·4885	·001042	60·14	27·11	416·8	1·70
313	1·4503	·002248	57·87	27·52	418·2	1·72
333	1·4108	·004356	55·60	27·94	419·9	1·74

Acetone, C_3H_6O. M. wt. 58.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	·8186	·0$_3$2339	131·8	196·6	1437	1·73
293	·7960	·0$_3$5688	127·2	200·7	1455	1·75
313	·7731	·001215	121·4	203·1	1469	1·75
333	·7497	·002372	117·2	208·5	1481	1·79

Ethyl formate, $C_3H_6O_2$. M. wt. 74.

T.	ρ_1.	ρ_2.	L.	$\frac{L}{\rho_1^2-\rho_2^2}$	E.	K_4.
273	·9480	·0$_3$3152	99·50	110·8	1056	1·70
333	·8689	·003356	87·56	116·0	1064	1·76
353	·8409	·006061	82·54	116·7	1069	1·77
373	·8112	·01031	76·83	116·8	1075	1·76
393	·7796	·01656	71·33	117·4	1082	1·76
413	·7448	·02558	65·63	118·2	1090	1·76
433	·7058	·03876	58·80	118·0	1095	1·75
453	·6610	·05747	51·64	118·1	1100	1·74
473	·6066	·08621	42·54	118·0	1112	1·72
493	·5290	·1379	29·59	113·4	1104	1·66
503	·4635	·1890	19·51	100·1	1028	1·62
507	·4117	·2353	11·89	104·3	1082	1·57

The third column of Table III. contains the mean value of $\frac{L}{\rho_1^2-\rho_2^2}$ of each liquid contained in Table II. According to equation (9) this quantity is equal to

$$\frac{U}{m^{7/3}\rho_c^{2/3}}(\Sigma\sqrt{m_1})^2.$$

TABLE III.

Name of Liquid.	ρ_c.	$\frac{L}{\rho_1{}^2-\rho_2{}^2}$.	$\frac{2073(\Sigma\sqrt{m})^2}{m^{7/3}\rho_c^{2/4}}$.	E.	$\frac{258{\cdot}8(\Sigma\sqrt{m_1})^2}{m^{4/3}\rho_c^{2/3}}$.
Chlorobenzene	·3654	71·49	66·83	1049	938·7
Pentane	·2323	209·4	217·7	1951	1960
Heptane..................	·2341	185·0	158·6	2246	1982
Stannic chloride	·7419	6·779	7·009	237·0	228·2
Hexane	·2344	193·3	178·7	2094	1923
Ethyl oxide	·2604	163·3	171·3	1507	1582
Benzene..................	·3045	134·3	126·3	1357	1228
Iodo-benzene............	·5814	17·45	16·67	463·4	424·4
Hexamethylene	·2735	151·8	191·8	1661	2014
Carbon dioxide.........	·464	57·37	66·43	322·7	365·1
Octane	·2327	176·2	165·5	2393	2358
Ethyl propionate	·286	115·3	122·5	1410	1559
Carbon tetrachloride.	·5576	19·74	17·95	403·7	344·9
Ethyl acetate	·2993	115·3	119·8	1239	1308
Di-isobutyl	·2366	161·7	179·1	2247	2552
Fluor-benzene	·3541	81·44	82·30	1001	987·4
Bromobenzene	·4853	30·53	30·39	621·0	595·7
Methyl formate	·3489	115·4	106·3	893·9	796·2
Ethyl formate	·315	113·9	115·8	1092	1069

The values of the latter quantity were calculated, and are given in the fourth column of the table, U being put equal to 2073. The value of U is the mean of the values obtained by equation (9) for the liquids. The agreement between the two sets of values is fairly good, and equation (9) may therefore be used to obtain the approximate internal latent heat of evaporation of a liquid at any given temperature.

The values of $\frac{L}{\rho_1^2-\rho_2^2}$ for a large number of liquids have a tendency to increase slightly with the temperature. It was therefore thought desirable to test the expression using a different power of ρ than 2, preferably less than 2. The values of $\frac{L}{\rho_1^{5/3}-\rho_2^{5/3}}$ have therefore been calculated for carbon tetrachloride and ethyl propionate, and are contained together with the values of $\frac{L}{\rho_1^2-\rho_2^2}$ in Table IV. It will be seen that

TABLE IV.

Carbon tetrachloride.											
$\frac{L}{\rho_1^2-\rho_2^2}$ ...	18·12	19·31	19·47	19·65	19·73	20·00	20·01	20·28	20·54	20·4	19·63
$\frac{L}{\rho_1^{5/3}-\rho_2^{5/3}}$ ...	21·34	21·77	21·74	21·69	21·53	21·31	21·31	21·30	21·23	20·77	19·54
Ethyl propionate.											
$\frac{L}{\rho_1^2-\rho_2^2}$ ...	108·9	114·7	115·0	114·8	115·0	116·5	118·3	118·9	116·8	113·8	
$\frac{L}{\rho_1^{5/3}-\rho_2^{5/3}}$ ...	114·1	105·6	104·8	102·4	101·1	101·3	100·2	99·4	95·4	89·9	

the values of the former expression are more constant than those of the latter for carbon tetrachloride, but the opposite is the case with ethyl propionate. The equation for the latent heat according to the former expression is

$$L=U_1\{\rho_1^{5/3}-\rho_2^{5/3}\}\frac{(\Sigma\sqrt{m_1})^2}{m^{7/3}\,\rho_c^{1/3}}.$$

It appears therefore that in some cases this equation will be in better agreement with the facts than equation (9), while in other cases equation (9) will be in better agreement.

Since $P_n=L/\rho$, we may now write

$$P_n=42\times 2073\,\frac{\rho^3}{m^{7/3}}(\Sigma\sqrt{m_1})^2,$$

and the equation of state becomes

$$p+87066\,\frac{\rho^3}{m^{7/3}\rho_c^{2/3}}(\Sigma\sqrt{m_1})^2=\frac{RT\rho}{m(1-b\rho)}, \quad . \quad . \quad (10)$$

taking b first of all as constant. From the equations expressing the conditions for equal roots we have

$$p_c = \frac{87066}{2}\left(\frac{\rho_c}{m}\right)^{7/3}(\Sigma\sqrt{m_1})^2 \quad \text{and} \quad p_c = \frac{\mathrm{R}T\rho_c}{m1\cdot5}.$$

These two equations, we see, are of the required form but the numerical constants have not the proper value. We will therefore, as before, assume $b=(n-n_2\rho)$. From the equations of condition for equal roots we then have that if we put

$$n_1 = \frac{u_1}{\rho_c}, \text{ and } n_2 = \frac{u_2}{\rho_c^2},$$

we obtain two equations of the above form connecting the critical constants; and if we further put $u_1 = \cdot06$ and $u_2 = \cdot602$ the numerical constants in the equations will have the proper value. The above equation of state and the one given previously will be further discussed later in this paper and in subsequent papers. It may be noticed here that

$$\frac{1}{\rho_c}\left(\cdot602 - \frac{\rho}{\rho_c}\cdot06\right),$$

the expression obtained for b, is of the same form as the value obtained previously, viz.:

$$\frac{1}{\rho_c}\left(\cdot734 - \frac{\rho}{\rho_c}\cdot176\right).$$

The reason that the part *b c d* of the curve in the figure is not realized in practice does not seem to have yet been made quite clear. It is intimately connected with the property of a liquid and vapour to be able to exist in equilibrium side by side ; in fact, it appears that in all cases where two portions of matter of different densities can be in equilibrium in contact with one another, the states corresponding to the intermediate densities cannot be realized in practice. According to the equation of condition of a molecule in the liquid or gaseous state, it follows that if each molecule is in the same condition, two portions of matter of different densities cannot exist in equilibrium in contact with one another. The matter of less density would condense upon that of the greater density. Therefore, since a vapour can exist in contact with the liquid, the molecules must differ from one another in some way. The explanation is that the molecules differ from one another in their velocity of translation; further, the velocity of each molecule is continually changing, the distribution of velocities among the molecules at any instant being given by Maxwell's law or some law similar to it. A certain number of molecules will therefore each second obtain sufficient kinetic energy to be able to get away from the attraction of the molecules of the liquid, equilibrium being produced when the number shot out of the liquid is equal to the number returning from the vapour. When the volume of the vapour is decreased by compression its density must remain the same, for the number of molecules shot from the surface of the liquid per cm.^{2} is unaltered by the process, and therefore the number coming from the vapour must also remain unaltered, and a portion of the vapour must therefore condense to keep the density constant.

Now, suppose a cylinder which has one end closed and in which a piston works contains some saturated vapour of a liquid, and suppose we endeavour by moving the piston to pass the vapour through those changes usually not realized in practice. From a consideration of the law of attraction of one molecule on another and the average density of rigid materials, it follows that the attraction of the material of the cylinder on the vapour will be very nearly equal to that of the liquid corresponding to the vapour. The surface of the cylinder will therefore be covered with a thin layer of vapour which will be nearly as dense as the liquid. A small increase of pressure only will therefore in general be required to increase the density of this thin film, so that it is equal to that of the liquid. When that stage is reached, condensation of the vapour upon this liquid film takes place, and its pressure then decreases till it is equal to that of the ordinary pressure of the vapour in contact with the liquid. The pressure remains constant on the volume of the vapour being further decreased, and the vapour thus does not pass through the relations between pressure and volume indicated by theory. It appears, therefore, that if it were possible to construct the cylinder out of material which has no molecular attraction, the vapour could be passed without difficulty through all the isothermal changes indicated by theory.

From the equations of state given in this paper we can deduce some relations of interest and importance. Referring to the figure, it follows from thermodynamics[*] that the amount of external work done in passing along the isothermal from b to d is equal to the work done in passing from b to d

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[*] Winckelmann, *Handbuch der Physik, Wärme*, p. 654, second edition.

along the straight line. This well known condition is expressed by the equation

$$\int_{v_2}^{v_1} p \, . \, dv = p(v_1 - v_2).$$

Substituting for p on the left-hand side of the equation from equation (10) and integrating, we obtain an equation which may be written

$$\frac{\mathrm{P}}{2}(\rho_1^2 - \rho_2^2) - \frac{\mathrm{RT}}{m} \log \frac{\rho_1}{\rho_2} + h = p(v_2 - v_1),$$

where h is a positive quantity much smaller in magnitude than the term which precedes it, and

$$\mathrm{P} = \frac{87066}{\rho_c^{2/3} m^{7/3}} (\Sigma\sqrt{m_1})^2.$$

Now $\mathrm{P}(\rho_1^2 - \rho_2^2)$ is the internal heat of evaporation per gram of substance and $p(v_2 - v_1)$ the external work done during evaporation, and the latter quantity is therefore much smaller than the former. The quantity $(p(v_2 - v_1) - h)$ is therefore probably very small in comparison with the first term in the equation, and the first two terms therefore of the same magnitude. We may therefore suppose

$$\frac{x\mathrm{P}}{2}(\rho_1^2 - \rho_2^2) + p(v_2 - v_1) - h = 0$$

in the equation, where x is a very small fraction which is taken as constant, and we therefore have

$$\mathrm{E}(\rho_1^2 - \rho_2^2) = \mathrm{T} \log \frac{\rho_1}{\rho_2}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where E is a constant. This equation was tested in the case of a number of substances over considerable ranges of temperature. The result is given in the sixth and thirteenth columns of Table II., which contain the values of E calculated by means of this equation. It will be seen that E is remarkably constant for each substance. This equation thus gives very accurately the relation between ρ_1, ρ_2, and T, for different temperatures of a liquid.

The value of E is proportional to $\frac{\mathrm{P}m}{\mathrm{R}}$, and therefore proportional to $\frac{(\Sigma\sqrt{m_1})^2}{m^{4/3}\rho_c^{2/3}}$. The fifth column of Table III.

contains the mean values of E of each liquid in Table II., and the sixth column contains the values of

$$258{\cdot}8\frac{(\Sigma\sqrt{m_1})^2}{m^{4/3}\rho_c^{2/3}}.$$

It will be seen that the two sets of values agree approximately with one another. The constant 258·8 was obtained by dividing the values of E in Table III. by the corresponding values of $\frac{(\Sigma\sqrt{m_1})^2}{m^{4/3}\rho_c^{2/3}}$ and taking the mean of the values obtained.

In the equation expressing the equality of the work done in passing from *b* to *d* in the figure either along the straight or curved part, if we substitute for *p* from equation (6) and integrate we obtain, assuming that the sum of certain terms in the equation is zero, in a similar way as before, that

$$S(\rho_1^{4/3}-\rho_2^{4/3})=T\log\frac{\rho_1}{\rho_2}, \quad . \quad . \quad . \quad . \quad (12)$$

where

$$S=dK_2\frac{(\Sigma\sqrt{m_1})^2}{m^{4/3}},$$

and *d* is a numerical constant. This equation should be in approximate agreement with the facts, since it is simply the left-hand side of equation (11) expressed in a different way. The-left hand sides of both equations (11) and (12) are, according to equations (3) and (9), it will be observed, equal to L*m* multiplied by a numerical constant. K_2 we have seen is a function of the temperature only and is approximately given by $(7222-4422\frac{T}{T_c})$. Its exact form will be investigated in a subsequent paper.

At the critical point the value of E given by equation (11) is an indeterminate fraction, and it will therefore be of interest to determine its limiting value at that point. Let $\rho_2=x\rho_1$ and we have

$$2{\cdot}3E=\frac{T_c}{\rho_c^2}\left[\frac{\log_e\left(\frac{1}{x}\right)}{1-x^2}\right]_{\mathrm{Lt}\ x=1}=\frac{T_c}{\rho_c^2}\left[\frac{1}{2x^2}\right]_{\mathrm{Lt}\ x=1}=\frac{T_c}{\rho_c^2 2},$$

changing in the beginning the logarithm from the base 10 to the base e. Now, E must have the same value at the critical temperature as at lower temperatures. Substituting for E its value

$$258{\cdot}8\,\frac{(\Sigma\sqrt{m_1})^2}{m^{4/3}\rho_c^{2/3}}$$

in the above equation, we have

$$T_c = 1189{\cdot}6\left(\frac{\rho_c}{m}\right)^{4/3}(\Sigma\sqrt{m_1})^2.$$

This relation between T_c, ρ_c, m, and m_1, has already been obtained by the writer in a previous investigation *. The numerical coefficient in the equation obtained in the above way is also of the proper magnitude. Thus the value of the coefficient calculated by means of the equation using the critical data of ether is 1127, which is approximately the same as that given above. Equation (12) also leads to the above equation.

We have seen that each of the left-hand sides of equations (11) and 12 is equal to Lm multiplied by a numerical constant. This gives another formula for the internal heat of evaporation which may be written

$$L = K_4\,\frac{RT}{m}\log\frac{\rho_1}{\rho_2}, \quad \ldots\ldots \quad (13)$$

where K_4 is a numerical constant. If x in the equation

$$\frac{xP}{2}(\rho_1^2-\rho_2^2)+p(v_2-v_1)-h=0$$

is zero, then it follows from the equation from which equation (11) is derived that K_4 is equal to 2. The actual value of K_4 was found to be equal to about 1·75. This is shown by the seventh and fourteenth columns of Table II., which contain values of K_4 calculated by means of equation (13). It will be seen that K_2 is not quite independent of the temperature, it usually increases slightly with the temperature till near the critical point and then decreases again. The constancy of K_4 is further tested in Table V. for several

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* Phil. Mag. Dec. 1909, p. 906; (*a*) pp. 783–787.

TABLE V.

Di-isopropyl.		Isopentane.		Propyl formate.		Methyl propionate.		Propyl acetate.		Methyl butyrate.	
T.	K_4.	T.	K_4.	T.	K_4.	T.	K_4.	T.	K_4.	T.	K_4.
273	1·68	273	1·70	273	1·68	273	1·71	273	1·72	273	1·73
333	1·74	293	1·67	363	1·78	353	1·80	373	1·84	383	1·78
353	1·74	313	1·67	383	1·77	373	1·80	393	1·85	403	1·80
373	1·70	333	1·68	403	1·78	393	1·80	413	1·86	423	1·81
393	1·73	353	1·69	423	1·77	413	1·80	433	1·86	443	1·81
413	1·73	373	1·69	443	1·76	433	1·81	453	1·86	463	1·83
433	1·72	393	1·69	463	1·78	453	1·81	473	1·86	483	1·84
453	1·73	413	1·69	483	1·78	473	1·82	493	1·86	503	1·85
473	1·73	433	1·69	503	1·80	493	1·82	513	1·86	523	1·86
489	1·70	449	1·66	523	1·78	513	1·79	533	1·84	543	1·83
498	1·64	458	1·61	533	1·79	528	1·69	546	1·76	553	1·72

liquids not mentioned in Table II. The values of ρ_1, ρ_2, and L, used in the calculations, are not given in the table: they can be obtained from tables given by Mills, which were quoted previously in this paper. The calculations have been carried out up to a few degrees below the critical temperature. It will be seen by inspection that the mean value of K_4 for each liquid depends slightly on the nature of the liquid.

It should be mentioned here that Jäger, Voigt, and Dieterici [*] have arrived at equations for the internal latent heat which resemble more or less equation (13). These equations were obtained from considerations of the kinetic equilibrium between the molecules shot out of the liquid into the surrounding vapour and the molecules returning from the vapour to the liquid. Dieterici, in the paper mentioned, by making certain assumptions to simplify the result arrives at the same equation as the above. The application of the equation to a few liquids showed that K_4 is equal to about 1·7. A much more comprehensive test of the equation is given in this paper.

Cambridge,
June 2, 1910.

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[*] *Ann. der Phys.* xxv. p. 569 (1908).

LXXIV. *The Scattering of Waves by a Cone. By* Professor H. S. Carslaw, *The University of Sydney, N.S.W.*[*]

In view of the interest at present taken in the question of the scattering of waves by a sphere, the corresponding problems for a cone may have some slight value. Recently I have obtained the expression in series which gives the solution for the cone, but I have not yet been able to reduce my results to a form suitable for numerical discussion. The method which I follow is similar to that of a former paper on Diffraction[†], and is suggested by Dougall's work on Potential[‡]. The proof is hardly suitable for these pages, and I confine myself for the present to a statement of one of the results obtained.

The vertex of the cone is taken as the origin. Its surface is given by $\theta = \theta_0$, and its axis by $\theta = \pi$.

We start with a source at the point on the axis produced, at a distance r' from the vertex. This is the point $(r', 0, 0)$ in spherical coordinates.

The disturbance in the infinite medium due to this source is defined by

$$u_0 = \frac{e^{-i\kappa R}}{R},$$

where $$R^2 = r^2 + r'^2 - 2rr' \cos\theta.$$

This can be written

$$u_0 = \frac{2e^{i\frac{\pi}{4}}}{\sqrt{rr'}} \sum_0^\infty e^{ni\frac{\pi}{2}} (n+\tfrac{1}{2}) K_{n+\frac{1}{2}}(i\kappa r')\, J_{n+\frac{1}{2}}(\kappa r)\, P_n(\mu),$$

for $r < r'$, with the usual notation for the Bessel's Functions[§].

On replacing this series by an equivalent Contour Integral, and associating with it the solution required by the surface condition $u = 0$ at $\theta = \theta_0$, we obtain the following result:—

$$u = -\frac{2\pi}{\sqrt{rr'}} e^{i\frac{\pi}{4}} \sum_n e^{ni\frac{\pi}{2}} K_{n+\frac{1}{2}}(i\kappa r')\, J_{n+\frac{1}{2}}(\kappa r) \frac{P_r(-\mu_0)\, P_n(\mu)}{\sin n\pi \frac{d}{dn} P_n(\mu_0)},$$

for $r < r'$, the summation being for the values of $n > -\frac{1}{2}$ which make $P_n(\mu_0)$ vanish.

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[*] Communicated by the Author.

[†] Phil. Mag. (6) vol. v. (1903).

[‡] Proc. Edinburgh Math. Soc. vol. xviii. (1900).

[§] *Cf.* Macdonald, 'Electric Waves,' p. 91.

A relation between $P_n(-\mu_0)$ and $\frac{d}{d\mu_0}P_n(\mu_0)$ exists in this case, and allows us to put this result in the form

$$u = -\frac{4e^{i\frac{\pi}{4}}}{\sqrt{rr'}}\sum_n e^{ni\frac{\pi}{2}}\,K_{n+\frac{1}{2}}(i\kappa r')\,J_{n+\frac{1}{2}}(\kappa r)\,\frac{P_n(\mu)}{(1-\mu_0^2)\,\frac{d}{dn}P_n(\mu_0)\,\frac{d}{d\mu_0}P_n(\mu_0)}$$

for $r<r'$, the values of n being as above.

The symbols r, r' have to be interchanged when $r>r'$, and if the source were at (r', θ', ϕ') instead of at $(r', 0, 0)$, a corresponding, but more complicated, result would hold.

The problems in conduction of heat analogous to these lend themselves to the same treatment.

Sydney, June 1910.

LXXV. *The Number of α Particles emitted by Uranium and Thorium and by Uranium Minerals. By* Hans Geiger, *Ph.D., and* Professor E. Rutherford, *F.R.S.*[*]

In previous papers we have shown that the number of α particles emitted per second from radioactive materials can be counted either by the electrical or scintillation method. It has been shown that one gram of radium itself, and each of the three α ray products in equilibrium with it, emits $3{\cdot}4\times10^{10}$ α particles per second. Since Rutherford and Boltwood [†] have shown that in an old unaltered mineral there is $3{\cdot}4\times10^{-7}$ gram of radium per gram of uranium, it is possible to deduce the number of α particles emitted per second from one gram of uranium and also from a mineral containing one gram of uranium. In this calculation it is supposed that uranium is the ultimate parent of radium, and that the mineral is in radioactive equilibrium. If a uranium atom, like a radium atom, emits one α particle in its transformation, the number of α particles emitted per second per gram of uranium should be $3{\cdot}4\times10^{10}\times3{\cdot}4\times10^{-7}$, or 11,600. We shall for convenience call this number N.

As a result of a very careful analysis of the radioactive constituents of uranium minerals, Boltwood [‡] has shown that the total activity of uranium, measured by the electric method, is about twice as great as would be expected if

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[*] Communicated by the Authors.

[†] Amer. Journ. Sci. vol. xxii. p. 2 (1906); also Boltwood, Amer. Journ. Sci. vol. xxv. p. 296 (1908).

[‡] Boltwood, Amer. Journ. Sci. vol. xxv. p. 270 (1908).

uranium emits one α particle for one from the radium itself in equilibrium with it. This suggests that the uranium atom in its transformation emits at least two α particles. In the present state of our knowledge it is not certain whether this can be ascribed to the existence of an additional α ray product which is always separated with the uranium, or to the expulsion of two or more α particles in the transformation of the uranium atom.

Supposing, for the purpose of calculation, that the uranium in a mineral emits two α particles for one from each of the subsequent six α ray products, viz. ionium, radium emanation, radium A, radium C, radium F (polonium), the number of α particles emitted per second per gram of uranium in a mineral is 8 N, or four times the number emitted by ordinary purified uranium. In this calculation no account has been taken of the actinium which occurs in all uranium minerals, and which Boltwood has shown stands in a genetic relation with uranium. However, Boltwood (*loc. cit.*) has found that the actinium and its four α ray products contributes an activity to the mineral equal to only ·21 of that of the uranium. The relative number of α particles is still smaller, for the α particles from actinium have an average range of about 5·7 cms. of air, while the α rays of uranium, according to Bragg, have a range of 3·5 cms. Taking as a first approximation that the ionization due to an α particle is proportional to its range, the number of α particles emitted by the actinium in a mineral should be about ·17 of that from uranium. The total number of α particles emitted by a mineral containing one gram of uranium should consequently be $2{\cdot}34\,\mathrm{N} + 6\,\mathrm{N} = 8{\cdot}34\,\mathrm{N}$. Since N by calculation is 11,600, the total number of α particles emitted per second from a mineral containing one gram of uranium should be $9{\cdot}67 \times 10^4$, and the number per second from one gram of ordinary purified uranium should be $2{\cdot}32 \times 10^4$.

It was the object of the present experiments * to determine the number of α particles experimentally, and to test the agreement with the calculated number.

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* The experiments described later were, for the most part, completed more than a year ago. Recently, J. N. Brown (Proc. Roy. Soc. vol. A. lxxxiv. p. 151, 1910) has counted the scintillations from a uranium mineral and found a value per gram of uranium of $7{\cdot}36 \times 10^4$, which is somewhat smaller than our experimental value given later, viz. $9{\cdot}6 \times 10^4$

Arrangement of Experiment.

The scintillation method was adopted in order to count the number of α particles from a known weight of active material. A small quantity of the material under examination was finely powdered in an agate mortar, and then mixed with alcohol or ether and deposited as a thin uniform film on a thin sheet of aluminium or glass. The method adopted was similar to that first used by McCoy. Care was taken that the powder suspended in the liquid was well stirred in order to avoid a separation of the lighter from the denser portions. The weight of the active film was determined by weighing the plate before and after the active material had been removed. It was desirable to use very thin films in order that all the α particles might emerge without much loss of their range. In the case of uranium, however, the number of α particles emitted was so small that they were difficult to count with accuracy. For this reason thicker films were in some cases purposely employed. The efficiency of the zinc sulphide screen was tested by counting the number of α particles emitted from a definite quantity of radium C. The number of scintillations observed was found to be 8 per cent. less than the actual number of α particles incident on the screen. The latter value was calculated from the known result that one gram of radium and each of its products emits $3{\cdot}4 \times 10^{10}$ α particles per second. In the initial experiments the number of scintillations was counted by placing the screen close to the active material. In this case, the number of α particles striking the screen is equal to one half the total number emitted from an area of the active film equal to the area of screen seen in the microscope. This method is open to some objections, for it requires that the film should be very uniformly spread and, in addition, very thin, for otherwise the particles emitted at an oblique angle suffer a considerable loss of range in the active material itself. The lack of uniformity of the film can be corrected for by counting at different points parts of the film, but this involves much labour.

In most of the experiments the active matter was spread in a circular area, and the small zinc sulphide screen was placed parallel to the film and opposite to its centre.

If a = radius of circular film,
d = distance of screen from centre of film,
A = area of screen observed in field of microscope,
σ = total number of particles emitted per second per square centimetre of surface of film,

then, by a simple integration, it can be shown that the number n of α particles incident per second on the area A is given by

$$n = \frac{\sigma A}{2}\left(1 - \frac{d}{\sqrt{a^2+d^2}}\right).$$

A simple example will serve to illustrate the method of calculation. The uranium film No. 1 (see table later) contained 10·43 milligrams of uranium oxide (U_3O_8) spread on an area of 5·9 square cms. 515 scintillations were counted, and the average number of scintillations observed corresponded to 5·16 per minute, and per second ·086. Making the 8 per cent. correction for the imperfection of the screen, the corrected value becomes ·093. This is the value of n to be substituted in the formula.

$A = 3{\cdot}16$ sq. mms. $\quad d = 2{\cdot}06$ cms. $\quad a = 1{\cdot}37$ cms.

Substituting these values in the formula,

$$\sigma = 35{\cdot}0.$$

Now the weight of film per square centimetre was 1·77 mg. U_3O_8, or 1·50 mg. uranium. Consequently, from this experiment, the total number of α particles emitted per second per gram of uranium is $2{\cdot}33 \times 10^4$.

The chief difficulty of the experiments lay in counting accurately a sufficiently large number of scintillations. The number of scintillations observed in the microscope varied from one to five per minute in the case of uranium or thorium. While different observers agreed closely in counting scintillations due to radium or polonium when 30 to 50 scintillations were seen per minute, the agreement was not so good for uranium films. This difference is in part due to the fact that the eye becomes quickly fatigued when only a few scintillations appear on the screen per minute. This was especially marked in counting the scintillations from uranium, which are relatively much fainter than those from radium C. In the case of uranium and thorium minerals, where the scintillations are on the average much brighter than those from uranium, the counting was relatively easy. The brightness of scintillations of course depends on the range of the α particle striking the screen. We shall see later that the range of the α particle, and consequently the intensity of the scintillations from uranium, is less than from any other radioactive substance.

The active materials used in these investigations were kindly presented to us by Professor Boltwood, and were fractions of larger quantities analysed by him. We desire to express our indebtedness to Professor Boltwood for the use of these materials.

(1) Uranic-uranose oxide (U_3O_8) prepared from uranium nitrate which had been crystallized fifteen times. The least soluble fraction was taken and ignited at a high heat in a current of oxygen.

(2) Uraninite—a selected sample from Joachimsthal. This contained 61·7 per cent. of uranium. The mineral, when finely powdered, lost 6·2 per cent. of its emanation. The sample employed had been finely ground for several years, and during this time the emanation had steadily escaped. Under these conditions it can be simply deduced that the emission of α particles from the mineral is about three per cent. less than if the mineral had retained all its emanation. A correction of this amount has consequently been made to the counted number of α particles.

(3) Thorium oxide prepared from thorite. This was tested five weeks after its chemical separation. Since, in the chemical process of purification, the mesothorium is removed from the thorium, the α-ray activity of the purified thorium decays with time due to the decay of its product radiothorium. Since the half period of decay of the latter is about 737 days, a positive correction of about two per cent. is necessary to give the correct number of α particles emitted from thorium oxide in radioactive equilibrium. The activity of the thorium oxide in the form of a thin film was compared with that of a film of the mineral thorite of known composition, and gave nearly the ratio to be expected from their relative content of thorium.

The results of the observations are included in the following Table (p. 696).

Since only about 900 scintillations were counted altogether, the agreement between the three uranium films is closer than could be expected, considering the possible errors in the experiment. In the case of the mineral films 2000 scintillations were counted in all, and about an equal number for the thorium films. Before and after each set of observations the screen was carefully tested to determine the number of scintillations observed when the active material was removed. The correction for the screen employed was small, and usually corresponded to one scintillation in three or four minutes. All the counting experiments were checked among themselves by measuring the activity of the films in an α-ray electroscope. The activity measured in this way was found to be proportional to the weight of the film for thin films, but for the thicker films the activity was relatively smaller on account of absorption.

Radioactive Substances.	Number of α particles emitted per second per gram of Uranium or Thorium.	
Uranium film No. 1. 10·43 mgrs. U_3O_8 on area 5·9 cm.^{2}	$2\cdot33\times10^4$	Average $2\cdot37\times10^4$
Uranium film No. 2. 2·85 mgrs. U_3O_8 on area 12·8 cm.^{2}	$2\cdot36\times10^4$	
Uranium film No. 3. 3·04 mgrs. U_3O_8 on area 14·9 cm.^{2}	$2\cdot43\times10^4$	
Mineral film No. 1. 10·95 mgrs. Uraninite. (Joachimstahl) on area 5·9 cm.^{2}	$9\cdot5\times10^4$	Average $9\cdot6\times10^4$
Mineral film No. 2. 12·73 mgrs. Uraninite. (Joachimstahl) on area 5·9 cm.^{2}	$9\cdot7\times10^4$	
Thorium film No. 1. 4·43 mgrs. ThO_2 on 6·1 cm.^{2}	$2\cdot55\times10^4$	Average $2\cdot7\times10^4$
Thorium film No. 2. 1·21 mgrs. ThO_2 on 6·4 cm.^{2}	$2\cdot84\times10^4$	
Thorium film No. 3. 3·58 mgrs. ThO_2 on 6·15 cm.^{2}	$2\cdot65\times10^4$	

It will be seen that there is a good agreement between the experiments and the numbers calculated on the assumption considered in the beginning of this paper. This is brought out by the Table below.

	Number of *a* particles per gram of Uranium per second. Calculated.	Observed.
Uranium	$2\cdot32\times10^4$	$2\cdot37\times10^4$
Uranium mineral	$9\cdot67\times10^4$	$9\cdot6\times10^4$
Thorium, number of α particles per gram :		$2\cdot7\times10^4$

No doubt the agreement is closer than would be expected under the conditions of the experiments.

The agreement between theory and experiment confirms in another way the correctness of Boltwood's conclusion that uranium emits two α particles for one from each of its later products. The experiments are not of sufficient accuracy to confirm the data on the relative activity of actinium and radium. There is no doubt, however, that the number of α particles to be ascribed to actinium is very small compared with that to be expected if actinium and its series of products emitted one α particle for one from radium. The connexion of actinium with the uranium-radium series is difficult to determine, and remains one of the chief outstanding problems in the analysis of radioactive changes.

Production of Helium by Uranium, Uranium Minerals, and Thorium.

Since the α particle is a charged atom of helium, it is a simple matter to deduce the rate of production of helium from the active materials considered. Calculation and experiment show that one gram of radium in equilibrium with its three α-ray products produces 158 cubic mm. of helium per year. Since radium and each of its products emits $3{\cdot}4 \times 10^{10}$ α particles per gram per second, uranium, which emits $2{\cdot}37 \times 10^{4}$ α particles per gram per second, produces $2{\cdot}75 \times 10^{-5}$ cubic mm. per year. The rate of production of helium for the different materials is given below.

	Production of Helium per gram per year.
Uranium	$2{\cdot}75 \times 10^{-5}$ cubic mm.
Thorium	$3{\cdot}1 \times 10^{-5}$,,
Uranium mineral in equilibrium	$11{\cdot}0 \times 10^{-5}$,,
Radium in equilibrium ...	158 ,,

A simple calculation allows us to estimate the production of helium for a mineral like thorianite containing both uranium and thorium.

Range of the α particles from Uranium.

The range of the α particles from uranium has been difficult to determine directly on account of the smallness of the activity of the thin films of the substance. By observations of the decrease of the ionization due to a layer of uranium when sheets of thin aluminium were placed over it, Bragg * deduced that the range in air of the α particle from uranium was about 3·5 cms. In the course of counting the scintillations from a thin film of ionium, it was observed that

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* Bragg, Phil. Mag. 1906, xi. p. 754.

the scintillations were as bright if not brighter than those from a thin film of uranium. Boltwood has found that the range of the α particle from ionium is 2·8 cms., so that it appeared probable that the range of the α particles from uranium had been overestimated. This conclusion was confirmed by finding that the α rays from a thin film of uranium were more readily absorbed by aluminium than those from ionium. By a special method, the range of the α particle from uranium has been measured and found to be about 2·7 cms., while the range of the α particle from ionium is a millimetre or two longer. Further experiments are in progress to determine the range of the α particle from uranium accurately, and to examine carefully whether two sets of α particles of different range can be detected.

University of Manchester,
July 1910.

LXXVI. *The Probability Variations in the Distribution of α Particles.* *By* Professor E. RUTHERFORD, *F.R.S., and* H. GEIGER, *Ph.D.* *With a Note by* H. BATEMAN [*].

IN counting the α particles emitted from radioactive substances either by the scintillation or electric method, it is observed that, while the average number of particles from a steady source is nearly constant, when a large number is counted, the number appearing in a given short interval is subject to wide fluctuations. These variations are especially noticeable when only a few scintillations appear per minute. For example, during a considerable interval it may happen that no α particle appears; then follows a group of α particles in rapid succession; then an occasional α particle, and so on. It is of importance to settle whether these variations in distribution are in agreement with the laws of probability, *i. e.* whether the distribution of α particles on an average is that to be anticipated if the α particles are expelled at random both in regard to space and time. It might be conceived, for example, that the emission of an α particle might precipitate the disintegration of neighbouring atoms, and so lead to a distribution of α particles at variance with the simple probability law.

The magnitude of the probability variations in the number of α particles was first drawn attention to by E. v. Schweidler [†]. He showed that the average error from the mean number of α particles was $\sqrt{N\,.\,t}$, where N was the number of particles emitted per second and t the interval under consideration. This conclusion has been experimentally verified by several

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[*] Communicated by the Authors.

[†] v. Schweidler, Congrès Internationale de Radiologie, Liège, 1905.

observers, including Kohlrausch [*], Meyer and Regener [†], and H. Geiger [‡], by noticing the fluctuations when the ionization currents due to two sources of α rays were balanced against each other. The results obtained have been shown to be in good agreement with the theoretical predictions of von Schweidler.

The development of the scintillation method of counting α particles by Regener, and of the electric method by Rutherford and Geiger, has afforded a more direct method of testing the probability variations. Examples of the distribution of α particles in time have been given by Regener [§] and also by Rutherford and Geiger [‖]. It was the intention of the authors initially to determine the distribution of α particles in time by the electric method, using a string electrometer of quick period as the detecting instrument. Experiments were made in this direction, and photographs of the throws of the instrument were readily obtained on a revolving film; but it was found to be a long and tedious matter to obtain records of the large number of α particles required. It was considered simpler, if not quite so accurate, to count the α particles by the scintillation method.

Experimental Arrangement.

The source of radiation was a small disk coated with polonium, which was placed inside an exhausted tube, closed at one end by a zinc sulphide screen. The scintillations were counted in the usual way by means of a microscope on an area of about one sq. mm. of screen. During the time of counting (5 days), in order to correct for the decay, the polonium was moved daily closer to the screen in order that the average number of α particles impinging on the screen should be nearly constant. The scintillations were recorded on a chronograph tape by closing an electric circuit by hand at the instant of each scintillation. Time-marks at intervals of one half-minute were also automatically recorded on the same tape.

After the eye was rested, scintillations were counted from 3 to 5 minutes. The motor running the tape was then stopped and the eye rested for several minutes; then another interval of counting, and so on. It was found possible to count 2000 scintillations a day, and in all 10,000 were recorded. The records on the tape were then systematically

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[*] Kohlrausch, *Wiener Akad.* cxv. p. 673 (1906).

[†] Meyer and Regener, *Ann. d. Phys.* xxv. p. 757 (1907).

[‡] Geiger, Phil. Mag. xv. p. 539 (1908).

[§] Regener, *Verh. d. D. Phys. Ges.* x. p. 78 (1908); *Sitz. Ber. d. K. Preuss. Akad. Wiss.* xxxviii. p. 948 (1909).

[‖] Rutherford and Geiger, Proc. Roy. Soc. A. lxxxi. p. 141 (1908).

examined. The length of tape corresponding to half-minute marks was subdivided into four equal parts by means of a celluloid film marked with five parallel lines at equal distances. By slanting the film at different angles, the outside lines were made to pass through the time-marks, and the number of scintillations between the lines corresponding to 1/8 minute intervals were counted through the film. By this method correction was made for slow variations in the speed of the motor during the long interval required by the observations.

In an experiment of this kind the probability variations are independent of the imperfections of the zinc sulphide screen. The main source of error is the possibility of missing some of the scintillations. The following example is an illustration of the result obtained. The numbers, given in the horizontal lines, correspond to the number of scintillations for successive intervals of 7·5 seconds.

									Total per minute.
1st minute :	3	7	4	4	2	3	2	0	25
2nd ,,	5	2	5	4	3	5	4	2	30
3rd ,,	5	4	1	3	3	1	5	2	24
4th ,,	8	2	2	2	3	4	2	6	31
5th ,,	7	4	2	6	4	5	10	4	42

Average for 5 minutes ... 30·4

True average .... 31·0

The length of tape was about 14 cms. for one minute interval. The average number of particles deduced from counting 10,000 scintillations was 31·0 per minute. It will be seen that for the 1/8 minute intervals the number of scintillations varied between 0 and 10 ; for one minute intervals between 25 and 42.

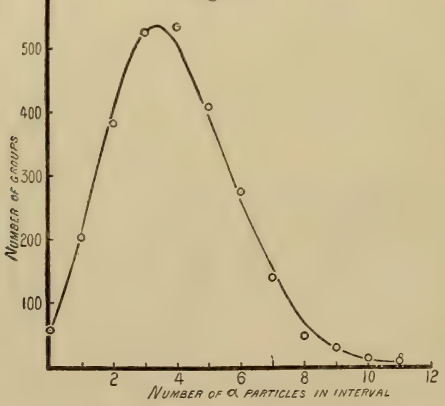
The distribution of α particles according to the law of probability was kindly worked out for us by Mr. Bateman. The mathematical theory is appended as a note to this paper. Mr. Bateman has shown that if x be the true average number of particles for any given interval falling on the screen from a constant source, the probability that n α particles are observed in the same interval is given by $\frac{x^n}{n!}e^{-x}$. n is here a whole number, which may have all positive values from 0 to ∞. The value of x is determined by counting a large number of scintillations and dividing by the number of intervals involved. The probability for n α particles in the given interval can then at once be calculated from the theory. The following table contains the results of an examination of the groups of α particles occurring in 1/8 minute interval.

Number of α particles.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Number of α particles.	Number of intervals.	Average number.
I.	15	56	106	152	170	122	88	50	17	12	3	0	0	1	0	3179	792	4·01
II.	17	39	88	116	120	98	63	37	4	9	4	1	0	0	0	2334	596	3·92
III.	15	56	97	139	118	96	60	26	18	3	3	1	0	0	0	2373	632	3·75
IV.	10	52	92	118	124	92	62	26	6	3	0	2	0	0	1	2211	588	3·76
Sum	57	203	383	525	532	408	273	139	45	27	10	4	0	1	1	10097	2608	3·87
Theoretical values.	54	210	407	525	508	394	254	140	68	29	11	4	1	4	1			

For convenience the tape was measured up in four parts, the results of which are given separately in horizontal columns I. to IV.

For example (see column I.), out of 792 intervals of 1/8 minute, in which 3179 α particles were counted, the number of intervals giving 3 α particles was 152. Combining the four columns, it is seen that out of 2608 intervals containing 10,097 particles, the number of times that 3 α particles were observed was 525. The number calculated from the equation was the same, viz. 525. It will be seen that, on the whole, theory and experiment are in excellent accord. The difference is most marked for four α particles, where the observed number is nearly 5 per cent. larger than the theoretical. The number of α particles counted was far too small to fix with certainty the number of groups to be expected for a large value of n, where the probability of the occurrence is very small. It will be observed that the agreement between theory and experiment is good even for 10 and 11 particles, where the probability of the occurrence of the latter number in an interval is less than 1 part in 600. The closeness of the agreement is no doubt accidental. The relation between theory and experiment is shown in fig. 1 for the results given in Table I., where the o represent observed points and the broken line the theoretical curve.

Fig. 1.



The results have also been analysed for 1/4 minute intervals. This has been done in two ways, which give two different sets of numbers. For example, let A, B, C, D, E represent the number of α particles observed in successive 1/8 minute intervals. One set of results, given in Table A, is obtained by adding A + B, C + D, &c.; the other set, given in Table B,

TABLE A.

Number of particles.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	Whole number of scintillations.	Whole number of intervals.	Average number in one interval.
I.	0	3	4	7	17	35	42	60	71	49	46	22	19	11	2	5	1	2	0	0	0	0	3182	396	8·04
II.	0	2	3	6	19	33	34	56	32	34	27	24	11	7	5	3	1	1	0	0	0	0	2330	298	7·82
III.	0	0	6	8	25	39	39	51	42	38	26	17	11	6	5	2	1	0	0	0	0	0	2373	316	7·51
IV.	0	1	7	11	14	30	40	47	48	36	27	18	8	4	1	0	1	1	0	0	1	0	2214	294	7·53
Sum	0	6	20	32	75	137	155	214	193	157	126	81	49	28	13	10	4	4	0	0	1	0	10099	1304	7·74

TABLE B.

I.	0	2	4	9	21	35	46	56	68	48	35	30	15	12	6	8	0	0	0	0	1	0	3180	396	8·03
II.	0	1	5	7	21	27	38	46	40	38	28	16	12	9	3	5	0	1	0	1	0	0	2333	298	7·83
III.	0	0	5	12	32	38	32	41	36	50	32	14	11	6	5	1	0	0	0	0	0	1	2371	316	7·50
IV.	0	0	3	18	25	26	35	44	36	37	36	15	6	8	2	0	1	0	2	0	0	0	2210	294	7·52
Sum	0	3	17	46	99	126	151	187	180	173	131	75	44	35	16	14	1	1	2	1	1	1	10094	1304	7·74
Sum of Tables A & B	0	9	37	78	174	263	306	401	373	330	257	156	93	63	29	24	5	5	2	1	2	1	20193	2608	7·74
Theoretical values.	1·1	9	34	88	170	263	339	372	363	312	242	170	110	65	36	19	9	4	1·8	·72	·28	·10			

by starting 1/8 minute later and adding B+C, D+E, &c. The results are given in the appended Tables. In the final horizontal columns are given the sum of the occurrences in Tables A and B and the corresponding theoretical values.

In the cases for 1/4 minute intervals, the agreement between theory and experiment is not so good as in the first experiment with 1/8 minute interval. It is clear that the number of intervals during which particles were counted was not nearly large enough to give the correct average even for the maximum parts of the probability curve, and much less for the initial and final parts of the curve, where the probability of an occurrence is small. However, taking the results as a whole for the 1/8 minute and the 1/4 minute intervals, there is a substantial agreement between theory and experiment, and the errors are not greater than would be anticipated, considering the comparatively small number of intervals over which the α particles were counted. We may consequently conclude that the distribution of α particles in time is in agreement with the laws of probability and that the α particles are emitted at random. As far as the experiments have gone, there is no evidence that the variation in number of α particles from interval to interval is greater than would be expected in a random distribution.

Apart from their bearing on radioactive problems, these results are of interest as an example of a method of testing the laws of probability by observing the variations in quantities involved in a spontaneous material process.

University of Manchester,
July 22nd, 1910.

NOTE.

On the Probability Distribution of α Particles.

By H. BATEMAN.

LET λdt be the chance that an α particle hits the screen in a small interval of time dt. If the intervals of time under consideration are small compared with the time period of the radioactive substance, we may assume that λ is independent of t. Now let $W_n(t)$ denote the chance that n α particles hit the screen in an interval of time t, then the chance that $(n+1)$ particles strike the screen in an interval $t+dt$ is the sum of two chances. In the first place, $n+1$ α particles may strike the screen in the interval t and none in the interval dt. The chance that this may occur is $(1-\lambda dt)W_{n+1}(t)$. Secondly, n α particles may strike the screen in the interval t

and one in the interval dt; the chance that this may occur is $\lambda dt W_n(t)$. Hence

$$W_{n+1}(t+dt) = (1-\lambda dt) W_{n+1}(t) + \lambda dt W_n(t).$$

Proceeding to the limit, we have

$$\frac{dW_{n+1}}{dt} = \lambda(W_n - W_{n+1}).$$

Putting $n=0, 1, 2 \ldots$ in succession we have the system of equations:

$$\frac{dW_0}{dt} = -\lambda W_0,$$

$$\frac{dW_1}{dt} = \lambda(W_0 - W_1),$$

$$\frac{dW_2}{dt} = \lambda(W_1 - W_2),$$

$$\cdots\cdots$$

which are of exactly the same form as those occurring in the theory of radioactive transformations *, except that the time-periods of the transformations would have to be assumed to be all equal.

The equations may be solved by multiplying each of them by $e^{\lambda t}$ and integrating. Since $W_0(0)=1$, $W_n(0)=0$, we have in succession:

$$W_0 = e^{-\lambda t},$$

$$\frac{d}{dt}(W_1 e^{\lambda t}) = \lambda, \qquad \therefore \quad W_1 = \lambda t e^{-\lambda t},$$

$$\frac{d}{dt}(W_2 e^{\lambda t}) = \lambda^2 t, \qquad \therefore \quad W_2 = \frac{(\lambda t)^2}{2!} e^{-\lambda t},$$

and so on. Finally, we get

$$W_n = \frac{(\lambda t)^n}{n!} e^{-\lambda t}.$$

The *average* number of α particles which strike the screen in the interval t is λt. Putting this equal to x, we see that the chance that n α particles strike the screen in this interval is

$$W_n = \frac{x^n}{n!} e^{-x}.$$

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* Rutherford, 'Radioactivity,' 2nd edition, p. 330. The chance that an atom suffers n disintegrations in an interval of time t is equal to the ratio of the amount of the nth product present at the end of the interval to the amount of the primary substance present at the commencement.

The particular case in which $n=0$ has been known for some time (Whitworth's 'Choice and Chance,' 4th ed. Prop. 51).

If we use the above analogy with radioactive transformation, the theorem simply tells us that the amount of primary substance remaining after an interval of time t is $e^{-\lambda t}$ if a unit quantity was present at the commencement.

The *probable* number of α particles striking the screen in the given interval is

$$p=\sum_{n=1}^{\infty} n\mathrm{W}_n = xe^{-x}\sum_{n=1}^{\infty}\frac{x^{n-1}}{(n-1)\,!}=x.$$

The *most probable* number is obtained by finding the maximum value of W_n.

Since $\dfrac{\mathrm{W}_n}{\mathrm{W}_{n-1}}=\dfrac{x}{n}$, this ratio will be greater than 1 so long as $n<x$. Hence if $n \lesseqgtr x$,

$$\mathrm{W}_n \gtreqless \mathrm{W}_{n-1}\,;$$

if $n=x$, $\mathrm{W}_n=\mathrm{W}_{n-1}$. The most probable value of n is therefore the integer next greater than x; if, however, x is an integer, the numbers $x-1$ and x are equally probable, and more probable than all the others.

The value of λ which is calculated by counting the total number of α particles which strike the screen in a large interval of time T, will not generally be the true value of λ. The mean deviation from the true value of λ is calculated by finding the mean deviation of the total number N of α particles observed in time T from the true average number $\lambda\mathrm{T}$. This mean deviation D (mittlerer Fehler) is, according to the definition of Bessel and Gauss, the square root of the probable value of the square of the difference $\mathrm{N}-\lambda\mathrm{T}$, and so is given by the series

$$\mathrm{D}^2=\sum_{n=0}^{\infty}(\mathrm{N}-\lambda\mathrm{T})^2\frac{(\lambda\mathrm{T})^{\mathrm{N}}}{\mathrm{N}\,!}\,e^{-\lambda\mathrm{T}}$$

$$=e^{-\lambda\mathrm{T}}\sum_{\mathrm{N}=0}^{\infty}\left[\frac{(\lambda\mathrm{T})^{\mathrm{N}}}{(\mathrm{N}-2)\,!}+\frac{(\lambda\mathrm{T})^{\mathrm{N}}}{(\mathrm{N}-1)\,!}-2\frac{(\lambda\mathrm{T})^{\mathrm{N}+1}}{(\mathrm{N}-1)\,!}+\frac{(\lambda\mathrm{T})^{\mathrm{N}+2}}{(\mathrm{N})\,!}\right]=\lambda\mathrm{T}.$$

Hence $\mathrm{D}=\sqrt{\lambda\mathrm{T}}$, and the mean deviation from the value of λ is accordingly

$$\frac{D}{T}=\sqrt{\frac{\lambda}{T}};$$

it thus varies inversely as the square root of the length of the interval of time. This result is of the same form as the classical one used by E. v. Schweidler in the paper referred to earlier.

The probable value of $|N-\lambda T|$ (der durchschnittlicher Fehler) is much more difficult to calculate.

LXXVII. *A New Radiant Emission from the Spark.* By R. W. Wood, *Professor of Experimental Physics in the Johns Hopkins University*[*].

[Plate XIV.]

I SCARCELY know how to designate the peculiar type of radiation referred to in the present paper, which was first discovered over two years ago in the course of some experiments made with a view of ascertaining whether the Schumann waves from the spark gave rise to any fluorescence of the air by which they were absorbed. It is now known that there is a feeble ultra-violet luminosity of air or nitrogen gas surrounding a small mass of radium, in other words the radium renders the gas luminescent. To test for a fluorescence due to the absorption of very short light-waves, the condenser spark between aluminium electrodes was passed behind and very close to a vertical strip of metal which completely concealed the spark, but which enabled observation, either visual or photographic, of the air in its immediate vicinity. If the air in the room was free from dust and smoke absolutely nothing could be seen with the eye, even after prolonged resting in the dark. A photograph, however, made with a small camera provided with a quartz lens, showed that the air around the spark was a source of a powerful actinic radiation, which was completely stopped by the intervention of a glass plate between the camera and the spark. The first photograph of the phenomenon which was obtained is reproduced on Pl. XIV. fig. 6. The narrow strip of metal between the two wider strips was about 1 cm. in width; the spark discharge was concealed behind this.

Two hypotheses immediately presented themselves: (*a*) we are dealing with a scattering of the shortest waves by the

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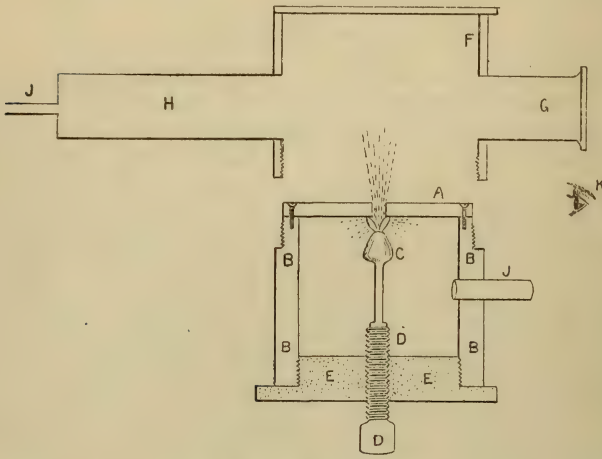
[*] Communicated by the Author.

air molecules or microscopical dust particles, as in case of blue-sky; (*b*) ultra-violet fluorescence of the air caused by the absorption of the Schumann waves. As a matter of fact neither hypothesis turned out to be tenable, but I mention them to show that they have been carefully considered.

If the emission of ultra-violet light by the air was merely a scattering, its spectrum should be identical with that of the spark: if, on the contrary, it is a fluorescence phenomenon, its spectrum would be totally different. In the spectroscopic work it was necessary to get as close as possible to the spark, and yet run no risk of having its direct light enter the slit of the instrument. To meet this requirement the apparatus shown in fig. 1 was constructed. A disk of aluminium, 3 mm. thick, was perforated with a hole 1·5 mm. in diameter and fastened to a short brass cylinder B. The aluminium electrode C was carried by a screw D, which passed through the ebonite cap E. The spark discharge passed between C and the inner rim of the hole in the aluminium disk. If the spark chamber is hermetically sealed the explosive expansions of the air are apt to force the spark aureole, which is pale green in the case of the aluminium spark, out through the hole. The small lateral tube J prevents this, and serves as well for the introduction of various gases. The length of the spark must be so adjusted that no visible portion is forced out through the hole, when viewed from the position K.

Fig. 1.



A second brass cylinder F, closed at the top and fitted with two lateral tubes H and G, can be screwed to the spark chamber when it is desired to study the emission in dry filtered air or some other gas. The tube G is closed with a quartz window, while H terminates in a smaller tube J for the introduction of gas. The emission is quite invisible in dust-free air, yet it can be photographed with an exposure of one or two minutes with a quartz lens of 2 cm. aperture and 15 cm. focus. In arranging the position of the quartz camera the focal plane should be examined with an eyepiece in a dark room to make sure that no part of the lens receives light from the edge of the hole; in other words, the top of the lens must be just below the plane of the aluminium disk A.

In order to get an idea of the appearance of scattered light, the air around the apparatus was filled with smoke and the spark discharge started. The photograph obtained in this way is reproduced on Pl. XIV. fig. 1. Fig. 2 was obtained when the air was free from smoke or dust, and shows the appearance of the emission with which we are concerned. A comparison of these two photographs shows us at once that the emission does not extend nearly so far out from the aperture as does the luminous region of light-scattering smoke. It appears as if it were rapidly absorbed by the air. That this is not due to differences in the time of exposure is shown by the original negatives, for fig. 2 has a density nearly double that of fig. 1 in the immediate proximity of the aperture in the disk. An experiment was next made to ascertain the nature of the light given out by the emission. A fine thread of fused quartz, about 2 mm. in length, was mounted at the edge of the aperture by means of a small drop of soluble glass. This scattered the light of the spark, forming a narrow linear source of spark light located at the centre of the base of the emission. The slit tube of a small quartz spectrograph was removed, and the luminous quartz thread brought into its place. The resulting photograph is shown in fig. 3, a continuous band of light, the spectrum of the quartz fibre, with the emission above it and about at its centre. This picture proved that the light given out by the emission embraced a limited range of wave-lengths in the region 300–310. This picture was secured with an exposure of only fifteen minutes, which made it seem probable that the spectrum of the emission could be obtained with a fairly narrow slit. Fig. 5 shows a spectrogram obtained with a wide slit, the aluminium lines showing faintly as a result of diffused light: the lower spectrum is that of the spark for comparison. The spectrum of the emission consists of two broad bands, one very strong, the other (to the right) much weaker. These were found to be identical with the so-called "water bands" of the oxy-hydrogen flame, as is clearly brought out by fig. 9, in which the upper spectrum is that of the oxy-hydrogen flame, the lower that of the emission. In addition to these bands I obtained on one plate lines at wave-lengths 3576, 3537, and 3369, which are identical with lines attributed to nitrogen in the spectrograms published by Eder and Valenta of the spark between wet carbon electrodes. There is, in addition, a line which is imbedded in the water-band, as shown in figs. 7 and 8. In fig. 7 the upper spectrum is that of the oxy-hydrogen flame (over-exposed), below it the aluminium spark, and at the bottom the spark emission. The nitrogen lines come out very clearly in this case. The spectrum by Eder and Valenta, which is practically identical with that of the emission, was obtained by passing the discharge of an induction-coil between wet carbon electrodes, and differs from that of the oxy-hydrogen flame in that it shows the nitrogen lines above referred to.

It looked very much as if the emission might be due to the fluorescence of nitrogen and water vapour, resulting from the absorption of the Schumann waves; this would explain its failure to penetrate the air to any considerable distance. To test this point the auxiliary tube was attached to the spark chamber, the emission being studied through the quartz window attached to the tube G. The apparatus was first filled with air carefully dried by passage through a tube filled with phosphorus pentoxide, and then with air passed through a plug of wet cotton. The emission was photographed in each case, but no difference in the intensity of the images could be detected. Oxygen and nitrogen were then tried in succession. In the former there was almost no trace of the emission, while in the latter it was much brighter and extended to a greater distance from the aperture than in air. Photographs of the phenomenon in these two gases are reproduced on Pl. XIV. fig. 4. The emission is photographed against the very black background furnished by the long tube H, in fig. 1. The time of exposure was the same in each case, and the two plates were developed together. The aperture is to the right in each picture, the emission shooting out towards the left. The crescent of light is the inner edge of the tube H illuminated by diffused light.

The next question was to determine whether the presence of oxygen prevented the formation of the emission, or whether the gas exerted an absorbing action. This was a difficult matter to determine, since numerous experiments showed that no substance was transparent to the emission.

A plate of white fluorite, 0·5 mm. in thickness, which had been found very transparent for the Schumann waves by Dr. Lyman, who very kindly placed it at my disposal, together with an end-on hydrogen tube for the production of Schumann waves, when placed over the aperture was found to destroy all trace of the emission. This disposed of the theory that we were dealing with a fluorescence produced by the short waves. Thin aluminium foil, such as is used with the Lenard tubes, was found to be equally opaque. It is therefore a difficult matter to start the emission in a given gas and pass it into a different one. The problem was finally solved by an experiment designed to test one of the theories that I had evolved to explain the phenomenon. It occurred to me that we might be dealing with hydrogen ions, shot off from the electrodes, which, by combination with the oxygen of the air, gave rise to a spectrum similar to that of the oxy-hydrogen flame. We might in this way explain the lessened effect in oxygen as a result of the circumstance that the "combustion" of the ions took place almost entirely within the small tube with which the disk of aluminium was perforated. If this were the case, it seemed probable that if the emission were formed in air, and a small jet of oxygen were directed across it transversely, we should observe a more intense action at the point where the emission met the oxygen jet. The experiment was tried, and it was found that the gas jet merely interrupted the emission, killed it in other words, precisely as if it absorbed it. If the emission was started in air and a jet of nitrogen blown gently against the aperture, the emission was found to shoot out much farther and to be of greater intensity. The magnetic field appeared to be without action on it, though the experiment was found to be attended with difficulties on account of the action of the magnet on the spark.

It is still more difficult to study the action of an electrostatic field. The material constituting the emission is evidently shot from the aperture at a very high velocity, for it is impossible to blow it aside with a strong jet of air; moreover, if air is forced continuously into the auxiliary chamber, passing through the aperture in the aluminium disk at a high velocity, the emission does not appear to be held back in the slightest degree.

I am unable to explain its reactions with oxygen and nitrogen, and the apparent failure of the presence or absence of water vapour to modify the intensity of the spectrum, which is made up chiefly of the so-called water-bands. These bands appear when hydrogen burns in oxygen, and yet oxygen destroys the luminosity of the emission. This fact appears to be of the greatest importance in connexion with the origin of these bands. If I remember rightly, the introduction of chlorine gas into a sodium flame destroys its emission of the D lines, and there may be some analogy between the two phenomena. I intend sometime to photograph the spark directly utilizing the principle of the spectroheliograph. An image of the spark obtained with monochromatic light of the wave-length of the water-band may tell us something about the origin of the emission. In the meantime I hope that some study of the phenomenon will be made by others, as it appears to be of considerable importance in connexion with the origin of radiation.

It seems quite likely that the "Entladungsstrahlen" may be identical with the emission, for they are absorbed by oxygen. One great difficulty in the investigation is the apparent impossibility of separating the emission from the ultra-violet and visible light which goes out with it.

LXXVIII. *Some Experiments on Refraction by non-homogeneous Media. By* R. W. Wood*.

[Plate XIV. fig. 10.]

THAT the apparent diameter of a body surrounded by a refracting atmosphere is slightly larger than its true diameter is well known. An extreme case is the mercury thread of a thermometer. At the other extreme we have the earth as seen from the moon.

This magnification by a non-homogeneous atmosphere, in which there is no sharply defined refracting surface (as in the case of the earth's atmosphere) can be very nicely shown in the following way :—

Make a small rectangular glass tank by cementing five squares of glass together with sealing-wax. Fill it with melted gelatine and support an empty test-tube in the fluid with a clamp stand. The bottom of the test-tube should be within half a centimetre of the bottom. After the jelly has solidified, pour hot water into the test-tube, and immediately withdraw it. It will leave a cylindrical hole in the jelly, with a hemispherical bottom. Now pour a mixture of glycerine and powdered chalk into the cavity until it is half full. Fill the remainder with water to which a few drops of milk have been added. The glycerine will gradually

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* Communicated by the Author.

diffuse into the gelatine, increasing its refractive index. The condition at the end of a few minutes will be not unlike that of a white body surrounded by a dense atmosphere, for the refractive index will be high at the boundary between the jelly and glycerine, gradually decreasing as we pass out into the jelly. The magnification resulting can be seen by looking through the side of the trough, the lower portion of the cavity appearing swollen out like a mushroom. If we perform the experiment with pure glycerine and clean water the same thing happens. By placing an arc light behind the tank and throwing an image of the cavity upon a piece of ground glass with a camera objective, placed at the centre of the shadow of the tank, we can see the bright ring of light which appears to surround the bottom of the cavity. This is analogous to the ring of light which would be seen surrounding the earth by an observer on the moon during a lunar eclipse, or rather a solar eclipse. As the glycerine penetrates into the jelly this ring of light eventually separates from the line of the cavity. Photographs of this experiment are reproduced in fig. 10, Plate XIV.

Exner has described experiments with pseudo-lenses made by immersing gelatine cylinders in water, and drying sections of gelatinous cylinders. These I described in 'Physical Optics,' but have since improved the method by the use of glycerine. The whole experiment can now be performed within the limits of the lecture hour.

A handful of photographic gelatine is soaked in clean water until thoroughly softened. The excess of water is poured off and the mass is then heated until quite fluid, and filtered through a funnel with a small piece of absorbent cotton placed at the bottom of the cone. If the gelatine refuses to run through, add a little more boiling water. Pour a small quantity into a test-tube, and let it stand until solid. Evaporate the remainder over a small flame, stirring constantly until it is of the consistency of syrup. This means boiling it down to one-third or less of its original volume. Now add an equal volume of glycerine, and pour the mixture into a second test-tube. After the jellies have set, crack the bottom of the tubes by a sharp blow, warm them by the momentary application of a Bunsen flame and push out the cylinders.

Cut the cylinders into disks of different thicknesses, with a warm pen-knife. The best thickness is about two-thirds of the diameter. Mount the disks between small squares of thin plate-glass (window glass will do), warming the plates slightly, to insure getting the jelly into optical contact.

It may be found necessary to prop the upper plate in position until the surface in contact with the glass has "set." The cylinders which are made of gelatine and water are now to be immersed in glycerine, the glycerine jelly cylinders in cold water. The glycerine should be stirred occasionally, as the layers in contact with the jelly take up the displaced water. The action will be found to be well under way in a quarter of an hour, the glycerine gradually diffusing into the jelly, driving out the water, and the water gradually replacing the glycerine. A jelly containing glycerine has a higher refractive index than one containing water, consequently the cylinders soaked in glycerine act as concave, while those soaked in water act as convex lenses.

The focal length will be found to be only 8 or 10 cms., and very sharp images of the filament of an incandescent lamp or a gas-flame can be obtained with them.

Interesting refraction effects can be observed by nearly closing the ends of a tin pipe 3 or 4 metres long and 10 or 15 cms. in diameter with plate glass, inclining the tube and pouring in sufficient gasolene (petrol) to wet the entire bottom of the tube. On tilting the tube back into the horizontal position, the cross section of the circular end appears deformed into an ellipse when viewed through the opposite end with the eye near the bottom, and external objects are seen much distorted. Proximity of a flame is to be avoided.

LXXIX. *On a Method of Counting the Rulings of a Diffraction Grating.* *By* G. W. C. Kaye, *B.A.*, *D.Sc.* The National Physical Laboratory *.

[Plate XV.]

It would appear from a review of the earlier determinations of wave-lengths by the use of diffraction gratings, that most of the results were vitiated by an imperfect knowledge of the value of the grating-space rather than by inaccurate measurement of angular deviation.

This was the case with the pioneer work of Fraunhofer (1814–1823) with wire and later with glass gratings; of Ditscheiner (1864, 1866) with one of Fraunhofer's gratings; and of Mascart (1864), Ångström (1864), and van der Willigen (1868), each of whom worked with Nobert's gratings †.

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* Communicated by Dr. R. T. Glazebrook, F.R.S.

† For a bibliography see Bell, Phil. Mag. xxv. p. 250 (1888).

Most of Nobert's gratings, however, were small and inaccurately ruled, they all gave very imperfect definition and showed numerous "ghosts." There does not seem to have been any special trouble in ruling lines as close together as need be; for example Nobert, who jealously guarded his machine and methods as a trade secret, succeeded in ruling as many as 100,000 lines to the inch. The real difficulty was to secure uniformity of spacing.

It was about forty years ago that Rutherfurd, a New York lawyer, by attention to the accuracy of the feeding-screw of his ruling machine, was able to make a great advance in the art of ruling gratings. The best of Rutherfurd's gratings, however, were still faulty in respect of uniformity of spacing, and his larger gratings are not satisfactory.

As is well known, Rowland's success at Baltimore in ruling gratings was largely attendant on the success of his method to secure perfection in his feeding-screw. As at present made, the Rowland gratings are usually ruled with 10,000, 14,438, or 20,000 lines to the inch. Practically all are on speculum metal (*c.* 7 Cu, 3 Sn) which, permitting a high polish, yields gratings of great brilliance and definition, and being soft is not severe on the ruling diamond. On the other hand, speculum metal is not a simple alloy—a state of things which tends to local heterogeneity—it is heavy (which necessitates thick and rather massive gratings to prevent distortion), and further it has a considerable thermal coefficient of expansion ($19 \cdot 3 \times 10^{-6}$)—a fact which introduces some uncertainty into the certified grating-space for those gratings whose temperature of ruling is unknown.

A determination of the grating-space involves (1) the measurement at a known temperature of the overall length of a selected number of rulings, (2) the counting of those rulings. The first part presents no difficulty for the modern comparator fitted with suitable high-power micrometer microscopes. It was to carry out what threatened to be a hopelessly tedious and fatiguing task in the counting of the rulings that the following method was employed in the case of a plane Rowland grating about 8 cms. long on speculum metal, belonging to Mr. J. W. Gifford, and for which ignorance of the ruling temperature made the certified value (14,438 lines to the inch) not so certain as was required.

With some of Rowland's gratings every fiftieth and hundredth rulings are differentiated by being shorter and longer than the rest. Others have all the rulings the same length; this was the case with Mr. Gifford's grating.

Accordingly, quite close up to one edge of the grating were ruled by the Laboratory dividing-engine short fine equidistant reference-lines each about ⅓ mm. long and at such a distance apart as to include about 100 grating lines.

Each fifth reference-line was a trifle longer than its neighbours, and each tenth line longer still. Every fiftieth line was distinguished by the addition of an appropriate number of fine dots, so that afterwards there was very little trouble in picking up under the microscope any particular reference-line required.

The counting of the grating rulings was carried out with the aid of the projection microscope. The grating was mounted on the stage of the microscope and an image of the graduated edge of the grating was thrown upon a screen: with the magnification of 1200 employed the lines stood out in sharp relief about 2 mm. apart on the screen. A 4 mm. objective was used, and about 150 grating lines and two reference-lines were in focus in the field of view. On the screen was drawn a scale of divisions of which the central 100 were emphasized. The length of each scale-division was equal to the distance apart of the lines in the projected image of the grating. Thus by slight adjustment of the screen to one side or the other, and so securing coincidence between the lines of the scale and of the grating image, 100 (or so) lines could be counted merely at a glance. There was no difficulty, therefore, in noting the number of rulings (always near 100) between each successive pair of reference-lines, the grating being racked along each time on the stage of the microscope by a convenient amount.

Fig. 1 (Pl. XV.) is a photograph with a magnification of 450, and will give an idea of the appearance of the edge of the grating together with two of the reference-lines.

The method proved to be very expeditious. Without interruption 1000 lines could be counted in 4 minutes; in a 2½ hours sitting 22,000 lines were enumerated without fatigue. A good fraction of this time was taken up with such things as attention to the illuminating arc of the microscope, renewal of carbons, refocussing, &c.

It may perhaps not be without interest to add that in the case of Mr. Gifford's grating, two independent countings and a supplementary check counting agreed in giving a total of 45,668 rulings.

At 16°·0 C. on the hydrogen scale, these rulings occupied a length of 8·03618 cms., as the result of a comparison against the Standard Invar Metre of the National Physical Laboratory which has been repeatedly verified at Sèvres. This is at the rate of 5,682·57 spacings to the cm. or 14,433·7 to the inch at 16°·0 C., which may be compared with Brashear's certified value of 14,438 rulings to the inch, temperature unknown.

For Mr. Gifford's grating the mean spacing value over the whole of the grating was determined, but there would of course be no difficulty in obtaining its value over any particular region should local variation be suspected.

In most of the accompanying photographs (taken wi ha magnification of 690, which is reduced in the reproductions to about 450) the crystalline structure of the speculum metal shows up strongly.

Fig. 1 (Pl. XV.) shows the remarkably straight edge formed by the points where the ruling diamond was set down at the beginning of each stroke. The other and far more irregular edge where the diamond was lifted from the metal is seen in fig. 2. The two sides of each furrow in the metal and the remains of the "cuttings" can be plainly seen at the ends of some of the longer rulings. It is evident that the rulings are not very light ones, and that the original flat surface of the speculum has been completely replaced by a succession of fully developed V-shaped furrows with no intervening plane surface. This renewal of the surface is further illustrated by fig. 3, which shows a corner of the grating. The scratch across the corner was, as will be seen, almost entirely removed by the rulings. We should expect with such a surface that the apparent width of the ruling would depend on the obliquity of the illumination. Such variation from line to line in the width of the rulings is noticeable in some of the photographs. Fig. 4 shows a blemish on the grating. The diamond appears to have got fouled for a number of strokes and has lacerated the surface in some rulings and failed to rule at all elsewhere.

I wish to thank Mr. Gifford for his permission to include in this paper the photographs and measurements of his grating, and I am indebted to Dr. Glazebrook for his interest in the work.

The National Physical Laboratory,
Teddington.

LXXX. *The Expansion and Thermal Hysteresis of Fused Silica.* *By* G. W. C. KAYE, *B.A.*, *D.Sc.* The National Physical Laboratory *.

FUSED silica or quartz glass has assumed such importance, and has been applied to so many purposes in physics and chemistry, that a study of its thermal expansion may perhaps be of general interest.

As is well known, quartz, which in the crystalline state has a considerable coefficient of expansion, assumes when fused a smaller coefficient of expansion than that of any other known substance, good invar alone excepted †. For example, at ordinary temperatures the expansion coefficients are

quartz,	$\parallel$ axis	$7{\cdot}5 \times 10^{-6}$ ‡
,,	$\perp$,,	$13{\cdot}7$,,
fused silica,		c. $0{\cdot}4$,,

Owing to the extreme smallness of the expansion coefficient of fused silica, most observers have adopted modifications of Fizeau's interference method, more especially when for some reason it was convenient to work with small samples.

I. THE COEFFICIENT OF EXPANSION.

Moderate Temperatures.

Chappuis and Scheel have each determined the coefficient of expansion at moderate temperatures. Chappuis § (1903) for the range 0° to 83° C. obtained the expression

$$\frac{l_t - l_0}{l_0} = ({\cdot}385t + {\cdot}00115t^2)\,10^{-6},$$

where l_t is the length at $t°$, l_0 that at 0°.

Scheel ‖ in 1903 derived for the range 0° to 100° C. the formula

$$\frac{l_t - l_0}{l_0} = ({\cdot}322t + {\cdot}00147t^2)\,10^{-6}.$$

In 1907¶ Scheel repeated his measurements with a new

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* Communicated by Dr. R. T. Glazebrook, F.R.S.

† Invar is obtainable as such in three grades, covering a range of coefficients of from about $-0{\cdot}3 \times 10^{-6}$ to $+2{\cdot}5 \times 10^{-6}$.

‡ Benôit, *Trav. et Mém. du Bur. Intl.* i. 1881; vi. 1888. Scheel, *Ann. der Phys.* ix. p. 837 (1902). Randall, Phys. Rev. xx. p. 10 (1905).

§ Chappuis, *Procès Verbaux, Inter. Comm. des Poids et Mesures*, 1903, p. 75.

‖ Scheel, *Deut. Phys. Gesell. Verh.* v. p. 119, March 1903.

¶ Scheel, *ibid.* ix. p. 718, Dec. 1907; *Zeit. Inst.* xviii. p. 107 (1908).

cylinder of silica prepared by Zeiss. His new formula reads

$$\frac{l-l_0}{l_0}=(\cdot 388t+\cdot 001682t^2-\cdot 0_5504t^3)\,10^{-6},$$

which gives results in good agreement with Chappuis' over the same range.

The results in Table I. give for the range 0° to 100° some values of $(l_t-l_0)/l_0$, derived from the above formulæ.

A result of Randall's (see later) at 80° is also tabulated.

TABLE I.

Temp. (t).	$(l_t-l_0)/l_0$.			
	Chappuis. 1903.	Scheel.		Randall. 1910.
		1903.	1907.	
	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
10° C.	4·0	3·4	4·0	
16	6·4	5·5	6·6	
20	8·2	7·0	8·4	
50	22	20	23	
80	38	35	39	33
100	50*	47	50	

* Extrapolated.

Low Temperatures.

At low temperatures the experiments of Scheel and of Dorsey claim attention. In January 1907 Scheel[†] published some results dealing with the expansion over the range −190° to +16° C. of a silica cylinder made by Heraeus. These were embodied in the formula

$$\frac{l_t-l_0}{l_0}=(\cdot 217t+\cdot 00238t^2)\,10^{-6},$$

which indicates a minimum length at −46°.

Later in the year Scheel[‡] gave the results of experiments on a silica cylinder made by Zeiss. They are represented

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[†] Scheel, *Deut. Phys. Gesell. Verh.* ix. p. 3, Jan. 1907.

[‡] Scheel, *ibid.* ix. p. 718, Dec. 1907.

over the range −190° to +100° C. by the formula (also given above)

$$\frac{l_t-l_0}{l_0}=(\cdot 388t+\cdot 001682t^2-\cdot 0_5504t^3)\ 10^{-6},$$

which indicates a minimum length at −84°, and that the length at −157° is equal to the length at 0°.

Dorsey* in 1907, using Fizeau's method, worked over a range of −170° to +10° C. with two samples of silica tubing, one transparent, the other not. The latter shows results which are out of sequence. The results for the transparent specimen are given by Dorsey as coefficients of expansion for isolated ranges of 20° round and about various temperatures selected. To facilitate comparison these results have been graphically interpolated by the writer, and so caused to yield the expansions at a suitable number of equidistant temperatures—from which by summation the values of $(l_t-l_{10})/l_{10}$, and thence of $(l_t-l_0)/l_0$, were obtained by making use of Chappuis' and Scheel's results (above) for the range 0 to 10°. A selection of these final values thus obtained are tabulated (along with Scheel's) in Table II.

TABLE II.

Temp. (t).	$(l_t-l_0)/l_0$.		
	Scheel, 1907.		Dorsey, 1907.
	(Heraeus.)	(Zeiss.)	
	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
−10° C.	−1·9	−3·7	−3·2
−20	−3·4	−7·0	−6·1
−50	−4·9	−14·6	−12·9
−80	−2·1	−17·7	−14·7
(−84)	(+0·6)	(−17·7)	(−14·6)
−100	+2·1	−14·9	−13·4
−150	+21	−3·4	+ 4·0
−190	+47	+21·6	+17·2 (−170°)

Their graph indicates a minimum length at −77° and gives $l_{-145}=l_0$, Dorsey's non-transparent specimen also showed a minimum length at about −80°. Having regard to the

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* Dorsey, Phys. Rev. xxv. p. 88, July 1907.

above method of reduction of Dorsey's results, their agreement with Scheel's corresponding values for his Zeiss specimen must be regarded as very satisfactory. A mean of Scheel's Zeiss values and Dorsey's reduced values for low temperatures is probably not far from the truth.

High Temperatures.

Le Chatelier [*] in 1900 was the first to make systematic measurements on the expansion of fused silica at high temperatures. Subsequent work has not confirmed his results, which depend on the expansion of porcelain. When plotted, his readings indicate a maximum length at 750° and a mean expansion coefficient of $\cdot 67 \times 10^{-6}$ for the range 0 to 1000° C.

Callendar [†] in 1901 obtained the value $\cdot 59 \times 10^{-6}$ for the mean coefficient of expansion between room temperature and 1000° C. of a silica rod 40 cms. long. He states that the expansion is uniform up to 1000° C., increases rapidly from 1000° to 1400°, and changes to a contraction beyond 1400° [‡]. The length was measured by a micrometer microscope, and the temperature was estimated by the expansion of a surrounding platinum cylinder which was used to heat the silica. Callendar's result reduced to the interval 0° to 1000° is noted in Table III.

Holborn and Henning [§] in 1903 used a rod of silica 52 cms. long, and by a microscope method measured the length at room temperature, 250°, 500°, 750°, and 1000°. The rod was heated electrically in a porcelain tube, and the temperatures at different points of the rod were measured by a thermocouple. The results have been reduced and brought into line with those of observers in Table III.

Minchin [‖] in 1907 found $\cdot 45 \times 10^{-6}$ as the uniform coefficient of expansion between room temperature and 950°. Certain errors have, however, since been found in his work.

Randall [¶] has recently completed a comprehensive series of measurements using Minchin's specimen of silica. He employed an interference method over the range 16° to 1100°. The silica (a ring about 10 mm. long made by Zeiss) was heated in vacuo by an electric furnace; temperatures were taken by a Pt-Rh thermocouple. The experiments

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[*] Le Chatelier, *Compt. Rend.* cxxx. p. 1703 (1900).

[†] Callendar, Chem. News, lxxxiii. p. 151 (1901).

[‡] Shenstone, 'Nature,' lxiv. p. 65 (1901), gives this temperature as 1200°.

[§] Holborn and Henning, *Ann. der Phys.* x. p. 447 (1903).

[‖] Minchin, Phys. Rev. xxiv. p. 1 (1907).

[¶] Randall, Phys. Rev. xxx. p. 216 (1908).

appear to have been conducted with great care, and the results are entitled to considerable weight. They have the advantage of not depending on any assumptions as to the effect of temperature and pressure on the refractive index of air at high temperatures*; such effects are of the same order as that due to the expansion of the silica. Randall's final values, reduced as before to the range ($t°-0°$) by the aid of Chappuis' and Scheel's values for the interval $0°-16°$ are given in Table III.

Table III.

Temp. (t).	$(l_t-l_0)/l_0$.		
	Randall, 1910.	Holborn & Henning†, 1903.	Callendar, 1901.
	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
200° C.	100		
250	......	118	
300	161		
400	222		
500	281	276	
600	336		
700	389		
750	......	404 : 402	
800	434		
900	481		
1000	541	537	587
1100	641		

In fig. 1 the expansion per unit length $(l_t-l_0)/l_0$ is plotted against temperature (t). The results of Randall, Scheel (Zeiss specimen), Dorsey, Chappuis, Holborn and Henning, and Callendar are utilized.

The excellence with which the curve represents the different results will be noticed. The values of Holborn and Henning, and of Randall at high temperatures are in close agreement, as are those of Scheel and Dorsey at low temperatures, and of Scheel and Chappuis at moderate temperatures. It would appear that the curve represents with a considerable degree of accuracy the expansion of clear, transparent, annealed silica from $-190°$ to $+1100°$ C. The inset gives a portion of the expansion curve on a larger scale.

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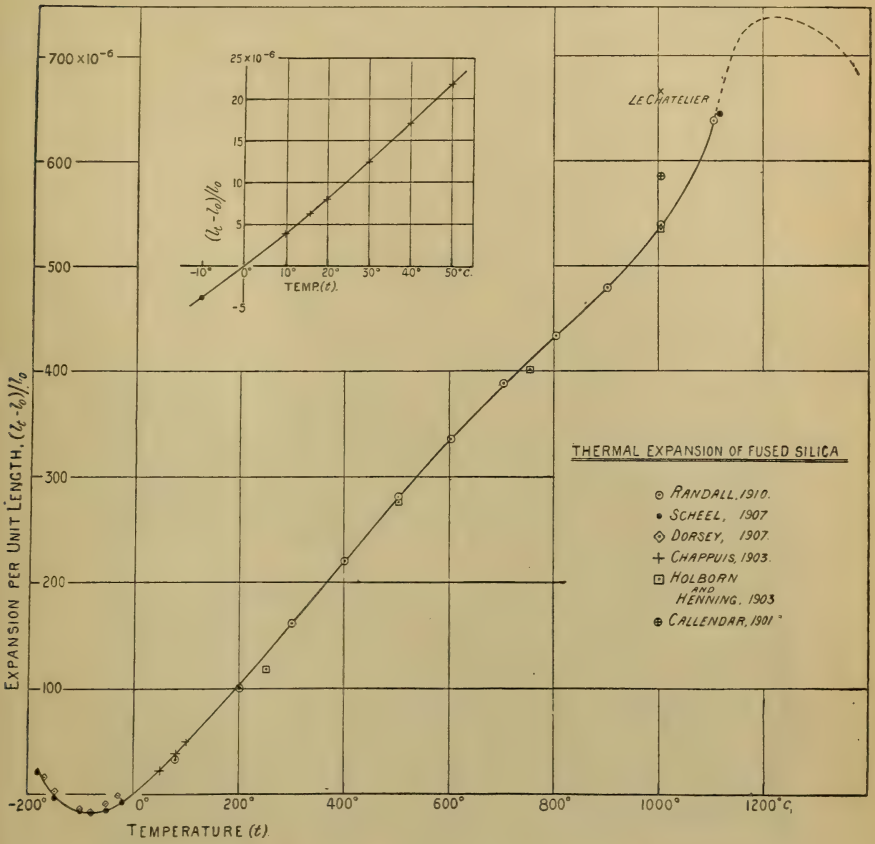
* Pulfrich's formula (*Zeit. Inst.* xiii. p. 455, 1893) has not been tested for temperatures above 100° C.

† Henning, *Ann. der Phys.* xxii. p. 638 (1907) quotes values which when reduced read 132, 267, 402, 537×10^{-6} for the temperatures given in this column.

Randall's value at 1100° confirms Callendar's statement as to the rapid increase in the expansion of silica at temperatures above 1000°. The dotted portion of the curve beyond 1100° is qualitative only and is an expression of Callendar's observations.

Fig. 1.



The slope of the tangent to the curve at any point gives, of course, a measure of the coefficient of expansion

$$\left(\alpha = \frac{1}{l} \cdot \frac{dl}{dt}\right)$$

at that temperature, and the curve shows that α is negative below −80°, zero at −80°, slowly increases to a maximum at about 500°, diminishes somewhat up to about 900°, and afterwards rapidly increases.

From the curve, one may derive the mean coefficient of expansion over any desired range between −190° and 1100° C. The following values have been obtained from the original curve which has been greatly reduced in fig. 1.

Temp. range.	Expansion coefficient α.
−160° to −120° C.	$-{\cdot}43 \times 10^{-6}$
−120 to − 80	−·11 ,,
− 80 to − 40	+·14 ,,
− 40 to 0	·31 ,,
0 to 30	·42 ,,
30 to 100	·53 ,,
100 to 500	·58 ,,
500 to 900	·50 ,,
900 to 1100	·80 ,,

These results refer to clear, transparent, annealed silica. It is probable that want of annealing is the cause in most cases of the anomalous results which have been obtained by some observers. This view is supported by the experiments carried out in this Laboratory on the behaviour of specimens subject to a first heating as contrasted with their behaviour on subsequent heatings.

In regard to the expansion of the translucent or satin-like variety of silica, information is forthcoming from some experiments of Mr. A. Blackie at the National Physical Laboratory, who has recently measured the relative expansions of the two kinds of silica, the transparent and the translucent. He finds that for temperatures below about 500° C. the translucent variety expands slightly more than the transparent, while for temperatures above 500° C. the reverse is true. The difference, however, is very small, not more, for example, than 30 parts in a million at 800°.

II. Change Points.

It would appear from the expansion curve of fused silica that it shows at least two change-points, one at about 1000° C. the other at about −80° C. The former result agrees with the conclusion of Day and Shepherd*, who showed that for

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* Day and Shepherd, Amer. Journ. Sci. xxviii. p. 1089 (1906).

all temperatures above about 1000°, quartz and fused silica devitrify into crystalline tridymite[*], which above this temperature is the stable phase.

At −80° Scheel noted a maximum density as well as a minimum length. There is no analogue of this point in the expansion curve of crystalline quartz [†].

As to the existence of a third change-point in fused silica at about 500°, the expansion curve, it is true, indicates a maximum value of the coefficient of expansion at that temperature. But the maximum is not very pronounced and the certain existence of a change-point can scarcely be inferred. It is useful to note Mallard and Le Chatelier's [‡] measurements on the expansion of quartz crystal at high temperatures. Their results when plotted give an expansion curve which steepens up rapidly [§] in the neighbourhood of 500° to a well marked maximum length at about 670°; in fact, the expansion curve of crystalline quartz at 500° is very much like that of fused quartz at 1100°.

A recalescence point at about 500° is well marked with quartz crystal, but a thermo-junction embedded in powdered fused silica does not, according to Rosenhain, support the same claim for fused quartz.

Perhaps it would be right to infer that the maximum at 500° in the expansion curve of fused silica is a residual effect, and that the change from crystalline to amorphous quartz, though apparently complete as judged by other tests [||], is not so complete as to avoid recognition by the very delicate means that Fizeau's method affords.

However, the point, such as it is, may be useful in setting a limit to the temperature that should be employed in annealing a silica standard of length intended for use at ordinary temperatures. Moreover, as will be seen later, the thermal hysteresis exhibited by silica is much less for temperatures below about 500° than for higher temperatures. *A propos* of this, Blackie's observation (above) as to the reversal at 500° of the relative expansibilities of the transparent and translucent varieties of silica may also be noted.

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[*] The densities of the various varieties of silica are:—Quartz 2·65, tridymite 2·32, transparent fused silica 2·21, translucent fused silica 2·07. The optical constants and crystalline forms of quartz and tridymite are very similar. See Dana's 'System of Mineralogy.'

[†] See Scheel, *Deut. Phys. Gesell. Verh.* ix. p. 3, Jan. 1907.

[‡] Mallard and Le Chatelier, *Compt. Rend.* cviii. p. 1046 (1889).

[§] See also Randall, Phys. Rev. xx. p. 10 (1905).

[||] Mr. Blackie has obtained some interesting results at the N. P. L. from a microscopic examination with polarized light.

III. Thermal Hysteresis.

Having regard to the expansion curve of fused silica, we should expect that any thermal hysteresis it may exhibit would depend very considerably on the temperature treatment. Callendar[*] remarks that if the temperature be kept constant at any point above 1000°, silica continues slowly to expand; and furthermore, after such an expansion it does not return to its original length on cooling, but remains slightly longer. Randall[†] has noticed that this gradual lengthening at constant temperature in the region of 1100° is accompanied by anisotropic expansion, the worked surfaces of the silica ceasing to be plane. The distortion is moreover permanent and remains even after cooling. These results are of course not surprising in view of the existence of a change-point at 1000° C.

At low temperatures, Dorsey[‡] noticed that for a range of about 60° on either side of −80°, fused silica shows this peculiarity; above −80°, when warmed it first contracts slightly and then expands; similarly when cooled, it first expands a trifle and afterwards contracts. For temperatures below −80° the converse of this is true. Dorsey could not trace the effect below about −140° or above about −20°, nor did he notice it in any other substance.

With temperature treatment which is not extreme, one may infer from a review of the observations of Holborn and Henning, Minchin, and Randall (see above), that the residual length alteration after a temperature cycle would be very slight if the silica has been annealed and if the temperature has not exceeded say 400° or 500°. The existence of such hysteresis for moderate temperature ranges has been definitely established and measured at the National Physical Laboratory by Mr. L. F. Richardson.

To fix one's ideas quantitatively, thermal hysteresis may be defined as follows:—Let l be the original length of a specimen, which is subjected to a rise of temperature of t°, and is maintained at that temperature for say a day or two. If, when it is cooled to the original temperature, its length (after half an hour or so) is found to be $(l+\delta l)$, then $\frac{\delta l}{l}\cdot\frac{1}{t}$ is adopted as a measure of the linear thermal hysteresis H.

Since the mean coefficient of expansion $=\frac{\Delta l}{l}\cdot\frac{1}{t}$, where Δl

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[*] Callendar, Chem. News, lxxxiii. p. 151 (1901).

[†] Randall, Phys. Rev. xxx. p. 216 (1910).

[‡] Dorsey, Phys. Rev. xxv. p. 88, July 1907.

is the linear expansion for a rise of temperature of $t°$, H may be looked upon as the residual variation of the expansion coefficient.

Specimens of annealed fused silica both clear and translucent were obtained in the form of end-measure rods about 45 cms. long. They were subjected for periods of from 1 to 90 hours to various temperatures over a range of from about $-190°$ to $400°$ C. For annealed specimens, H, as defined above, came out between 1×10^{-9} and 5×10^{-9}, which is less than 1 per cent. of the expansion coefficient at ordinary temperatures. Usually H was negative, which means that after heating and then cooling to the original temperature, the contraction was greater than the preceding expansion. This is in accordance with the observations of Minchin and of Randall, and is, of course, one of the characteristics of invar.

As will be seen below, silica compares very favourably with the two common Jena thermometry glasses specially designed to show a small after-effect. To extend the comparison, Guillaume's figures for invar are added.

Substance.	Temp. Range.	Linear Hysteresis H.	Authority.
Jena 16‴ * ...	0° to 50°	42×10^{-9}	Thiesen & Scheel.
Jena 59‴ † ...	0 to 50	23 ,,	,, ,,
Invar ‡	0 to 25	-81 ,,	Guillaume.
,, ...	0 to 50	-162 ,,	,,
Fused Silica ...	0 to 400	-1 to -5 ,,	N. P. L.
,, ,, ...	0 to 800	-17 ,,	,,
,, ,, ...	0 to >1000	+values	Callendar.

* $H=(34+0{\cdot}16t)\,10^{-9}$. † $H=(27-0{\cdot}08t)\,10^{-9}$. ‡ $H=-3{\cdot}25t \times 10^{-9}$.

Thus in regard to linear after-effect, silica over the range 0° to 400° has nothing to fear in comparison with either invar or Jena thermometry glasses subjected, as will be seen, to much less severe temperature conditions. There is practically nothing to choose between the different kinds of fused silica; the cheaper satin-like variety is as good as the more expensive clear transparent kind.

In justice to invar, it ought to be added that Guillaume's observations on after-effect extended over months, while the measurements on silica were included in the space of a few hours.

It will be seen that fused silica has qualities which commend it for use as a material for standards of length. A silica standard metre is on the point of completion at the National Physical Laboratory, and there is good reason to believe that its adoption will be attended with success.

The National Physical Laboratory,
Teddington.

LXXXI. *Pendulum Motion and Spherical Trigonometry.*

By G. Greenhill [*].

MR. ROSE-INNES has developed the relation between the revolution of a pendulum in a plane and the projection of the motion on a spherical surface, and he shows that the argument of the elliptic function required can be represented by an area on the sphere which grows uniformly with the time (Phil. Mag. June 1910).

In a change to the polar reciprocal, the time will then be represented by a spherical arc, as discussed here in § 9.

1. Consider a circle AQD on the vertical diameter AD, and a particle Q circulating round it under gravity with velocity due to the depth KQ below a horizontal line HK; the motion of Q will represent a pendulum making complete revolutions, like a bicycle-wheel on its ball-bearings, put out of balance by an iron bar in the spokes (fig. 1).

The lettering and notation is that employed in my 'Elliptic Functions,' fig. 13, where, with $\mathrm{ADQ}=\phi$,

$$(1)\quad \mathrm{KQ}=\mathrm{AE}-\mathrm{AN}=\mathrm{AE}-\mathrm{AD}\sin^2\phi$$

$$=\mathrm{AE}(1-\kappa^2\sin^2\phi)=\mathrm{AE}\,.\,\Delta^2\phi,\ \kappa^2=\frac{\mathrm{AD}}{\mathrm{AE}},$$

$$(2)\quad (\text{vel. of Q})^2=\left(\mathrm{AD}\frac{d\phi}{dt}\right)^2=2g\,.\,\mathrm{KP}$$

$$=2g\,.\,\mathrm{AE}\,.\,\Delta^2\phi,\ \left(\frac{d\phi}{dt}\right)^2=\frac{g}{\mathrm{AC}}\,.\,\frac{\Delta^2\phi}{\kappa^2},$$

$$(3)\quad \int_0\frac{d\phi}{\Delta\phi}=\frac{nt}{\kappa}=u,\quad \phi=\mathrm{am}\,u,\quad n=\sqrt{\frac{g}{\mathrm{AC}}};$$

so that n/π is the number of beats per second in small oscillation; and the elliptic argument u grows uniformly with the time t, starting from the lowest point A.

Draw the circle, centre E and radius EB, orthogonal to

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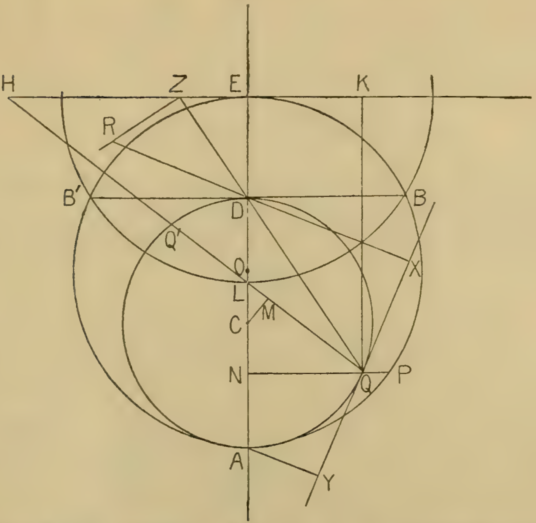
[*] Communicated by the Author.

Fig. 1.

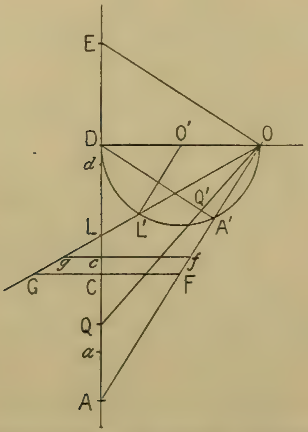


the circle AQD, cutting AD in L, the limiting point or Landen point; then

(4) $$ED \, . \, EA = EL^2, \quad \text{and } HQ \, . \, HQ' = HL^2,$$

(5) $$\begin{aligned} QL^2 &= (HQ - HL)^2 = HQ^2 - 2HQ \, . \, HL + HQ \, . \, HQ' \\ &= (HQ + HQ' - 2HL) HQ = (2HM - 2HL) HQ \\ &= 2LM \, . \, HQ = 2LC \, . \, KQ \\ &= 2LC \, . \, AE \, . \, \Delta^2\phi = AL^2 \, . \, \Delta^2\phi. \end{aligned}$$

Fig. 2.



2. Turn the vertical circle about the diameter AD through a right angle, so as to bring DB to DO in fig. 2, and project

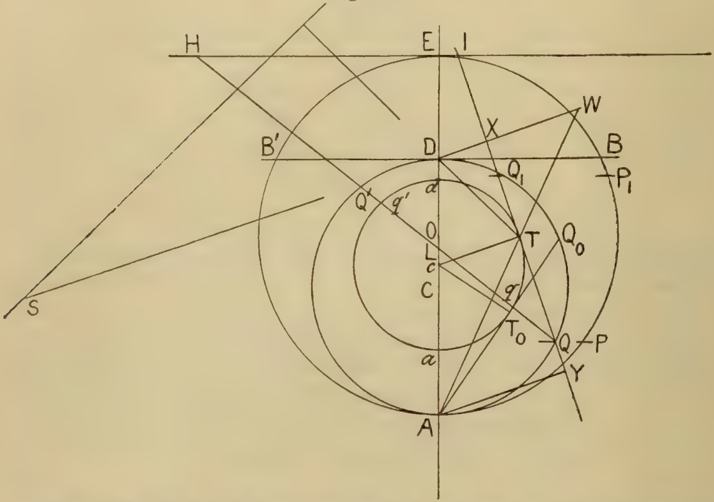
in Mr. Rose-Innes's manner on a sphere, by lines drawn from the centre O; corresponding points on the sphere in fig. 4 and the plane AQD of fig. 1 may be represented without confusion by the same letter, in most cases. Then

$$(1) \qquad \kappa^2 = \frac{\mathrm{AD}}{\mathrm{AE}} = \frac{\mathrm{AD}^2}{\mathrm{AO}^2} = \sin^2 \mathrm{AOD};$$

so that AOD is the modular angle, denoted by c; and EO=EL, and OL bisects the angle AOD.

Invert with respect to O, making $\mathrm{OQ} \cdot \mathrm{OQ}' = \mathrm{OD}^2$; the

Fig. 3.



vertical plane AQD inverts into a sphere on the diameter OD, and the circle AQD into another circle A′Q′D in a plane perpendicular to OA, so that these circles are circular sections of the cone, vertex O and base AQD.

Now AQ is perpendicular to the plane ODQ, so that the planes OAQ, ODQ are at right angles, and the angle AQD on the sphere in fig. 4 is a right angle.

If DX is the perpendicular on the tangent at Q, QDX= QDA=ϕ in figs. 1 and 4; so also in fig. 4, if AY is the perpendicular from A on the tangent at Q, QAY=QAD=ϕ', but ϕ' is the angle Q′A′D in fig. 2, or ADQ′ in fig. 1.

3. In fig. 4, by Spherical Trigonometry,

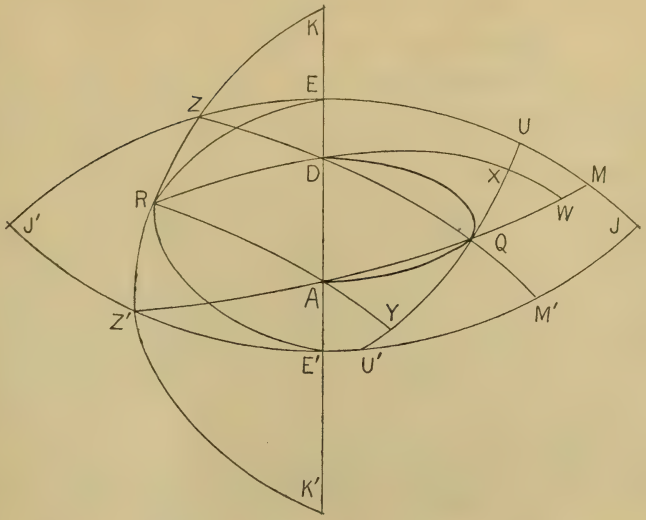
$$(1) \quad \sin \mathrm{AQ} = \sin \mathrm{AD} \sin \mathrm{ADQ} = \kappa \sin \phi, \ \cos \mathrm{AQ} = \Delta\phi,$$

$$(2) \quad \sin \mathrm{DQ} = \kappa \sin \phi', \quad \cos \mathrm{DQ} = \Delta\phi',$$

$$(3) \quad \cos \mathrm{AQ} \cos \mathrm{DQ} = \cos \mathrm{AD} = \cos c, \quad \Delta\phi\, \Delta\phi' = \kappa',$$

$$(4) \quad \phi' = \mathrm{am}\,(\mathrm{K} - u), \quad \text{with } \phi = \mathrm{am}\, u.$$

Fig. 4.



With EJ the polar circle of A, and E'J of D, and from (3) § 1, when Q makes a small advance to q, and M, M' to m, m',

$$(5)\qquad du=\frac{d\phi}{\Delta\phi}=\frac{\Delta\phi' d\phi}{\kappa'}=\frac{\cos \mathrm{DQ}}{\cos c}d\phi$$

$$=\frac{\text{spherical area QM}'m'q}{\cos c},$$

$$(6)\quad -du=\frac{d\phi'}{\Delta\phi'}=\frac{\Delta\phi d\phi'}{\kappa'}=\frac{\cos \mathrm{AQ}}{\cos c}d\phi'$$

$$=\frac{\text{spherical area QM}mq}{\cos c},$$

$$(7)\qquad u=\frac{\text{area AE}'\text{M}'\text{Q}}{\cos c},\quad \mathrm{K}-u=\frac{\text{area DEMQ}}{\cos c},$$

$$(8)\qquad \mathrm{K}=\frac{\text{area AE}'\text{JDQA}}{\cos c}.$$

The point Q describes a sphero-conic, with EJ, E'J the cyclic arcs, since

$$(9)\qquad \cos \mathrm{AQ}\cos \mathrm{DQ}=\sin \mathrm{QM}\sin \mathrm{QM}'=\cos c,$$

(Salmon, 'Solid Geometry,' Chap. X.), and the tangent UQU' intercepted by the cyclic arcs is bisected at Q, and cuts off a constant area $UJU' = \pi - 2c$; so that the angles JUU', $JU'U$ are equal to the angle UJU', and then

$$JQ = QU = QU',\ JM = MU,\ JM' = M'U'.$$

Since AU is a quadrant and AYU a right angle, YU is a quadrant, and so also is XU′; and $XU' = YU$, $QX = QY$.

If DX cuts AM in W, the spherical triangles XQW, YQA are equal, and

$$(10) \qquad DWQ = QAY = DAQ = \phi', \quad DW = DA,$$

$$(11) \qquad DW = DX + XW = DX + AY = DA = c.$$

4. So much for the geometry of the sphero-conic AQD, as developed in Salmon's 'Solid Geometry' and by Mr. Rose-Innes; returning to the vertical circle AQD, draw another interior circle *aqd*, centre *c*, with the same limiting point L and radical axis HEK, cutting QLQ′ in *q*, *q′*; then (fig. 3)

$$(1) \quad Hq \,.\, Hq' = HL^2 = HQ \,.\, HQ',$$

$$\begin{aligned}(2) \quad Qq \,.\, Qq' &= (HQ - Hq)(HQ - Hq') \\ &= HQ^2 - (Hq + Hq')HQ + HQ \,.\, HQ' \\ &= (HQ + HQ' - Hq - Hq')HQ \\ &= 2Mm \,.\, HQ = 2Cc \,.\, KQ.\end{aligned}$$

If QT is the tangent to this inner circle, cutting the outer circle again in Q_1,

$$(3) \qquad QT^2 = 2Cc \,.\, KQ, \quad QL^2 = 2CL \,.\, KQ,$$

$$(4) \qquad \frac{QT^2}{QL^2} = \frac{Cc}{CL} = \frac{Q_1T^2}{Q_1L^2},$$

and LT bisects the angle QLQ_1; also $IT = IL$, if QQ_1 cuts HE in I, giving a simple construction of the inner circle for a given QQ_1.

As the tangent QTQ_1 moves round, cutting the outer circle at equal angles,

$$(5) \qquad \frac{\text{vel. of } Q_1}{\text{vel. of } Q} = \frac{Q_1T}{QT} = \sqrt{\frac{K_1Q_1}{KQ}},$$

and this is the ratio of the velocity under gravity of two particles, Q and Q_1, describing the circle in the same manner, so that Q and Q_1 will remain simultaneous positions of the particles if QQ_1 is a tangent of the inner circle; and putting $ADQ_1 = \psi = \text{am}\, u_1$, then

$$(6) \qquad u_1 - u = w, \text{ a constant.}$$

5. Draw *gcf* in fig. 2 through *c* perpendicular to the plane AQD, cutting OA in *f*, and OL in *g*; the circle, centre *f* and

radius fO will pass through a and d, since

(1) $Ea \, . \, Ed = EL^2 = EO^2$,

and

(2) $aOL = EOL - EOa = ELO - EdO = dOL$,

so that OL bisects the angle aOd, and passes through g on the circle round Oad.

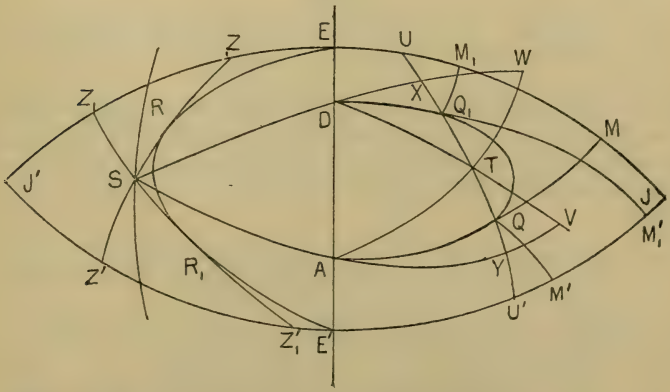
Then gLa, gaO are similar triangles, and $gL \, . \, gO = ga^2$, so that L and O are inverse points with respect to the sphere, centre g and radius ga; thence LT : TO is a constant ratio, equal to $La : aO$, and similarly LQ : QO is the constant ratio LA : AO round the circle AQD, and $OQ = OA \, . \, \Delta\phi$.

The inverse of the circle aTd with respect to O is another circle $a'T'd'$ parallel to $A'Q'D$; for $L'T' : OL' = LT : OT$, a constant ratio, so that $L'T'$ is constant, L' being the point inverse to L.

Conversely the inverse of a system of parallels of latitude on a sphere with respect to a point O on the sphere is a system of dipolar circles in a plane, as the circles of latitude on the stereographic representation of a hemisphere.

6. The line $O'T'$ from O', the centre of the sphere on the diameter OD, makes a constant angle, c', with $O'L'$, and the angle $DO'T'$ is double the angle DOT'; so that if the arc DT in fig. 5 in the representation on a sphere, centre O, is produced to double length to V, OV will make a constant angle c' with OA, which is parallel to $O'L'$, and the arc $AV = c'$.

Fig. 5.



Then in fig. 5, by Spherical Trigonometry,

(1) $\cos AT \, . \, \cos DT = \frac{1}{2}(\cos AD + \cos AV) = \frac{1}{2}(\cos c + \cos c')$,

a constant; so that T describes another sphero-conic, interior to that described by Q, and with the same cyclic arcs, so that its tangent QQ_1 cuts off from the cyclic arcs a triangle UJU′ of constant area, and UU′ is bisected at T (Salmon, 'Solid Geometry,' §§247, 248).

But since, in figs. 2, 3,

$$(2)\qquad \frac{QT}{TQ_1}=\frac{QL}{LQ_1}=\frac{QO}{OQ_1},$$

OT bisects the angle QOQ_1, and T in fig. 5 is the midpoint of QQ_1, so that (Salmon, § 252) QQ_1 cuts off a constant area from the outer sphero-conic.

With constant $u_1-u=w$, the area QMM_1Q_1 is constant, so that the spherical quadrilateral QMM_1Q_1 is constant, and this implies that the sum of the angles DQQ_1, DQ_1Q or DQV is constant, and this is found in § 8 to be $\operatorname{am}(K-w)+\frac{1}{2}\pi$.

As before in fig. 4, XU′ and YU are quadrants, $QY=Q_1X=p$ suppose, $Q_1Y=QX=q$ suppose;

$$DX=YV,\ DX+AY=AV=DW=c'.$$

7. The angle $ADX=\phi+\psi$ in fig. 5, as in fig. 3; $QDX=\psi$, $Q_1DX=\phi$.

Similarly $DAY=\phi'+\psi'$, $Q_1AY=\phi'$, $QAY=\psi'$.

Then in the spherical triangle AQV in fig. 5,

$$(1)\qquad \sin QV=\sin DQ_1=\kappa\sin\psi',\quad \sin AQ=\kappa\sin\phi,$$

$$(2)\qquad \frac{\sin QV}{\sin QAV}=\kappa=\frac{\sin AQ}{\sin QVA}=\frac{\kappa\sin\phi}{\sin QVA}=\frac{\sin AV}{\sin AQV},$$

so that $QVA=\phi$; this is seen also from the equality of the triangles QYV, Q_1DX, in which $QY=Q_1X$, $YV=DX$, so that $QVY=Q_1DX=\phi$; this is the equivalent of Mr. Rose-Innes's theorem (III.).

Also

$$(3)\qquad \sin AQV=\frac{\sin c'}{\kappa},\quad \sin AQV=\sin MQV=-\cos DQV,$$

since DQM is a right angle; and so we put, as in (8) § 8,

$$(4)\qquad AQV=\operatorname{am}(K+w),\qquad MQV=\operatorname{am}(K-w),$$

$$\sin c'=\kappa\operatorname{sn}(K+w)=\kappa\operatorname{sn}(K-w),$$

$$\cos c'=\operatorname{dn}(K+w)=\operatorname{dn}(K-w).$$

8. The addition formula of the elliptic function follows at once from a Legendre spherical triangle, in the manner employed by Mr. Kummell ('Analyst,' 1878); for in the spherical triangle AQV,

$$(1)\quad \sin p = \sin \mathrm{QY} = \sin \mathrm{AQ} \sin \mathrm{QAY} = \kappa \sin\phi \sin\psi',$$

$$\cos p = \sqrt{(1-\kappa^2 \sin^2\phi \sin^2\psi')},$$

$$(2)\quad \cos \mathrm{AY} = \frac{\cos \mathrm{AQ}}{\cos \mathrm{QY}} = \frac{\Delta\phi}{\cos p},$$

$$\sin \mathrm{AY} = \frac{\sin \mathrm{AQ} \cos \mathrm{QAY}}{\cos \mathrm{QY}} = \frac{\kappa \sin\phi \cos\psi'}{\cos p},$$

$$(3)\quad \cos \mathrm{YV} = \frac{\cos \mathrm{QV}}{\cos \mathrm{QY}} = \frac{\Delta\psi'}{\cos p},$$

$$\sin \mathrm{YV} = \frac{\sin \mathrm{QV} \cos \mathrm{QVY}}{\cos \mathrm{QY}} = \frac{\kappa \sin\psi' \cos\phi}{\cos p},$$

$$(4)\quad \cos c' = \cos \mathrm{AV} = \cos(\mathrm{AY}+\mathrm{YV})$$

$$= \frac{\Delta\phi\Delta\psi' - \kappa^2 \sin\phi \cos\phi \sin\psi' \cos\psi'}{1-\kappa^2 \sin^2\phi \sin^2\psi'}$$

$$= \mathrm{dn}(u+\mathrm{K}-u_1) = \mathrm{dn}(\mathrm{K}-w) = \mathrm{dn}(\mathrm{K}+w).$$

In a similar manner, with Spherical Trigonometry,

$$(5)\quad \cos \mathrm{AQY} = \frac{\sin \mathrm{QAY} \cos \mathrm{AQ}}{\cos \mathrm{QY}} = \frac{\sin\psi'\Delta\phi}{\cos p},$$

$$\sin \mathrm{AQY} = \frac{\cos \mathrm{QAY}}{\cos \mathrm{QY}} = \frac{\cos\psi'}{\cos p},$$

$$(6)\quad \cos \mathrm{VQY} = \frac{\sin \mathrm{QVY} \cos \mathrm{QV}}{\cos \mathrm{QY}} = \frac{\sin\phi\Delta\psi'}{\cos p},$$

$$\sin \mathrm{VQY} = \frac{\cos \mathrm{QVY}}{\cos \mathrm{QY}} = \frac{\cos\phi}{\cos\psi},$$

$$(7)\quad \cos \mathrm{AQV} = \cos(\mathrm{AQY}+\mathrm{VQY})$$

$$= \frac{\sin\phi\Delta\phi \sin\psi'\Delta\psi' - \cos\phi \cos\psi'}{1-\kappa^2 \sin^2\phi \sin^2\psi'}$$

$$= -\mathrm{cn}(u+\mathrm{K}-u_1) = -\mathrm{cn}(\mathrm{K}-w) = \mathrm{cn}(\mathrm{K}+w),$$

$$(8)\quad \mathrm{AQV} = \mathrm{am}(\mathrm{K}+w), \quad \mathrm{DQV} = \tfrac{1}{2}\pi + \mathrm{am}(\mathrm{K}-w).$$

9. In the reciprocal diagram of fig. 4, drawn on the left hand, R is the pole of XY, and the perimeter of the triangle

ARD is π; the tangent intercept ZZ′ by the cyclic arcs is $\frac{1}{2}\pi$, so that QZZ′ is a spherical triangular octant; RZ=ZK, RD=DK, RA=AK′; and if R, Z moves to r, z, as Q advances to q, and Dz crosses ZR in z',

$$(1)\quad \cos c\, du = \cos \mathrm{DQ}d\phi = \sin \mathrm{DZ}d\phi = \mathrm{Z}z'$$
$$= \text{arc } \mathrm{R}r - rz + \mathrm{RZ},$$

$$(2)\quad u \cos c = \text{arc } \mathrm{ER} - \mathrm{RZ},$$

thus representing the time by the difference of the arc ER and RZ.

In the reciprocal part of the diagram in fig. 5, where the tangents at R, R_1 intersect in S,

$$(3)\quad \mathrm{AS} + \mathrm{DS} = \pi - c',$$

$$(4)\quad (u_1 - u)\cos c = \text{arc } \mathrm{RR}_1 - \mathrm{R}_1\mathrm{Z}_1 + \mathrm{RZ};$$

$$(5)\quad \text{arc } \mathrm{RR}_1 = \mathrm{SR} + \mathrm{SR}_1 - \text{constant (Salmon, § 252)},$$

$$(6)\quad (u_1 - u)\cos c + \text{a constant} = \mathrm{SZ} - \mathrm{SZ}_1 = \mathrm{SZ} + \mathrm{SZ}_1' - \tfrac{1}{2}\pi.$$

The Spherical Trigonometry interpretation is the same as before in § 8; since

$$(7)\quad q = \mathrm{XQ} = \mathrm{XSQ} = \tfrac{1}{2}\pi - \mathrm{DSZ} = \tfrac{1}{2}\pi - \mathrm{ASZ}_1',$$
$$\sin q = \sin \mathrm{DQ} \sin \mathrm{QDX} = \kappa \sin\phi' \sin\psi,$$

$$(8)\quad \cos \mathrm{SZ} = \frac{\cos \mathrm{ZDS}}{\sin \mathrm{DSZ}} = \frac{\cos\psi}{\cos q},$$

$$\sin \mathrm{SZ} = \frac{\sin \mathrm{ZDS} \sin \mathrm{DZ}}{\sin \mathrm{DSZ}} = \frac{\sin\psi\Delta\phi'}{\cos q},$$

$$(9)\quad \cos \mathrm{SZ}_1' = \frac{\cos \mathrm{Z}_1'\mathrm{AS}}{\sin \mathrm{ASZ}_1'} = \frac{\cos\phi'}{\cos q},$$

$$\sin \mathrm{SZ}_1' = \frac{\sin \mathrm{Z}_1'\mathrm{AS} \sin \mathrm{AZ}_1'}{\sin \mathrm{ASZ}_1'} = \frac{\sin\phi'\Delta\psi}{\cos q},$$

$$(10)\quad \sin(\mathrm{SZ} + \mathrm{SZ}_1') = \frac{\sin\psi\cos\phi'\Delta\phi' + \sin\phi'\cos\psi\Delta\psi}{\cos^2 q}$$
$$= \mathrm{sn}\,(\mathrm{K} - u + u_1) = \mathrm{sn}\,(\mathrm{K} + w),$$
$$\mathrm{SZ} + \mathrm{SZ}_1' = \mathrm{am}\,(\mathrm{K} + w).$$

And with

$$(11)\quad p=\mathrm{XQ}_1=\mathrm{XSQ}_1=\tfrac{1}{2}\pi-\mathrm{DSZ}_1=\tfrac{1}{2}\pi-\mathrm{ASZ}',$$

$$(12)\quad \sin \mathrm{SZ} = \cos \mathrm{SZ}' = \frac{\cos \mathrm{SAZ}'}{\sin \mathrm{ASZ}'} = \frac{\cos \psi'}{\cos p},$$

$$\cos \mathrm{SZ} = \frac{\sin \mathrm{SAZ}' \sin \mathrm{AZ}'}{\sin \mathrm{ASZ}'} = \frac{\sin \psi' \Delta\phi}{\cos p},$$

$$(13)\quad \cos \mathrm{SZ}_1 = \frac{\cos \mathrm{SDZ}_1}{\sin \mathrm{DSZ}_1} = \frac{\cos \phi}{\cos p},$$

$$\sin \mathrm{SZ}_1 = \frac{\sin \mathrm{SDZ}_1 \sin \mathrm{DZ}_1}{\sin \mathrm{DSZ}_1} = \frac{\sin \phi \Delta\psi'}{\cos p},$$

$$(14)\quad \sin(\mathrm{SZ}-\mathrm{SZ}_1) = \frac{\cos\phi\cos\psi' - \sin\phi\sin\psi'\Delta\phi\Delta\psi'}{\cos^2 p}$$
$$= \mathrm{cn}(u+\mathrm{K}-u_1) = \mathrm{cn}(\mathrm{K}-w),$$

$$(15)\quad \mathrm{SZ}-\mathrm{SZ}_1=\tfrac{1}{2}\pi-\mathrm{am}(\mathrm{K}-w),$$
$$\mathrm{Z}_1\mathrm{Z}_1'=\tfrac{1}{2}\pi=\mathrm{am}(\mathrm{K}+w)+\mathrm{am}(\mathrm{K}-w)-\tfrac{1}{2}\pi,$$

$$(16)\quad \mathrm{SZ}+\mathrm{SZ}_1'=\mathrm{am}(\mathrm{K}+w).$$

Thus the constant in (6) is $\mathrm{am}(\mathrm{K}+w)-\tfrac{1}{2}\pi-\kappa' w$.

The sphero-conic ERE′ of fig. 4 is the projection on the sphere of the polar reciprocal of the circle AQD of fig. 1 with respect to D, and this is the parabola ER; while the sphero-conic S in fig. 5 will be the projection of the hyperbola of S in fig. 3, polar reciprocal of the circle $a\mathrm{T}d$.

10. The motion of P at the same level as Q in fig. 1, oscillating on the arc BAB′ of the circle on the diameter AE, will represent the associated motion of a pendulum, swinging through an angle $4c$, and then if θ denotes the inclination of the pendulum OP to the vertical

$$(1)\quad \sin^2 \tfrac{1}{2}\theta = \frac{\mathrm{AN}}{\mathrm{AE}} = \frac{\mathrm{AD}}{\mathrm{AE}} \cdot \frac{\mathrm{AN}}{\mathrm{AD}} = \kappa^2 \sin^2\phi,$$

$$\cos\tfrac{1}{2}\theta=\Delta\phi=\cos \mathrm{DQ},\quad \tfrac{1}{2}\theta=\mathrm{DQ},\quad \text{in fig. 4.}$$

Draw a circle through B and B′, centre o, in fig. 6; draw PB, and PpB′ crossing this circle at p; and draw PH and Oq perpendicular to BB′ and PB′.

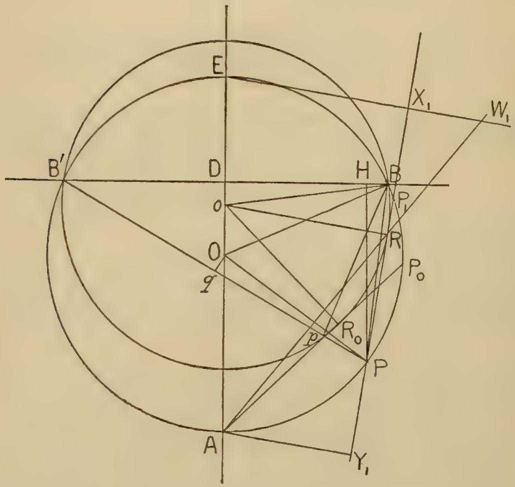
The triangles PpB and OoB are similar, and so are the triangles PHB, PqO; so that

$$(2)\qquad \frac{\mathrm{P}p}{\mathrm{O}o}=\frac{\mathrm{PB}}{\mathrm{OB}}=\frac{\mathrm{PB}}{\mathrm{PO}}=\frac{\mathrm{PH}}{\mathrm{P}q}=\frac{2\mathrm{PH}}{\mathrm{PB}'},$$

and if PRP_1 is tangent to this circle,

$$(3)\quad \mathrm{PR}^2=\mathrm{P}p\,.\,\mathrm{PB}'=2\mathrm{O}o\,.\,\mathrm{PH},\quad \mathrm{P}_1\mathrm{R}^2=2\mathrm{O}o\,.\,\mathrm{P}_1\mathrm{H}_1.$$

Fig. 6.



If P and P_1 are particles oscillating with the velocity due to the level BB′,

$$(4)\qquad \frac{\text{vel. of P}}{\text{vel. of P}_1}=\sqrt{\frac{\mathrm{PH}}{\mathrm{P}_1\mathrm{H}_1}}=\frac{\mathrm{PR}}{\mathrm{P}_1\mathrm{R}},$$

so that, as before in § 4, PP_1 will continue to touch the circle, centre o, during the subsequent motion; and the centre o has been chosen so as to bring P_1 to the same level as Q_1, and then PQ, $\mathrm{P}_1\mathrm{Q}_1$ will continue to be horizontal, by a suitable arrangement of gravity.

11. It is desirable to have a geometrical interpretation of the addition formula of (4) and (7), § 8, on the plane in figs. 3 and 6; this is seen by drawing AT, AR to meet DX and EX_1 produced, drawn perpendicular to QQ_1 and PP_1, in W and W_1.

Then if P_1 and Q_1 come to P_0 and Q_0 when P and Q are starting together from A, when

$$u=0,\ u_1=w,\ \text{and}\ ADQ_0=\gamma=\operatorname{am} w, \quad \cos AEP_0=\Delta\gamma,$$

$$(1)\quad \frac{DW}{DA}=\frac{cT}{cA}=\frac{cT_0}{cA}=\frac{DQ_0}{DA}=\cos ADQ_0=\cos\gamma, \quad DW=DQ_0\,;$$

$$(2)\quad \frac{EW_1}{EA}=\frac{oR}{oA}=\frac{oR_0}{oA}=\frac{EP_0}{EA}=\cos AEP_0=\Delta\gamma, \quad EW_1=EP_0.$$

$$(3)\quad AQ=AD\sin\phi, \quad DQ=AD\cos\phi,$$
$$AP=AE\,.\,\kappa\sin\phi=AB\sin\phi, \quad EP=AE\,.\,\Delta\phi,$$

so that, by Euclid VI. C,

$$(4)\quad DX=\frac{DQ\,.\,DQ_1}{AD}=AD\cos\phi\cos\psi,$$

$$AY=\frac{AQ\,.\,AQ_1}{AD}=AD\sin\phi\sin\psi,$$

$$(5)\quad AY_1=\frac{AP\,.\,AP_1}{AE}=AE\,.\,\kappa^2\sin\phi\sin\psi$$
$$=AD\sin\phi\sin\psi=AY,$$

$$EX_1=\frac{EP\,.\,EP_1}{AE}=AE\,.\,\Delta\phi\Delta\psi.$$

$$(6)\quad \cos\gamma=\frac{DW}{AD}=\frac{DX}{AD}+\frac{XW}{AD}=\frac{DX}{AD}+\frac{AY}{AD}\cdot\frac{XW}{AY},$$

$$\frac{XW}{AY}=\frac{XT}{TY}=\frac{Dc}{cA}=\frac{Q_0T_0}{T_0A}=\frac{Q_0L}{LA}=\Delta\gamma,$$

$$(7)\quad \cos\gamma=\cos\phi\cos\psi+\sin\phi\sin\psi\Delta\gamma.$$

$$(8)\quad \Delta\gamma=\frac{EW_1}{AE}=\frac{EX_1}{AE}+\frac{X_1W_1}{AE}=\frac{EX_1}{AE}+\frac{AY_1}{AE}\cdot\frac{X_1W_1}{AY_1},$$

$$(9)\quad \frac{X_1W_1}{AY_1}=\frac{X_1R}{RY_1}=\frac{Eo}{oA}=\frac{P_0R_0}{R_0A}=\sqrt{\frac{DN_0}{DA}}=\cos\gamma,$$

$$(10)\quad \Delta\gamma=\Delta\phi\Delta\psi+\kappa^2\sin\phi\sin\psi\cos\gamma.$$

Here (7) and (10) are the well-known formulas of Legendre; and thence, as before in (7) and (4), § 8,

$$(11)\quad \cos\gamma=\cos\phi\cos\psi+\sin\phi\sin\psi(\Delta\phi\Delta\psi+\kappa^2\sin\phi\sin\psi\cos\gamma)$$

$$\cos\gamma=\frac{\cos\phi\cos\psi+\sin\phi\sin\psi\Delta\phi\Delta\psi}{1-\kappa^2\sin^2\phi\sin^2\psi};$$

$$(12)\quad \Delta\gamma=\Delta\phi\Delta\psi+\kappa^2\sin\phi\sin\psi(\cos\phi\cos\psi+\sin\phi\sin\psi\Delta\gamma),$$

$$\Delta\gamma=\frac{\Delta\phi\Delta\psi+\kappa^2\sin\phi\sin\psi\cos\phi\cos\psi}{1-\kappa^2\sin^2\phi\sin^2\psi}.$$

Or, geometrically,

$$(13)\quad \frac{\cos\gamma-\cos\phi\cos\psi}{\sin\phi\sin\psi}=\frac{\mathrm{XW}}{\mathrm{AY}}=\frac{\mathrm{EW}_1}{\mathrm{AE}}=\frac{\mathrm{EX}_1}{\mathrm{AE}}+\frac{\mathrm{X}_1\mathrm{W}_1}{\mathrm{AE}}$$
$$=\Delta\phi\Delta\psi+\kappa^2\sin\phi\sin\psi\cos\gamma,$$

$$(14)\quad \frac{\Delta\gamma-\Delta\phi\Delta\psi}{\kappa^2\sin\phi\sin\psi}=\frac{\mathrm{X}_1\mathrm{W}_1}{\mathrm{AW}_1}=\frac{\mathrm{DW}}{\mathrm{AD}}=\frac{\mathrm{DX}}{\mathrm{AD}}+\frac{\mathrm{XW}}{\mathrm{AD}}$$
$$=\cos\phi\cos\psi+\sin\phi\sin\psi\Delta\gamma,$$

equivalent to (11) and (12) above.

So also the formula for $\sin\gamma=\operatorname{sn} w$ can be interpreted.

LXXXII. *The Optical Determination of Stress. By* E. G. COKER, *M.A., D.Sc., Professor of Mechanical Engineering, City and Guilds of London Technical College, Finsbury*[*].

THE principal advances in our experimental knowledge of the strength and properties of materials have been made by the use of mechanical apparatus for applying stress and measuring strain, and instruments of this class are now in general use possessing a sufficient degree of accuracy for the most refined measurements, but whatever applications purely mechanical methods may have, they possess a common characteristic feature that measurements must be taken over a definite length, area, or volume maintained in a standard condition throughout in order that the state of stress or strain may be referred to some standard measure possessed by the instrument, or by which it is calibrated. Whatever the arrangement may be, it is not in general possible to measure the stress or strain at a point, if the body is subjected to stress varying from point to point.

This defect in purely mechanical devices is one which from the nature of the case is hardly likely to be overcome entirely, yet in the great majority of the problems which arise in practice the stresses change very rapidly from point to point, and experimental information, if it exists, has almost invariably been obtained by using mechanical apparatus incapable of determining the stress at a point. Mathematical researches of the state of stress and strain in bodies give exact solutions of a variety of complicated problems; but some of the simplest forms of practical construction offer problems of the greatest difficulty, as for example the determination of the stresses in hooks, chain links, and rivetted

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[*] Communicated by the Author: read in abstract at the British Association, Sheffield.

plates, the effect of notches and holes of various forms in tension and compression members, beams, pillars, and shafts, the distribution of stress in built up structures such as plate girders, rivetted frames, masonry dams, and the like.

In most of these cases the distribution of stress has not been completely solved.

One of the most suggestive and instructive experimental methods is suggested by the differential equations of plane strain which, under certain conditions, have identically the same forms as the equations of stream-line motion in a perfect fluid. Thus in irrotational plane strain when u and v are the displacements in the direction of the axes of x and y, we obtain

$$\partial v/\partial x-\partial u/\partial y=0, \quad \partial u/\partial x+\partial v/\partial y=0,$$

while if u and v are the displacements of a perfect fluid moving irrotationally we obtain similar equations. The stress problem has therefore an analogous problem in hydrodynamics, but the restrictions to which the analogy is subjected seriously limit its applications.

Many experimental researches on the behaviour of materials have also been made using models shaped in rubber, and by measurements of the comparatively large strains produced in this material under various conditions of loading, the stresses in the structure have been determined.

A method invented by Brewster depends on the application of polarized light for observing the condition of a specimen made of glass, and he suggested that models of arches might be made of this material and their optical properties examined under stress.

This matter has received a considerable degree of development at the hands of Neumann* and Maxwell†; but the difficulty and expense of making objects in glass has hindered the progress of the experimental method.

In an attempt to obtain an optical verification of the mathematical theory of the stresses at the principal section of a hook, one or two models were shaped from a square of glass, and their behaviour under stress examined by polarized light. The experiments showed that to produce any measurable effect the glass must be very thick and the stresses dangerously near the breaking stress of the material.

Several other materials were tried, and a suitable material was ultimately found in "xylonite," which possesses most of

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* "Die Gesetze der Doppelbrechung des Lichts," F. E. Neumann, *Abhandlungen der K. Akademie der Wissenschaften zu Berlin*, 1841.

† "On the Equilibrium of Elastic Solids," J. C. Maxwell, Collected Papers.

the desirable features of glass, with the additional advantage of being easily cut into shape without suffering any injury of its elastic or optical properties.

Xylonite is a preparation of nitrocellulose of widely extended use, and it can be obtained in sheets several square feet in area free from initial stress except at the edges, so that it shows no colour effect in polarized light.

It is not quite so transparent as glass, and it is usually slightly tinted, but this is not found to be a disadvantage in practice.

Specimens may be cut from the sheet by ordinary wood and metal working tools, and with a little practice any object capable of being represented in a plane may be fashioned with ease. The material is fairly isotropic in character, and although a sheet appears to show a distinct grain, this is apparently a mere surface effect due to the sheet being cut from a plastic slab ; it is afterwards subjected to treatment which renders it semielastic, and its surface is finally polished before use.

Xylonite is much more compressible than glass, and it possesses the useful property of not readily breaking under stress. Up to a stress of about 4000 lbs. per square inch it may be subjected to repeated stresses without injury or change of its optical character, but beyond this it shows signs of residual stress when the load is removed.

Its elastic behaviour under stress is not so perfect as that of glass, and the values of Young's modulus and Poisson's ratio are very different.

This will be readily seen when the results of experiments on specimens of both materials are compared.

The following table gives the values obtained in a tension specimen of xylonite 8 ins. long between measuring-points, 0·49 in. wide and 0·123 in. thick.

TABLE I.

Load, pounds.	Extensions, ins.	Differences.	Contraction of width, ins.	Differences.
0	0		0	
40	·017	·017	·0004	·0004
80	·035	·018	·00085	·00045
120	·052	·017	·0013	·00045
160	·071	·019	·0017	·0004
120	·055	·016	·0014	·0003
80	·037	·018	·0001	·0004
40	·020	·017	·00055	·00045
0	·001	·019	·0001	·00045

These readings give a mean value for Young's modulus of 299,100 in lbs. and inch units, and for Poisson's ratio a value 0·39.

For comparative purposes a set of similar values are given in Table II. for a piece of plate-glass which when examined between crossed nicols showed very little trace of internal stress, and in this respect it was very similar in character to xylonite.

The specimen* was 1·016 ins. by 1·008 ins. in section and 1·25 ins. of measured length.

TABLE II.

Load, pounds.	Compressions in millionths of an inch.		Lateral extensions, millionths of an inch.	
1000	0		0	
		240		42
3000	240		42	
		240		44
5000	480		86	
		240		48
7000	720		134	
		220		44
9000	940		178	
		220		43
7000	720		135	
		240		46
5000	480		89	
		240		49
3000	240		40	
		240		40
1000	0		0	

and the mean value of E obtained from these readings was 10,380,000 and for Poisson's ratio 0·233.

If a homogeneous beam of plane-polarized light passes through a plate of unstressed glass, xylonite, or other like transparent material, it suffers no decomposition; but the application of a tension or compression stress causes the material to behave like a double refracting substance, and the plane-polarized beam breaks up into plane-polarized rays having their directions of vibration parallel and perpendicular to the axes of principal stress. These rays have different velocities in the material, and their relative retardation R is proportional to the indices of refraction μ_0 and μ_ϵ of the two rays and the thickness T of the plate of material through which they pass; this is expressed by

$$R=(\mu_0-\mu_\epsilon)T. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Experiments on glass show that the difference of the refractive indices is proportional to the difference of the principal

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* Specimen "d," p. 65, of "An Investigation into the Elastic Constants of Rocks," by Adams and Coker, Proceedings of the Carnegie Institution, Washington.

stresses X and Y in the plate, and if therefore we write

$$\mu_0 - \mu_\epsilon = \mathrm{C}(\mathrm{X} - \mathrm{Y}), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

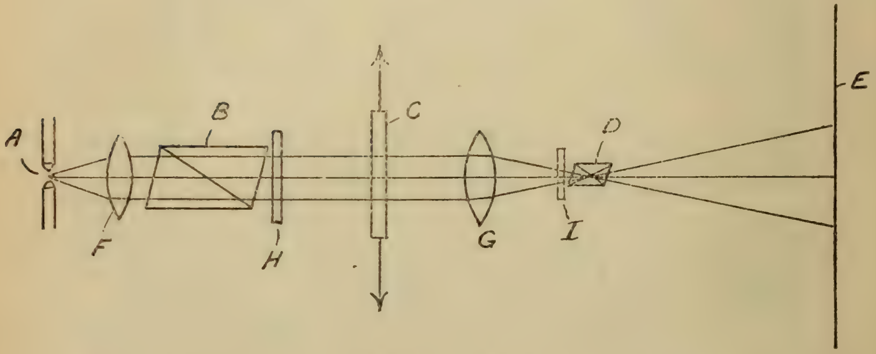
where C is an optical coefficient, the value of which can be determined by experiment, we obtain

$$\mathrm{R} = \mathrm{C}(\mathrm{X} - \mathrm{Y})\mathrm{T}.$$

Wertheim's[*] experiments showed that the optical coefficient is independent of the wave-length of the light used, but the later experiments of Pockels[†] and Filon[‡] show that a variation exists which in very accurate experiments must be taken into account. For the purposes of this paper the variation of the optical coefficient is neglected, and the retardation is assumed to follow the law stated by equation 2.

A convenient arrangement for examining the effects of stress is shown by fig. 1. Light from a point source A is plane-polarized by its passage through a Nicol's prism B, and is transmitted through a transparent plate C of the material under examination. This transmitted light is analysed by a second Nicol's prism D, and the image showing the colours produced by the interference of the ordinary and extraordinary rays is projected on a sheet E of squared paper, or is photographed as may be convenient. Condensing lenses F and G are also provided for focussing purposes. A very

Fig. 1.



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[*] *Annales de Chimie et de Physique*, Series 3, vol. xl.

[†] "Über die Änderung des optischen Verhaltens verschiedener Gläser durch elastische Deformation," *Annalen der Physik*, Series 4, vol. vii.

[‡] Camb. Phil. Soc. Proc. vols. xi. and xii.

convenient form of apparatus for this work is described by Cheshire*, and his arrangement was used for the experiments.

If the value of the optical coefficient is known, and the retardation is measured for a given thickness of the material, the difference between the principal stresses at a point may be obtained, or in the case of simple tension or compression where one of the principal stresses is zero the absolute value of the stress can be directly determined.

For most purposes, however, it is more convenient to proceed in a different manner by a process of comparison of colours. A scale may be readily formed in which the relation between say tension or compression and colour due to interference is obtained experimentally. Thus, for example, a specimen 0·49 in. wide and 0·123 in. thick gave the following colour-scale in tension.

TABLE III.

Load in pounds per sq. inch.	Colour.	Load in pounds per sq. inch.	Colour.
0	Dark field.	2020	Reddish yellow.
340	Faint white.	2170	Reddish purple.
670	Intense white.	2350	Purple.
1018	Faint yellow.	2510	Sky-blue.
1340	Lemon-yellow.	2690	Very light blue.
1680	Orange-yellow.	3020	Nearly white.

and these loadings were repeated at different times with the same results as far as could be judged.

It is difficult, however, to independently estimate most of these colours, with the possible exception of purple, which is usually well defined; and it is necessary for accuracy to arrange the experiment, so that the colours produced in the object under examination may be directly compared with a colour produced by uniform stress.

It is not difficult to arrange a standard specimen and the object under test so that they may appear close together in the same field of view, and this allows of much greater accuracy as the colours produced may be matched in the same manner as in photometric work.

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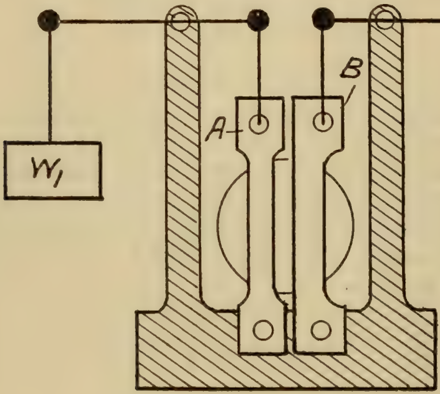
* "Some new Optical Projection Apparatus," by F. J. Cheshire. Optical Society, 1908.

The usual arrangement adopted is shown in fig. 2, in which a symmetrically loaded tension specimen A and another B with an eccentric load are both shown secured in the grips of miniature testing machines. In this example the specimens were cut from the same strip, and the interference effects were projected on to a squared paper screen so that the breadth of the eccentrically loaded specimen was 2 ins., corresponding to an actual breadth of 0·309 in.

Fig. 2.



The stresses produced at different points in the cross-sections were determined by loading the standard test-piece until the uniform colour produced in it agreed with that produced at a definite point in the cross-section of specimen B, and the stress was calculated from the load and the dimensions of the levers. This method requires no correction for the tension side of the specimen as the diminution of thickness due to the load is the same for both, but a small correction is required for the compression side as the relative retardation between the interfering rays is greater on account of the increase in thickness due to the stress.

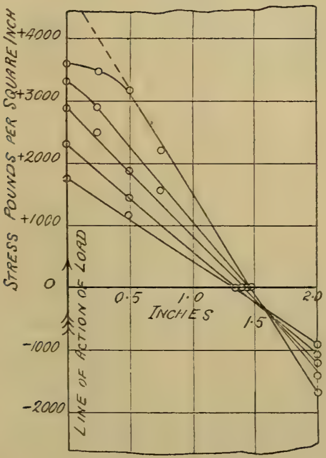
Measuring in this way, the following values (Table IV.) of the stress were obtained across the section of the specimen B, where the abscissæ refer to the projected dimensions measured from the line of application of the load, which in this case coincided with one edge of the specimen.

These values are plotted in fig. 3, and the diagram shows that the variation of stress in the specimen is approximately a linear one, except for the highest load, when the specimen failed on the tension side, thereby producing a change in the

TABLE IV.

	Abscissæ, inches.					
	0.	0·25.	0·5.	0·75.	Distance of neutral axis from zero line ins.	2·00.
Stress in pounds per square inch.	+1750	...	+1190	...	1·35	−960
	+2320	...	+1410	...	1·35	−1070
	+2880	+2540	+1880	...	1·39	−1190
	+3330	+2880	...	+1520	1·45	−1470
	+3560	+3450	+3160	+2200	1·47	−1640

Fig. 3.



properties of the material, which showed itself when the load was removed by its faint doubly refracting power. The highest values of the stress are therefore not correct, owing to their values having been obtained by comparison with a test piece differing in optical condition from the object.

The position of the neutral axis for the lower loadings agrees very well with that given by calculations using the ordinary formula for beams. It is also worthy of note that the neutral axis moved away from the tension side as the load increased—a result* which agrees with theoretical determinations.

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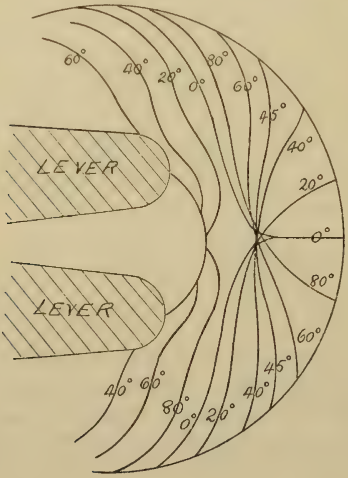
* Love's 'Theory of Elasticity,' p. 349.

As an example of a more complicated kind we may take a hook of very great curvature. This case differs optically from the preceding one in a very important way, as the principal stresses on each side of the principal section show considerable variation in angular position.

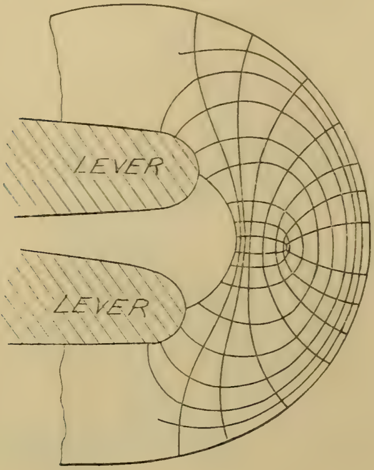
If, therefore, a plane-polarized beam passes perpendicularly through the plate with the intersection of its plane of polarization oblique to the directions of principal stress, it is resolved into components corresponding to these latter directions, and therefore in all parts of the specimen through which the plane-polarized light passes, the ray is resolved into two directions at right angles. The interference of these two rays produces colour fringes, except in those parts of the field where the directions coincide with the planes of the crossed nicols. Such bands, therefore, indicate the directions of the principal stresses, and by turning the nicols round while their planes of polarization remain at right angles to one another, a series of curves are obtained as shown, for example, by fig. 4, where these loci have been obtained for a hook having an outer radius of 0·75 in. and an inner radius of 0·277 in., the plate being 0·123 in. thick.

Fig. 4.



The effect thus produced is equivalent to superposing a black cross upon the interference colours produced by the stress, and it serves a useful purpose in that it enables curves of principal stress to be drawn graphically, or by calculation when these loci are determined with reference to the angular positions of the nicols. Such curves have been determined graphically in this case and are shown by fig. 5.

Fig. 5.

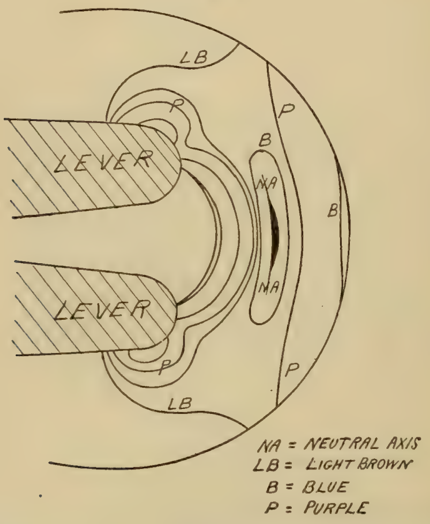


For measurement of the stress it is necessary to get rid of the distorting effect produced by the black cross, and I am greatly indebted to Professor Silvanus Thompson, F.R.S., for suggesting for this purpose the use of two quarter wave-plates (H, I, fig. 1) set with their axes inclined at 45° to the Nicol's prisms, whereby the plane wave issuing from the first nicol B is converted into circularly polarized light. The circularly polarized beam produced by this combination, whether right-handed or left-handed, has no special direction of polarization, and it therefore presents the same aspect to all parts of the object under stress. It is again converted to plane-polarized light by the inverse combination of quarter wave-plate and nicol and the interference fringes are still produced, while the black cross disappears. This arrangement has the further practical advantage that, except for a slight and invariable change of tint, the interference colours produced are independent of the angular position of the object.

Fig. 6 shows the general arrangement of the colour fringes presented by the hook when viewed by circularly polarized light, and the stresses at points of the central section can be determined in a similar manner to that described above.

The projected image of 0·473 in. actual width measured 2 ins. on the squared paper screen, and the stresses obtained are given in the annexed table.

Fig. 6.



	Abscissæ, inches.					
	0.	0·16 0·25.	0·5.	Neutral axis.	1·5.	2·0
Stresses in pounds per square inch.	2380	1970 at 0·1	...	0·7	...	640
	3370	2380 at 0·16	...	0·7	950	1270
	4060	2480 at 0·25	...	0·7	1460	1720
	4570	....	1460	0·75	1910	2730

and a plot of these values is shown in fig. 7.

The position of the neutral axis has been mathematically determined by Andrews and Pearson*, and its distance $\bar{y}_0$ from the centre of the section has been shown to be

$$\bar{y}_0=\rho_0\left\{1\Big/\left(\gamma_1-\frac{\rho_0}{c}\gamma_2\right)^{\frac{1}{\eta+1}}-1\right\},$$

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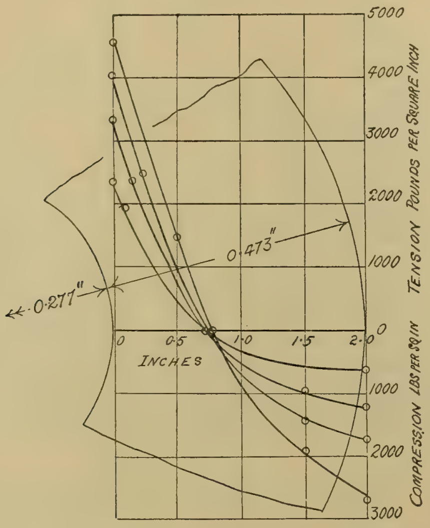
* Drapers' Company Research Memoirs. Technical Series. I. 1904.

where ρ_0 is the mean radius of curvature, c is the distance of the applied force from the centre of the section, and γ_1, γ_2 are constants depending on ρ_0, η, and T. In the present case $\gamma_1 = 1{\cdot}048$, $\gamma_2 = {\cdot}891$, where $\eta = {\cdot}39$, and the position of the neutral axis is ·055 in. from the centre on the tension side.

Fig. 7.



This agrees fairly well with the observed value of ·059 in. having regard to the fact that ρ_0 is increased about 10 per cent. of its original value by the load.

Owing to the uncertainty of the exact position of the forces when a ring of such great curvature is stressed and somewhat distorted by a load, it has not been possible with the apparatus at my present disposal to establish any very accurate relationship between the external and internal forces.

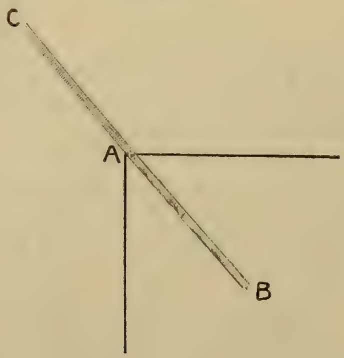
The present examples, however, serve to illustrate the practical uses which it is possible to make of this method of analysing the stresses produced in any object capable of being represented in a plane by a model cut from a sheet of transparent material.

LXXXIII. *Rays of Positive Electricity.*

By Sir J. J. THOMSON *.

I FIND that the investigation of the Positive Rays or Canalstrahlen is made much easier by using very large vessels for the discharge-tube in which the rays are produced. With large vessels the dark space around the cathode has plenty of room to expand before it reaches the walls of the tube; the pressure may therefore be reduced to very low values before this takes place, and in consequence the potential difference required to force the discharge through the tube at these low pressures is much lower than when the tubes are smaller. It is possible with large tubes to work with much lower pressures than with small ones, and at the lower pressures phases of the phenomena of the positive rays come to light which are absent or inconspicuous at higher pressures. With small tubes and therefore comparatively high pressures, when the arrangement used to investigate the rays is that described in my former paper (Phil. Mag. [6] xviii. p. 821, 1909), *i. e.* when the rays passing from a hole in the cathode through a long narrow tube fall on a phosphorescent willemite screen after passing through superposed magnetic and electric fields, the appearance on the screen is as follows.

Fig. 1.



The bright spot A which marks the place where the undeflected rays strike the screen is drawn out by the magnetic and electric forces, producing respectively vertical and horizontal displacements, into a straight band AB (fig. 1) of

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* Communicated by the Author. Read at the meeting of the British Association, Sept. 1, 1910.

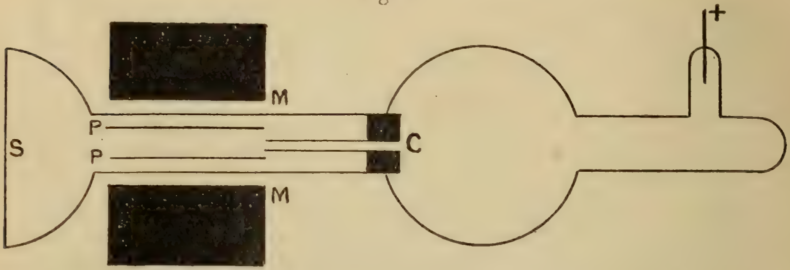
fairly uniform intensity; there is also a fainter prolongation AC of the band in the opposite direction to AB due to rays which carry a negative charge. The velocities and the values of e/m for the rays can be determined by measurements of this band. For if y and x are the vertical and horizontal deflexions of a ray striking the screen at P, then the velocity of this ray is equal to $c_1 y/x$ and the value of e/m to $c_2 y^2/x$, where c_1 and c_2 are constants depending on the strengths and positions of the electric and magnetic fields. I have shown (Phil. Mag. *loc. cit.*) that the velocity of the rays in this case is practically independent of the potential difference between the electrodes in the discharge-tube, and that we could increase the potential difference from 3000 to 40,000 volts without appreciably increasing this velocity. With small tubes the appearance I have just described is often the only effect to be observed even when the pressure is reduced close to the point at which it ceases to be possible to force the discharge through the tube.

When large discharge-tubes are used a much greater variety of effects can be observed. I have used tubes with a volume as large as 11 litres; these, however, are somewhat difficult to procure and not very convenient to work with. I have found flasks having a volume of 2 litres, such as are used for boiling-point determinations, large enough for most purposes.

A uniform and sensitive phosphorescent screen is of great importance as there is often a considerable amount of detail to be made out, and some of it too faint to be visible unless the screen is a very good one. My assistant Mr. Everett has lately succeeded in making very uniform screens by grinding the willemite into exceedingly fine powder, then shaking the powder up in alcohol and allowing it to settle slowly from the alcohol on to a flat glass plate; when the deposit has reached the requisite thickness the rest of the suspension is drawn off and the deposit allowed to dry; when dry it sticks quite firmly to the plate, and the deposit is much more uniform than that obtained by the method I formerly used of dusting powdered willemite on a glass plate smeared with water glass. The screens soon lose their sensitiveness if bombarded by the rays, and when any fine detail has to be made out it is advisable to use a new screen or a part of the screen not previously bombarded by the rays.

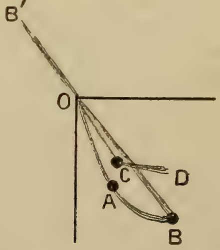
The discharge-tube is shown in section in fig. 2 (p. 754). The perforated cathode C protrudes well into the tube, the rays pass through the hole in the cathode through the fine tube and then travel between the poles MM of an electromagnet and the parallel plates PP which are connected with a battery

Fig. 2.



of small storage-cells; the rays after being deflected fall on the willemite screen S. With a tube of this kind the appearance on the screen as the pressure is gradually reduced is as follows, the rays being exposed to both magnetic and electric forces. At the highest pressure at which the phosphorescence is visible, the phosphorescent patch covers a considerable area, the left hand (the least deflected) boundary being fairly well defined while the other boundary is hazy. As the pressure is still further reduced we get the appearance shown in fig. 1; this persists for a considerable range of pressure, but as the pressure is still further reduced bright spots as described in my paper (Phil. Mag. [6] xiii. p. 561, 1907) begin to appear, while the luminosity appears to divide into two portions, the appearance being that represented in fig. 3.

Fig. 3.



The luminous band, which at the higher pressures was the sole representative of the phosphorescent, can still be seen in its old position though it is not so bright as when the pressure was higher, the negative continuation of it still persists. As the pressure is still further diminished this part of the phosphorescence with its negative accompaniment gets fainter and fainter but does not alter in position, showing that the velocity of the rays producing it is independent of the potential difference between the electrodes, finally when the pressure is very low it looks like a faint nebulous band over which brighter patches are superposed.

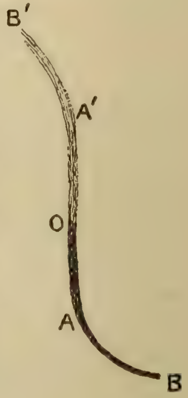
The relations between the positive and negative portions of the phosphorescent figures when the pressure is low are very interesting. The lower, more deflected portion has frequently two bright spots A and B for each of which $e/m = 10^4$: one at A which gradually moves, as the pressure is diminished, along a parabolic path to O, the position of the undeflected spot; the other, not quite so definite, at B, a point on the phosphorescent band which has survived from the higher pressure. The negative portion at these low pressures is not a replica of the positive portion as it was at the higher pressures, but remains unaltered in shape and position as the pressure diminishes, getting gradually fainter. There is no trace on it of the spot A; the spot B is, however, visible at B′, and the luminous band BB′ can be traced as a straight strip occupying the same position as it did at higher pressures when it was the only part of the phosphorescence visible.

There is nothing on the negative side corresponding to the portion OCD on the positive, or at any rate if it exists it is so very much fainter, that I have never been able to satisfy myself of its existence, even when the negative part OB′ was quite bright.

I think there is exceedingly strong evidence to show that the straight band of phosphorescence which alone is seen at higher pressure and which lingers on with diminished intensity when the pressure is reduced, has a different origin from the phosphorescence which shows itself as bright spots on an isolated streak of phosphorescence, and which is due to rays whose velocity, unlike that of those producing the first kind of phosphorescence, depends upon the potential difference between the electrodes.

Such evidence is afforded by the following experiments, the first of which shows the complete symmetry between the positive and negative parts of the first kind of phosphorescence, and also that much of this kind of phosphorescence is due to secondary rays produced after the primary rays have passed through the cathode. In this experiment, the magnetic and electric fields, instead of being as in the previous experiments arranged so that when a particle was exposed to a magnetic force it was simultaneously exposed to an electric one, were made to overlap. The poles MM of the electromagnet were pushed nearer the screen so that they extended on the screen side beyond the parallel plates PP which produced the electric field. With this arrangement a particle, after leaving the space between the plates, enters a region where it is exposed to magnetic but not to electric forces, *i. e.* when it is deflected vertically but not horizontally. In this case the appearance presented by the phosphorescence patch at the pressure, when under normal circumstances it would be as represented in fig. 1, is shown in fig. 4.

Fig. 4.



There is now a vertical portion OA due to rays which have been deflected vertically but not horizontally, *i. e.* which have been acted upon by magnetic but not by electric forces, and which must therefore have been produced between the ends of the parallel plates and the screen. Connected with the vertical piece OA there is a curved part AB due to rays which have been deflected by the electrostatic as well as the magnetic forces. The rays falling on the portion of AB near to A have been produced inside the parallel plates close to the end next the screen, and have only been exposed to the electric force for a small portion of their path. As we approach B the corresponding rays have been produced nearer the cathode, while the rays at the very end were already produced before the space between the plates was entered, for we find that the end B of the phosphorescent patch is in the same position as where the fields of action of the magnetic and electric forces were coincident.

If we reverse both the electric and magnetic forces so as to bring the negatively charged particles on to the part of the screen previously occupied by the positive ones, we find that the phosphorescent band due to the negative rays is an exact reproduction in shape, size, and position of that due to the positively charged particles.

If this experiment is repeated when the pressure has been reduced to the stage when the phosphorescence splits up into two bands as in fig 3, the contrast between the behaviour of the two bands is very instructive. The lower band (*i. e.* the one where the magnetic deflexions are the greatest) is bent in the way we have just described, and is below the position it occupied when the magnetic and electric fields were coincident. The upper band on the other hand is bent in the opposite way and is above the position it occupied when the fields coincided. The appearance of the phosphorescence is represented in fig. 5, where the dotted lines show the positions of the bands when the magnetic and electric fields coincide, the continuous lines their position when the magnetic

Fig. 5.

field is pushed forward towards the screen. The shape of the lower band can be explained as we have seen by supposing that it is due to secondary rays which are continually being produced as the undeflected rays travel from the cathode to the screen. The configuration of the upper band can be explained by supposing that it is due to primary rays coming through the cathode, and that these are not recruited by secondary rays, but on the other hand gradually get neutralized by combining with negative corpuscles. For if this were the case the rays which strike the screen near O are not, as in the previous case, rays which have been produced near the ends of the electric and magnetic fields, but are rays which have been neutralized soon after entering these fields. As the deflexions of such rays are due to the forces which act on the charged particle immediately after it leaves the tube and enters the space between the plates, the effect of pushing the magnetic field forward away from the tube will be to diminish the magnetic force on these particles while the electric force is unaltered : this will clearly tend to make the luminous band more nearly horizontal than it was before the magnets were pushed forward, and we see from fig. 5 that this is just the effect produced.

The upper band also differs from the lower one in not having, so far as I have been able to observe, any negative portion connected with it.

The difference between the properties of the rays which constitute the two bands is also shown by the following experiment. Two systems of magnets and parallel plates instead of one are placed between the cathode and the screen, the fields in these could be excited separately. The deflexion due to the magnet next the cathode is horizontal, that due to the magnet next the screen vertical. The electric fields are at right angles to the corresponding magnetic fields. Suppose that the magnetic field nearest the cathode is excited, the phosphorescent patch will be drawn out into a horizontal line, the most deflected portion of which, B, will be due to particles which were charged when they passed through the cathode. Now let the magnet next the screen be excited, the appearance on the screen is as in fig. 6; those rays which were charged when they passed through the first field and were deflected by it are still further deflected along the line BC, but in addition to this the stream of neutral particles as it passed between the two magnets has produced new secondary rays and these are deflected along OA. Thus all the rays which were charged when they passed through the cathode are found on the line BC, while OA consists exclusively of those which have been produced or which have acquired their charge after they left the first magnet. If now we put on the electric field in the system next the screen, we find that, at low pressures, the portion BC, which consists of rays charged when they passed through the cathode, is broken up into the two bands of which we have been speaking, and which were seen when only one system of electric and magnetic forces was used. On the other hand, the band OA, due to rays which were produced nearer the screen than the first magnet, does not bifurcate but consists of only one branch for which the maximum value of $e/m = 10^4$. The appearance of the phosphorescence is shown in fig. 7.

Fig. 6.

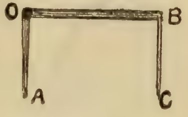
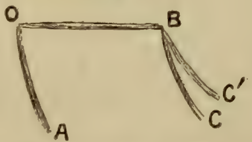


Fig. 7.



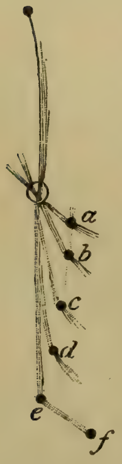
I have hitherto spoken only of two bands, but when the pressure is low there seem with these large tubes to be parabolic bands corresponding to every gas in the tube. By using very sensitive screens I have been able to detect the bands corresponding to hydrogen, helium, carbon, air, oxygen, neon, and mercury vapour. The appearance on the screen when there are several gases in the tube is almost like a spectrum, and I think this effect may furnish a valuable means of analysing the gases in the tube and determining their atomic weights. There is a band on the screen corresponding to a value of e/m about $\frac{1}{7}\times 10^4$, due to the air in the tube; the arrangement I was using was not suitable for applying the most intense magnetic fields and I could not detect that this spot was double, with one constituent corresponding to the atom of nitrogen, the other to the atom of oxygen. When CO was put into the tube, however, the band in this region was clearly double although the constituents were very close together, one constituent I suppose corresponding to oxygen the other to carbon.

One interesting feature in these experiments is that the bright spots on the bands are all in the same vertical line, showing that the electrostatic deflexion is the same for them all, and therefore that this energy of the particles which form the bright spots corresponding to the different gases is due to a fall through the same potential difference. The velocity of the rays forming these bright spots varies with the potential difference between the electrodes.

The bright spots come I think from the negative glow at the outer boundary of the dark space; they are weakened by any arrangement which prevents the portion of the negative glow straight in front of the cathode having free access to the cathode. Thus, if the anode A is a disk placed in front of the cathode, the spots do not appear unless the anode is pushed back so as to be outside the dark space; the continuous band due to the secondary radiation is, however, well developed when the anode is put forward.

Another interesting feature of these bright bands is that some of them have negative tails connected with them while others have not. This is shown in fig. 8, which represents the appearance in a tube containing mercury vapour, air, helium, and hydrogen; *a*, *b*, *c*, *d*, are the spots corresponding to these substances, the spot *f* is on the part due to secondary radiation: it will be noticed that this secondary radiation has a negative tail, there are no tails corresponding to the lighter elements, but the air and mercury bands have a well developed tail.

Fig. 8.



The details of the measurements of the values of e/m for the different elements are given at the end of this paper; it may be noted here, however, that with the exception of hydrogen all the charged particles of the different gases seemed to be atoms and not molecules of the gas. In working with the heavier atoms it is desirable to have very intense magnetic fields, otherwise the magnetic deflexion is very small. I am making arrangements for experiments in which the magnetic forces will be much greater than those I have hitherto used.

The preceding considerations show I think that we may divide the positive rays into the following classes :—

1. The undeflected rays, *i. e.* rays which are not affected by electric or magnetic forces; we cannot determine directly the velocity or the value of e/m for these rays.

2. Secondary rays produced by the rays (1). As the rays of the first type pass through a gas and collide against the molecules they produce secondary rays; whether they do this by splitting up themselves or by dissociating the molecules against which they strike, is uncertain. The rays of this class have a constant velocity 2×10^8 cm./sec. roughly; whatever may be the potential difference between the electrodes, they have a constant maximum value of $e/m = 10^4$. At the higher pressures and when the discharge-tube is small, these rays predominate and swamp the others; they get fainter and fainter as the pressure is reduced below a certain amount. We shall call the rays of this type secondary positive rays.

3. Rays characteristic of the gases in the tube. These are seen at low pressures, they produce bright spots on the screen; with each spot a thin parabolic band of luminosity is connected, the separate bands forming a kind of spectrum characteristic of the gases in the tube. The velocity of these rays depends on the potential difference between the electrodes, and the value of e/m is inversely proportional to the atomic weight of the gas from which they are derived. Their kinetic energy is that due to the potential difference between the negative glow and the cathode, in a mixture of gases the electrostatic deflexion of the rays from each gas is the same.

The retrograde rays which start from the cathode and travel away from it in the same direction as the cathode rays belong to classes (1) and (2). I have never seen the bright spots characteristic of class 3 in the retrograde rays.

In addition to the positively charged rays there are negatively charged ones of type 2 and in some cases of type 3. The different gases show great variations in the brightness of the negative tails connected with the rays peculiar to the atoms of the element, some elements show the negative tail readily while I have never seen it with others.

If we suppose that the undeflected rays are formed by the recombination of positive and negative particles and that these by collision with the molecules of the gas through which they pass form rays of type (2), either by splitting up themselves or by dissociating the molecules against which they strike, we can explain why the velocity of these rays should be independent of the potential difference between the electrodes in the tube. For in the first place, the positive and negative charges will not unite unless their relative velocity falls below a certain value which does not depend upon the strength of the electric field, and in the next place if the velocity were less than a limiting value they would not dissociate themselves nor could they dissociate other molecules by collisions when moving through a gas. The first condition gives a superior limit to the velocity, the second an inferior one; and both are independent of the strength of the electric field.

I shall now proceed to give the details of the measurements of the values of e/m and v. These constants were determined by measuring the magnetic and electrostatic deflexion of the rays. If y is the deflexion due to the magnetic force, e the charge on the particle and v its velocity,

$$y=\frac{e}{mv}\int_0^l (l-x)\mathrm{H}dx,$$

where x is the distance, measured along the undeflected ray, from the end of the tube through which the rays enter the magnetic field, H the magnetic force at the point x, and l the distance of the screen from the end of this tube. The value of $\int_0^l (l-x)\mathrm{H}dx$ was determined by measuring the magnetic induction through a triangular coil with its base at the end of the tube and its apex at the screen (see Phil. Mag Nov. 1909). If n is the number of turns in this coil, d the base and l the perpendicular from the apex on the base, I the magnetic induction through the coil, then

$$\mathrm{I}=\frac{nl}{d}\int_0^l (l-x)\mathrm{H}dx;$$

hence if we know I we can deduce the value of the integral; the coil was made so narrow that for a given value of x the magnetic force was constant over the coil.

The induction was measured by means of a Grassot fluxmeter, using for the sake of greater accuracy the deflexions of a beam of light reflected from the back of the instrument instead of the usual index and scale.

The fluxmeter was standardized, (1) by measuring by means of it the induction through one of a pair of coaxial solenoids when a known current was broken in the other, the coefficient of mutual induction for these coils had been carefully determined by Mr. Searle; (2) by means of a Duddell induction-meter which had been standardized at the National Physical Laboratory and which was kindly lent to me by the Cambridge Scientific Instrument Co. The two methods gave results agreeing within less than 1 per cent,

With regard to the electrostatic deflexion we have to allow for the irregularity of the field near the edges of the plate; the case is one for which a complete solution is given by the Schwartzian transformation

$$\frac{dz}{dt} = \mathrm{C}\frac{t}{t+1} \quad \text{where} \quad z = x + iy,$$

or

$$x + iy = \mathrm{C}(t - \log(1+t) + i\pi),$$

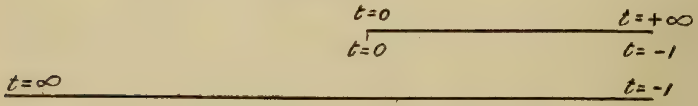
$$\frac{dw}{dt} = \frac{\mathrm{B}}{t+1} \quad \text{where} \quad w = \phi + i\psi,$$

or

$$\phi + i\psi = \mathrm{B}\{\log(1+t) - i\pi\},$$

where $y = \mathrm{C}\pi$ is the equation to one plane and $y = -\mathrm{C}\pi$ to the other, $y = 0$ is the plane midway between them; ψ is the potential and ϕ the current function, $2\mathrm{B}\pi$ the difference of potential between the plates. The range of t over one of the semi-infinite planes and the plane midway between them is shown in fig. 9. t ranges from $+\infty$ to 0 on the upper, from $t = 0$ to -1 on the lower surface of the semi-infinite plate, and from $t = -1$ to $t = -\infty$ on the plane midway between the two plates.

Fig. 9.



We shall suppose that the undeflected path of the particle is in this median plane. The equation of motion is

$$m\frac{d^2y}{dt^2} = \mathrm{Y}e,$$

or approximately

$$mv^2\frac{d^2y}{dx^2} = \mathrm{Y}e,$$

where Y is the electric force perpendicular to the plates,

$$\mathrm{Y} = \frac{d\psi}{dy} = \frac{d\phi}{dz}.$$

Hence

$$mv^2\frac{d^2y}{dx^2}=e\frac{d\phi}{dx},$$

hence

$$mv^2\frac{dy}{dx}=e(\phi_P-\phi_0),$$

where $\frac{dy}{dx}$ is the value of $\frac{dy}{dx}$ at a point P; ϕ_P is the value of ϕ at P and ϕ_0 the value of ϕ at the place where the rays leave the narrow tube inserted in the cathode; the value of $\frac{dy}{dx}$ at this place is assumed to be zero. Hence if y is the displacement of the particle on the screen,

$$mv^2y=\int_0^{-l}e(\phi_P-\phi_0)dx,$$

$$=e\int_0^{-l}\phi_P dx+el\phi_0,$$

where l is the distance of the screen from the end of the tube. Along the median plane

$$\frac{dx}{dt}=\frac{Ct}{t+1},$$

$$\phi_P=\mathrm{B}\log(1+t);$$

hence

$$e\int_0^{-l}\phi_P dx=e\mathrm{BC}\int\frac{t}{t+1}\log(1+t)dt$$

$$=e\mathrm{BC}\Big[(1+t)\log(1+t)-(1+t)-\tfrac{1}{2}\log^2(1+t)\Big]_0^{\mathrm{A}},$$

where A refers to the screen and 0 to the end of the tube.

Hence

$$\frac{mv^2}{e}y=\mathrm{BC}\Big[(1+t)\log(1+t)-(1+t)-\tfrac{1}{2}\log^2(1+t)\Big]_0^{\mathrm{A}}+\mathrm{B}\log(1+t_0)l.$$

If the distance of the end of the tube from the edge of the plates is a considerable multiple of the distance between the plates an approximate value of t_0 is -1.

Let $t_0 = -1-\xi$, let b be distance from the end of the tube to the edge of the plate, then

$$b = C(-1-\xi-\log\xi),$$

an approximate solution is

$$\xi = e^{-\left(\frac{b+C}{C}\right)},$$

$$\log(1+t_0) = -\left(\frac{b+C}{C}\right).$$

If d is the distance of the screen from the edge of the plate, t_A is given by the equation

$$-d = C(t_A - \log(1+t_A)),$$

and when d is large compared with C, we can easily get a solution of this equation by successive approximation.

Two sets of plates were used in the course of the experiments. For one set 2·5 cm. long and ·2 cm. apart,

$$C\pi = \cdot 1, \qquad l = 8\cdot 7,$$

$$b = 2\cdot 5,$$

$$d = 6\cdot 2,$$

for these we find

$$t_A = -189\cdot 46 \log(1+t_0) = -79\cdot 5,$$

this gives

$$y = \frac{e}{mv^2} X\ 19\cdot 7,$$

where X is the potential difference divided by the distance between the plates.

For the second pair of plates, which were 5·0 cm. long and 3 cm. apart,

$$C\pi = \cdot 15,$$

$$b = 5\cdot 0,$$

$$d = 3\cdot 7,$$

$$l = 8\cdot 7,$$

for them

$$t_A = -73\cdot 42 \log(1+t_0) = -105\cdot 7,$$

hence

$$y = \frac{e}{mv^2} X\ 32\cdot 2.$$

We shall now proceed to consider the values of e/m for the different types of rays. First, with regard to the secondary rays. The values of e/m were measured when there was a well-marked spot which was visible on both the positive and negative side (this is the spot *f* in fig. 8). When the conditions were most favourable to accurate measurements, it was found that increasing the potential difference between the plates from 100 to 200 volts increased the horizontal deflexion of the spot by 3 millimetres when the second system of plates was used. While an increase of 3 millimetres in the vertical deflexion was produced by increasing the current through the electromagnet by 1 ampere. The measurements of the magnetic induction by the fluxmeter showed that this increase in the current corresponded to an increase of $5{\cdot}05 \times 10^4$ in the value of

$$\int_0^l (l-x)\mathrm{H}dx,$$

hence we have

$$\cdot 3 = \frac{e}{mv} \times 5{\cdot}05 \times 10^3,$$

$$\cdot 3 = \frac{e}{mv^2} \times \frac{10^{10}}{\cdot 3} \times 32{\cdot}2,$$

giving $$v = 2{\cdot}1 \times 10^8,$$

$$e/m = 1{\cdot}24 \times 10^4.$$

It was found that the values of *e*/*m* for this spot always came out a little greater than 10^4, and as the spot was not quite at the extreme end of the straight band of phosphorescence due to the secondary rays, the value of *e*/*m* for the rays at the tip of this band would be still greater; for the tip the values of *e*/*m* ranged up to $1{\cdot}5 \times 10^4$, but as the tip is somewhat ill-defined the values of *e*/*m* for it could not be measured with the same accuracy as when there was a spot. The larger values of *e*/*m* were more frequent for the negative secondary rays than for the positive ones; these larger values would be accounted for if some of the particles had acquired a double charge for part of their course.

For the spot *e* the magnetic deflexion for a current of 2 amperes through the electromagnet

$$\left(\text{value of} \int_0^l (l-x)\mathrm{H}dx = 1{\cdot}1 \times 10^4\right)$$

was 4·4 millimetres, and for 200 volts an electrostatic deflexion of 3·5 millimetres. This gives

$$\cdot 44 = \frac{e}{mv} \times 1\cdot 01 \times 10^4,$$

$$\cdot 35 = \frac{e}{mv^2} \times \frac{2 \times 10^{10}}{3} \times 32\cdot 2;$$

or

$$v = 2\cdot 66 \times 10^8,$$

$$e/m = 1\cdot 16 \times 10^4.$$

The value of v for this spot depends upon the pressure in the tube. The spot d had the same electrostatic deflexion as e, so that the values of e/m for the spots d and e will be as the squares of the magnetic deflexions.

The corresponding magnetic deflexions for d and e and the square of their ratio is given in the following table:

Deflexion of *e*.	Deflexion of *d*	Square of ratio.
3·5	2·5	1·96
5·3	3·7	2·06
6·8	4·7	2·09
6·0	4	2·25
7·0	5	1·96

Thus the value of e/m for d is half that for e; hence if the charges are the same, the mass of the carriers producing the spot d is twice that of those producing e, hence we ascribe d to the hydrogen *molecule*.

The spot c is the helium spot, and the value of e/m as I showed in my earlier paper is $\frac{1}{4}$ that of the spot e.

We can compare the mass of the carriers for the spot b with those of d by comparing the magnetic deflexions, the following are corresponding values:

Spot *d*.	Spot *b*.	Square of ratio.
9·0	3·3	7·4
4·7	1·8	6·8
9·2	3·5	6·9
9·5	2·4	7·8
8·0	3	7·1

Thus if the charges are the same, the mass of the carriers of b is about seven times that of d; if, as we supposed, the carrier of d is the hydrogen molecule, then the carrier of b will be an atom either of nitrogen or oxygen. I am inclined to think that this is a double spot and will be resolved by the application of stronger magnetic fields.

When the air in the tube was replaced by CO there was a spot in approximately the same position as b, on increasing the field it was resolved into two with magnetic deflexions 6·0 and 5·3 millimetres; the square of the ratio of these deflexions is 1·28, the ratio of the atomic weights of O and C is 1·33, which agrees with the preceding value within the accuracy of the experiments. The spot *a* was compared with *b*, the corresponding magnetic deflexions are:

b.	*a.*	Square of the ratio.
5·0	1·5	11·1
5·0	1·3	13·6
	Mean	12·35

For mercury vapour the square of the ratio would have been 14 if the spot *b* were due to nitrogen, 12 if it were due to oxygen. The deflexion of the spot *a* with the magnetic force available was too small to admit of accurate measurement, but there can, I think, be little doubt that the spot *a* is due to mercury vapour. It disappears very quickly when liquid air is put around some charcoal in a side tube.

Thus we see that on the assumption that the charges are equal, we see that all the carriers with the exception of those for spot *d* are in the atomic condition; a very remarkable result, and one which has an important bearing on the dissociation of gases in the discharge-tube. It will be interesting to liberate the different elements from compounds of different types when they have different valencies, and from carbon compounds where the bands are different, and see whether the value of *e/m* remains unaltered.

The absence of the negative part of the phosphorescence indicates a reluctance on the part of the atoms of some gases to acquire a negative charge; this is also brought out by Franck's discovery that in some gases from which oxygen has been carefully excluded the velocity of the negative ion was very many times greater than when oxygen was admitted, while the positive ion was not affected. This indicates that negative corpuscle does not readily attach itself to the molecules of these gases.

I had occasion in the course of the work to investigate the secondary Canalstrahlen produced when primary Canalstrahlen strike against a metal plate. I found that the secondary rays which were emitted in all directions were for the most part uncharged, but that a small fraction carried a positive charge.

I have much pleasure in thanking Mr. F. W. Aston, of Trinity College, Cambridge, and Mr. E. Everett, for the kind assistance they have given me with these experiments.

LXXXIV. *Vacuum Spectrometer.*

By Professor AUGUSTUS TROWBRIDGE *.

[Plate XVI.]

FOR the purpose of spectroscopic investigation in the extreme ultra-violet region of the spectrum it has been found necessary, on account of atmospheric absorption, to employ some form of vacuum spectrometer, either of the mirror type or of that where collimation is effected by lenses of some transparent material.

The instruments employed in the well-known work of Schumann and of Lyman could hardly be improved on were one to design an instrument for research in the ultra-violet region exclusively, and I therefore only venture to describe an instrument which I have recently had constructed because of its wider range of usefulness.

In research work in the infra-red region of the spectrum, it is customary to use a mirror spectrometer of the fixed arm type with a rock-salt prism and Wadsworth mirror. The energy measuring instruments most commonly employed use the bolometer or the thermopile. It is generally necessary to shield either of these very carefully by means of screens from irregular changes of temperature, and it is not uncommon in the use of the bolometer to mount it in an air-tight case with a transparent window. Some observers have worked with the bolometer *in vacuo* in order better to secure constant temperature conditions.

If rock-salt be employed as the prism substance it is necessary to protect it against moisture, and this requires that the prism be enclosed in a case with the necessary openings for the passage of the light and suitable arrangements for preserving a moisture-free atmosphere within it.

From the above it is evident that a vacuum spectrometer would be advantageous, though not of course absolutely essential, in securing good working conditions in infra-red investigations as well as in work in the ultra-violet.

The instrument described in the present paper is designed to be used with either a prism or a grating, and attachments are provided which allow the use of either bolometer or thermopile for work in the infra-red or a photographic plate carrier for work in the ultra-violet.

Referring to the first of the figures, which are photographic reproductions of the shop drawings, and are one-quarter of

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* Communicated by the Author.

the natural size. C is the main conical bearing of the spectrometer—it carries on its upper end (not shown in Pl. XVI. fig. 1) the grating or prism-holder and near its lower end a large divided circle D. Readings are taken on this circle by means of micrometer microscopes MM, one division on the head of which is one second of arc. Less accurate readings may be rapidly obtained from the setting of the drum N mounted on the axis of the worm W, which engages the gear-wheel WW rigidly attached to the cone and divided circle. The worm W is mounted on the bed-plate B, which is bolted to the three legs of the instrument. The worm may be thrown out of gear by a suitable mechanism.

Pl. XVI. fig. 3 is an elevation of the upper part of the instrument, showing a section of the evacuated region and arrangement for leveling the grating or prism-holder H. This holder may be centered by means of the screws *c*, and it may be rotated about the axis of the cone C′, which is approximately coaxial with the cone C.

Pl. XVI. fig. 2 shows a horizontal section of the instrument through the axis of collimation; SC is the carrier of the slit —this brass casting which carries the slit SS′ is provided with a window W of suitable transparent material and the necessary conical plugs to admit of adjustment of the slit from the outside as regards height, width, and position. The details of this are not given as I have followed the construction devised by Schumann. The slit carrier SC is held on the collimator tube O by means of the ground conical gearing provided with the screw-ring R_1. The collimator tube is provided with appropriate diaphragms, and is soldered with the main bronze casting excentrically as shown in the figure. M_1 and M_2 are concave mirrors, of silvered glass for the work in the infra-red, and of speculum metal for ultra-violet work, so placed as to render the beam falling on the grating parallel, and then to bring the image of the slit on the bolometer strip mounted in the cone BC.

In case a prism be used instead of a grating the mirror M_2 is placed at M_2', and the bolometer case BC and the cap B′C′ exchange positions. The details of construction of the carriers of the mirrors M_1 and M_2 are given in the margin of fig. 3. A diagram of the electrical connexions of the bolometer is given in the margin of fig. 2. $b_1 \ldots b_2$ represent the bolometer strips 1–4, and 4 and 3 the balancing coils of manganin wire which are bifilar wound and occupy the capsule $c \ldots c$ shown in the bolometer case BC. For final adjustment of balance one of the coils is shunted with the high resistance R′.

A glass window is provided at the back of the bolometer case so that the exposed bolometer strip may be viewed at any time by means of a low power microscope (shown in fig. 4).

For work in the ultra-violet spectrum a plate-carrier case replaces the bolometer case BC. The details of this plate carrier are not given, as I have here also followed the construction devised by Schumann.

The instrument has been in use for several months as a spectrobolometer, and has proved in every way satisfactory. The gain in speed of observation over that possible with a bolometer subjected to disturbances due to air currents more than compensating for the loss of time in pumping out the instrument.

No annoyance whatever has been experienced from "leak," though of course the instrument is not perfectly air-tight. The leak, chiefly at the rock-salt window on the slit-case, does not exceed one millimetre of mercury in forty-eight hours. In practice a Gaede pump is run continuously during observation at a speed just sufficient to take up the leak.

LXXXV. *The Echelette Grating for the Infra-Red.* By R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University* *.

[Plate XVII.]

ONE of the most important problems in Optics is the question of the distribution of intensity among the spectra of different orders produced by a diffraction grating. Practically no rigorous experimental investigation has been made, owing to the impossibility of determining the actual form of the groove ruled by a diamond point on a glass or metal surface. It is very difficult to learn anything from a microscopical examination, and it is by no means certain that the form of the groove will conform to what we believe to be the shape of the ruling point. It occurred to me that a promising method of attack would be to manufacture gratings with grooves of such large size as to make the determination of their exact form, width, &c. a matter of certainty, and then investigate the energy distribution by means of the long heat-waves discovered by Rubens and his collaborators. By employing the residual rays from quartz and a grating with 1000 lines to the inch, we should have about the same ratio of wave-length to grating space as obtains in the case of a Rowland grating with 14,000 lines to the inch, and red

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* Communicated by the Author.

light. Gratings with constants varying from 0·1 mm. to ·01 mm. could be studied by means of residual rays, or narrow regions of the infra-red spectrum, isolated by a salt-prism spectrometer, and the relation between the intensity distribution and the form of the groove determined. Methods were worked out by which a groove of any desired form could be ruled, with optically flat sides (a very important point), the angular slope of each side of the groove measured, and the exact nature of the ruling determined, *i. e.* whether the metal had been forced up between the grooves, or whether the angle between the opposed faces was equal to the angle between the edges of the ruling knife. This by no means follows, as the ruling of groove No. 2 may force the metal to one side and increase the angle of slope of the adjacent side of groove No. 1. Gratings were finally obtained, which have proved so efficient in the investigation of infra-red spectra that it seems worth while to designate them by a name of their own. They throw a large percentage of the energy into one or two spectra to the left of the central image, and show little or no trace of any energy to the right of it. With visible light they send the greater part into a group of spectra, say, from the 12th to the 16th, or from the 24th to the 30th order. Thev may thus be regarded as reflecting echelons, of comparatively small retardation, and I propose the name "echelette," to distinguish them from the ordinary grating and the Michelson echelon.

Various methods were tried for their production. The first were made by punching the grooves with a steel die, two adjacent surfaces of which had been ground flat and highly polished. The die was a block of hard steel measuring 3 × 2 × 1·5 cms., and the gratings were punched with an ordinary milling machine, the die being clamped at the proper angle in a fixed position, and a polished plate of some soft metal pushed up against it from below. This method is analogous to the one used by Mr. Thorpe, in making his gratings for the demonstration of predominant spectra, but it did not give very satisfactory results.

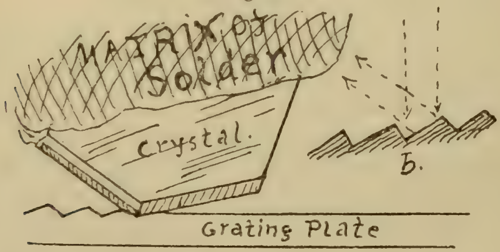
After considerable experimenting with various metals and ruling points, I came to the conclusion that soft alloys must be avoided, for it appeared to be impossible to cut a groove with optically flat sides. The crystalline structure of the metal caused the point to rule a groove, the sides of which undulated more or less, causing more or less reflexion in directions parallel to the grooves.

The method finally adopted was the following:—A sheet of polished copper plate, such as is used by photo-engravers for the half-tone process, was gold-plated and polished. The plates were found sufficiently flat for the purpose and had a much better optical surface than anything that I was enabled to produce on a copper plate by grinding and polishing, for the final polishing always produced irregular undulations (possibly owing to variations in the hardness), and I was unable to get any suggestions from professional opticians accustomed to the polishing of glass and speculum metal. If any one has worked out a method of getting a flat optical surface on such metals as copper or gold, I shall be very glad to hear of it, as it will doubtless improve the quality of the gratings.

A carborundum crystal was used for the ruling point, and the ruling, in the case of the gratings of very large constant, was done on a small laboratory dividing-engine by hand. This machine had bad periodic errors, and the best gratings were made with Rowland's first machine, with a 7-tooth and a 15-tooth cam, which gave 2062 and 962 lines to the inch respectively.

The hexagonal carborundum crystals were selected by breaking up a mass of the substance as it comes from the furnace. Specimens of these iridescent crystalline masses are to be found in most chemical or mineralogical museums. The crystals have the form shown in figure 1, and are mounted as shown in the figure. The natural edges are so straight that they rule a groove with optically perfect sides. Everything depends upon the nature of the edge and the angle at which it is set with respect to *the direction of the line*, *i. e.* the tilt forwards or back. Some edges will not rule properly at any angle, "chattering" over the surface and tearing off a thread of metal. *No metal is removed* when the ruling is going on properly, the groove being formed by compression of the metal. If the edge is properly chosen, mounted at the proper angle and correctly weighted, a beautiful groove is made with a very little elevation of the

Fig. 1.



metal above the original surface at the edges. The first gratings were ruled on copper and subsequently gold-plated to prevent tarnish, but it was found that even the lightest polishing on the buffing wheel destroyed the sharpness of the edges and caused the development of strong central images.

It was found, however, that even with an exceedingly thin deposit of gold (about the lightest plating ever done commercially) it was possible to rule very deep grooves without uncovering the copper. This solved the difficulty, and excellent gratings could be produced at a very small cost. The copper plate was varnished with asphalt on the back to save gold, and gilded in as large pieces as the gilding establishment could handle. These large sheets were then cut up to the required size with a circular saw. They performed fairly well optically, giving almost as good images as an ordinary plate-glass mirror, in spite of the rather rough treatment to which they had been subjected. It is important to instruct the gilder to do as little buffing as possible. My first plates were spoiled by having too thick a deposit of gold and too vigorous buffing or burnishing. The best treatment is the one which they give to the thinnest coats, which would be completely removed if polished by the methods employed for thicker deposits. If a thick deposit is given and polished in the usual way, the optical surface is ruined by the formation of undulations, though it is hard to convince the gilder that it is unsatisfactory. I mention these details for the benefit of others undertaking the manufacture of these gratings, for it took me nearly a week to convince the gilder that he could be taught anything about the nature of metals and how they should be treated. To obtain a better optical surface, or rather a flatter one, I had a polished flat plate of speculum metal, such as is used for making Rowland gratings, silver-plated and polished. The circumstance that the first plate which I placed in the hands of the plater flew into three pieces as soon as he put it in the hot alkaline solution which they use for cleaning thin metalwork, convinced him that there was something about metals to be learned, and he was more willing to take advice thereafter. By this method it was possible to get a beautiful optical surface of soft metal, in which the grooves could be cut. So far as I could see by a rather superficial examination, the optical perfection of the surface had not been materially affected.

The angle of the ruling edges of the carborundum hexagonal plates is 120°, consequently the sides of the groove make approximately this angle. By placing the crystal in various positions we obtain grooves of various shapes, one side, for example, sloping at an angle of 12° with the original surface, the other at 48°. These angles are subsequently determined with a small spectrometer or by simply mounting the gratings on a graduated circle, and observing the reflexion of a lamp-flame in them. In the best ones no trace of the central image can be seen, which is what we should expect if the edges of the grooves were sharp and none of the original plane surface remained. The sum of the two angles of slope did not always add up to 60°, as they should do if the ruling had been done with a 120° point. This is probably due to the circumstance that the edges of the carborundum crystals are usually bevelled as shown in fig. 1. I have not made a study of the angles at which these small planes meet, but it seems likely that with certain crystals we may have a ruling point the edges of which meet at an angle larger than 120°.

Of the eight gratings which I have measured thus far, the angles of the edges and their sum are shown in the following Table :—

11	20·5	22	29	11	12	17	43
49	27·5	30	18	44	46	37	11
60	48	52	47	55	58	54	54

In addition to knowing the angle of slope of the two sides of the groove it is necessary to determine whether they make a sharp angle, *i.e.* whether they meet in a knife-edge at the top, or whether there is some of the original surface remaining between them, or a ridge of more or less roughed surface due to the squeezing up of metal by the compression resulting from the action of the carborundum crystal.

Some difficulty was found in interpreting the appearance of the surface under the microscope until the following method, which gave beautiful results, was tried. Two electric lamps were placed just above the stage of the microscope, to the right and left of the tube, in such positions that the edges of the grooves reflected light vertically into the objective. A red glass was placed in front of one lamp, and a green glass in front of the other. The edges of the grooves appeared brilliantly illuminated in complementary colours, with no dark region, if they met at the top, but if not, each pair of red-green strips was separated from the neighbouring pair by a dark line, due to the fact that the level surface between the grooves was not at the proper angle to reflect light from either lamp into the objective. The appearance of the gratings illuminated in this way was similar to that of one of the screens used in the Joly process of colour-photography. If the grating showed no central image with light, it was safe to assume that the metal along the dark line had been forced up and the original surface destroyed. This was usually the case when the grooves were very nearly in contact. If strong central images were exhibited, it indicated that a portion of the original flat surface remained between the grooves. The width of this portion in comparison with that of the roughened portion could be determined by placing the grating at an angle under the microscope and reflecting light from the linear strips between the grooves. In this way a very perfect knowledge of the exact nature of the ruled surface could be obtained. Another method of studying the surface is to make a cast of it in celluloid or a paraffin composition and section this with a microtome. The optical method gave the best results, however.

In the majority of cases the crystal was mounted so as to rule a groove one edge of which made an angle of 20° or less with the original surface. With normal incidence this gives us a concentration of energy at an angle of 40°, with practically no energy thrown off from the other edges of the groove, owing to the steepness of the angle. This case is shown in fig. 1 *b*. The best gratings show no reflexion in the normal direction, *i. e.* they give no central image. They give, however, a very good reflected image of one's face, when held at an angle of 20°, the image being uncoloured, but slightly diffused by diffraction in a direction perpendicular to the grooves. The image is so sharp, however, that the pupil of the eye can be seen without difficulty.

The gratings behave, with infra-red radiation of wave-lengths, above, say 3 μ, precisely as an ideally perfect grating, that is they give spectra similar to what we should have with an ordinary grating which threw practically all of the light into one or two orders on one side of the central image.

With visible light their behaviour is most curious and interesting. The central image is usually absent, and we get a blaze of light when the grating is turned at the proper angle. With a symmetrical groove the blaze is seen on both sides, at angles of 45° for normal incidence. This blaze we may term the oblique image.

If the source of light is white, a lamp flame, for example, the appearance is as shown in fig. 2 *d* (Pl. XVII.), which is for a grating with a constant of ·05 mm. The position of the central image is indicated by an arrow. It is very faint or barely visible, however. To the right and left are the oblique images, but very slightly broadened by diffraction owing to the width of the reflecting edges, which in this case make equal angles with the surface.

In fig. 2 *a* we have the appearance of things with a grating of constant ·0123 mm. The central image is indicated by an arrow, and is bordered on each side by the ordinary grating spectra, which are close together on account of the coarseness of the ruling. They are much fainter than I have indicated on the plate. Well to one side, at an angle of about 40° with the normal, we see a very bright and greatly broadened white image of the flame, accompanied by lateral spectra. These are shown by a coloured plate in the forthcoming edition of my 'Physical Optics.'

These are not grating spectra, but the first class spectra (as Fraunhofer termed them) due to a single slit, or in this case to a single reflecting edge of a groove. With a sodium flame the appearance is as shown in fig. 2 *b*. We have in this case three orders of spectra in the region occupied by the central maximum of the spectra of the first class. Their order is indicated below. One or two orders to the right and left of this group are absent, since they fall in the region of the minimum due to a single slit. They are the "absent spectra" of grating theory. Other groups of orders appear in the regions occupied by the first class coloured spectra, their intensity being much less, however, than the intensity of the ones falling within the region of the central maximum. The existence of these images of the soda flame shows us that the perfection of ruling is such that interference, with a path difference of about 30 wave-lengths, is still taking place. In other words, our grating is acting as a reflecting echelon with steps 15 wave-lengths in height. This was observed only in the case of the gratings ruled on the Rowland machine. Those ruled on the small laboratory machine by hand showed only a confused jumble of overlapping images, which formed an almost continuous band of yellow light. The grating constant was ·0123 mm. in the case represented in figs. 1 and 2. With a larger constant the central maximum of the spectra of the first class was narrower and brighter, the lateral rainbow coloured fringes being less in evidence.

The width of the region in which we have these maxima and minima of the first class becomes less as we increase the width of the reflecting steps of the grating. In the case of a grating of such a small constant as ·0123 mm., this region of diffraction of the energy from each individual element covers a range of fully ten degrees, embracing as many as 12 or more orders of second class spectra. In the case of the Michelson echelon, the width of the step is from 0·5 to 1 mm., and the range of diffraction is so small that but one or two orders of spectra are included within it. By the study of these echelette gratings we can pass gradually from the case of the ordinary grating to that of the echelon.

The results appear to me to indicate that with a simple groove, such as we have here, we cannot secure a concentration of light in a region narrower than the diffraction range from a single reflecting element. This question will be more fully discussed in a subsequent paper treating of the energy distribution among spectra of different orders produced by these gratings, with visible light and very long heat waves.

Some of the gratings, with a constant of ·0123 mm. gave strongly coloured images, and lateral spectra of low order in which a certain colour or colours were wholly absent. The first order spectrum on one side, for example, may contain no yellow-green, a broad dark band bisecting the spectrum. A third order spectrum may have two dark bands, one in the yellow, and another in the greenish-blue.

In one case the oblique image or the central maximum of the spectra of the first class, instead of being white, was distinctly blue, while the maxima immediately to the right and left of it contained only red, orange, and yellow light, as shown in fig. 2 *c* (Pl. XVII.).

This curious distribution of colour was observed in the case of one grating only, and its explanation gave a good deal of trouble. To explain it we must devise some type of reflecting element which will give, in the case of red light, zero illumination at the centre of symmetry, with strong lateral maxima, and with blue light a strong maximum at the centre, bordered by minima which occupy the positions of the red maxima, and maxima in the positions of the red minima. This can apparently be brought about only by an element consisting of two parts, in other words a double reflecting strip, with a half-wave retardation for red light, as in the case of the laminary grating. The central maximum will vanish in this case for red light, as can be easily seen by constructing the diffracted wave-fronts. If blue light is used the retardation becomes very nearly a whole wave, and we have the centre of the system bright. An examination of the grating with a microscope showed that there were in fact two reflecting strips in contact which together formed one side of the groove, the grating being built up of paired reflecting elements separated by inoperative strips of about the same width. Just how the carborundum crystal managed to rule such a groove I am unable to say. A coloured drawing of this very remarkable set of spectra will be found in 'Physical Optics.'

These cases will be more fully discussed in a subsequent paper, in which a full report of an investigation made in collaboration with Prof. A. Trowbridge, of Princeton, with his remarkably perfect vacuum spectrometer will be given. This investigation has shown that these gratings give far higher resolving powers in the infra-red than have ever been available previously, combined with great efficiency. The emission band of CO_2 from the flame of a Bunsen burner, which has been observed only as a single band up to this time, was easily resolved into three or possibly four component bands.

Further experimenting will probably improve the quality of the gratings and open up a large field of work in the infra-red region. The gratings yield excellent replicas which can be mounted on flat plates of glass and gold-plated by the cathode discharge. The replicas will very possibly have flatter surfaces than the original gratings, if properly mounted.

LXXXVI. *Some experiments on the Absorption of Radium Emanation by Coconut Charcoal. By* JOHN SATTERLY, *A.R.C.Sc., B.Sc., B.A., St. John's College, Cambridge*[*].

DURING the performance of some experiments[†] by the author on the measurement of the amount of radium emanation in atmospheric air by the charcoal absorption method, the following interesting points came up for consideration :—

(*a*) Is the amount of emanation absorbed from the air always the same fraction of the total amount in the air whatever that amount may be, other experimental conditions remaining the same?

(*b*) In the case when the air flowing to the charcoal contains a constant percentage of emanation, is the amount absorbed by the charcoal proportional to the time the air-current is flowing, or does the charcoal show signs of saturation?

(*c*) Does the amount of emanation absorbed from the air depend on the humidity of the air?

(*d*) What is the percentage of emanation absorbed in any particular case?

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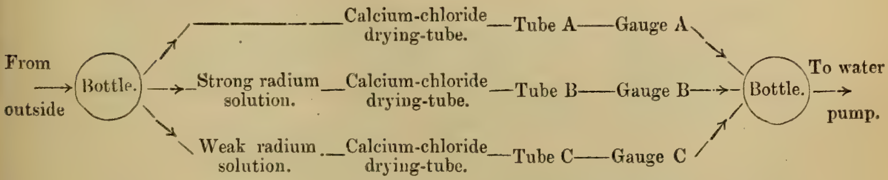
[*] Communicated by Sir J. J. Thomson, F.R.S.

[†] See Phil. Mag. Oct. 1908 and July 1910.

I.

Experiments to test the first point were made in Dec. 1907–Jan. 1908 and July–Aug. 1908. The apparatus used was that described in my earlier experiments *. Two radium solutions were made up as follows:—126 c.c. of a certain radium solution was taken and divided into two parts of 43 and 83 c.c. (it was intended to be 42 and 84), so that the radium contents were as 1 : 1·93. Each part was made up to 136 c.c. and placed in exactly similar bottles fitted with inlet and outlet tubes so that air could be bubbled through the solutions. Three exactly similar charcoal tubes, A, B, C (porcelain tubes 60 cm. long, 1·6 cm.^{2} cross-section, central foot filled with 39 gm. charcoal) were joined up in a circuit as shown below:—



Air was drawn through the three tubes by a water-pump. The air-streams through the tubes were measured by means of three gauges and adjusted to be of the same strength. After the air-streams had been flowing for some hours they were stopped and the tubes taken and heated. The amount of emanation the charcoal had absorbed was then measured in the usual way.

Let H = amount of emanation in the quantity of air that passed along to tube A,

and E = amount of emanation generated by the weaker solution in the given time of exposure.

Then the amounts of emanation arriving at tubes C and B were H + E and H + 1·93 E respectively. Let the amounts of emanation caught by the tubes A, B, C be denoted by $n\mathrm{H}$, $n_1(\mathrm{H}+1{\cdot}93\,\mathrm{E})$, $n_2(\mathrm{H}+\mathrm{E})$. Then, if

$$\frac{n_1(\mathrm{H}+1{\cdot}93\,\mathrm{E})-n\mathrm{H}}{n_2(\mathrm{H}+\mathrm{E})-n\mathrm{H}}=\frac{1{\cdot}93}{1},$$

it follows that $n=n_1=n_2$; *i. e.*, the same fraction of the emanation was absorbed in each case.

Throughout the paper the amount of emanation is expressed in the same arbitrary unit. The numbers are the leaks per minute produced in my testing vessel by the emanation and read on the scale provided to the electrometer.

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* See Phil. Mag. Oct. 1908 and July 1910.

The following are the results :—

(1) Dec. 20, 1907. Duration of exposure 2 hrs.
Air-stream $=\cdot5$ litre per min.

$$\left.\begin{array}{lll}\text{Tube A,} & n\mathrm{H} & = \cdot3\\ \text{,, B,} & n_1(\mathrm{H}+1\cdot93\mathrm{E}) & = 27\cdot0\\ \text{,, C,} & n_2(\mathrm{H}+\mathrm{E}) & = 20\cdot0\end{array}\right\}\ \therefore\ \frac{n_1(\mathrm{H}+1\cdot93\mathrm{E})-n\mathrm{H}}{n_2(\mathrm{H}+\mathrm{E})-n\mathrm{H}}=\frac{26\cdot7}{19\cdot7}=1\cdot4-$$

(2) Jan. 21, 1908. Duration of exposure 80 min.
Air-stream $=\cdot5$ litre per min.

$$\left.\begin{array}{lll}\text{Tube A,} & n\mathrm{H} & = \cdot3\\ \text{,, B,} & n_1(\mathrm{H}+1\cdot93\mathrm{E}) & = 13\cdot6\\ \text{,, C,} & n_2(\mathrm{H}+\mathrm{E}) & = 9\cdot4\end{array}\right\}\ \therefore\ \frac{n_1(\mathrm{H}+1\cdot93\mathrm{E})-n\mathrm{H}}{n_2(\mathrm{H}+\mathrm{E})-n\mathrm{H}}=\frac{13\cdot3}{9\cdot1}=1\cdot4+$$

From (1) and (2) it follows that with the given solutions, n, n_1, n_2 are not equal. Weaker solutions were now tried. The strong solution was mixed with two-thirds of the weak and new solutions were made up, one twice as strong as the other. Call them $2\mathrm{E}_1$ and E_1.

(3) July 22, 1908. Duration of exposure $2\frac{3}{4}$ hrs.
Air-stream $=\cdot5$ litre per min.

$$\left.\begin{array}{lll}\text{Tube A,} & n\mathrm{H} & = \cdot7\\ \text{,, B,} & n_1(\mathrm{H}+2\mathrm{E}_1) & = 14\cdot9\\ \text{,, C,} & n_2(\mathrm{H}+\mathrm{E}_1) & = 10\cdot7\end{array}\right\}\ \therefore\ \frac{n_1(\mathrm{H}+2\mathrm{E}_1)-n\mathrm{H}}{n_2(\mathrm{H}+\mathrm{E}_1)-n\mathrm{H}}=\frac{14\cdot2}{10\cdot0}=1\cdot4.$$

Again made new solutions : one-third of E_1 was taken for the new weak solution and two-thirds of E_1 for the new strong solution.

(4) July 31, 1908. Duration of exposure $2\frac{1}{4}$ hrs.
Air-stream $=\cdot5$ litre per min.

$$\left.\begin{array}{lll}\text{Tube C,} & n\mathrm{H} & = \cdot3\\ \text{,, B,} & n_1(\mathrm{H}+\frac{2}{3}\mathrm{E}_1) & = 5\cdot3\\ \text{,, A,} & n_2(\mathrm{H}+\frac{1}{3}\mathrm{E}_1) & = 2\cdot8\end{array}\right\}\ \therefore\ \frac{n_1(\mathrm{H}+\frac{2}{3}\mathrm{E}_1)-n\mathrm{H}}{n_2(\mathrm{H}+\frac{1}{3}\mathrm{E}_1)-n\mathrm{H}}=\frac{5\cdot0}{2\cdot5}=2\cdot0.$$

(5) Aug. 5. Same solutions used. Duration of exposure $2\frac{1}{4}$ hrs.
Air-stream $=\cdot5$ litre per min.

$$\left.\begin{array}{lll}\text{Tube A,} & n\mathrm{H} & = \cdot4\\ \text{,, C,} & n_1(\mathrm{H}+\frac{2}{3}\mathrm{E}_1) & = 5\cdot1\\ \text{,, B,} & n_2(\mathrm{H}+\frac{1}{3}\mathrm{E}_1) & = 2\cdot8\end{array}\right\}\ \therefore\ \frac{n_1(\mathrm{H}+\frac{2}{3}\mathrm{E}_1)-n\mathrm{H}}{n_2(\mathrm{H}+\frac{1}{3}\mathrm{E}_1)-n\mathrm{H}}=\frac{4\cdot7}{2\cdot4}=2\cdot0.$$

The results of Experiments (4) and (5) show that for solutions of the strengths used and for the other experimental conditions, the amount of emanation absorbed by the charcoal is practically proportional to the emanation content of the air sent through the charcoal. For stronger solutions as used in (1),(2), (3), the amount absorbed does not increase in the same proportion as the emanation content of the air; it certainly looks as if the charcoal were approaching saturation.

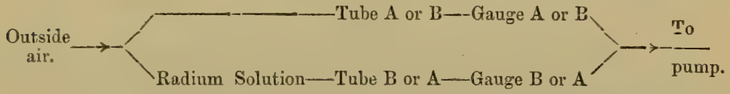
The strength of the solution $\frac{1}{3}E_1$ is very nearly the same as that of a solution containing $3{\cdot}14 \times 10^{-9}$ gm. radium which was given to the author by Professor Rutherford; for that solution gave me a reading 2·5 for a 2-hours run [*]. The solution $\frac{1}{3}E_1$ therefore contains about 3×10^{-9} gm. radium, and the emanation it would yield in $2\frac{1}{4}$ hours would have a volume of 3×10^{-14} c.c. It is hard to imagine that charcoal would be saturated even with a volume many hundred times this [†]; but it must be remembered that an air-stream is passing through the charcoal all the time and that this air has two effects: (1) it is absorbed by the charcoal, thus leaving less room for any other gas, and (2) it tends to blow out any other gas that has been absorbed.

It follows that if for solutions of strengths 3×10^{-9} and 6×10^{-9} gm. radium the amount absorbed is proportional to the strength of the solution, this proportionality would also hold for weaker solutions and also for the radium content in the air, thus justifying the method of calculation employed in my paper in the Phil. Mag. of October 1908.

II.

Experiments made to find out whether the fraction of the emanation absorbed, when the emanation is supplied from a constant source by a steady stream of air, is independent of the time of exposure.

In this series of experiments two silica tubes, A and B, (each 60 cms. long, 8·0 sq. cm. in cross-section, and containing about 130 gm. of coconut charcoal in the central foot) were coupled up as shown in the accompanying diagram



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[*] Phil. Mag. Oct. 1908, p. 599.

[†] At 10° C. one gram of coconut-charcoal absorbs 3×10^{-5} c.c. of radium emanation (Rutherford, Manch. Lit. Phil. Soc. Dec. 1908). This is, of course, a statical result.

with a radium solution in series with one of the tubes, and exposures were made of different periods but with air-streams of the same strength (·5 litre per minute). The radium solution used contained $\frac{3{\cdot}14}{5} \times 10^{-9}$ gm. of radium. Sometimes the solution was in series with Tube A, sometimes with Tube B. In calculating the last column, allowance has been made for the fact that Tube B absorbs about 10 per cent. more than Tube A[*].

TABLE I.

		Air alone.			Air+Solution.			
Date, 1909.	Period of exposure	Tube.	Vol. of air in litres.	Emanation caught.	Tube.	Vol. of air in litres.	Total Emanation caught.	Emanation caught from the solution.
Oct. 26–27.	22¼ hrs.	A	633	1·1	B	660	4·7	4·7−1·2=3·5
„ 27–28.	21 „	B	607	·9	A	640	4·1	4·1− ·8=3·3
„ 28–29.	15 „	A	452	·7	B	448	3·6	3·6− ·7=2·9
Nov. 2	7 „	A	212	1·3	B	214	3·2	3·2−1·4=1·8
„ 2–3 ...	21 „	B	647	2·2	A	657	5·2	5·2−2·0=3·2
„ 3–4 ...	21 „	A	637	2·6	B	631	7·2	7·2−2·9=3·8
„ 5	7 „	B	211	·6	A	213	2·0	2·0− ·5=1·5
„ 10 ..	7 „	A	210	1·1	B	209	2·8	2·8−1·1=1·7

From the figures in the second and last columns the following curves (fig. 1) have been plotted. If for exposures of all the periods named the fraction of emanation absorbed was the same, the curves would be practically straight. (There would be a slight falling away from the straight line owing to the decay of the emanation: this, however, is very slight, as is evidenced by the dotted line in fig. 1, which represents on an arbitrary scale the growth of radium emanation from a quantity of radium.)

Similar experiments made in July and August[†] with a 3-hours exposure and a solution of $3{\cdot}14 \times 10^{-9}$ gm. radium gave 4·5 for tube B and 4·4 for tube A. Therefore, assuming as is proved in I. that the amount absorbed from these solutions in a short time is proportional to the strengths of the

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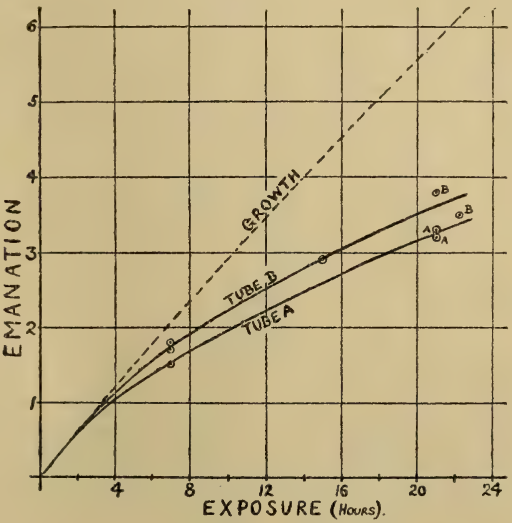
[*] See Phil. Mag. July 1910, pp. 15, 17.

[†] Phil. Mag. July 1910, p. 27.

solutions, the amount absorbed from the one one-fifth solution in 3 hours should be ·9 for tube B and a little less for tube A. This is in good agreement with fig. 1.

Fig. 1.



The results of these experiments show that in the early stages not much of the emanation is allowed to pass through the charcoal unabsorbed. In the later stages, however, much of the emanation is allowed to pass.

From fig. 1 it follows that if we suppose complete absorption to occur for exposures of 3 hours or less, then B for a 21-hours exposure absorbs about 62 per cent. of the emanation sent through it. The state of affairs is probably very similar to that discovered by McBain * for the absorption of hydrogen by charcoal, viz. that the absorption is twofold : a quick effect—a surface condensation—being followed by a slower effect—a diffusion into the interior.

III.

Effect of the Humidity of the Air.

As no drying agent was used in the experiments described in II., the results may be due to the fact that as time went on the charcoal tube attached to the radium solution would

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* Phil. Mag. Dec. 1909.

absorb more and more water, and thus its absorbing qualities for other gases might gradually diminish. Experiments were now made to test this point. The (silica) tubes A and B were placed in parallel, and air-streams of the same strength (·5 litre per minute) were passed through each. The humidity of the air going to the separate tubes was altered as shown in Table II. In the first three experiments the source of emanation was the air ; in the others this source was supplemented by bubbling the air through a radium solution containing $\frac{4}{5}$ of $3{\cdot}14 \times 10^{-9}$ gm. radium. The duration of the exposure was about 21 hours in each case.

TABLE II.

TUBE A.	Emanation caught.	TUBE B.	Emanation caught.
Outer air, humidity unaltered	1·5	Outer air bubbled through 6 in. water.	1·6
Outer air, dried by calcium chloride, then bubbled through 6 in. water.	1·4	Outer air dried by same calcium chloride as used with A......................	1·5
Outer air, humidity unaltered	·9	Outer air sent through 40 cm. wet cotton-wool.	1·1
Laboratory air bubbled through the solution....................................	16·2	Laboratory air bubbled through the solution and sent through 100 cm. of wet cotton-wool.	18·7
Outer air bubbled through the solution	6·8	Outer air bubbled through solution and then dried by calcium chloride.	9·2
Outer air bubbled through the solution and then dried by calcium chloride.	7·8	Outer air bubbled through the solution	7·0
Outer air bubbled through the solution, then dried by calcium chloride, then saturated by passing through 100 cm. wet cotton-wool.	7·3	Outer air bubbled through the solution, then dried by same calcium chloride as used with A	9·2
Outer air bubbled through the solution, then dried by calcium chloride......	11·8	Outer air bubbled through the solution, then dried by same calcium chloride as used by A, then saturated by passing through 100 cm. wet cotton-wool.	13·9

From these results it is clear that, allowing for the fact that under the same conditions tube B nearly always absorbs about 10 per cent. more emanation than tube A, the amounts of emanation absorbed in my experiments by the charcoal are independent of the humidity of the air carrying the emanation.

IV.

Experiments with two charcoal tubes in series to find out how the relative amounts of emanation absorbed by each of the tubes depend on the duration of the exposure.

The silica tubes were connected up as follows :—

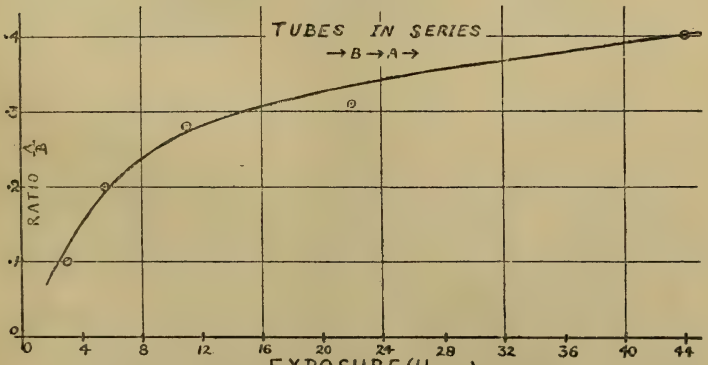
Outer air ——→Radium Solution→1 metre of calcium chloride→Tube B→Tube A→Gauge A→Pump.

Table III.

Duration of Exposure.	Amount of Emanation caught by B.	Amount of Emanation caught by A.	Ratio, $\frac{A}{B}$.	Means.
3 hours.	5·0	·2	·04	·10
" "	4·8	·7	·14	
" "	4·9	·6	·12	
5½ hours.	7·1	1·7	·24	·20
" "	8·0	1·3	·16	
11 hours.	12·2	3·4	·28	·28
22 hours.	18·5	11·1	·6 *	
" "	22·4	7·0	·31	·31
44 hours.	29·9	13·0	·45	·40
" "	34·9	12·4	·36	

* Neglected in finding the mean.

Fig. 2.



and the air sent through it at a constant rate (·5 litre per minute). The radium solution used contained $\frac{4}{5}$ of $3{\cdot}14 \times 10^{-9}$ gm. radium.

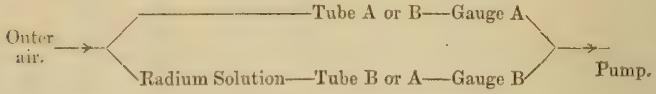
The results are represented in fig. 2, and it is clearly shown that the charcoal in the first tube (B) approaches saturation when the exposure is long and the amount of emanation sent along the tube is high.

V.

Percentage of Emanation absorbed by Coconut Charcoal.

It is of interest to find what percentage of the emanation given off by a radium solution is absorbed by the charcoal under the conditions of my experiments.

Using a solution containing $\frac{2}{5}$ of $1{\cdot}57 \times 10^{-9}$ gm.[*] radium, six experiments were made with the silica tubes containing the coconut charcoal arranged as shown below :—



The air-streams were adjusted to ·48 litre per minute through each branch, and the exposure was continued for exactly 21 hours. Subtracting the amount of emanation caught in the tube in the "air alone" arm from the amount caught in the tube in the other arm, we get the amount caught by the charcoal from the solution.

Before beginning this set of experiments the tubes had been emptied and made up afresh with 130 gms. of charcoal in each, so that the results are not absolutely comparable with earlier results.

The results were :—

Tube A	5·1	4·5	4·9	Mean 4·8,
Tube B	4·1	4·5	4·1	„ 4·2,

the amounts being expressed in terms of the leaks produced in the testing vessel expressed in cms. per minute of my electrometer scale, and reduced to a common sensitiveness (90 divisions per volt).

It now remained to find the total amount of emanation produced by the same solution in 21 hours. To do this the bottle R containing the solution was connected up to a condenser C and heated in a brine bath (b.p. 105° C.), as

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[*] This was a portion of a fresh radium solution kindly supplied to the author by Professor Rutherford.

shown in the accompanying diagram (fig. 3). When the brine had been boiling for some time the clip T was opened, air bubbled through the solution, and the emanation drawn off from the solution and collected in the aspirator A and tested in the usual way.

Fig. 3.

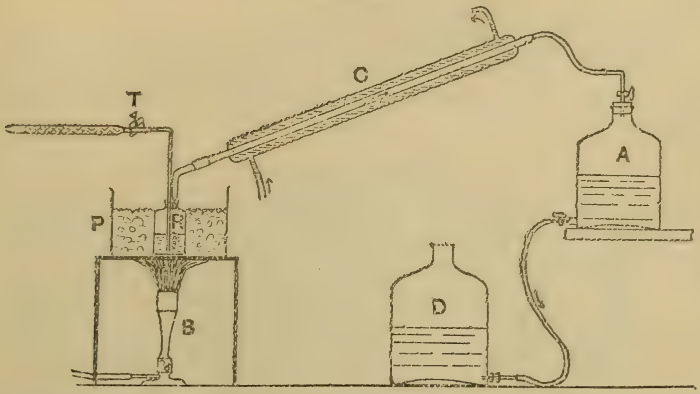

Table IV. gives the results, the leaks being reduced to the same electrometer sensitiveness as before. The last column is calculated from the second, by the help of tables similar to those given in my earlier papers *.

TABLE IV.

Interval solution had been resting since last heating.	Emanation generated in this interval.	Emanation generated in 21 hours.
20½ hours.	7·1	7·3
74¾ ,,	20·0	6·7
23¼ ,,	8·4	7·4
24⅓ ,,	8·4	7·4
47½ ,,	14·0	6·7

Mean ...... 7·1

The radium generates therefore an amount of emanation represented by 7·1 in 21 hours; and with an air-stream of ·48 litre per minute the charcoal in (silica) tubes catches only

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* See also Kolowrat, *Le Radium,* 1909, pp. 193-5.

4·5 (mean of A and B). The percentage caught is therefore $\frac{450}{71}$, or 63 per cent. (See also II. p. 783.) This is at the ordinary laboratory temperatures.

Further experiments with air streams of magnitudes ·11, ·25, and ·80 litre per minute showed that at these speeds the amounts of emanation caught were 86, 73, and 23 per cent. respectively.

Summary.

Experiments have been made on the absorption of radium emanation by coconut charcoal, the emanation being carried to the charcoal by a stream of air. It has been found

(*a*) that with weak solutions the amount of emanation absorbed in short exposures of the same time for the same strength of air-stream is proportional to the strength of the solution ;

(*b*) that with the same solution and strength of air-stream the amount absorbed for exposures of different times does not increase in proportion to the time of exposure but falls off, showing that the charcoal is getting saturated ;

(*c*) that under the conditions of the experiments the amount of emanation absorbed does not depend on the humidity of the air ;

(*d*) that with tubes 8 sq. cm. in cross-section containing a column 30 cms. long of coarsely powdered coconut-charcoal the amount of emanation absorbed when the air-stream is ·5 litre per minute and the exposure is 21 hours, is only about 62 per cent. of the total amount of emanation carried by the air to the tube.

In conclusion the author wishes to express his best thanks to Professor Sir J. J. Thomson for permission to carry out the above research at the Cavendish Laboratory.

Cambridge, June 17, 1910.

LXXXVII. *On Displacements in the Spectrum due to Pressure.* *By* Andrew Stephenson [*].

It has been suggested in connexion with the peculiar resonance effects exhibited in the spectra of sodium and other vapours, that a series of lines is, in certain cases, the spectroscopic analysis of the individual oscillatory motion of a single coordinate under the disturbing influence of some

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[*] Communicated by the Author.

distinct normal motion. Under such influence, consisting in a periodic variation in the spring of the coordinate, the free motion changes from the simple oscillation

$$\mathrm{A}\cos(\mu t+\epsilon)$$

to the complex oscillation represented by

$$\sum_{-\infty}^{\infty} a_r \cos\{(\mu+p+rn)t+\epsilon\},$$

where p and the ratios of the a's are determined by the frequency and intensity of the disturbance. With regard to forced oscillations the coordinate absorbs energy from a direct force of frequency equal to that of any element in the series, storing it as a free (complex) oscillation—the property leading to the hypothesis.

In the phenomena referred to n is small compared with μ, and it is evident from the general method of analysis that even with a small variation in spring, the elementary amplitudes $\ldots a_{-1}, a_0, a_1 \ldots$ are comparable. The general solution may, however, be obtained by a very simple method:—

$$x = \mathrm{A}\,(\cos ct+\alpha\sin nt+\epsilon),$$

where A and ϵ are arbitrary, is the solution of

$$\ddot{x}+\frac{\alpha n^2\sin nt}{c+\alpha n\cos nt}x+(c^2+\tfrac{1}{2}\alpha^2n^2+2\alpha cn\cos nt+\tfrac{1}{2}\alpha^2n^2\cos 2nt)x = 0,$$

an equation determining the motion of a system of natural spring $c^2+\frac{1}{2}\alpha^2n^2$, subject to positional and motional forces the strengths of which are periodic functions of the time. n being small the periodic terms in n^2 are negligible compared with those in n; thus

$$\ddot{x}+(\mu^2+2\alpha\mu n\cos nt)x = 0$$

gives
$$x = \mathrm{A}\cos\left\{\left(\mu-\frac{1}{4}\,\frac{\alpha^2n^2}{\mu}\right)t+\alpha\sin nt+\epsilon\right\},$$

indicating a reduction in frequency of the second order of small quantities. The square of the amplitude of spring variation is proportional to the energy of the normal motion producing it; and such motion being subject to dissipation according to the exponential law, for a steady state its energy must be proportional to the pressure—the temperature being assumed constant. Thus the reduction in the frequency of the series is directly proportional to the pressure.

Although the equation of motion can always be reduced to the above form, the quantity directly affected when the disturbance is slow, is the reciprocal of the spring, which in general undergoes (i.) a change in its mean value proportional to the pressure, and (ii.) a periodic variation: the latter gives an increase in frequency, the former either an increase or diminution. Thus we can assert only that there is a change of frequency proportional to the pressure.

Reductions proportional to the pressure have been observed in the case of iron vapour *, but the hypothesis does not appear of marked value in this instance owing to the absence of specially selective effects. Evidently the statical influence of the pressure is predominant.

In the case of sodium many resonance series appear to have the same frequency difference. From the present standpoint it seems probable, therefore, that the vapour would strongly absorb long waves of this frequency, $n/2\pi$, and show selective refraction in its neighbourhood. Such absorption would be accompanied by displacements of the series towards the violet end of the spectrum under the influence of the intensified periodic variation in the reciprocal of the spring.

It is hardly necessary to point out that slow normal oscillations within the vibrating system are sufficient to account for the complexity of linear spectra, and the variations in relative brightness at different pressures.

July 1910.

LXXXVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 544.]

February 23rd, 1910.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S., President, in the Chair.

THE following communication was read:—

'Metamorphism around the Ross of Mull Granite.' By Thomas Owen Bosworth, B.A., B.Sc., F.G.S.

The Ross of Mull granite is a coarsely crystalline plutonic mass, forming the western portion of the Ross of Mull and extending over some 20 square miles.

The intrusion is conspicuously later than the Moine rocks, and

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* W. G. Duffield, "On the Effect of Pressure on the Arc Spectrum of Iron," Phil. Trans. 1907.

is regarded as one of the 'newer granites'. The rock shows very little evidence of faulting or movement of any kind, and is traversed by sheets of mica-trap. The eastern boundary of the granite is a very intricate line of junction with typical Moine Schists and Gneisses, into which it has been intruded. Injection-breccias occur along the margin, where the granite is crowded with schist-inclusions.

The changes in the pelitic schists are of two kinds, and are considered under separate headings (*a*) and (*b*) below.

(*a*) Impregnation.—The schists have been impregnated with the granite in a very intimate manner:—(1) Along irregular cracks; (2) Along bedding-planes; (3) Along strain-slip; and (4) Along foliation.

Variously banded rocks have been thus produced, which suggest how readily these processes, carried out on a large scale, would convert pelitic sediments from the state of schists into crystalline igneous gneisses.

(*b*) Thermal Metamorphism.—In some places the pelitic gneiss in contact with the granite, and commonly the masses included in the granite, have been very highly altered. The new minerals formed are sillimanite, andalusite, cordierite, and green spinel; and these are present in such amount that their formation must have been accompanied by much recrystallization among the quartz, felspar, and mica also.

Sillimanite is the most abundant new mineral, and occurs not only as fibrolite throughout the rock, but also in larger crystals which are often grouped together in prismatic aggregates. These aggregates weather out as conspicuous knobs, measuring about an inch across.

Under the microscope, the sillimanite is seen to enclose large numbers of grains of green spinel. The cross-sections of sillimanite are diamond-shaped, and show a pinacoidal cleavage; their colour between crossed nicols is a very low grey, and good interference-figures are obtained.

The association of minerals in the schists is the same as that noticed at the margin of the Ben Cruachan 'newer granite'-mass, and also at the margin of 'newer granite' at Netherly in Elgin.

Tourmaline, kyanite, and staurolite also occur in the Moine Schists of Mull, but are in no way connected with the granite.

March 9th.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S.,
President, in the Chair.

The following communication was read:—

'The Carboniferous Succession in Gower (Glamorganshire).' By Ernest Edward Leslie Dixon, B.Sc., F.G.S., and Arthur Vaughan, B.A., D.Sc., F.G.S.

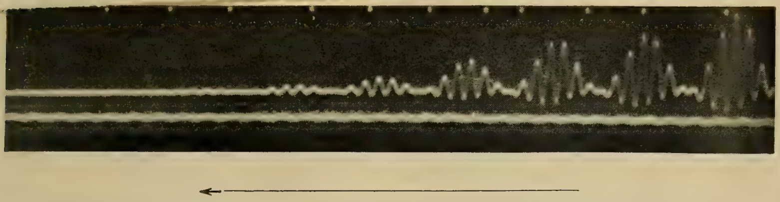
The succession in three districts in Gower is described, the districts being so situated that a comparison of their respective developments can be interpreted in the light of the fact that, during Avonian time, the nearest coast lay to the north, with a general east-and-west trend. With the description of the lithological sequence are included notes on some breccia-like limestones, characteristic of D, and on 'lagoon-phases' and the origin of radiolarian cherts. To the faunal lists are added notes on the D_2–D_3 phase of the *Dibunophyllum* Zone, which distinguishes Gower from the rest of the South-Western Province at present known, and on the correlation of that zone with the Upper Bernician of Northumberland. From the faunal sequence it is concluded that the zones Z, C, S, D_1 and D_2 (the K Zone is poorly exposed) are characterized by the same assemblages as in the Bristol area.

The lithological sequence shows (1) that over the whole area the depth of the Carboniferous sea underwent a complete cycle of intermittent change during Lower Avonian time, the initial deepening being followed by gradual shallowing up to the top of the lower part, C_1, of the *Syringothyris* Zone, which was deposited almost at sea-level; (2) that a similar cycle marked the ensuing period up to the top of the *Seminula* Zone; (3) that a similar but smaller cycle took place in the *Dibunophyllum* Zone, the latter actually reaching the surface; and (4) that a fourth cycle, commencing with a far-reaching physiographic change, characterized the *Posidonomya* Zone.

Further, a comparison of the sequences and thicknesses in the three districts shows that, not only were the downward movements of the sea-bottom during the first two cycles greater in the south than in the north, but also that the axis on which the movement during the first cycle hinged was different in direction from the axis during the second cycle. The bearing of these movements on the question of the delimitation of the divisions of the Avonian is then discussed. They suggest that the base of the upper part, C_2, of the *Syringothyris* Zone should form the base of the Upper Avonian. On the other hand, the base of C_2 in at least two localities is closely connected, faunally, with the zones below, whereas the fauna of the main mass of C_2 passes into S_1 without appreciable change other than the introduction of *Lithostrotion*. It will, therefore, in all probability be decided that the break between the Lower and the Upper Avonian should be taken at a level within C, rather than at the base of the *Seminula* Zone. For the present, however, this question must be deferred, since it concerns the whole extent of the formation in Belgium, the North of France, and the British Isles.

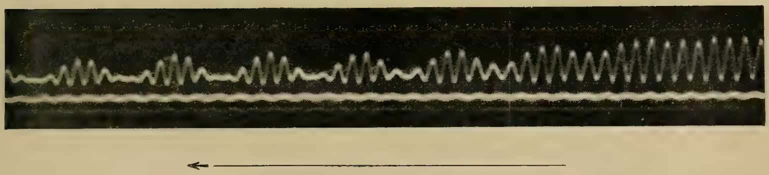
The paper concludes with notes on some of the corals and brachiopods, including one new species of coral and two new species and a new variety of brachiopod.

The plates belonging to this book are all here but not in their proper places.



$n_2 = \frac{4}{3} n_1$. $n_2 - n_1 = 200{\cdot}6$.

Fig. 2.



$n_2 = \frac{4}{3} n_1$. $n_2 - n_1 = 174{\cdot}8$.

Fig. 3.

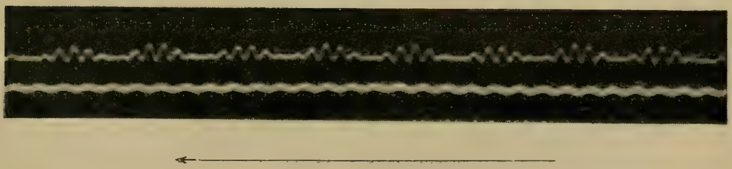


FIG. 1.

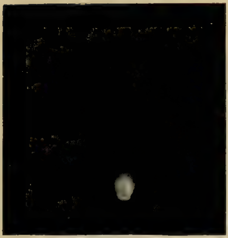


FIG. 2.

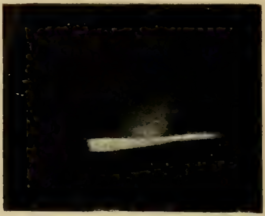


FIG. 3.

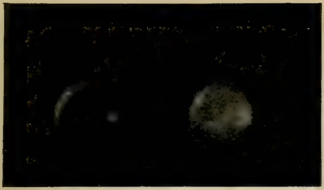


FIG. 4.

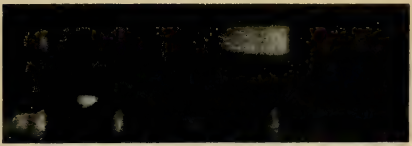


FIG. 5.

FIG. 6.

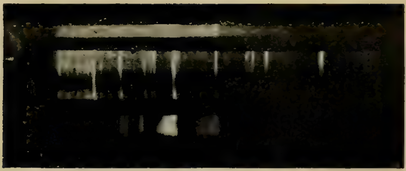


FIG. 7.

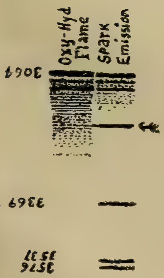


FIG. 8.

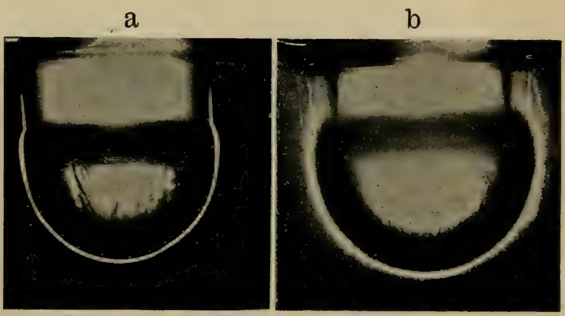


FIG. 10.

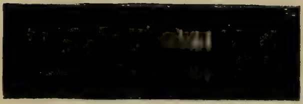


FIG. 9.

Fig. 1.

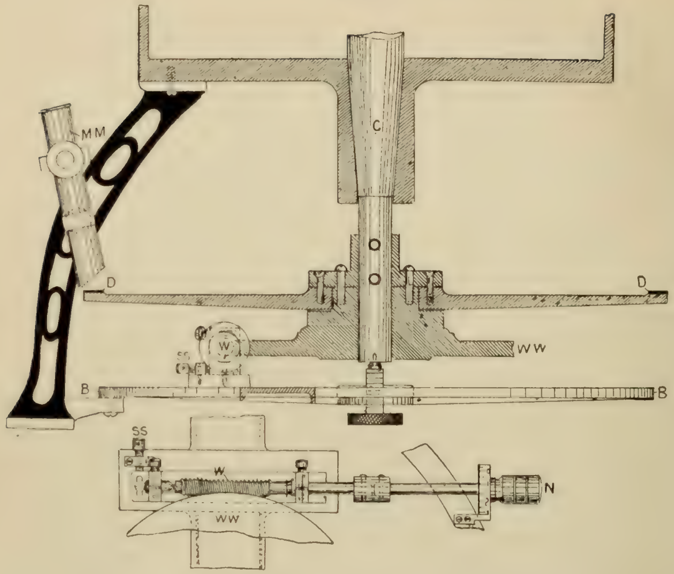

MM
C
D
D
W
SS
WW
B
B
SS
W
WW
N

Fig. 2.

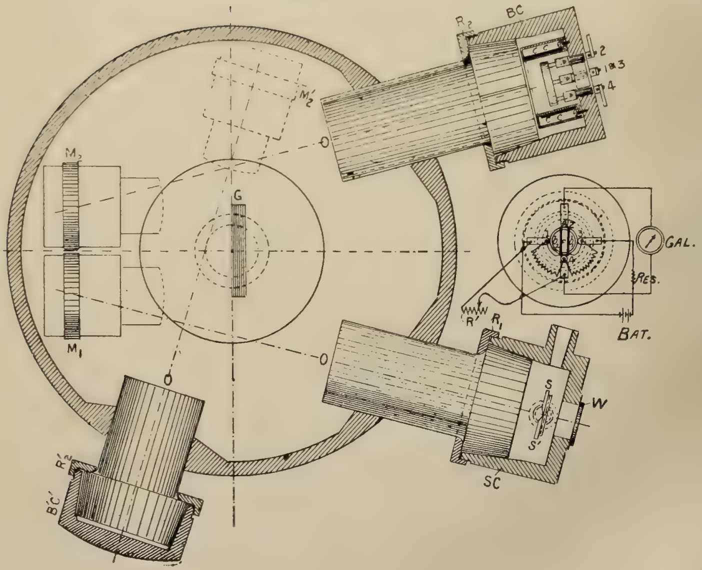

M_2'
R_2
BC
C C
2
1&3
4
C C
M_2
G
M_1
O
O
O
GAL.
RES.
R'
R_1
BAT.
S
W
S'
SC
R_2'
BC'

Fig. 3.

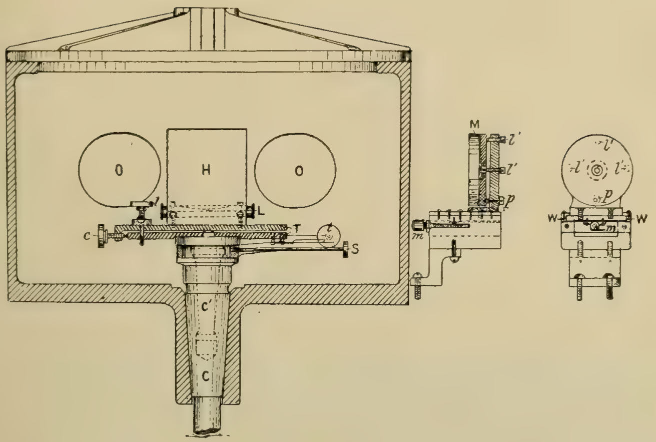


Fig. 4.

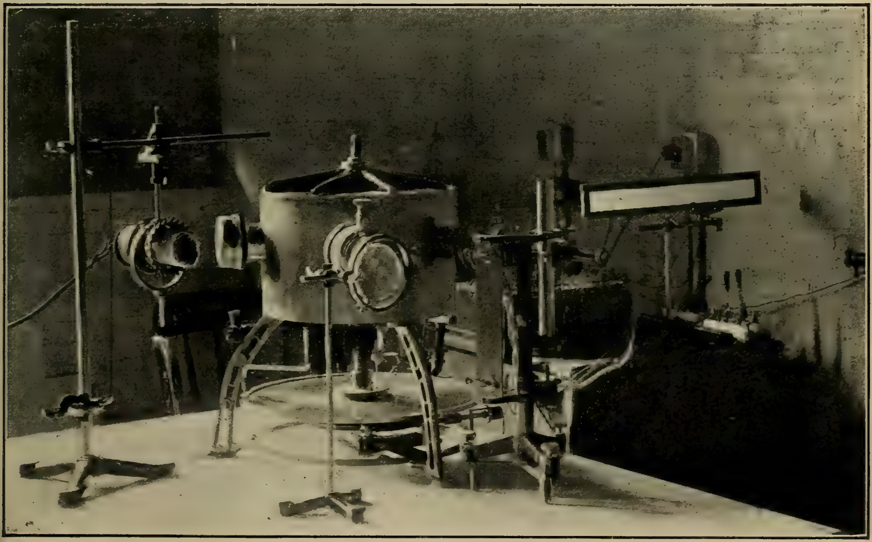
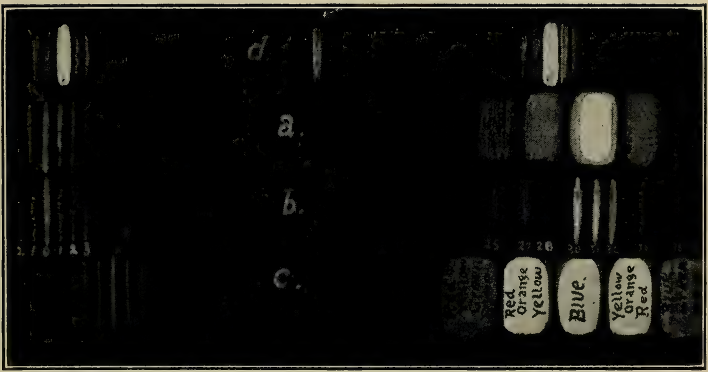
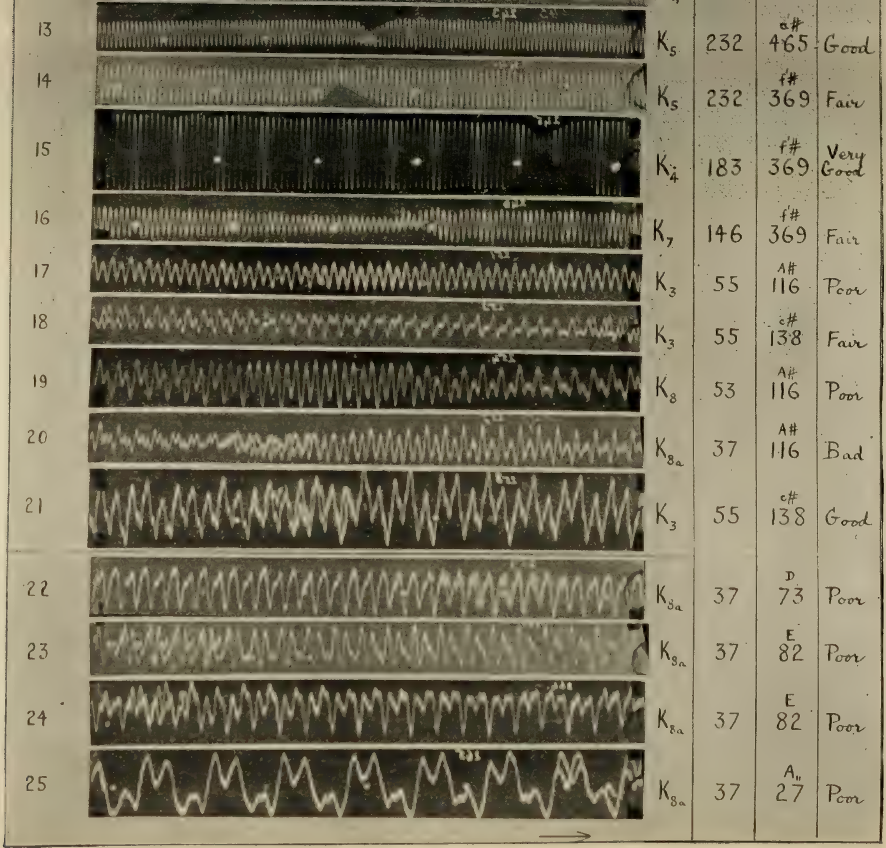


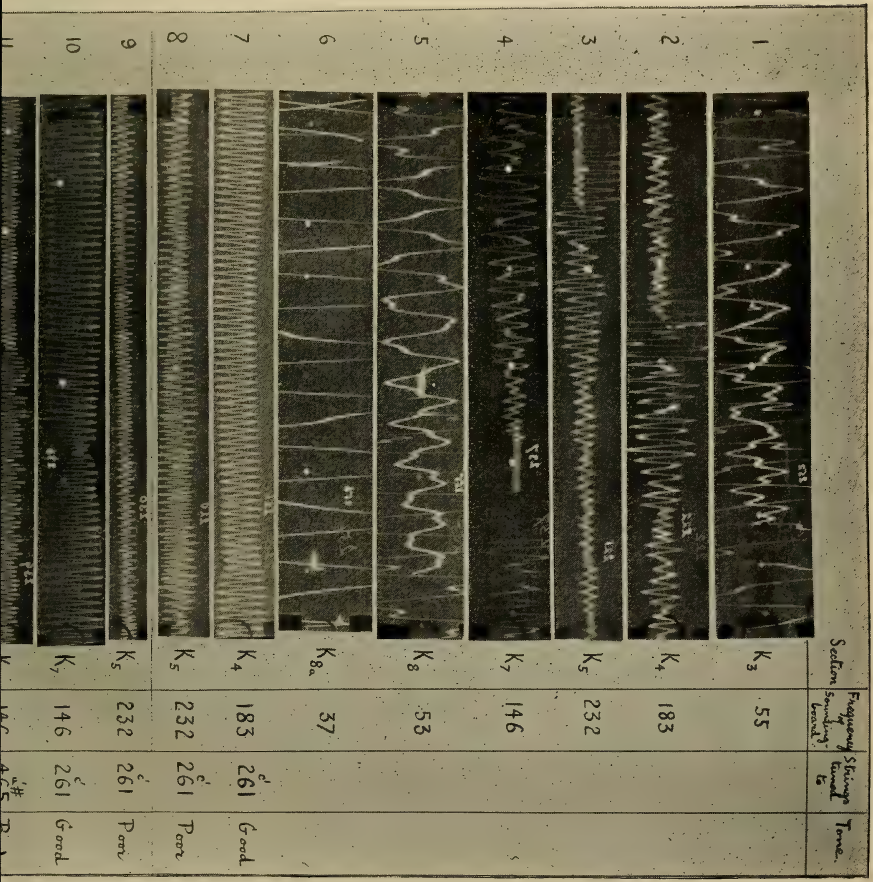
Fig. 2.



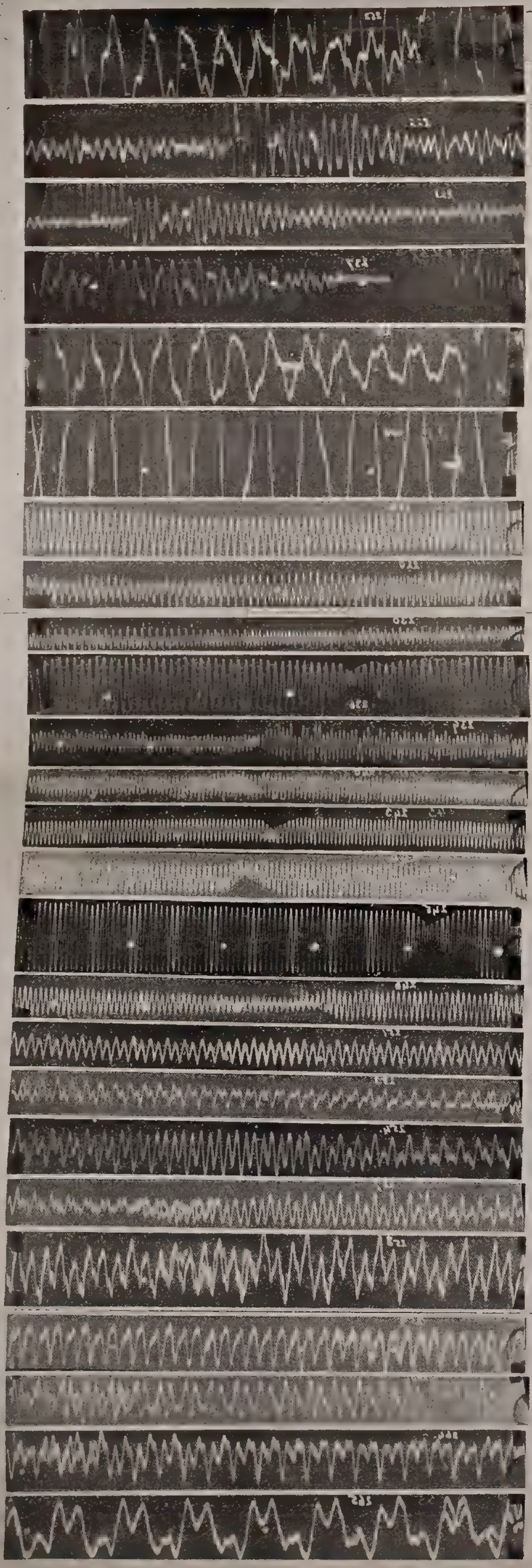


13	K_5	232	a# 465	Good
14	K_5	232	f# 369	Fair
15	K_4	183	f# 369	Very Good
16	K_7	146	f# 369	Fair
17	K_3	55	A# 116	Poor
18	K_3	55	c# 138	Fair
19	K_8	53	A# 116	Poor
20	K_{8a}	37	A# 116	Bad
21	K_3	55	c# 138	Good
22	K_{8a}	37	D 73	Poor
23	K_{8a}	37	E 82	Poor
24	K_{8a}	37	E 82	Poor
25	K_{8a}	37	A,, 27	Poor

Phil. Mag. Ser. 6, Vol. 20, Pl. XII.



	Section	Frequency of sounding-board	Strings tuned to	Tone
1	K_3	55		
2	K_4	183		
3	K_5	232		
4	K_7	146		
5	K_8	53		
6	K_{8a}	37		
7	K_4	183	$\overset{c'}{261}$	Good
8	K_5	232	$\overset{c'}{261}$	Poor
9	K_5	232	$\overset{c'}{261}$	Poor
10	K_7	146	$\overset{c'}{261}$	Good
11				



	Section	Frequency of Sounding-board	Strings tuned to	Tone.
1	K_3	55		
2	K_4	183		
3	K_5	232		
4	K_7	146		
5	K_8	53		
6	K_{8a}	37		
7	K_4	183	c' 261	Good
8	K_5	232	c' 261	Poor
9	K_5	232	c' 261	Poor
10	K_7	146	c' 261	Good
11	K_7	146	a'# 465	Bad
12	K_4	183	a'# 465	Good
13	K_5	232	a'# 465	Good
14	K_5	232	f'# 369	Fair
15	K_4	183	f'# 369	Very Good
16	K_7	146	f'# 369	Fair
17	K_3	55	A# 116	Poor
18	K_3	55	c# 138	Fair
19	K_8	53	A# 116	Poor
20	K_{8a}	37	A# 116	Bad
21	K_3	55	c# 138	Good
22	K_{8a}	37	D 73	Poor
23	K_{8a}	37	E 82	Poor
24	K_{8a}	37	E 82	Poor
25	K_{8a}	37	A„ 27	Poor

BERRY.

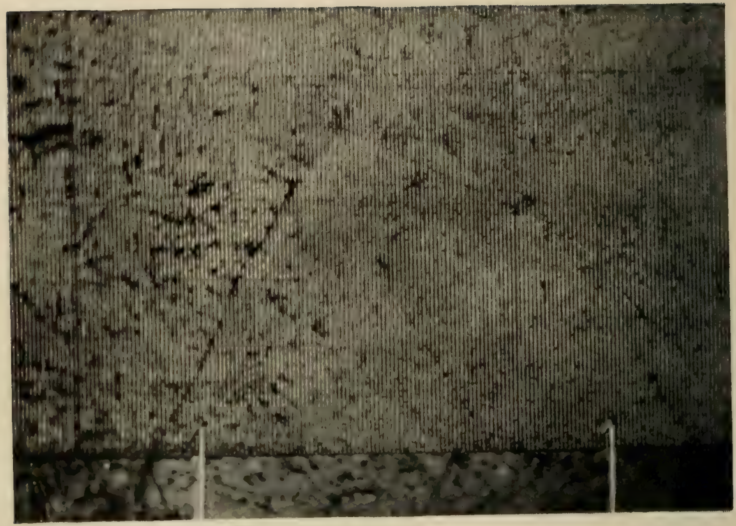
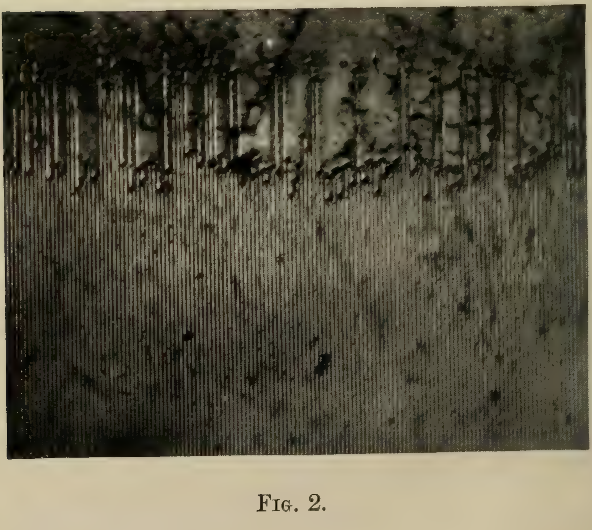


Fig. 1.



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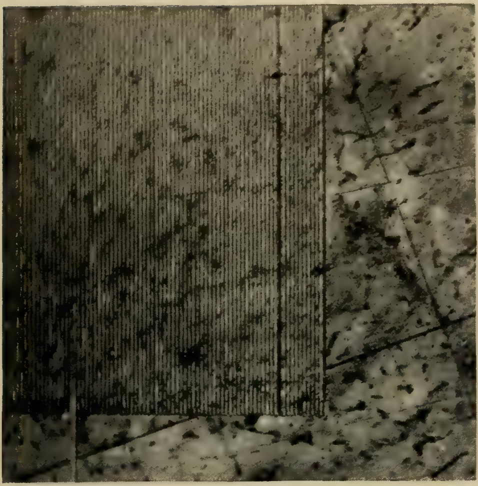


Fig. 3.

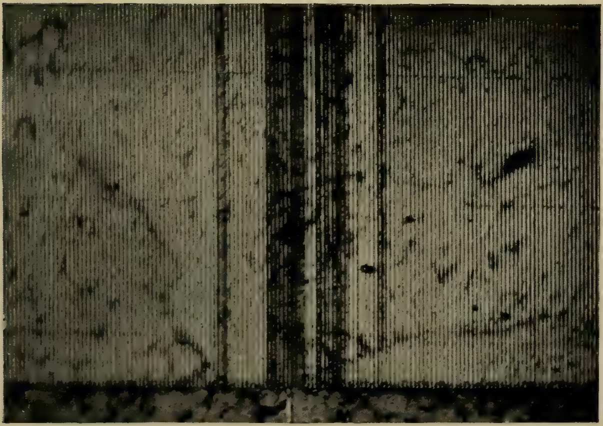


Fig. 4.

Fig. 2.

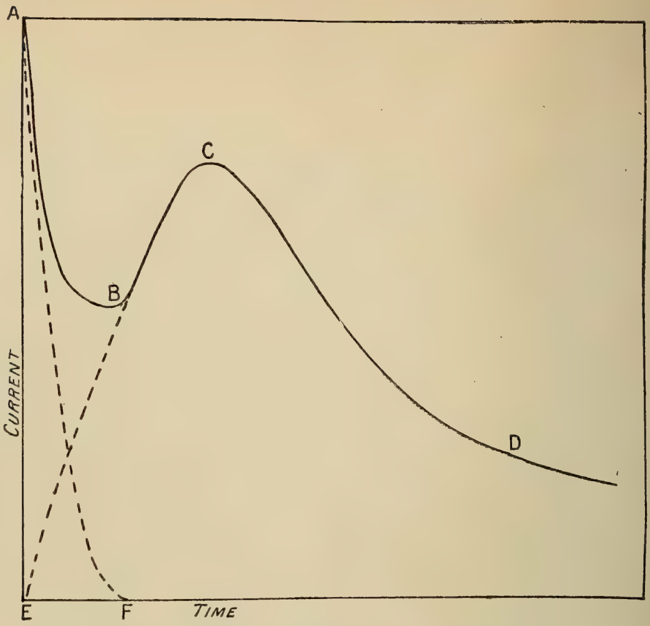

A
C
B
CURRENT
D
E
F
TIME

Fig. 4.

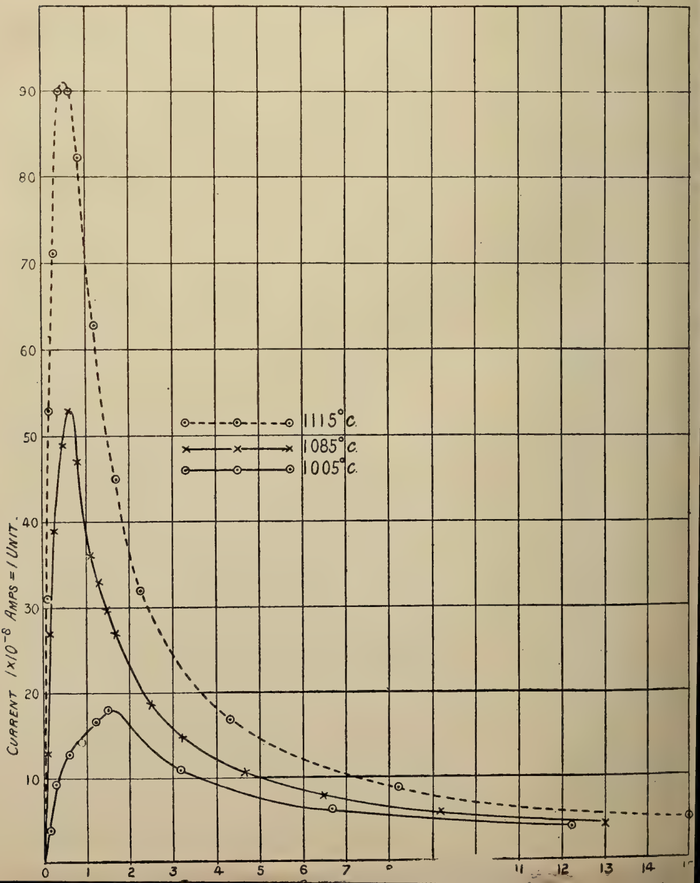

90
80
70
60
50
40
30
20
10
CURRENT 1×10⁻⁸ AMPS = 1 UNIT.
1115°c.
1085°c.
1005°c.
0
1
2
3
4
5
6
7
11
12
13
14

Fig. 3.

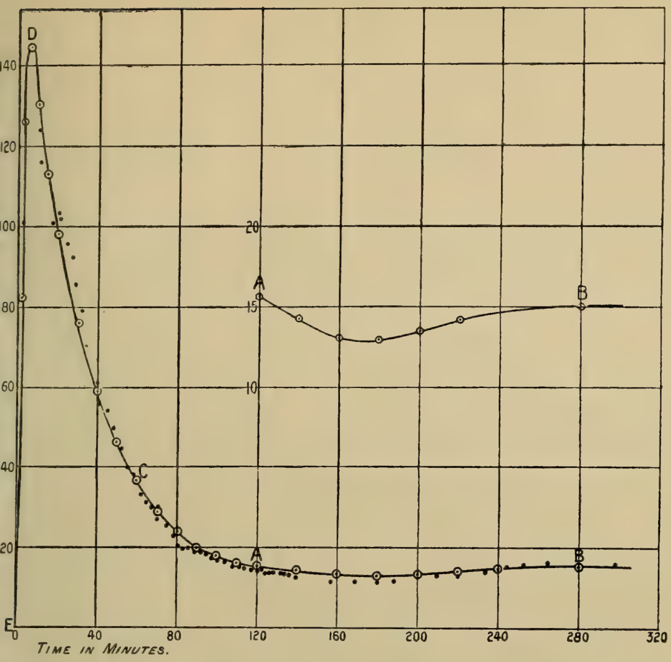
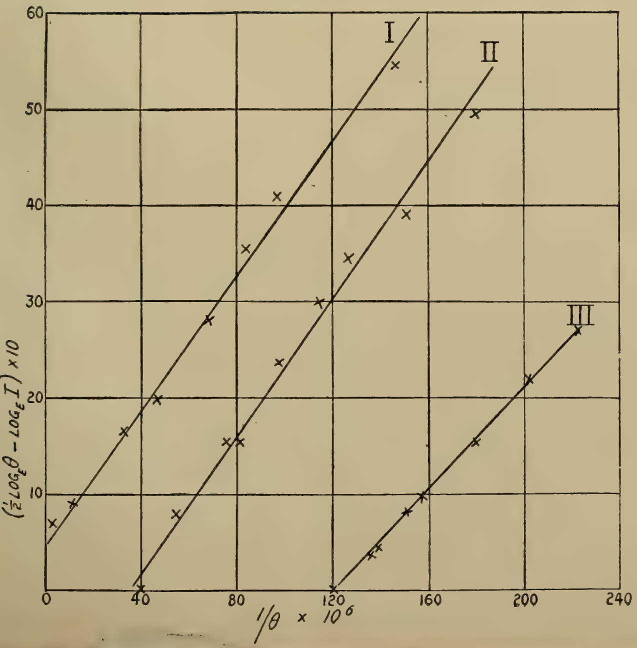

D
140
120
100
80
60
40
20
E
20
15
10
A
B
C
A
B
0
40
80
120
160
200
240
280
320
Time in Minutes.

Fig. 5.


I
II
III
60
50
40
30
20
10
0
40
80
120
160
200
240
$(\frac{1}{2}\log_e\theta - \log_e I) \times 10$
$1/\theta \times 10^6$

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

NOVEMBER 1910.

LXXXIX. *On the Critical Phenomena of Ether.*

By F. B. YOUNG, *B.A.*, *B.Sc.*[*]

IT has been observed by numerous investigators that when a liquid in contact with its vapour is heated to the critical temperature of vaporization, the meniscus disappears whilst the density of the liquid is still distinctly greater than that of the vapour, and that this difference of density may persist for an appreciable time even if the temperature is still further raised. According to the simple theory of continuity of state, the liquid and vapour should become identical at the critical temperature[†]. Various explanations of this phenomenon have been offered, some of which are intended to reconcile it with Andrews's theory, whilst others utilize it as evidence of the insufficiency of that theory. The chief views which have been presented are the following:—

A. Explanations involving no modification of Andrews's Theory.

(i.) Gouy (1) points out that owing to the influence of gravity the pressure in the substance is not uniform but increases from the top downwards. Since the substance when exactly at its critical state is quite abnormally compressible, an appreciable discontinuity may be produced in the density of the substance at that level at which the pressure is equal to the critical pressure.

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[*] Communicated by Prof. A. P. Chattock.

[†] S. Young has shown this to be true in the case of normal pentane (Trans. Chem. Soc. vol. lxxi. p. 446, 1897).

(ii.) Villard (2) points out that at the critical temperature and just above it, the dilatation with rise of temperature is extremely great. He attributes the difference of density to a slight but persistent difference in temperature. In support of his explanation he has reproduced the difference of density in a tube of ethylene by gently heating the upper portion. Since the mean specific volume was greater than the critical volume, the effect must have been quite distinct from that predicted by Gouy.

(iii.) Onnes and Verschaffelt (3) ascribe the phenomenon largely to the presence of traces of impurity in the substance. If the substance contain a slight admixture of some other more volatile substance, the latter might tend to collect in the vapour phase and, by its partial pressure, would produce an effect similar to that ascribed by Gouy to gravity.

B. Liquidogenic Hypotheses.

(iv.) Some investigators (amongst whom are De Heen and Traube) * consider that the difference of density corresponds to an actual difference of molecular structure. The liquid molecules or *liquidons* are of greater mass than the gaseous molecules or *gasons*; the meniscus disappears when the two phases become mutually soluble in all proportions, but homogeneity of molecular structure occurs only at a temperature (T_c), which is higher than that of the disappearance of the meniscus (θ_c). It is urged that the differences of density observed are both too great and too persistent to be due to differences either of pressure or of temperature, whilst it is claimed that impurities are eliminated by the methods of preparation.

The investigation to be described was undertaken with the purpose of examining the Cagniard-Latour phenomena in the light of the various explanations offered.

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* The results obtained by De Heen (Mathias, *Point Critique des Corps Purs*, p. 197, P. de Heen, *Bull. de l'Acad. roy. de Belgique* [3] t. xxxi. pp. 147 et 379, 1896), and by Teichner (*Ann. d. Physik*, Feb. 1904) have been critically examined in the laboratory of K. Onnes (*loc. cit.*), and the results of the inquiries warrant a strong presumption that the marked differences of density are to be attributed to the presence of a small percentage of impurity in the substance assumed to be pure. Since, however, Mathias regards the controversy between the Classical and Liquidogenic Theories as still an open one, additional experimental material relating to the critical phenomena of pure substances seemed to be highly desirable.

Elaborate precautions were taken to secure the purity of the ether, and especially to free it from the last traces of permanent gas. The submersed bell described in Section A proved a delicate means of detecting the slightest traces of gaseous impurity, and showed the precautions taken to be quite necessary for the attainment of the best results. It was possible thereby not only to test the efficiency of the means adopted for purifying the ether, but also to classify the tubes prepared according to the relative amounts of impurity contained. The observations made with these tubes proved that extremely slight traces of gaseous impurity might visibly modify the critical phenomena.

By means of the bell above mentioned the part played by hydrostatic pressure in the Cagniard-Latour phenomena was tested, and found to be probably negligible.

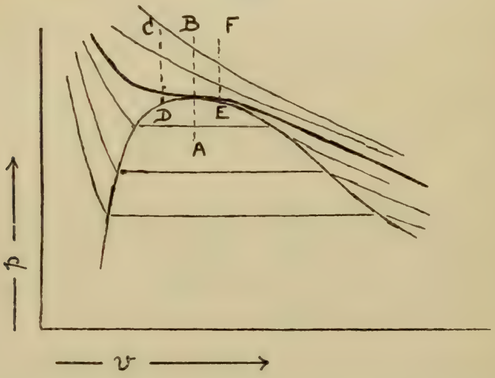
The effect produced by Villard with ethylene was reproduced in the tubes of ether, and the density difference so produced was carefully compared with that associated with the Cagniard-Latour phenomena in the pure substance. The conclusion arrived at was that these were essentially identical.

The opalescent phenomena were carefully examined, and explanations are suggested of some of the peculiar opalescent effects described by earlier investigators. Some account is also given of preliminary observations which were made with a view to determining the nature of the opalescent particles.

The investigation has led to the general conclusion that the phenomena observed in the pure substance may readily be explained in accordance with the theory of Andrews, whilst the phenomena, both qualitative and quantitative, which have been advanced as demonstrating most strongly the insufficiency of that theory are to be observed only in tubes which contain distinct traces of impurity.

Before proceeding to the experimental work, I would like to point out that if the differences of density can be adequately accounted for, the various other phenomena which have been held to invalidate the Classical Theory need present no difficulty. Cailletet and Collardeau (4) have shown that iodine dissolved in liquid CO_2 remains in solution in the denser substance above θ_c, although the less dense substance does not acquire the property of dissolving iodine. Hagenbach (5) found that the resistance of a very dilute solution of sodium iodide or bromide in sulphur dioxide remained less in the upper portion of the tube than in the lower for two or three hours after the temperature had been raised above the Cagniard-Latour temperature. Eversheim (6) observed similar effects in ammonia and SO_2, whilst the dielectric constant for H_2S differed also in similar fashion. If, however, the density differences can be explained in accordance with Andrews's theory these latter forms of evidence become inconclusive. For though, by definition, the liquid and vapour cease to exist above the Cagniard-Latour temperature, there is no cogent reason why their peculiar properties should forthwith disappear. The diagram of Andrews is apt to give an impression of discontinuity at θ_c which in practice is nonexistent. The ordinate AB (fig. 1), for which v is equal to the critical volume V_c, appears in meeting the saturation curve to strike a point of sudden transition; this is because of the impossibility of realizing the theoretical isothermals within that curve. In practice, however, as the explanations of both Gouy and Villard indicate, the bulk of the substance does not, during rise of temperature, pass through θ_c along the isothermal AB, but, roughly speaking, along two ordinates DC and EF, for which $v < V_c$ and $v > V_c$ respectively. In this case the discontinuity at θ_c ceases to be apparent. Hence it is not unreasonable to assume that the continued difference of density will be accompanied by a continued difference of properties; and if adequate causes for the observed persistency of the density difference can be found which are in accordance with Andrews's theory, the same causes may be held to produce indirectly the observed differences of electrical and chemical properties.

Fig. 1.



A. *Preparation of the Tubes.*

Fig. 2.

The tubes employed were of the design shown in figure 2. The Natterer tube AD is of Jena glass tubing about 1 mm. in thickness, about 8 or 10 mm. in internal diameter, and from 13 to 16 cm. in length. Inside AD slides freely a piece of Jena-glass tubing C about 3 cm. in length, which is closed at the upper end and thus forms a bell. The bell-tube is fused to a similar piece of tubing B in which are hermetically sealed some tightly packed iron filings; by means of a sufficiently powerful electromagnet, C and B may be raised at will. The ether is introduced through the constricted end D which is afterwards sealed off.

The special purpose of this design is explained later, but, as has already been stated, the bell proved to be a very efficient detector of gaseous impurities. If such impurity is present, it is to be found chiefly in the vapour. By inverting the tube and then slowly bringing it back to the position shown in fig. 2, the bell-tube may be made to fall into the liquid, carrying within it a portion of the vapour. If the vapour is pure it readily condenses, but if it is mixed with gas a bubble remains which dissolves very slowly, since it is subjected to a pressure of only a few centimetres of liquid ether. As a further test, C may be filled by ebullition. If the end D is gently heated, the ether boils briskly, whilst reflux condensation occurs at end A. By this means the gaseous impurity, if present, is brought mainly to the top of the tube, and C is filled with comparatively pure vapour from beneath. This sample of vapour may then be compared with that previously obtained.

In filling the earlier tubes various methods of removing the air were tried. In some cases, a large excess of ether was introduced and the surplus was pumped off with a Töpler pump. In other cases, the method described by Travers and Usher (7) was adopted: the ether was frozen with liquid air whilst the tube was exhausted, and the excess of ether was then pumped off before sealing the tube with the blowpipe. In all cases, however, very distinct traces of gaseous impurity were observable: the vapour brought down from end A was far more persistent than that produced in the bell-tube by ebullition, and in order to secure its condensation it was necessary to raise the pressure by gently heating the upper part of the tube.

Since the removal of gaseous impurity was of the utmost importance, the methods of filling were carefully examined. Tube XII. was filled with excess of ether and connected through a prolongation of the capillary D (fig. 2) and a short piece of rubber pressure-tubing to a Töpler pump. The ether having been frozen with liquid air, the tube was exhausted. When the ether was allowed to thaw a brisk effervescence of bubbles proceeded from the surface of the dwindling solid lump. This was the dissolved air which had separated out when the ether was frozen. Not all the air, however, escaped in this way. After a little of the ether had vaporized, the freezing and thawing were repeated and again bubbles were evolved, though fewer than before. Though the ether was frozen four times, a few bubbles rose after the final thawing. (In the case of another tube bubbles were evolved after the ninth freezing.) The trouble was largely due to the partial solution of the bubbles as they rose, for some of the smaller bubbles visibly dwindled in size as they ascended. The tube was finally sealed off at the constriction whilst the ether vapour was passing freely into the pump.

For purposes of comparison another tube A was filled with ether. The constricted end had been drawn out and bent so that the tip might be immersed in mercury. About two-thirds of the ether was boiled off and the tube was then sealed. Tubes XII. and A were then immersed in liquid air : when the ether thawed, an eye estimation of the bubbles evolved led to the conclusion that tube A contained rather more permanent gas than tube XII.

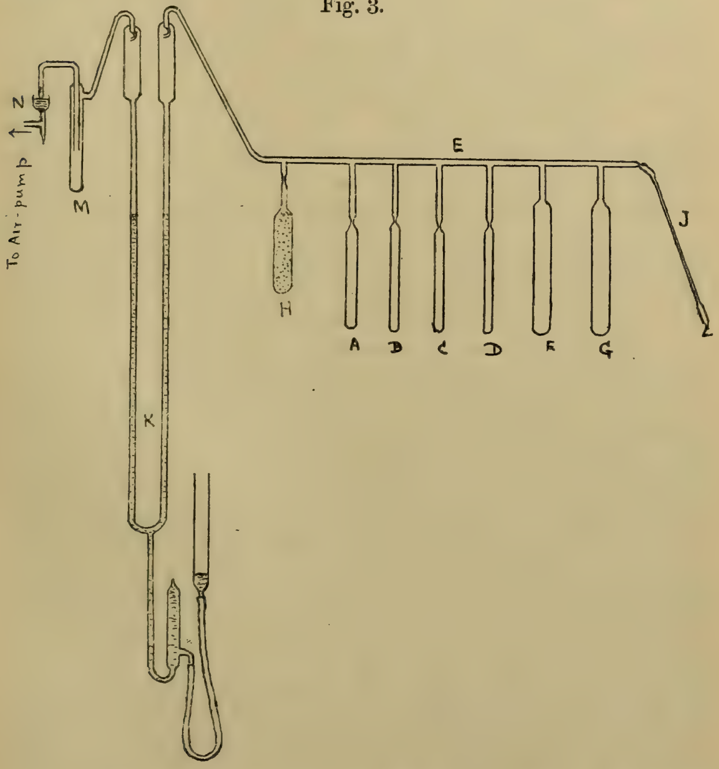
The importance of reducing the pressure to a minimum, if the freezing process is employed, was shown by freezing and thawing ether at atmospheric pressure. Though numerous bubbles appeared upon the surface of the solid lump as it melted away, scarcely one left the surface, so rapidly did they dissolve.

A further test showed the extreme solubility of air in ether at the atmospheric pressure. A tube which had been nearly freed from permanent gas in the manner above explained was detached from the pump, so that the ether was again exposed to the atmosphere. After a few moments it was replaced on the pump, care being taken to avoid shaking the tube more than was necessary. On freezing the ether and thawing it under reduced pressure, the effervescence was not perceptibly less than it had been originally.

These tests suggest that the test commonly relied upon for judging the absence of permanent gas—namely, the absence of bubbles in a capillary tube containing the ether—cannot be relied upon if the ether is under a pressure approaching that of the atmosphere.

In some of the earlier tubes, the traces of gaseous impurity were more distinct after the tubes had been raised to a high temperature than they were immediately after the process of filling. Since the ether which was used in these tubes had been kept for some months in a stoppered bottle placed in a desiccator, it is possible that it had been attacked by the atmospheric oxygen with the formation of products which decomposed at a high temperature. In filling the later tubes, the ether to be used was finally distilled over potassium and sodium alloy within an hour or two of the process of filling.

Fig. 3.



The following rather drastic method of filling the tubes was finally found necessary. The tubes to be filled (A, B, C, and D in fig. 3) were fused to a horizontal tube E, from which were suspended also the two reservoirs F and G and the bulb of charcoal H. One end of tube E terminated in the fine capillary tube J, the sealed tip of which was drawn out very thin and bent, so that it might readily be snapped by a gentle pressure. The other end of E communicated with a Töpler pump through the mercury trap K, the arms of which were about 90 cm. in height. Between K and the pump was interposed the trap M: this was immersed in liquid air, and by arresting the ether vapour prevented the fouling and consequent loss of efficiency of the pump. Since the experimental tubes were of Jena glass it was necessary to construct the whole of the filling apparatus of the same material. The connexion with the pump was made by means of the mercury-sealed ground joint N.

In order to free the tubes from moisture and adsorbed air, the apparatus from H to G was covered with asbestos millboard and heated over a tube furnace. The tubes were evacuated by means of the pump, and the trap K was left open so that they were in communication with the phosphorus-pentoxide tube attached to the pump. This process was repeated several times. Just before carrying out the filling operations the trap K was closed; the charcoal bulb was immersed in liquid air for about an hour and was then fused off, so that a Dewar vacuum was created in the tubes.

The apparatus from K to G was heated well above the boiling-point of ether. The capillary tube J was then introduced into the freshly prepared ether, and its tip was broken by pressure against the bottom of the bottle. The first portion of ether which ascended the capillary vaporized, until the internal pressure was equal to that of the atmosphere. The reservoir G was then cooled with water, the remainder of the apparatus being kept hot as before. When the desired amount of ether (about 45 c.c.) had collected in G, the flow was checked by immersing G in water at about 35° C., and the capillary tube was sealed off near the top.

The ether in G was then frozen with liquid air. The mercury in K, acting as a manometer, still showed a pressure in the tubes of 8·8 cm., this being almost entirely due to the air which had entered in solution. M having been surrounded with liquid air, K was opened and the air was pumped off. The ether was then allowed to thaw, and a first portion passed off as vapour through K. The bulk of the ether was condensed in F by means of liquid air; a little of the remainder was then condensed in the experimental tubes, after which the ether in F was allowed to thaw and the first portion of it passed off through K together with the ether in the experimental tubes and the remainder in G. The ether was distilled to and fro between F and G, the operations above described being repeated at each reversal. In this way the first and last fractions were each time removed, and the experimental tubes were flushed out with ether vapour. K was so manipulated as to prevent the return of any vapour from the pump. The distillation was accelerated, when necessary, by dipping the reservoir in a beaker of methylated spirit, and the spirit served the further useful purpose of keeping the reservoir free from frost, so that careful observation was possible. The bubbles evolved on thawing decreased at each successive distillation till at the commencement of the sixth distillation none were visible. The sixth distillate was then frozen and allowed to thaw, whilst one of the empty tubes was immersed in liquid air in order that the ether might thaw under a minimum pressure. As there was again an entire absence of bubbles, the process of the purification was considered complete. Each experimental tube in turn was then filled by condensation with a slight excess of ether; the excess was distilled off, and the tube sealed off at the constriction with the blowpipe.

Some of the tubes were sealed whilst the vapour was issuing freely; others were immersed, before sealing, in liquid air, so that the constriction was free from vapour. The latter tubes showed a slight but distinct superiority over the former when tested for the presence of permanent gas. From this it appears that the vapour in contact with the hot glass undergoes decomposition.

For the above process, Kahlbaum's ether distilled over sodium was used after further treatment. About a third of a litre of the ether was placed in a well-stoppered bottle with some sodium and potassium alloy. The bottle was wrapped in opaque paper and placed in a mechanical shaker, by means of which it was repeatedly shaken for several hours at a time. This plan was adopted in view of a suggestion that the efficiency of the solid metal is quickly impaired by the oxidation of the surface: by means of the shaking the surface of the liquid alloy was constantly renewed. After about three months of this treatment the ether was fractionated over the alloy three times through a five-section Young fractionating column. The ether was protected from atmospheric moisture by a guard-tube of phosphorus pentoxide, the receiver being ground to the condenser tube; and by introducing the liquid into the apparatus in the manner previously described, the necessity for pouring it through the air was avoided. The thermometer employed was graduated in tenths of a degree and was calibrated by means of a similar Reichsanstalt thermometer. The boiling-point of the selected fraction was 34°·53–34°·54 C. (N.T.P. at lat. 45°).

The B.P. is lower than the generally accepted value (34°·6 C.); but, according to Wade and Finnemore (8), whose work on the purification of ether was unfortunately not published until after the above preparation had been completed, the boiling-point of pure ether is very near 34°·50 C., and the ether prepared was therefore not really freed from the last traces of alcohol. This possibility is remembered in discussing the experimental results obtained.

The following are details of the various tubes to which reference has been or will be made in this paper :—

Tube VII. was filled with ether kindly supplied by Mr. Usher and prepared in the manner described by Travers and Usher (7); it had, however, been kept for some time. The tube was filled with the aid of liquid air and the simple Töpler pump, the ether being frozen seven times ; it was sealed with the vapour issuing.

Tube XII. was filled with ether freshly prepared by the method of Travers and Usher (7), sodium and potassium alloy, however, being substituted for potassium wire. It was filled in the same way as tube VII., the ether being frozen four times.

Tube XIII. was filled with Kahlbaum's ether treated with sodium and potassium alloy. It was filled by means of the special apparatus described and sealed whilst the vapour was issuing.

Tube XIV. was filled in the same manner and at the same time as tube XIII., but was sealed whilst the ether was frozen.

For purposes of comparison, tubes VII., XII., XIII., and XIV. were fastened side by side and immersed in a tank of water at a temperature of about 10° C. After immersion for about 15 minutes, the bell-tubes were filled simultaneously by inversion of the experimental tubes, and observations were made of the condensation of the vapour carried down by the bells. Tubes XIII. and XIV. were markedly superior to tubes VII. and XII., whilst XIV. was distinctly freer from permanent gas than XIII. The observations are tabulated in Table I.

It may be mentioned that the head of liquid under which the vapour condensed was roughly the same except in the case of tube XII., in which it was about one-half as great as in the other tubes. Hence the apparent similarity of tubes VII. and XII. implies that tube XII. is somewhat superior to tube VII. In every case the bubbles could be made to vanish by gently warming the upper layers of ether and thus adding the vapour pressure to the hydrostatic pressure, so that had the vapour been tested under atmospheric pressure it would probably have completely condensed in every case.

Table I.

No. of Tube.	Observations of condensation of vapour.		Fraction of tube occupied by liquid at 0° C.	Critical Temperature (of reappearance of meniscus).
	Bell filled by inversion.	Bell filled by ebullition.		
VII.	$\frac{2}{3}$ remained after 13 mts. ($\frac{3}{5}$ remained after 90 mts.)	Vapour condensed in 1 mt.	0·335	193°·59 C.
XII.	$\frac{2}{3}$ remained after 13 mts.	Vapour condensed in $2\frac{3}{4}$ mts.	—	—
XIII.......	$\frac{1}{10}$ remained after 13 mts. ($\frac{1}{20}$ remained after 90 mts.)	Vapour condensed in $2\frac{1}{2}$ mts.	0·385	193°·58 C.
XIV.	Condensation complete in $1\frac{1}{2}$ mts.	Vapour condensed in $2\frac{1}{3}$ mts.	0·345	193°·59 C.

The bell-tubes were then filled by ebullition. The bells having been filled with liquid, the experimental tubes were placed point downwards over a hot-water coil for five minutes. They were then plunged, still point downwards, into the water-tank. In this case the vapour in tube VII. condensed more readily than that in the remaining tubes, the condensation being probably assisted by the partial pressure of the gaseous impurity. The distinctly greater persistence of the vapour in tube XIV. may be accounted for by the additional time required for the preliminary establishment of equilibrium of temperature. The time required for the condensation of the vapour in tube XIV. does not seem unduly great when it is considered that to maintain the two menisci in equilibrium at the average difference of level (about 6 cm.) a difference in temperature of only 0°·2 C. between the menisci was necessary, or a difference in temperature of 0°·1 C. between either meniscus and the water-bath. During the process about 0·1 of a calorie was absorbed at the upper meniscus and evolved at the lower ; the dissipation of heat from the bell, moreover, occurred through two thicknesses of glass separated by a thin film of liquid.

The tests have only a rough quantitative value since the tubes were not identical in their dimensions. They suffice to show, however, that (*a*) the ether should be prepared shortly before being placed in the tubes ; (*b*) the last traces of gaseous impurity can be removed only with the utmost difficulty ; (*c*) if the tubes are to be sealed with the blowpipe the pressure of the ether vapour should previously be reduced to a minimum. Each of the above experiments was checked by duplicate tubes.

In Table I. are included for reference the proportions of the tubes filled by the liquid at 0° C. and the critical temperature of the ether in tubes VII., XIII., and XIV. (Tube XII. exploded before observations could be made.)

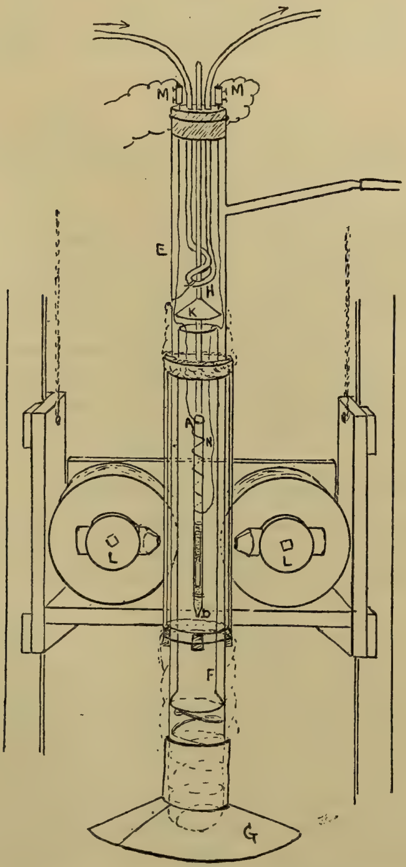
The temperature given is that at which the meniscus was first perceived as the ether was very slowly cooled. Since in neither of the tubes was the mean density exactly equal to the critical density, the actual Cagniard-Latour temperature (θ_c) is probably slightly higher than that given. The critical temperature for tube XIV. is the mean of seven observations, and the critical temperatures for tubes VII. and XIII. are obtained by direct comparison with tube XIV., the tubes being observed simultaneously.

B. *Disposition of Apparatus.*

The tube under observation was supported on a glass rod in the vapour jacket E (fig. 4). This jacket was surrounded by two guard-tubes forming a double air jacket, whilst an inner tube F, which was widened at the bottom to fit the vapour jacket rather closely, still further protected the tube from temperature disturbances. A coil of metal tube H acted as a condenser, a stream of cold water being passed through it. The tin cone K deflected any drops of condensed liquid to the sides of the vapour jacket. The asbestos cone G protected the vapour from the heat of the flame which was placed beneath. The vapour jacket was placed between the poles L of a powerful electromagnet which was mounted on a small counterpoised lift so that it could be readily raised or lowered. By means of the magnet the bell C (fig. 2) could be raised at will. The upper portion of the experimental tube was in some cases surrounded by an open coil of fine iron wire N having a resistance of about 2 ohms, the ends of which were connected through the needles M to electrical terminals. The vapour jacket was connected, through the side tube, with an arrangement for maintaining constant the internal pressure (*v.* Appendix).

The liquid used in the vapour jacket was aniline. For this purpose Kahlbaum's Aniline was redistilled and the middle fraction was employed. The temperatures were obtained from the vapour-pressure readings given by Travers and Usher (7). In the few cases in which these readings were exceeded, it was considered sufficient to extrapolate the given values, since in those cases an approximate temperature sufficed for the purpose.

Fig. 4.



The tube F was sufficiently wide to accommodate two experimental tubes side by side, and where comparisons are made between two tubes, the tubes were heated simultaneously, so that the conditions of temperature were identical.

C. *General Phenomena.*

A brief statement is given of the general phenomena observed in tube XIV. in the neighbourhood of the critical temperature.

(1) If the tube was slowly cooled after being maintained at a temperature about 3° C. above θ_c :—

(*a*) A faint opalescent haze appeared throughout the tube and gradually became denser, at first very slowly, but more rapidly as the temperature θ_c was approached. Just above that temperature a dense opaque fog pervaded the tube and the substance appeared greatly agitated.

(*b*) At θ_c a faint, flat meniscus was perceived slowly rising around the plunger B (fig. 2). A brisk ebullition of fine bubbles was generally discernible through the dense opalescence which still persisted after the appearance of the meniscus.

(*c*) As the temperature was further reduced the opalescence became fainter and at length disappeared. The ebullition became more marked, while condensation was apparent in the vapour. The meniscus gradually rose, becoming at the same time clearer and assuming a concave shape. (If the reduction of temperature was effected in sudden drops of about 0°·02 the tube became filled each time with an oily cloud which dissolved into a rain of bubbles and drops rising and falling respectively into the meniscus.)

These appearances may be regarded as belonging to conditions of equilibrium, since by arresting the fall of temperature the changes described could be arrested at any point.

(2) If the temperature was raised extremely slowly (*e.g.* 0°·01 C. in 5 mts.) it was possible to approximate to a reversal of the phenomena of slow cooling, the condensation phenomena in the vapour phase excepted. It was difficult, however, to avoid the effects of lag detailed in (3) and (4).

(3) If the temperature was raised as quickly as possible to the neighbourhood of θ_c, the liquid quickly became opalescent and after a few minutes the vapour also became opalescent. At the same time the meniscus fell and, given sufficient time, fell below the top of the plunger, beyond which point its movements were difficult to follow.

(4) If the temperature was rapidly raised a little above θ_c (say 0°·2 C.) and then maintained constant, the meniscus quickly became indefinite in outline and nebulous in appearance; it assumed at the same time a slightly convex

appearance (*v.* Section E). The substance beneath the disappearing meniscus quickly became densely opalescent; the top of the opalescent column slowly became less defined, and the substance above it also grew opalescent till the opalescence was uniform. The higher the temperature was the more rapidly did the meniscus fade and the less marked were the opalescent phenomena. In each case the final appearance was that produced by slowly cooling the tube as in 1 (*a*) to the same temperature. The height at which the meniscus faded varied considerably with the rapidity with which the temperature was raised to the desired temperature. The more rapidly the temperature was raised the greater was this height, which might be as much as 3·5 cm. above the plunger.

(5) If the temperature was quickly raised as in (4) and was then allowed to fall steadily before the liquid phase had become opalescent, an opalescent zone gradually appeared at the level at which the meniscus was fading and became denser as θ_c was approached, till at length a meniscus appeared within the zone and the opalescence then faded away. The phenomena were practically a rapid repetition of those described in 1 (*a*) (*b*) and (*c*), confined, however, to a very short length of tube. The more promptly these operations were carried out, the shallower and more definite was the zone, the upper and lower limits of which sometimes had almost the sharpness of a meniscus.

In tubes VII. and XIII. the equilibrium phenomena were similar to those of tube XIV. except that in tube XIII. the meniscus was higher, the more nearly the temperature approximated to θ_c. The variations in the transitory phenomena are dealt with in later sections.

D. *Influence of Gravity.*

The tube described in Section A was designed for the purpose of testing the extent to which the abnormal compressibility at the critical volume predicted by Gouy from Clausius's equation accounted for the observed phenomena. The intention was to raise the bell to such a height that the meniscus disappeared within it, giving place to a zone of transition. The bell would then be gently lowered, carrying with it the transition zone. In this way the pressure at that zone would be increased by the hydrostatic pressure of the column of ether through which it was lowered, and theoretically the zone should then rise in the bell.

It was essential that the last traces of permanent gas should be removed. The earlier tubes distinctly showed effects due to the presence of such traces. The observations made with tube VII. may be taken as typical. When the vapour jacket was first heated, the aniline vapour, as it rose round the tube, produced a reflux condensation which, as before explained, had the effect of collecting the bulk of the gaseous impurity at the top of the tube, whilst the bell was filled with comparatively pure vapour. The tube was then maintained at a constant temperature of about 185° C. The meniscus was observed to rise slowly in the bell; after 7 minutes it had risen about halfway, and after 20 minutes about three-quarters of the way up the bell. The bell was next raised above the liquid so that it was filled with vapour from above. It was then lowered to the bottom, and the meniscus was again observed. The meniscus now remained at the mouth of the bell and had not risen at all at the expiration of 30 minutes.

Tube XIV. was heated simultaneously with tube VII., and in both of the above tests the meniscus remained at the mouth of the bell. It is evident, therefore, that the meniscus in tube VII. had in the first case been driven upwards by the partial pressure of the enclosed gas, while this partial pressure was lacking in tube XIV.

Theoretically, the meniscus should have slowly risen in the bell of tube XIV. owing to the pressure of the liquid ether upon the vapour in the bell. From the data given by Ramsay and Young (9) may be calculated the difference in temperature of the two menisci which is necessary to maintain them in equilibrium at a given difference of level. The difference of temperature is 0°·0008 C. for 1 cm. difference of level, or 0°·0064 C. for the difference of level of 8 cm. which existed in the tube. The difference was probably a little greater than this, for very occasionally a bubble escaped from the mouth of the bell, showing that slow vaporization was in progress. Thus the tube acts as a delicate differential thermoscope whose delicacy increases as the mean temperature rises, since not only does the density of the ether decrease with rise of temperature but the slope of its vapour pressure becomes steeper. The difference of temperature persisted in spite of all precautions taken. About one-tenth of this temperature variation may be ascribed to the effect of the hydrostatic pressure of the aniline vapour upon its own tension; the remainder must be due to other causes.

If the temperature of the tube was suddenly raised, the meniscus quickly travelled a certain distance up the bell and then remained practically stationary. Doubtless the vapour in the bell, being supplied with heat less rapidly than that above, maintained equilibrium of temperature by partial condensation. By suitable manipulation it was possible near the critical temperature to have two menisci in the tube at different levels—one in the bell and one above the plunger. It was thus unnecessary to bring the meniscus down from above as originally contemplated. If the temperature was then raised a little above θ_c, sensibly the same phenomena occurred in both menisci as have been described in Section A (4). Hence there were two levels differing by about 6 cm. at which zones of transition appeared and persisted for several minutes until the opalescence became uniform. Nor did the zone in the bell show any perceptible tendency to rise.

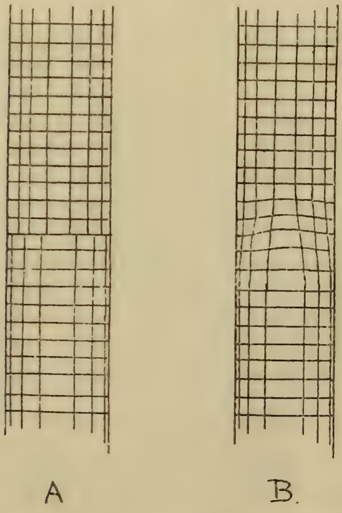
These phenomena favour the conclusion that the part played by hydrostatic pressure in the production of the transition zone is quite a subsidiary one. According to Gouy's prediction there may be one level in the tube at which $\frac{dv}{dp}$ is very great, but there can be only one such level. The existence of temperature differences in the vapour jacket, it is true, makes this conclusion somewhat uncertain. If the variation of temperature with height is uniform, the only effect will be a tendency to annul the effect of hydrostatic pressure and to prevent the formation of the transition zone; but if, owing to the separation of the tube into two sections by the plunger, each portion of the ether tends to assume a uniform temperature which is slightly higher for the lower portion than for the upper, the portions may be considered as representing short lengths of two isothermals in Andrews's diagram separated by a very small temperature difference; and in this case it is conceivable that each column may include the level at which $\frac{dv}{dp}$ is a maximum for the given isothermal. It is probable, however, that, as in Villard's experiment (*v.* page 794), this level of maximum value for $\frac{dv}{dp}$ was not contained within the limits of the tube. The behaviour of the meniscus at its appearance during slow cooling, or its disappearance during very slow rise of temperature, seems to show that the mean specific density was so much less than the critical density that the level in question would be somewhat below the bottom of the tube.

The possibility of making the zone of transition form at varying heights (*v.* Section C. 4) in the tube also seems to point to the inadequacy of the explanation of Gouy.

E. *Influence of Difference of Temperature.*

The experiments to be described were practically repetitions of Villard's experiments with ethylene. By passing a current of electricity through the coil N (fig. 4) it was possible to raise the temperature of the upper half of the tube slightly above that of the lower half. In the experiments which were carried out with tube XIV. the lower limit of the coil was about 3 cm. above the top of the plunger. The variations of optical density in the ether were observed, when possible, by means of a strip of squared paper placed behind the vapour jacket. The appearance of the lines when viewed through the tube maintained at a temperature slightly below θ_c is shown in figure 5 A; the vertical lines are sharply broken at the meniscus. If the temperature is raised rapidly to some point above θ_c the broken verticals become connected by a curve as shown in B; the curve gradually spreads upwards and downwards, and at the same time the upper and lower portions of the lines gradually open and close respectively until their appearance is uniform throughout. When the presence of opalescence made the observations difficult or impossible, the degree of uniformity of density of the ether

Fig. 5.



was judged by the degree of uniformity of the opalescence; this method is justified in Section F.

The temperature of the tube was raised a little above θ_c and maintained for a few minutes. The plunger was vigorously raised and lowered several times in order to ensure complete uniformity. The ether was then uniformly opalescent throughout the tube. A current of about 0·5 ampere was then passed through the wire coil. It was observed that the opalescence gradually faded away whilst the lines seen through the tube assumed the appearance of fig. 5 B; the transition zone was just beneath the lower limit of the coil. After the heating current had been switched off, the appearance of the tube remained unaltered for about three minutes; a faint opalescence then appeared in the transition zone which soon spread and filled the lower part of the tube. The upper part of the ether then grew opalescent, and finally the appearance of the tube became the same as it had been before the coil was heated. The phenomena scarcely differed from those described in Section C (4).

The transition zone was reproduced as before. The heating current having been switched off, the temperature was slowly reduced. It was observed that the transition zone became opalescent, the limits of the opalescence being sharply defined; the opalescence grew denser until at length a meniscus appeared within it. The opalescence then faded away. The phenomena of Section C (5) were thus reproduced.

An attempt was then made to compare the relative persistencies of the natural and the artificial transition zones. The temperature was suddenly raised from about 193°·4 C. to 193°·73 C. in order to produce the phenomena of Section C (4). The time was then taken which elapsed before the zone of transition had lost all definition and the opalescence had spread to the top of the tube; this proved to be about 10 minutes. After a short interval during which the temperature remained at 193°·73 C., the heating current was switched on for two minutes, and the time was again taken which had elapsed before the appearance of the tube was sensibly the same as at the end of the former test: the period was about 8 minutes.

The tests with the heating coil show it to be highly probable that differences of density above θ_c which persist for as much as 8 or 10 minutes may be ascribed to residual temperature differences produced by vaporization.

Mention may be made of two effects observed when the heating coil was used below the critical temperature.

It was possible, by passing a stronger current through the coil, to cause the meniscus to disappear when the temperature of the vapour jacket was as much as 8° below θ_c, so that the lower portion of the ether was still presumably in the liquid state. Owing to the great difference in density the transition zone was then extremely well marked. Its depth was so slight that it had almost the appearance of a convex meniscus. Closer examination, however, led to the conclusion that the appearance of convexity was due to the refractive effect upon horizontal lines placed behind (fig. 5), the effect being produced by the presence in a cylindrical tube of a medium gradually increasing in density downwards. The apparent slight convexity of the meniscus mentioned in Section C (4) may have been due to this cause. The matter is here mentioned because a convexity of the meniscus in the neighbourhood of the critical temperature has previously been recorded (10) ; it is now suggested that in such cases the temperature θ_c had already been slightly exceeded and that the so-called meniscus was in reality a very narrow transition zone.

If the bell was filled with vapour at a temperature considerably below θ_c and the heating current was then switched on, the liquid was observed to rise and fill the bell (the upper meniscus was for this purpose embraced by the coil). If, however, the temperature was not far below θ_c the meniscus, after rising a short distance, became nebulous and faded away as it rose. A similar effect is mentioned by Amagat (11), who found it occur when carbon dioxide slightly below its critical temperature was subjected to slow compression. It was probably due to the evolution of heat by the vapour as it condensed under compression. By diminishing the heating-current and consequently the rapidity with which the meniscus rose, it was possible to make the meniscus rise higher before disappearing, the latent heat of vaporization having more time in which to dissipate.

F. *Opalescent Phenomena.*

(1) *Occurrence.* — The opalescent effects described in Section E afford some information concerning the conditions which favour the production of opalescence. On reducing the temperature to θ_c after the production of the artificial transition zone, a dense opalescence appeared in that zone only, no visible phenomena occurring above or below as the temperature fell. Although the temperature of the ether varied through the tube, each layer of ether passed through θ_c in turn ; since marked opalescence was exhibited only by that part of the ether in which the meniscus appeared, and

which, therefore, presumably possessed the critical density, it seems that opalescence can occur in ether only if the density approximates to the critical density. Again, since conversely in every case in which the intensity of the opalescence was not uniform the meniscus appeared in the part in which the opalescence was most marked, it may be inferred that the critical density is the density most favourable to the production of opalescence.

Travers and Usher (7) observed that if the mean density of filling differs from the critical density, so that as θ_c is approached the meniscus is either rising or falling in the tube, then the disappearing phase becomes markedly more opalescent than the increasing phase. They suggest an explanation based upon Donnan's theory concerning the surface-tension of small drops, and connect the localization of the opalescence with the motion of the meniscus. This phenomenon was strikingly apparent in tubes XIII. and XIV. when they were raised simultaneously to the critical temperature; the liquid phase in XIV. became intensely opalescent before the vapour showed more than faint indications, whilst in tube XIII. the conditions were reversed. The phenomenon, however, receives a simple explanation from the dependence of the intensity of the opalescence upon the density of the substance. Unless the mean specific volume is equal to the critical volume, the meniscus can only disappear within the limits of the tube if, at the time of disappearance, the two phases differ in density, and hence at θ_c only one of the phases can approximate to the critical volume. If the mean specific volume is less than V_c, this phase will be the phase of lesser density, *i. e.* the vapour phase, which is also the diminishing phase; it is this phase whose density will be more favourable to the existence of opalescence. The reverse is true if the mean specific volume is greater than the critical volume. This explanation is in effect identical with the conclusion of Sidney Young (12) that the position of maximum opalescence depends upon the mean specific volume, since of course the actual specific volume at any given height in the tube and the mean specific volume are interdependent.

That the presence of the meniscus is unnecessary for the production of the phenomenon is shown by the effects described in Section C (4) where the local opalescence appeared after the fading of the meniscus; under the conditions of Section C (4) the same striking difference was apparent between tubes XIII. and XIV. The same indeed was true when the transition zone produced above θ_c by means of the heating-coil was allowed to disappear. The effects of traces of permanent gas upon the intensity of the opalescence are mentioned in Section F; it seems probable that these effects are indirect and consequent upon the influence of the impurity upon the density of the ether.

The variation of the intensity of the opalescence with temperature was examined. It was observed that the intensity, which was greatest at θ_c, decreased as the temperature steadily rose above or fell below that temperature but decreased at a diminishing rate, so that the opalescence disappeared insensibly. It was, therefore, difficult to determine the limiting temperatures, particularly as the opalescence was viewed through six layers of glass. The lower limit, however, appeared to be about $0^{\circ}\cdot5$–$0^{\circ}\cdot6$ below θ_c, whilst there was a suspicion of opalescence at the highest temperature reached, *i. e.* about 3° above θ_c.

The Nature of Opalescence.

Various explanations of the nature of the opalescence have been suggested.

Some investigators have considered it to consist merely of an emulsion of one phase in the other (13, 14). Just below the critical temperature the liquid and vapour differ so little in density that either phase may exist dispersed throughout the other in the form of fine particles. Donnan (15) supports this view, but suggests certain conditions of surface tension which might account for the stability of the opalescent particles.

Küster (16) suggests that the opalescence is due to the variation in the temperatures of the individual molecules according to the kinetic theory. Let the mean temperature of the substance be just above the critical temperature; then, according to the theory of probabilities, many of the molecules will be moving with a velocity much lower (or higher) than corresponds to the mean temperature. When a sufficient number of slow-moving molecules occur together for an instant they constitute a minute drop of liquid. Any individual drop will only have a momentary existence since by hypothesis the drop has a lower temperature than its surroundings, but new drops will be created incessantly throughout the substance. In this way the opalescence above the critical temperature is accounted for; the opalescence in the liquid and vapour phases just below the critical temperature may readily be explained in a similar manner.

The theories stated have some interest in connexion with the present inquiry inasmuch as they implicitly assign different values to the critical temperature. Whilst neither of the theories makes any assumption either in favour of or contrary to the liquidogenic hypothesis, the theories of Altschul and Donnan imply that the Cagniard-Latour temperature is below either the temperature of complete mutual solubility of the liquidogenic hypothesis or that of uniformity of state of the simple classical theory ; Küster's theory, however, would imply that the Cagniard-Latour temperature coincides with one or the other of these. The fact that ebullition may proceed concurrently with the existence of opalescence of considerable intensity (*v.* Section C (1 *b*)) is scarcely in accord with Altschul's simple explanation, since it implies that an appreciable difference of density exists between the phases. An observation of the condensation phenomena also leads to the conclusion that there is a difference in kind between the stable opalescent cloud observed above or below θ_c and the cloud of condensation produced at the moment of separation of the meniscus. If the tube, first raised above θ_c, is steadily and fairly slowly cooled down, the opalescence increases in intensity as θ_c is approached but retains a "dry" nebulous appearance. At the moment of appearance of the meniscus, however, the condensation cloud appears to be superposed upon the opalescent cloud, sometimes flashing through the tube, sometimes spreading rapidly from the bottom upwards. This is particularly evident when the opalescence is localized, by the various means described, to a shallow zone. The "dry" fog instantaneously changes to a "wet" fog in a manner difficult to describe. When the condensation cloud has settled, the opalescent cloud is still visible enclosing the meniscus. The opalescent particles probably supply the condensation nuclei, but seem themselves to be something other than mere liquid drops or vapour bubbles. This phenomenon may perhaps be explained in accordance with Donnan's theory, if it is supposed that under suitable conditions of cooling the increase in the bulk of the opalescent material may tend to proceed rather by the increase in the size of the existing particles than by the formation of new aggregates, and that at length a certain proportion grow beyond the limits of size for which the peculiar conditions of surface tension which secure stability are true.

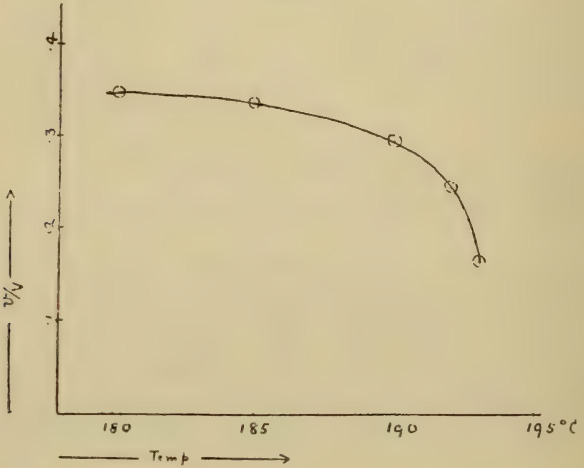
The consideration of the intensity of opalescence as a function of the temperature may, however, afford some criterion in deciding between the theories stated :—

Let a tube of capacity V contain 1 g. of the substance at a temperature below θ_c ; if the volume of liquid is v whilst u and u_1 are the specific volumes of liquid and vapour respectively, then the proportion by volume of the liquid present is given by

$$\frac{v}{V}=\frac{uu_1-uV}{V(u_1-u)}.$$

Figure 6 shows the graph of $\frac{v}{V}$ with temperature when V is greater than V_c. The graph is plotted from the experimental values of u and u_1 given by Ramsay and Young (20),

Fig. 6.

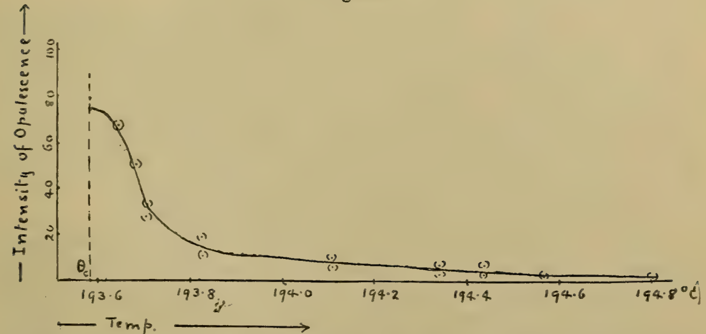


V being taken as 4·5, but its shape is characteristic of such a graph derived from a saturation curve of the form given in Andrews's diagram, *i.e.* a simple curve of negative curvature. It shows that the volume of the liquid diminishes with increasing rapidity, the temperature of disappearance being sharply marked. A similar graph would be obtained by plotting $\frac{V-v}{V}$ with temperature in the case where $V<V_c$. According to Altschul's simple explanation, either the bulk of opalescent material present should disappear in a similar manner with increasing rapidity and a well-marked point of disappearance, or the accepted form of the saturation curve requires modification and that curve must be given a peaked form. The assumptions of Donnan concerning surface-tension do not seem greatly to affect the nature of the graph. The optical intensity of the opalescence will, it is true, doubtless depend not only upon the bulk of the

opalescent material but also upon the difference of optical density between that material and the surrounding medium. Since the optical densities of the liquid and vapour, however, tend to equalize with increasing rapidity as θ_c is approached, the sharpness of the point of disappearance would be still further accentuated.

It was observed that the intensity of the opalescence above the Cagniard-Latour temperature decreased rapidly at first with rise of temperature, but with diminishing rapidity as the temperature became higher. To obtain some experimental record a rough graph showing the intensity of the opalescence at various temperatures was made in the following manner. A number of tubes of similar dimensions were filled with water containing a proportion of milk varying from 0·02 to 10 per cent. If one of these was held before the plate-glass observation window in a suitable position and under suitable conditions of illumination, an image could be obtained, close to the experimental tube, which resembled very closely a tube of opalescent ether. The series of tubes formed a rough scale of opalescence, with which the opalescent ether was compared at various temperatures. In fig. 7 the ordinates represent the intensity of the opalescence in terms of the proportion of milk contained in the tube whose image matched it most nearly (10 per cent. milk = 100). The curve shows sufficiently well the manner in which the opalescence varied with the temperature, and the form of the curve is altogether different in character from that of fig. 6.

Fig. 7.



The curve of opalescence is rather of the character which might be predicted from Küster's theory. According to that theory, there would probably be some connexion between the intensity of the opalescence and the distribution of velocities of translation according to Maxwell's theorem. The proportion of molecules having less than a given velocity k, which is itself less than the mean velocity of translation K, diminishes as k is taken further from K, but the rate of diminution is less rapid as $(K-k)$ becomes greater. This matter will, however, probably be further investigated.

G. *Effects of Impurity.*

Dwelshauvers-Dery (17) maintained a tube of carbon dioxide at various temperatures above θ_c and then allowed the tube to cool. A zone of emulsion appeared in the neighbourhood of the point at which the meniscus had disappeared, and as the temperature to which the tube was raised became higher, the zone of emulsion which was formed on cooling became broader. The emulsion, however, was not uniform throughout the tube even when the temperature had been raised 20° above θ_c. He inferred from his observations of carbon dioxide that the two states of the substance persisted even to the highest temperature reached. The zones of opalescence were regarded by him as zones in which mutual diffusion of the gasons and liquidons had occurred, so that when the temperature was lowered a cloud was formed by the separation of the two kinds of molecules.

Andrews (18), however, has obtained similar opalescent zones in working with mixtures of carbon dioxide and small proportions of nitrogen, though under rather different experimental conditions. The similarity of these results suggested that the phenomena of opalescence might be closely associated with, if not entirely dependent upon, the presence of impurity. It was partly with the object of testing this that special efforts were made to free the ether from impurity.

It was found, however, that the formation of opalescence is retarded rather than assisted by the presence of impurity. As the ether was obtained purer it more readily showed signs of general opalescence when its temperature was raised. When tubes VII. and XIV. were together raised in temperature slightly above θ_c, some time after the opalescence in XIV. had become general, tube VII. showed only a slight opalescence throughout the tube, whilst a denser cloud appeared in the neighbourhood of the point at which the meniscus had faded. If the ether was stirred, however, both tubes immediately appeared equally opalescent. The influence of traces of impurity upon the opalescent phenomena is probably indirect. If a trace of gas is present in the upper part only of the tube, it produces, by its partial pressure, a difference of density of the ether which may be so great that only the layers of ether at the junction of the two masses is of the density most favourable to the production of opalescence. The rate at which the opalescence spreads is dependent upon the rate of diffusion of the gaseous impurity, which is very slow. Even the slight impurity contained in tube XIII. seemed sufficient to delay visibly the establishment of equilibrium. If tubes XIII. and XIV. were raised simultaneously slightly above θ_c both tubes quickly showed opalescence in one portion (in tube XIII. this was above the transition zone), but the opalescent column in XIII. remained well defined for a few minutes after that in XIV. had become diffuse. It appears then that the readiness with which the opalescence becomes uniform throughout the substance, when the tube is heated slightly above θ_c, may be taken as a criterion of the freedom of the substance from gaseous impurity.

For the purpose of exaggerating the effects of impurity a tube XVII. was filled with ether contaminated with 5 per cent. of alcohol. The air was expelled from the tube, preparatory to sealing, by boiling off the excess of ether over mercury. The ether was heated, however, near the surface, so that the lower layers were unaffected and retained the dissolved air. The critical temperature θ_c for this tube was approximately 196°·2 C. It was maintained at the highest temperature for which the thermostat was constructed (about 196°·7 C.) for 30 mts. At the end of that time a very well-marked transition zone was still made evident by the squared paper placed behind ; it extended through a height of about 10 mm. only and was slightly opalescent. The temperature was then very slowly reduced, the reduction of 0°·5 occupying about 30 mts. ; at the same time the transition zone was watched carefully through a telescope containing a scale eyepiece. It was observed that the transition zone contracted slightly in height, whilst the relative displacement of the upper and lower parts of the vertical lines became more marked. The opalescence in the zone became gradually denser and more sharply defined. At the same time it became shallower : at 196°·4 C. it was a dense cylinder about 2·5 mm. in height, and at 196°·2 C. its height was scarcely 1 mm. The opalescence appeared to have contracted into the upper part of the transition zone, for the curvature of the vertical lines was still visible underneath. At 196°·2 C. the meniscus appeared in the opalescent zone. The transition zone had persisted for an hour, and at the end of that time was still clearly marked. The concentration of the opalescent material was probably only apparent, and the zone of opalescence became narrower simply owing to the increase in the slope of density through the transition zone, produced by the fall in temperature ; when uniformity of density was produced by stirring, the opalescence likewise became uniform and showed no tendency to become localized. The opalescent effects produced without stirring were very much like those produced in tube XIV. with the aid of the heating-coil, but were far more lasting.

It is necessary to observe caution in applying the results obtained with one substance to the explanation of phenomena observed in another. So far, however, as this may be done, it seems probable that the phenomena observed in tubes of carbon dioxide by Dwelshauvers-Dery might readily be produced if the experimental substance contained strong traces of some much more volatile impurity. It is unnecessary to regard the opalescent zone as a zone of separation of impurity from the ether, or the opalescence as consisting of the impurity in suspension. The opalescence is conditioned by the diffusion of the impurity only in so far as such diffusion produces a graduation of density in the substance, and hence the intensity of the opalescence or the bulk of opalescent material may be altogether out of proportion to the quantity of impurity present.

H. *The Liquidogenic Theories.*

Though it cannot be claimed that the experiments recorded by any means settle the liquidogenic controversy, yet they have some evidential value.

Travers and Usher (7) have criticised experimentally the results of Battelli by means of which he showed that, in the case of ether, θ_c decreases progressively as the mean density of filling increases. It is to be observed that the mean densities of filling chosen by Travers and Usher were contained within much narrower limits (0·244–0·281) than those taken by Battelli (0·2409–0·3043). Though the former investigators do not explicitly state the fact, one's own observations lead to the conclusion that if the tubes approaching the higher limit taken by Battelli were filled with ether sensibly pure and free from permanent gas, it would be impossible to make the meniscus disappear within the limits of the tube without raising the temperature of the thermostat so rapidly, in order to exaggerate the Villard effect, as to make accurate observations impossible. In tube XIII. it was found that with sufficiently slow rise of temperature the meniscus rose to within ·5 cm. of the top of the tube, though the mean density of filling was only 0·285 (density of ether at 0° C. being taken as 0·7362). If, however, sufficient traces of permanent gas or other impurities were present the task would be simple—it is quite probable that in tube XIII. the reluctance of the meniscus to ascend to the top was due to the trace of permanent gas known from the tests of Section A to be present—but in this case the results would no longer necessarily apply to the pure substance.

The slight difference in θ_c for the tubes XIII. and XIV. is not to be taken as lending support to Battelli's results. The values given in Table 1. are for the appearance of the meniscus with fall of temperature. If the ordinates, or lines of constant volume, are traced on Andrews's diagram for various values of v in the neighbourhood of V_c, it becomes evident that since the separation into two phases can only occur when the given ordinate reaches the saturation curve, the meniscus should appear at temperatures varying with the specific volume and diminishing as the specific volume differs more from V_c. Since in tubes XIII. and XIV. the meniscus appeared invariably at the upper and lower extremities of the respective tubes, V_c evidently lay between the two specific volumes, and if it lay nearer to the specific volume of tube XIV. the slight difference of temperature might be predicted from Andrews's theory. It was difficult to determine the exact temperature of disappearance on raising the temperature, partly because of the gradual nature of the change, partly because of the opalescent effects which rendered observation difficult, but in general the temperature of disappearance in both tubes seemed slightly higher than that of appearance, and was certainly not lower for tube XIII. than for tube XIV.

Other observers, like Battelli, have observed remarkable differences of density at θ_c or slightly above. Since the difference in the mean densities of tubes XIII. and XIV. is about 11 per cent. and the menisci disappeared practically at the top and bottom of the respective tubes (given a sufficiently gradual rise in temperature), it follows that at the temperature of disappearance the difference of density could not have exceeded that amount.

Mathias (19) shows, however, in his analysis of the liquidogenic theories that it is quite possible to frame a theory which will coincide with the classical theory of Andrews in its predictions concerning the final states of equilibrium, whilst it will also account for the transitory differences of density which have been held to show the insufficiency of that theory. It is the theory according to which the ratios

h_1 and h of gasons to liquidons in the vapour and liquid phases respectively are in the final state functions of the temperature only, the functions being different for the respective phases. If the law of Avogadro is assumed to hold for both kinds of molecules, the temperature of uniform density is that at which the ratios become identical. As the temperature is raised the establishment of equilibrium involves a continuous reduction in the value of h_1 and a continuous increase in the value of h; the adjustment is produced by a combined process of diffusion and of transformation of one kind of molecule into the other. A lag in this adjustment will sufficiently account for the prolonged differences of density which have been observed.

Since this theory differs from the classical theory in its predictions concerning observable phenomena only in respect to the time required for the establishment of equilibrium, it is only possible to decide between them by observation of the time-factor. Though the fact that the transition zone may be reproduced by heating the upper portion decisively proves that diffusion must play a minor part in the establishment of uniformity, it cannot be regarded as crucial evidence agains the validity of the liquidogenic theory: the objection may reasonably be raised that the changes of temperature and pressure which are produced tend to produce dissociation in the heated portion and possibly association in the lower portion. It is, however, doubtful whether the time-factor must be necessarily greater on the assumption of the liquidogenic hypothesis than on the assumption of Andrews's theory. According to the latter, if we accept Villard's explanation of the transition zone as of predominant importance, the denser substance must expand and the less dense substance be compressed against the external pressure and the intramolecular forces combined: this involves virtually the transmission of energy from the upper to the lower part of the substance, the transmission probably occurring mainly through the walls of the tube. In addition to this, sufficient heat must pass to bring the substance to the temperature of the thermostat. The liquidogenic theory seems to differ from Andrews's theory only in substituting the force of chemical affinity for the cohesive force, and the time-factor involved will only differ greatly on the assumption that the energy absorbed in the disintegration of the liquidons is much greater than that absorbed in separating the molecules against the cohesive force.

In Table II. are given readings for plotting by means of Van der Waals's equation the isobar which passes at the

TABLE II.

v (normal vols.).	t.	$t-194{\cdot}55$.	$\frac{(V_c\pm v)\times 100}{V_c}$.
0·0170320	467·504	−0·046	5·55
·0172320	467·521	− ·029	4·44
·0174320	467·535	− ·015	3·33
·0176320	467·542	− ·008	2·22
·0178320	467·547	− ·003	1·11
·0180320 (V_c)	*467·550*	*·000*	*0·00*
·0182320	467·552	+ ·002	1·11
·0184320	467·556	+ ·006	2·22
·0186320	467·563	+ ·013	3·33
·0188320	467·574	+ ·024	4·44

critical volume through the temperature $\theta_c + 0^\circ{\cdot}15$. The constants a and b, as well as the theoretical critical volume V_c, are derived from the critical data given by Young (20) ($\theta_c=194{\cdot}4$; $P_c=35{\cdot}61$ atmospheres), and are $a=0{\cdot}0347314$, $b=0{\cdot}00601066$, $V_c=0{\cdot}0180320$. The temperatures (t) were then calculated for the volumes given in the table from the formula

$$t=\left(p+\frac{a}{v^2}\right)(v-b)/R,$$

where $p=\dfrac{R(273+194{\cdot}55)}{(V_c-b)}-\dfrac{a}{V_c^2}$.

From the table it appears that a difference of temperature of $0^\circ{\cdot}014$ C. between the two portions of the substance may produce a difference of density of about 4·5 per cent. Owing to the great pressure under which the changes of density occur and the small temperature slope through the glass walls of the tube, it may be expected that the establishment of equilibrium will be a slow process.

Tube XIV. was raised to a temperature of about $0^\circ{\cdot}13$ C. above θ_c; the time which elapsed before the opalescence became absolutely uniform in appearance was 14 minutes. This does not seem an unduly long period for the establishment of equilibrium and seems to render a liquidogenic hypothesis superfluous.

It must be acknowledged that the slight differences of temperature occurring in the thermostat would tend to accelerate the establishment of equilibrium, both by increasing the rate of transmission of heat through the walls of the tube and by producing convection currents, though the latter were not perceptible. Some quantitative knowledge of the relation between the intensity of the opalescence and the density of the substance is also desirable, but owing to the difficulties of purification of the ether and of exact measurements at the critical temperature, this of itself would involve lengthy research.

General Conclusions.

The experiments described have perhaps served rather to demonstrate the difficulty of realising theoretical conditions, than to lead to a decisive conclusion concerning the nature of the Cagniard-Latour phenomena. The results of the investigation, however, clearly favour the retention of the classical theory of Andrews.

It has been found that by the introduction of a temperature difference, the Cagniard-Latour phenomena may be reproduced with similar opalescent effects and approximately the same persistency.

The last traces of gaseous impurity have proved most difficult to eliminate, and extremely slight traces of such impurity have visibly accentuated the phenomena or delayed the establishment of equilibrium.

Since the differences of temperature involved are so slight, the period required for the establishment of equilibrium does not seem unduly long.

The intensity of the opalescence depends greatly upon the density of the substance, so that any cause which produces a small difference in density will produce visible qualitative effects which are great in proportion to that cause.

The investigation of the nature of the opalescence, so far as it has been carried, tends to favour the kinetic explanation of Küster rather than that of Altschul or Donnan, and thus far decides the Cagniard-Latour temperature to be the true critical temperature of vaporization.

It may be noted that the more recent investigations have in general tended to show that the more violent discrepancies from the predictions of Andrews's theory concerning the critical phenomena have been due to causes which are not out of accordance with Andrews's theory. Owing to the peculiar properties of the substance at the critical temperature, the approach to conditions which permit of theoretical results must of necessity be asymptotic, and therefore to formulate an hypothesis for the purpose of explaining such discrepancies as may now be considered to remain seems unnecessary, except perhaps in the case of those liquids whose surface-tensions point to association of their molecules

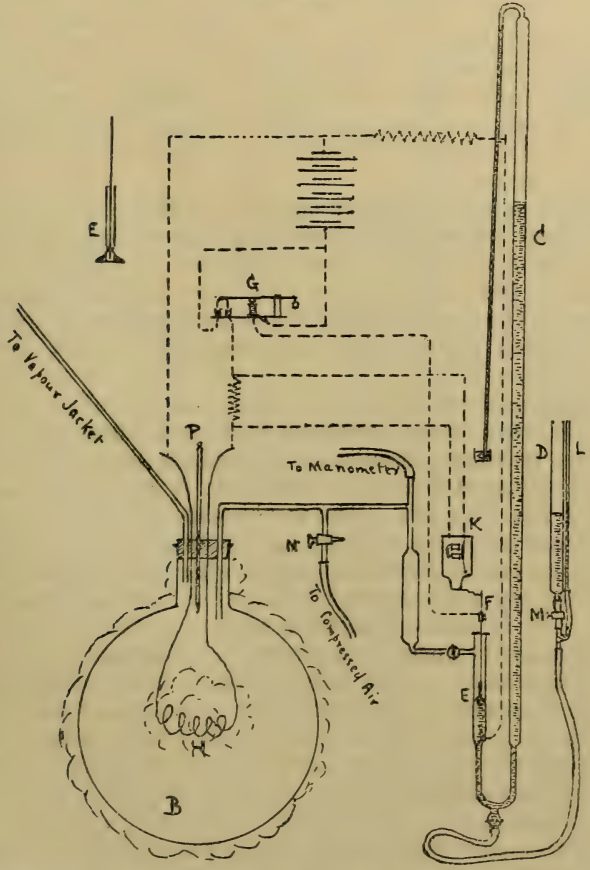
Appendix.

A Vapour Thermostat for work on Critical Phenomena.

In connexion with the vapour jacket shown in fig. **3** an arrangement was employed for maintaining the vapour at constant pressure, so that constant temperature was secured (fig. 8).

The vapour jacket communicates, through a large ballon B, with the closed mercury manometer C. The manometer

Fig. 8.



is fitted with a Töpler siphon-tube, so that the vacuum may be tested and, if necessary, renewed. In the short arm of the manometer is a float E, which makes electrical contact with a platinum-tipped needle F. The float consists of a light copper disk to the top of which is cemented a piece of thin-walled glass tubing, constricted near the bottom. On the top of the copper float is soldered a piece of platinum-foil; the under surface is amalgamated. When contact is made, a relay G is actuated and a current of about 1 ampere is sent through a 5-ohm coil of fine german-silver wire H contained in the ballon B and lightly wrapped in cotton-wool. The heat developed causes the air to expand until the consequent rise of pressure breaks the contact at E. If the temperature of the ballon is already rather higher than that of the atmosphere, the pressure again falls owing to radiation of heat, until contact is again made. The cotton wool has the effect of making the expansion less sudden, so that the mercury in the gauge may follow the changing pressure more closely. Since the height of the mercury in C can be regulated by means of the reservoir D, any desired pressure can be maintained in the apparatus.

A slight tendency to stick on the part of the contact E is corrected by means of the electromagnetic trembler K, which is placed as a shunt in the heating circuit. Its base-board is attached to the needle F by a wire whose tension is suitably adjusted. The tendency is reduced to a minimum by delicately poising the relay key and reducing the relay current to a minimum.

Tests have shown that the contact can be relied upon to make and break within a range of 0·035 mm. movement of the float, the maximum oscillation of pressure due to this cause being therefore 0·07 mm. of mercury; in general the oscillation is less than this. The troublesome effects due to the surface tension of the mercury are practically eliminated by making the manometer tubes rather wide (about 2 cm.), and by introducing a thin layer of 'Fleuss' oil over each mercury surface. It is also advisable to avoid depressing the float into the mercury during the process of adjustment.

The manometer is made independent of temperature variations by a suitable adjustment of its dimensions. Let P be the indicated pressure of mercury, S the area of cross-section of the longer limb, V the total volume of mercury, c the coefficient of cubical expansion of mercury, and a the coefficient of linear expansion of glass. Then, assuming the float to remain unmoved relatively to the glass tube, the change of pressure dp due to a change of temperature dt is given very approximately by

$$dp = \frac{\mathrm{V}(c-3a) \, . \, dt}{\mathrm{S}} + a \, . \, \mathrm{P} \, . \, dt - c \, . \, \mathrm{P} \, . \, dt.$$

The pressure is unaffected if

$$V=\frac{PS(c-a)}{c-3a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I.)$$

The movement of the float produced by the expansion of the needle is negligible for moderate lengths of the latter, since it depends upon the difference between the expansion of glass and that of steel.

Equation (I.) implies that if adjustment has been obtained for a given pressure P, in order to obtain adjustment for a pressure $P+p$, the increase v in the volume of mercury must be $\frac{pS(c-a)}{c-3a}$. If the two menisci move in cylindrical tubes of constant and equal cross-section, the point of the needle must be raised through a distance $\frac{1}{2}\left(\frac{v}{S}-p\right)$ or $\frac{pa}{c-3a}$ $(=p\times 0{\cdot}0554)$.

In practice the needle was soldered into a brass cap at the height corresponding to $P=965$ mm., which is the pressure of aniline vapour in the neighbourhood of the critical temperature of ether.

L is a narrow graduated tube which forms a subsidiary reservoir for fine adjustments of the mercury. If D is disconnected by closing slip M, small measured amounts of mercury can be introduced into the gauge or withdrawn from it. In this way it is possible to raise or lower the temperature of the thermostat by successive steps of 0°·01 or less, the pressure being adjusted by the heating-coil.

For considerable changes of pressure the reservoir D must be used, and air must be pumped into or withdrawn from the ballon through the three-way tap N. The heating-coil will satisfactorily maintain constant pressure only if the temperature of the air in the ballon as indicated by thermometer P is within certain limits (5° to 15° above the atmospheric temperature).

The irregularity of boiling adds considerably to the oscillation of pressure. In order to secure the best results it is necessary to employ a gas supply of steady pressure and to introduce broken porous ware into the aniline in the usual manner.

In a test lasting about three hours, during which the pressure was observed for a few minutes at frequent intervals by means of a water gauge, the extreme variation of pressure observed was ·29 mm. of mercury: this corresponds to a variation in temperature at 193–4° C. of 0°·12 C. If one reading is omitted, the variation was 0·19 mm. or 0°·008 C.

The oscillation of the pressure did not exceed 0·12 mm.; the period of oscillation (*i. e.* from contact to contact) varied from 6 sec. downwards.

In conclusion I desire to express my thanks for the facilities afforded me by the Physical and Chemical Departments of the University of Bristol, at which the research was conducted. I am greatly indebted to Professor A. P. Chattock and Dr. James W. McBain for constant advice, and to the latter for much personal assistance.

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XC. *The Accelerated Motion of a Dielectric Sphere.*

By J. W. Nicholson, *M.A.*, *D.Sc.*[*]

In a previous paper, a brief account was given of the motion of a conducting sphere whose mass is purely electrical, under the action of either a small uniform field of electric force or a small mechanical force. The solution was deduced as a limiting case from a more general problem treated by G. W. Walker[†], and it was shown that there are difficulties in the results of regarding any conductor as

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[*] Communicated by the Author.

[†] Roy. Soc. Proc. A. vol. lxxvii. p. 260 *et seq.*; Phil. Trans. A. 1910, p. 145 *et seq.*

perfect when its motion is accelerated. The perfect conductor of the usual theory leads to disturbing infinities when it has no Newtonian mass. The indications that the mass of a single electron can have a Newtonian element are not very securely established; and although certain experiments can be interpreted in accordance with this view, there is always a possibility of other interpretations which do not involve it. For example, it is possible that the particles in Kaufmann's experiments are electrons not free, but attached to matter. A comprehensive examination of the conditions of motion of a small body without a Newtonian mass is therefore desirable, and this was made in the case of a conductor under the action of a small force in the previous paper. Apart from indications there obtained, it seems unlikely on general grounds that an electron can be endowed with properties analogous to those of a conductor, for there is a difficulty of attaching a physical meaning to such properties in a single electron. Moreover, the rapidity of damping of the oscillations set up when the motion of the conductor is changed, supplies a strong adverse argument.

Some interest therefore attaches to the corresponding problem of a small sphere, with a surface charge, whose interior has the properties solely of a dielectric, with no conducting element.

In the present paper, the motion of such a sphere, devoid of Newtonian mass, is investigated, and it is shown to present none of the difficulties noticed in the case of the conductor. A small field of force can produce a finite acceleration, and will give the effect of a constant acceleration after a short time, if the dielectric coefficient be not too great. If this coefficient is great, the oscillations initially set up are very permanent, and the constant acceleration is not established by a uniform field within the time during which the equations are good approximations to the motion. The problem in this case bears some resemblance to that of the perfect conductor, for the disturbance inside the sphere tends to zero as the dielectric constant increases. But the problems do not become identical, for in the case of the conductor, the charge is allowed freedom of movement on the surface, and in fact does redistribute itself in the manner previously calculated. In the dielectric sphere, it remains uniformly distributed, and the problem thus corresponds to those of accelerated motion usually treated by the quasi-stationary principle, in whose application any redistribution is ignored.

The main outlines of the necessary analysis, when both kinds of inertia are present, have been given in Walker's second paper, although the special case is not examined. Let e be the charge on the sphere of radius a, κ its dielectric constant, and c', c the velocities of radiation inside and out, so that

$$\kappa c'^2 = c^2. \quad \ldots\ldots\ldots \quad (1)$$

ξ is the displacement of the sphere at time t, and F the force, of a mechanical origin. As for the conductor, the field outside can be expressed in terms of a function $\chi\,(ct-r)$, small like F, in the form, valid for a certain region,

$$(\mathrm{X, Y, Z}) = \frac{e}{r^3}(x, y, z) + \frac{e}{r^3}(-1, 0, 0)\left(r^2\chi'' + r\chi' + \chi - \frac{e\xi}{c}\right)$$

$$+ \frac{cx}{r^5}(x, y, z)\left(r^2\chi'' + 3r\chi' + 3\chi - 3\frac{e\xi}{c}\right). \quad \ldots \quad (2)$$

Inside the sphere, since there is no initial field, we may write, in terms of functions $\psi_1\,(c't-r)$ and $\psi_2\,(c't+r)$, both of which are required,

$$(\mathrm{X, Y, Z}) = \frac{c'}{r^3}(-1, 0, 0)\{r^2(\psi_1'' + \psi_2'') + r(\psi_1' - \psi_2') + \psi_1 + \psi_2\}$$

$$+ \frac{c'x}{r^5}(x, y, z)\{r^2(\psi_1'' + \psi_2'') + 3r(\psi_1' - \psi_2') + 3(\psi_1 + \psi_2)\}, \quad (3)$$

the axes moving with the sphere. In order that the internal field may be finite at the centre,

$$\psi_1(c't) + \psi_2(c't) = 0. \quad \ldots\ldots \quad (4)$$

The tangential electric and electromagnetic forces are identical to the order contemplated, and thus by the continuity of either at $r=a$,

$$c\left(a^2\chi'' + a\chi' + \chi - \frac{e\xi}{c}\right) = c'\{a^2(\psi_1'' + \psi_2'') + a(\psi_1' - \psi_2') + \psi_1 + \psi_2\}. \quad (5)$$

The difference of normal flux being $4\pi\sigma$ or e/a^2, it follows that

$$c\left(a\chi' + \chi - \frac{e\xi}{c}\right) = \kappa c'(a\psi_1' - a\psi_2' + \psi_1 + \psi_2). \quad \ldots \quad (6)$$

A determination of the mechanical force gives * for its

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* Walker, *l. c.* p. 174.

resultant along the direction of motion the value

$$-\frac{2}{3}\frac{ec}{a}\chi''(ct-a)\,;$$

so that

$$m\ddot{\xi}+\frac{2}{3}\frac{ec}{a}\chi''(ct-a)=\mathrm{F}. \quad . \quad . \quad . \quad . \quad (7)$$

The initial conditions are as before, $\xi=\dot{\xi}=0$ at $t=0$,

$$\chi(-a)=\chi'(-a)=0, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and the equations for determination of $(\chi\psi_1\psi_2)$ subject to these conditions become

$$c\left\{a^2\chi''+a\chi'+\left(1+\frac{m'}{m}\right)\chi-\frac{1}{2}\frac{e\mathrm{F}}{mc}t^2\right\}$$

$$=c'\{a^2(\psi_1''+\psi_2'')+a(\psi_1'-\psi_2')+\psi_1+\psi_2\}\,,$$

$$c\left\{a\chi'+\left(1+\frac{m'}{m}\right)\chi-\frac{1}{2}\frac{e\mathrm{F}}{mc}t^2\right\}$$

$$=\kappa c'\{a(\psi_1'-\psi_2')+\psi_1+\psi_2\}\,; \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and Walker's particular solution for χ involving only non-vibratory terms is

$$\chi(ct-a)=\frac{1}{2}\frac{e\mathrm{F}}{(m+m')c^3}\left\{c^2t^2-\frac{2mact}{m+m'}-2a^2\left(\frac{mm'}{(m+m')^2}+\frac{m}{(\kappa-1)(m+m')}\right)\right\}, \quad (10)$$

where $m'=\frac{2}{3}\frac{e^2}{ac^2}$ and is the usual electrical inertia for slow speeds.

The vibratory terms will be of the form

$$\left.\begin{aligned}\chi(ct-r)&=\mathrm{A}e^{-\lambda(ct-r+a)/a}\\ \psi_1(c't-r)&=\mathrm{B}e^{-\lambda\kappa^{\frac{1}{2}}(ct-r+a)/a}\\ \psi_2(c't+r)&=-\mathrm{B}e^{-\lambda\kappa^{\frac{1}{2}}(ct+r+a)/a}\end{aligned}\right\}, \quad . \quad . \quad . \quad (11)$$

or more strictly, summations of this form for the various values of λ satisfying the period equation

$$\frac{\tanh\kappa^{\frac{1}{2}}\lambda}{\kappa^{\frac{1}{2}}\lambda}=1+\kappa\lambda^2\left(1+\frac{m'}{m}-\lambda\right)\Big/\left\{(\kappa-1)\left(1+\frac{m'}{m}-\lambda\right)-\kappa\frac{m'}{m}\lambda+\kappa\lambda^3\right\}, \quad . \quad . \quad . \quad (12)$$

the real part of the summations being taken, λ being complex.

The equation may be shown to have a root zero, but no others except complex values whose real part is positive. Thus the vibratory terms ultimately decay.

We proceed to the case of a sphere without Newtonian mass. Taking the mass at first as very small, the non-vibratory part of $\frac{1}{2}\mathrm{F}t^2-\frac{2}{3}\frac{e}{ac}\chi$ becomes, on reduction,

$$\frac{m\mathrm{F}}{2m'c^2}\left\{c^2t^2+2act+2a^2\frac{\kappa}{\kappa-1}\right\},$$

and by (7) this is the non-vibratory part of $m\xi$. The vibratory portion is of the form

$$m\Sigma \mathrm{D}e^{-\lambda ct/a}\sin\left(\frac{\mu ct}{a}+\epsilon\right), \quad . \quad . \quad . \quad . \quad (13)$$

where the root of the period equation is now written $\lambda\pm\iota\mu$, and D and ϵ depend on λ and μ.

In order that ξ may satisfy the appropriate conditions at $t=0$, it is necessary that

$$\Sigma\mathrm{D}\sin\epsilon=-\frac{m}{m'}\cdot\frac{a^2\mathrm{F}}{c^2}\cdot\frac{\kappa}{\kappa-1},$$

$$\Sigma(\mu\mathrm{D}\cos\epsilon-\lambda\mathrm{D}\sin\epsilon)=-\frac{a^2\mathrm{F}}{m'c^2}, \quad . \quad . \quad . \quad (14)$$

the summation being for all roots $\lambda\pm\iota\mu$ of the period equation

$$\frac{\tanh\kappa^{\frac{1}{2}}x}{\kappa^{\frac{1}{2}}x}=1+\frac{\kappa x^2}{\kappa-1-\kappa x}. \quad . \quad . \quad . \quad . \quad (15)$$

The acceleration is always finite, whatever the distribution of the vibrations among the possible periods. The determination of this distribution is difficult, but is not necessary for the present purpose. In addition to the decrease in amplitude which may be expected as the vibrations recede from the fundamental, there will be increased damping in the higher modes. When κ is not too great, the damping will not be slight even for the fundamental, which will then be the only vibration needing attention. If this is so, and if the amplitude of this vibration is sufficiently preponderant, we may write

$$\xi=\frac{\mathrm{F}}{2m'c^2}\left(c^2t^2+2act+\frac{2a^2\kappa}{\kappa-1}\right)+\mathrm{D}e^{-\lambda ct/a}\sin\left(\frac{\mu ct}{a}+\epsilon\right),$$

where
$$D \sin \epsilon = -\frac{a^2 F}{m'c^2} \cdot \frac{\kappa}{\kappa - 1},$$

$$\mu D \cos \epsilon = -\frac{a^2 F}{m'c^2}\left(1 - \frac{\lambda\kappa}{\kappa - 1}\right),$$

and for moderately large values of κ, $\epsilon = \mu$, and

$$\xi = \frac{F}{2m'c^2}(c^2t^2 + 2act + 2a^2) - \frac{Fa^2}{m'c^2\mu} e^{-\lambda ct/a} \sin \frac{\mu}{a}(ct + a). \quad (16)$$

The period equation is practically $\tanh \kappa^{\frac{1}{2}} x = \kappa^{\frac{1}{2}} x$, whose fundamental solution is $\kappa^{\frac{1}{2}} x = \pm 4{\cdot}493\iota$, so that $\mu = 4{\cdot}493/\kappa^{\frac{1}{2}}$ of the order assumed above. For period equations of the present type, the real part of the solution is much smaller. A similar case is given by Lamb [*].

We see, therefore, that for a dielectric sphere under a small mechanical force, the vanishing of the Newtonian mass causes no difficulty as regards the acceleration; and in view of the fact that the presence of this mass is doubtful, and that its absence would tend towards simplicity in the construction of the ideal electron, it seems possible that the postulation of dielectric rather than conducting property in an electron will be of service.

Such an electron, moreover, by virtue of the rigidity of its electrification, would fulfil one of the necessary conditions for the validity of the quasi-stationary principle for small accelerations. It is the possibility of redistribution of the charge which is the main difficulty of this principle, and the problems treated by Walker are sufficient to show conclusively that redistributions will ordinarily take place for conductors in accelerated motion. Now a fairly large value of κ for the dielectric interior of a sphere secures that the internal vectors shall be nearly zero, and this, combined with the rigidity of the charge, should be sufficient. It has been tacitly supposed throughout that the Lorentz contraction does not take place, although it is the belief of the writer that the contracted electron gives the best representation of fact, and a recent investigation by Bucherer [†] tends to prove this.

If the dielectric sphere with a surface charge thus fulfils the conditions of that for which the quasi-stationary principle has been used, it may be expected to yield Abraham's expression for the transverse inertia when the sphere has a

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[*] Camb. Phil. Trans., Stokes Commem. volume.

[†] *Phys. Zeit.* 1908, p. 775.

uniform motion, and an accelerating force is applied perpendicular to that motion. Now Walker has shown in the case of the conductor, that when the surface condition is the evanescence of the tangential electromagnetic force, Abraham's expression does not follow as the result of a direct calculation from the primary electromagnetic equations. This disproves the quasi-stationary principle for the initial motions of a conductor at least, although the initial condition, involving the instantaneous creation of a uniform field, is somewhat artificial.

The equations valid for a dielectric in variable motion are not yet free from doubt, and a direct calculation of the inertia in this case, as Walker points out, is not at present possible; but he concludes that the inertia of the dielectric with a large value of κ would be practically the same as for a conductor with equal charge, by the following argument *.

"Since there is continuity of normal flux of disturbed electric force at the surface, the functions which determine the disturbance inside the sphere are of order κ^{-1} as compared with those which determine the outside field. Hence the tangential component of electric force inside, and therefore also outside, is very nearly zero. Thus since the equations for the æther are not modified by the motion of the sphere, the equation of motion and the surface forces outside differ by terms of order κ^{-1} from those for a perfect conductor. If this argument is valid, the assumption of perfect conduction, or of a high value of κ for the charged particle, would equally well explain Kaufmann's results, and give the same value for the electric inertia without limitation as to speed."

This argument appears to dispense with the necessity for complete analytical treatment. The inertia in question is that derived by Walker's analysis of the conductor with the other, and in the opinion of the writer, less likely condition in that case, that the tangential electric force is zero. Quoting the results, the initial longitudinal inertia becomes

$$\frac{e^2}{16ac^2}\left\{\frac{4-5k^2+4k^4}{k^3(1-k^2)^{\frac{3}{2}}}\sin^{-1}k-\frac{4-13k^2+6k^4}{k^2(1-k^2)}\right\}, \quad . \quad (17)$$

and the transverse inertia is

$$\frac{e^2}{8ac^2}\left\{\frac{4k^2-1}{k^3(1-k^2)^{\frac{1}{2}}}\sin^{-1}k+\frac{1+2k^2}{k^2}\right\}; \quad . \quad . \quad . \quad (18)$$

and these are the initial values to be regarded as true for a

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* Phil. Trans. 1910, A, p. 178.

dielectric sphere whose coefficient is large. They do not agree with the results deduced from a consideration of steady motions, without redistribution, but must apparently be regarded, with the corresponding values for a conductor, as the only values which have received a complete proof.

Meanwhile, as stated in the preface, it may well be of service, in any attempt to treat the electron as not subject to deformation, to endow it with dielectric rather than conducting properties. The analysis of this hypothesis presents no difficulty which does not appear to be shared by the other, and in a consideration of initial motions, it gives rise to great simplicity in the possible case of no Newtonian mass.

XCI. *The Electron Theory of the Optical Properties of Metals.*

By Prof. HAROLD A. WILSON, *F.R.S.*, *McGill University, Montreal**.

THE electron theory of the optical properties of metals has been developed by Drude, J. J. Thomson, H. A. Lorentz, J. H. Jeans, and others.

Let N denote the number of free electrons per c.c. in the metal, and let dN be the number in the group with velocities between V and $V+dV$. The number dN remains nearly constant, although particular electrons are continually entering and leaving the group. Each such group may therefore be regarded as having a permanent existence. Since the mass of an atom is large compared with the mass of an electron, the velocity of an electron will not be much altered by collisions with atoms, and collisions with atoms must be much more numerous than collisions with electrons. Consequently the electrons in a particular group may be regarded as making many collisons, and still remaining in the same group or in a set of groups covering a small range of velocities.

When an electric force acts in the metal the electrons in each group will acquire an average velocity which will not be the same for the different groups. The motion of a group will be determined by a differential equation which will be of the same form for all the groups, but with different values of the constants for the different groups. It will therefore not be possible to represent the average velocity of all the N electrons by a single differential equation, unless we make the assumption that all the electrons have the same velocity of agitation.

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* Communicated by the Author.

Let u denote the velocity of a particular group due to an electric force X acting parallel to the x axis and suppose (*vide infra*)

$$\frac{d}{dt}(d\mathrm{N}mu) = d\mathrm{NX}e - d\mathrm{N}\beta u,$$

where β is a function of V, m the mass, and e the charge of an electron. If $\mathrm{N}u_0 = \int u d\mathrm{N}$, u_0 will be the average velocity of all the N electrons in the x direction and

$$\frac{d}{dt}(\mathrm{N}mu_0) = \mathrm{NX}e - \int \beta u d\mathrm{N}.$$

Jeans[*], in his very interesting and valuable investigation, obtained the equation

$$\frac{d}{dt}(\mathrm{N}mu_0) = \mathrm{NX}e - \mathrm{N}\gamma u_0,$$

so that

$$\gamma = \frac{\int \beta u d\mathrm{N}}{\int u d\mathrm{N}}.$$

Since u varies with the time, it follows that γ is not in general a constant. If, however, we take all the electrons to have the same velocity of agitation, we get $\gamma = \beta$. In Jeans' investigation he took γ to be independent of the time, which seems to be equivalent to ignoring the velocity distribution. If this is not done, then it is necessary to find β as a function of V, which requires special assumptions to be made.

Jeans obtained his equation on the assumption that the time dt in it is large compared with the time of a collision. If it is taken so large that during it a particular electron will have successively many velocities, then the velocity of all the electrons will be the same on the average over dt, and so the equation will be true. I think this requires dt to be large compared with the time between two collisions between one electron and other electrons (not atoms, since collisions with atoms do not alter the velocity much). If this is so, it means that Jeans' equation will only be strictly correct for vibrations of much smaller frequency than those in infra-red radiation. At the same time, of course, it will be approximately correct even for rapid vibrations, because the assumption that all the electrons have the same velocity of agitation represents the facts fairly well in such problems.

In view of these considerations, it seemed to be worth while to work out the theory on the lines followed by Jeans, but

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[*] Phil. Mag. June 1902, and July 1909.

assuming that collisions do not alter the velocities of the electrons in magnitude.

In the following paper the atoms are regarded as hard smooth spheres which remain at rest, while the electrons are also regarded as spheres and their mutual actions are neglected. These are the assumptions adopted by H. A. Lorentz* in his theory of the electrical and thermal conductivities of metals.

Let n denote the number of atoms per c.c. in a metal and N the number of negative electrons, each with a charge e. Also let R be the sum of the radii of an atom and an electron. Let ξ, η, ζ denote the velocity components of an electron and V its resultant velocity. Following Jeans, I shall begin by calculating the rate of increase in the momentum of the electrons due to an electric force X parallel to the x axis. Let $\delta\mathrm{N}$ be the number of electrons per c.c. having velocity components between ξ, η, ζ and $\xi+\delta\xi$, $\eta+\delta\eta$, and $\zeta+\delta\zeta$. Consider a particular atom and a small cone of solid angle $d\omega$ with its vertex at the centre of this atom. Let f be the angle between the axis of this cone and the axis x. The number of electrons in the group $\delta\mathrm{N}$ which collide with the atom in time dt, so that at the moment of the collision the line joining the centres of the atom and electron lies inside $d\omega$, is

$$\delta\mathrm{N}\,\mathrm{R}^2\,d\omega\cos\theta\,\mathrm{V}\,dt,$$

where θ is the angle between V and the axis of the cone.

The loss of momentum in the x direction at each such collision is $2m\mathrm{V}\cos\theta\cos f$, where m is the mass of an electron. Consequently the total loss of momentum by the group $\delta\mathrm{N}$ is

$$\begin{aligned} &2m\mathrm{V}^2\,\delta\mathrm{N}\,\mathrm{R}^2\,n\,dt\int\cos^2\theta\cos f\,d\omega \\ &=2m\mathrm{V}^2\,\delta\mathrm{N}\,\mathrm{R}^2\,n\,dt\,\pi\xi/2\mathrm{V}\,\dagger \\ &=\delta\mathrm{N}\,m\xi\mathrm{V}\,dt/l_m \text{ where } l_m=1/\pi n\mathrm{R}^2. \end{aligned}$$

Now let $d\mathrm{N}$ denote the number of electrons per c.c. which have velocities between V and $\mathrm{V}+d\mathrm{V}$, and let $u\,d\mathrm{N}=\int\xi\delta\mathrm{N}$ so that u is the mean value of ξ for the electrons in the group $d\mathrm{N}$. Then the loss of momentum by the electrons in this group is

$$\frac{m\mathrm{V}\,dt}{l_m}\int\xi\delta\mathrm{N}=\frac{m\mathrm{V}u\,dt\,d\mathrm{N}}{l_m}.$$

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* 'Theory of Electrons,' pp. 266–273.

† See H. A. Lorentz, 'Theory of Electrons,' p. 272.

The gain of x momentum due to the electric force is $Xe\,dN\,dt$, so that we have

$$\frac{d}{dt}(mu\,dN)=Xe\,dN-\frac{umV\,dN}{l_m}. \quad . \quad . \quad . \quad (1)$$

Let now u_0 denote the mean value of ξ for all the N electrons so that $Nu_0=\int u dN$; then, if we find u by means of equation (1), we can get u_0 by putting the value of u in $\frac{1}{N}\int udN$.

We also have from (1)

$$\frac{d}{dt}(mNu_0)=XeN-\frac{m}{l_m}\int VudN.$$

Comparing this with Jeans' equation we get

$$\gamma=\frac{\frac{m}{l_m}\int VudN}{\int udN}.$$

If we take all the electrons to have the same velocity V we get $\gamma=mV/l_m$. Jeans' results consequently agree with mine only if all the electrons are taken to be moving with the same velocity.

If X is constant then after a sufficient interval du/dt will be zero, so that $u=Xel_m/mV$, and

$$u_0=\frac{1}{N}\int\frac{Xel_m}{mV}dN.$$

If we assume dN to be given by Maxwell's law this gives

$$u_0=\frac{Xel_m}{m}4\pi\left(\frac{q}{\pi}\right)^{3/2}\int_0^\infty V\epsilon^{-qV^2}dV=2\left(\frac{q}{\pi}\right)^{1/2}\frac{Xel_m}{m},$$

where $q=3/2\overline{V}^2$.

Suppose now that $X=a\cos pt$, then (1) gives

$$u=\frac{ea\cos(pt-\delta)}{m(p^2+V^2/l_m{}^2)^{1/2}},$$

where $\tan\delta=pl_m/V$.

Hence again assuming Maxwell's law

$$u_0=4\pi\left(\frac{q}{\pi}\right)^{3/2}\frac{ea}{m}\int_0^\infty\frac{\cos(pt-\delta)\,\epsilon^{-qV^2}V^2dV}{(p^2+V^2/l_m^2)^{1/2}}. \quad . \quad . \quad (2)$$

The amount of heat produced per c.c. per sec. will be equal to the mean value of $\mathrm{N}eu_0 a \cos pt$ and to $\frac{1}{2}a^2\sigma$ where σ denotes the conductivity. Hence we get using (2) and taking the mean value

$$\sigma = 4\pi\mathrm{N}\left(\frac{q}{\pi}\right)^{3/2}\frac{e^2 l_m}{m}\int_0^\infty \frac{\mathrm{V}\epsilon^{-q\mathrm{V}^2}d\mathrm{V}}{1+p^2 l_m^2/\mathrm{V}^2}.$$

When $p=0$ this gives

$$\sigma_0 = 2\mathrm{N}\left(\frac{q}{\pi}\right)^{1/2}\frac{e^2 l_m}{m}*.$$

Hence

$$\sigma = 2q\sigma_0\int_0^\infty \frac{\mathrm{V}\epsilon^{-q\mathrm{V}^2}d\mathrm{V}}{1+\pi p^2 m^2 \sigma_0^2/4q\mathrm{V}^2\mathrm{N}^2 e^4}. \quad . \quad . \quad (3)$$

If we take all the velocities to be equal we get instead $\sigma_0 = \mathrm{N}e^2 l_m/m\mathrm{V}$, and

$$\sigma = \frac{\sigma_0}{1+p^2 m^2 \sigma_0^2/\mathrm{N}^2 e^4}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which is the expression found by Jeans. Drude expressed σ as a sum of terms like (4), one term for each class of electrons. If we regard each group $d\mathrm{N}$ as constituting a class, then Drude's expression becomes identical with (3) allowing for the change of notation. Drude got it by assuming the motion of the electrons in each class to be opposed by a viscous resistance proportional to u.

Equation (4) has been used by Schuster and Jeans to get estimates of N from the values of σ deduced from optical observations. The integral in (3) unfortunately cannot be expressed in finite terms, but it can be found of course by graphical methods. I find that (3) gives values of N about double those given by (4) in most cases.

The conductivity for any frequency can also be obtained in another way by calculating the heat produced directly. Suppose as before that the metal contains N free electrons per c.c., and let l denote the length of a free path and V the velocity of an electron. The kinetic energy of an electron will be altered during a free path by the action of the electric force. If we calculate the total gain of kinetic energy for all the free paths traversed by all the N electrons in one second, the result will be the amount of heat energy produced.

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* H. A. Lorentz, in 'Theory of Electrons,' gets σ_0 less by the factor 2/3.

Let $a\cos pt$ denote the electric force so that $m\,dv/dt = ae\cos pt$, where m is the mass, e the charge of an electron, and v its velocity component parallel to the electric force. Let t_0 denote the time at the beginning of a free path and $t_0+\tau$ that at the end. Then

$$m(v_\tau - v_0) = \frac{ae}{n}\left\{\sin p(t_0+\tau) - \sin pt_0\right\},$$

or

$$m(v_\tau - v_0) = \frac{2ae}{n}\cos\frac{p}{2}(2t_0+\tau)\sin\frac{p\tau}{2}.$$

Therefore

$$\tfrac{1}{2}m(v_\tau^2 - v_0^2) = \frac{2}{m}\left(\frac{ae}{p}\right)^2\cos^2\frac{p}{2}(2t_0+\tau)\sin^2\frac{p\tau}{2}$$
$$+\,2v_0\frac{ae}{p}\cos\frac{p}{2}(2t_0+\tau)\sin\frac{p\tau}{2}.$$

If now S denotes a summation for all the free paths described by one electron in one second, we get

$$S\tfrac{1}{2}m(v_\tau^2 - v_0^2) = S\frac{1}{m}\left(\frac{ae}{p}\right)^2\sin^2\frac{p\tau}{2},$$

because the mean value of $\cos^2 x$ is $\frac{1}{2}$ and of $\cos x$ 0, and we may make the addition in groups such that τ is constant in each group.

Suppose that the velocity V of a particular electron remains constant, then the number of free paths of length between l and $l+dl$ in one second is $V\epsilon^{-l/l_m}dl/l_m^2$, where l_m denotes the mean free path. Also $l = V\tau$. Hence

$$S\tfrac{1}{2}m(v_\tau^2 - v_0^2) = \int_0^\infty \frac{1}{m}\left(\frac{ae}{p}\right)^2\sin^2\frac{pl}{2V}\cdot\frac{V}{l_m^2}\,\epsilon^{-l/l_m}dl$$
$$= \frac{a^2e^2l_m}{2mV(1+p^2l_m^2/V^2)}.$$

The number of electrons for which V is between V and $V+dV$ is, according to Maxwell's law,

$$4\pi N\left(\frac{q}{\pi}\right)^{3/2}\epsilon^{-qV^2}V^2dV,$$

where $q = 3/2\overline{V}^2$ and $\overline{V}^2$ is the mean value of V^2. Hence the heat H produced per c.c. per sec. is given by

$$H=\frac{2\pi N a^2 e^2 l_m}{m}\left(\frac{q}{\pi}\right)^{3/2}\int_0^\infty \frac{V\epsilon^{-qV^2}dV}{1+p^2 l_m^2/V^2}=\tfrac{1}{2}a^2\sigma.$$

Hence

$$\sigma=\frac{4\pi N e^2 l_m}{m}\left(\frac{q}{\pi}\right)^{3/2}\int_0^\infty \frac{V\epsilon^{-qV^2}dV}{1+p^2 l_m^2/V^2},$$

as before.

If i denotes the current carried by the dN electrons which have velocities between V and V$+d$V, then $i=eu\,d\text{N}$, which with equation (1) gives

$$\frac{m}{e^2 dN}\frac{di}{dt}+\frac{mV}{l_m e^2 dN}i=X.$$

The theory of the propagation of light in the metal follows from this equation in Drude's manner*. If n denotes the refractive index and κ the coefficient of absorption, we get

$$n^2(1-\kappa^2)=1-16\pi^{1/2}q^{3/2}\frac{Ne^2 l_m^2}{m}\int_0^\infty \frac{\epsilon^{-qV^2}dV}{1+p^2 l_m^2/V^2},$$

and $n^2\kappa=2\pi\sigma/p$.

If all the V's are taken to be equal these equations reduce to the simpler form which applies when only one class of electrons is supposed present.

The emission of light by a metal has been discussed by several writers. H. A. Lorentz has given a calculation of it on the assumptions adopted in this paper but applicable to very long waves only. J. J. Thomson† worked out the emission for any wave-length on the assumptions that all the free paths occupy equal times and that the velocities of the electrons at the ends of each free path vary in a particular way.

Jeans (*loc. cit.*) gives two calculations. In the first he assumes equal free path periods while in the second free paths are not assumed at all, but the calculation is based on the equation which seems to be exactly correct only when all the electrons have the same velocity. The following calculation is very similar to that given by H. A. Lorentz‡, but it is not restricted to very long waves. It is therefore

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* 'Theory of Optics,' p. 397.

† 'Corpuscular Theory of Matter,' pp. 89–97.

‡ 'Theory of Electrons,' pp. 81–90.

only necessary to indicate where it differs from his and to give the final result.

Lorentz shows that the amplitude in the radiation of a given frequency from a thin plate of the metal can be represented in the form of a sum of terms; one term for each free path described by the electrons. Each term contains the factor

$$\int_t^{t+\tau} \mathrm{V}_x \cos\frac{s\pi}{\theta}\left(t+\frac{r}{c}\right)dt,$$

where τ is the time of describing a free path. Lorentz assumes that the frequency is so small that $\cos\frac{s\pi}{\theta}t$ can be regarded as constant during a free path, and so (page 87) puts this factor equal to

$$\tau \mathrm{V}_x \cos\frac{s\pi}{\theta}\left(t+\frac{r}{c}\right).$$

To make the calculation apply to greater frequencies it is only necessary to put the factor equal to

$$\frac{\theta}{s\pi}\mathrm{V}_x\left\{\sin\frac{s\pi}{\theta}\left(t+\tau+\frac{r}{c}\right)-\sin\frac{s\pi}{\theta}\left(t+\frac{r}{c}\right)\right\},$$

and carry out the calculation in the same way as H. A. Lorentz gives it.

In this way I get

$$a_s^2=\frac{s^2e^2}{2\theta^4c^4r^2}\mathrm{S}\left\{\frac{\mathrm{V}_x{}^2\theta^2}{s^2\pi^2}\sin^2\frac{s\pi}{2\theta}\tau\right\},$$

instead of Lorentz's (page 88)

$$a_s^2=\frac{s^2e^2}{24\theta^4c^4r^2}\mathrm{S}\,(l^2).$$

If the angle $\frac{s\pi\tau}{2\theta}$ is taken to be very small and $\tau^2\mathrm{V}_x{}^2$ put equal to $\frac{l^2}{3}$, the two expressions become identical as they should.

The evaluation of S is similar to that given above in getting the heat produced in the metal.

The final result for the perpendicular emissivity of the plate of small thickness Δ is

$$\mathrm{E}=\frac{p^4e^2\mathrm{N}\Delta l_m}{12c^4\pi^3}\left(\frac{q}{\pi}\right)^{3/2}\int_0^\infty\frac{\mathrm{V}^3\epsilon^{-q\mathrm{V}^2}d\mathrm{V}}{1+p^2l_m^2/\mathrm{V}^2},$$

which if p is taken to be very small reduces to Lorentz's expression.

If we take all the electrons to be moving with the same velocity V we get instead

$$\mathrm{E}=\frac{\mathrm{N}e^2l_m p^4\mathrm{V}\Delta}{48\pi^4c^4(1+p^2l_m^2/\mathrm{V}^2)}$$

The coefficient of absorption A of a very thin plate is shown by Lorentz to be equal to $\sigma\Delta/c$, where σ denotes its conductivity. Hence using the value found for σ when all the V's are equal we get

$$\mathrm{A}=\frac{\mathrm{N}e^2l_m\Delta}{cm\mathrm{V}(1+p^2l_m^2/\mathrm{V}^2)}\,.$$

Hence we get for the energy density E_λ per unit range of wave-length in full radiation, after putting $m\mathrm{V}^2=2\alpha\mathrm{T}$ and $p=2\pi c/\lambda$,

$$\mathrm{E}_\lambda=\frac{8\pi}{c}\,\frac{\mathrm{E}}{\mathrm{A}}=\frac{16\pi\alpha\mathrm{T}}{3\lambda^4},$$

which is the value found by H. A. Lorentz for very long wave-lengths, and also by Jeans.

If the formulæ allowing for the distribution of V according to Maxwell's law are used instead, we get

$$\mathrm{E}_\lambda=\frac{8\pi m}{3\lambda^4}\,\frac{\displaystyle\int_0^\infty\frac{\mathrm{V}^3\epsilon^{-q\mathrm{V}^2}d\mathrm{V}}{1+p^2l_m^2/\mathrm{V}^2}}{\displaystyle\int_0^\infty\frac{\mathrm{V}\epsilon^{-q\mathrm{V}^2}d\mathrm{V}}{1+p^2l_m^2/\mathrm{V}^2}}.$$

It appears, therefore, that the extension of the calculation to shorter wave-lengths gives no indication of a diminution of E_λ. Both the emission and the absorption are diminished, but the diminution of the one compensates for that of the other.

On the assumptions that the atoms are hard spheres which do not move and that the electrons do not collide with each other on which the above calculations are based, the electrons only gain or lose energy from the radiation. Consequently, those electrons which are moving with a greater velocity than the average will gradually lose energy, while those which are moving with a less velocity than the average will gradually acquire energy. After a time, therefore, all the electrons will acquire the same velocity, and the energy density will be given by $16\pi\alpha\mathrm{T}/3\lambda^4$ exactly. The assumption of a velocity distribution given by Maxwell's law is therefore not really consistent with the other assumptions made. In reality of course the atoms do move to some extent and the electrons do influence each other, so that Maxwell's law no doubt really holds good, but the absorption and emission are not exactly the same as those calculated. It seems likely that the absorption and emission calculated should be such as to make $E_\lambda = 16\pi\alpha T/3\lambda^4$ exactly. The variation from this obtained above when Maxwell's law is assumed is no doubt due to the neglect of the motion of the atoms and the mutual influence of the electrons.

The value $E_\lambda = 16\pi\alpha T/3\lambda^4$ is obtained exactly when the assumptions made and their consequences are strictly adhered to throughout, that is when all the velocities are taken to be equal. If Maxwell's law is assumed, then the mutual encounters between the electrons should also be allowed for to obtain an exact result.

The equation $E_\lambda = 16\pi\alpha T/3\lambda^4$ has been very fully discussed by Jeans (*loc. cit.*), together with reasons why it fails in practice for short waves. It now seems very probable that the electron theory in its present form cannot account for the observed values of E_λ. The observed values fall below those calculated for wave-lengths which are very large compared with those of Röntgen rays, which latter are still long enough to be strongly absorbed by dense matter. Short ultra-violet light is even strongly absorbed by air.

XCII. *On the Intensity of Periodic Fields of Force.*

By Andrew Stephenson *.

1. THE nature of the motion of a system about a position of equilibrium in a periodic field of force depends upon the intensity of the field. In general, there is cumulative effect within each of a series of ranges of intensity, the period of the motion in the odd ranges being twice that of the field, and in the even ranges equal.

If the field is an even function of the time, the equation of motion may be written

$$\ddot{x} + 2\alpha n^2 \sum_0^\infty a_r \cos rnt \,.\, x = 0,$$

where α is regarded as a parameter measuring the intensity.

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* Communicated by the Author.

The limits of the odd ranges are given by

$$\begin{vmatrix} 2a_0+a_1-\frac{1}{4a} & a_1+a_2 & a_2+a_3 & . \\ a_1+a_2 & 2a_0+a_3-\frac{9}{4a} & a_1+a_4 & . \\ a_2+a_3 & a_1+a_4 & 2a_0+a_5-\frac{25}{4a} & . \\ . & . & . & . \end{vmatrix}=0, \quad . \quad . \quad . \quad \text{(i.)}$$

$$\begin{vmatrix} 2a_0-a_1-\frac{1}{4a} & a_1-a_2 & a_2-a_3 & . \\ a_1-a_2 & 2a_0-a_3-\frac{9}{4a} & a_1-a_4 & . \\ a_2-a_3 & a_1-a_4 & 2a_0-a_3-\frac{25}{4a} & . \\ . & . & . & . \end{vmatrix}=0, \quad . \quad . \quad . \quad \text{(ii.)}$$

and of the even ranges by

$$\begin{vmatrix} 2a_0-a_2-\frac{1}{a} & a_1-a_3 & a_2-a_4 & . \\ a_1-a_3 & 2a_0-a_4-\frac{4}{a} & a_1-a_5 & . \\ a_2-a_4 & a_1-a_5 & 2a_0-a_6-\frac{9}{a} & . \\ . & . & . & . \end{vmatrix}=0, \quad . \quad . \quad . \quad \text{(iii.)}$$

$$\begin{vmatrix} a_0 & a_1 & a_2 & . \\ a_1 & 2a_0+a_2-\frac{1}{a} & a_1+a_3 & . \\ a_2 & a_1+a_3 & 2a_0+a_4-\frac{4}{a} & . \\ . & . & . & . \end{vmatrix}=0 \quad . \quad . \quad . \quad \text{(iv.)}$$

The motion within the ranges is of form

$$\mathrm{A}e^{pt}\{\phi(t)-\psi(t)\}+\mathrm{B}e^{-pt}\{\phi(t)+\psi(t)\}, \quad . \quad . \quad (1)$$

where $\phi(t)$ and $\psi(t)$ are even and odd functions of t.

2. For a simple periodic field, $\ddot{x}+2\alpha n^2 \cos nt \,.\, x=0$, the first three ranges of cumulative effect are $0{\cdot}454 \ngtr 2\alpha \ngtr 3{\cdot}76$; $3{\cdot}79 \ngtr 2\alpha \ngtr 10{\cdot}64$; $10{\cdot}65 \ngtr 2\alpha \ngtr 20{\cdot}95$. The relative smallness of the ranges of stability is noteworthy.

3. In the case of an alternating impulsive field

$$\ddot{x}+2\alpha n^2\sum_0^\infty \cos(2r+1)nt\,.\,x=0.$$

Equation (i.) gives $2\alpha=1\Big/\sum_0^\infty\dfrac{2}{(1+2r)^2}=\dfrac{4}{\pi^2}$, and (ii.) has no positive root. Hence there is instability if the impulsive spring is not less than four times the reciprocal of its period. This result may be obtained directly. If a point with one degree of freedom is subject to changes of velocity $\beta\times$ displacement and $-\beta\times$ displacement at intervals τ, then if the initial velocity is properly chosen relatively to the displacement, the displacements at intervals 2τ increase or decrease in geometric progression provided $\beta\tau>2$, the ratio being

$$-\tfrac{1}{2}(\beta^2\tau^2-2\pm\beta\tau\sqrt{\beta^2\tau^2-4}).$$

The displacements at the impulses are

$$x,\ \mp kax,\ -k^2x,\ \pm k^3ax,\ k^4x,\ \dots,$$

where

$$k=\tfrac{1}{2}(\beta\tau\pm\sqrt{\beta^2\tau^2-4})\quad\text{and}\quad a=\sqrt{(\beta\tau-2)/(\beta\tau+2)}.$$

The general solution is of form (1) where the period is 4τ, and

$$-\phi(2\tau-t)=\phi(t)=\{1-(1-a/k_1)t/\tau\}e^{pt}$$
$$+\{1-(1+ak_1)t/\tau\}e^{-pt}\text{ between 0 and }\tau,$$

$$\psi(2\tau-t)=\psi(t)=\{1-(1-a/k_1)t/\tau\}e^{pt}$$
$$-\{1-(1+ak_1)t/\tau\}e^{-pt}\text{ between 0 and }\tau,$$

k_1 being the larger value of k, and $p=\dfrac{1}{\tau}\log_e k_1=\dfrac{1}{\tau}\cosh^{-1}\beta\tau/2$.

In the limiting case $\beta\tau=2$, the particular solutions are

$$A_1\phi_1(t)\text{ and }B_1\{t\phi_1(t)-\psi_1(t)\},$$

where ϕ_1 and ψ_1 are even and odd functions of t defined by

$$-\phi_1(2\tau-t)=\phi_1(t)=1-t/\tau\text{ between 0 and }\tau,$$
$$\psi_1(2\tau-t)=\psi_1(t)=\tfrac{1}{2}t(3-2t/\tau)\text{ between 0 and }\tau.$$

These give motions in which the displacements at the impulses are $b, 0, -b, 0, b\dots$ and $0, -c, -4c, c, 8c, \dots$, results which are easily verified.

The case in which the impulses are of the same sign may be treated similarly. Since in the above the steady motion at the limit of stability is unaffected by the omission of the negative portions of the spring, the condition for stability is, as before, that the impulsive spring be less than four times the reciprocal of its period.

4. When the period of the field is made up of intervals of constant strengths, the periodic motions which distinguish the limits of the ranges may be found directly. If, for example, the spring is alternately equal to $(\alpha n)^2$ and $-(\alpha n)^2$ during intervals π/n, the limits of the odd ranges are given by

$$e^{-\alpha\pi} = \tan\frac{\pi}{4}(2\alpha-1), \quad e^{\alpha\pi} = \tan\frac{\pi}{4}(2\alpha-1),$$

and of the even ranges by

$$-e^{\alpha\pi} = \tan\frac{\pi}{4}(2\alpha-1), \quad -e^{-\alpha\pi} = \tan\frac{\pi}{4}(2\alpha-1).$$

The ranges of cumulative effect lie about the integral values of α, and those of stability about the values differing from an integer by a half; the latter become small without limit as α is taken large. In the case of instability the value of p, equation (1), is

$$\frac{n}{4\pi}\log_e\frac{\cos(2\epsilon+\alpha\pi)}{\cos(2\epsilon-\alpha\pi)},$$

where

$$\cos 2e = \sin\alpha\pi\,\frac{e^{2\alpha\pi}+1}{e^{2\alpha\pi}-1}.$$

When the spring is alternately $(\alpha n)^2$ and zero for periods π/n, the ranges are given by $\cot\alpha\pi/2 = \alpha\pi/2$ and $\cos\alpha\pi/2 = 0$, the even by $\tan\alpha\pi/2 = -\alpha\pi/2$ and $\sin\alpha\pi/2 = 0$. Here the integral values of α give the upper limits of the ranges.

5. The problem under consideration is of importance in connexion with those motions which are maintained by a periodic field of force. Take, for example, the 'phonic wheel,' in which "the essential feature is the approximate closing of the magnetic circuit of an electromagnet, fed with an intermittent current, by one or more soft iron armatures carried by the wheel and disposed symmetrically round the circumference"[*]. "In some cases the oscillations of the motion about the phase into which it should settle down are very persistent and interfere with the application of the instrument. A remedy may be found in a ring containing water, or mercury, revolving concentrically."

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[*] Rayleigh, 'Sound,' i. § 63.

The methods of ensuring steadiness and their significance may be arrived at theoretically. We assume that there is no independent driving, and that the field is of impulsive type, being constant through an interval which is small compared with the period. The equation of motion is

$$\ddot{\theta}+2\kappa\dot{\theta}+f(nt)\sum_{0}^{\infty}a_{2r+1}\sin(2r+1)\frac{2\pi}{\epsilon}\theta=0,$$

where ϵ is the angle between consecutive positions of stable equilibrium, and $f(nt)$ is an even periodic function of period $2\pi/n$, equal to c^2 between 0 and τ, and zero between τ and π/n.

Putting $\frac{2\pi}{\epsilon}\theta=nt-\alpha+\frac{2\pi}{\epsilon}\phi$, we have

$$\ddot{\phi}+2\kappa\dot{\phi}+\frac{2\pi}{\epsilon}\Sigma\{(2r+1)a_{2r+1}\cos(2r+1)\alpha\}f(nt)\,.\,\phi$$
$$=\Sigma\{a_{2r+1}\sin(2r+1)\alpha\}f(nt)-\kappa n\frac{\epsilon}{2\pi},$$

where ϕ is small. The mean value of the right-hand side is zero if $\Sigma\, a_{2r+1}\sin(2r+1)\alpha=\kappa\epsilon/2c^2\tau$, which therefore gives the phase of the steady motion. The right now reduces to the even function equal to $\kappa\epsilon/2\tau$ between 0 and τ and $-n\kappa\epsilon/2\pi$ between τ and π/n; this gives the small periodic variation in the angular velocity due to the intermittency of the force. The steadiness of the motion depends upon the free oscillation of ϕ. From the concluding paragraph of § 3 it is evident that there is cumulative effect if the impulsive spring is of sufficient magnitude. For a given phase, α, stability is assured either by the introduction of frictional resistance, proportional to $\ddot{\theta}$, to absorb the energy communicated, as in the device cited above, or by a reduction in the spring to destroy the isochronism. The latter result may be attained by an increase in the radius of gyration.

For a specified motional resistance and strength of current there is a limit of frequency below which there is instability, and the greater the radius of gyration the slower the speed at which the instrument can be used.

If the field is not impulsive, but acts during an appreciable interval, *e. g.* half the period, steadiness might be reached in any case of instability, simply by a suitable *increase* of current.

July 1910.

XCIII. *Absorption and Reflexion of the β-Particles by Matter.* By ALOIS F. KOVARIK, *Ph.D.*[*]

RECENTLY considerable discussion has taken place on the law of absorption of the β-particles. Hahn and Meitner[†] have shown that the β radiations from radioactive elements are absorbed according to an exponential law, and according to their theory, namely, that radioactive elements emit rays of only one velocity, have concluded that such radiations are homogeneous. W. Wilson[‡] has shown that the β rays separated out by a magnetic field, and therefore consisting of practically one velocity, are not absorbed according to an exponential law. The results of Schmidt[§], Crowther[‖], and others have confirmed in some respects the experiments of one or the other. The question whether the β-particles from radioactive elements are homogeneous or complex is still an open one, and obviously quite complicated, involving in its solution several other questions, such as the effect of the reflected radiations and the variation of the ionizing power of the β-particle with its velocity, and possibly also with the path traversed.

Since the β radiations from most of the radioactive materials are absorbed very nearly according to an exponential law, this law becomes very convenient in determining the coefficients of absorption. The absorption curves are, however, influenced by different experimental arrangements, chiefly because under some conditions the scattered radiation is not properly taken into account in the ordinary methods of measurement.

The purpose of this investigation was (1) to determine the coefficients of absorption of the β-particles of different velocities under the most normal conditions; (2) to determine the effect of reflected rays on the coefficients of absorption; (3) to determine the variation of the amount of reflexion with the velocity as well as with the reflecting substance. In order to do this, it is necessary to have sources of β-particles of different velocities, and for this purpose the following were employed:—

Radium D+E which emits some weak rays probably from RaD but mainly the rays from RaE, whose coefficient of absorption by aluminium is 43·3 (cms.)$^{-1}$, corresponding to a

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[*] Communicated by Prof. E. Rutherford, F.R.S.

[†] Hahn and Meitner, *Phys. Zeit.* ix. x. p. 321 (1908).

[‡] W. Wilson, Proc. Roy. Soc., A. lxxxii. p. 612 (1909).

[§] H. W. Schmidt, *Jahrbuch d. Rad. u. Elek.* iv. 4 (20), p. 451 (1908).

[‖] J. A. Crowther, Proc. Camb. Phil. Soc. vol. xv. p. 442 (1910).

velocity represented by Hρ of about 1720, where H is strength of field and ρ radius of curvature of rays. On account of the long period of RaD this source is constant, and hence very convenient.

Actinium C, which emits rays whose coefficient of absorption by aluminium is 28·5, corresponding to a velocity represented by Hρ of about 2150. This was obtained by the recoil method for some experiments and by the use of actinium active deposit for others.

Radium B, which emits rays whose coefficient of absorption by aluminium is 75·0, corresponding to a velocity represented by Hρ of about 1200. This was obtained by the recoil method from radium A.

Thorium A + B + C + D, the thorium active deposit, which emits rays of at least two velocities whose coefficients of absorption by aluminium are 110 and 16·3, which would be represented by Hρ of about 900 and 2650, respectively.

Radium active deposit whose rays have a very wide range of velocities.

With all the sources used except Ra D + E, the work is quite laborious on account of the corrections for the decay since the periods of all of the others are quite short.

Generally, when the coefficients of absorption are obtained, the material is deposited on metals of considerable thickness. It will be shown in this paper that under such conditions the reflected rays play an important part in the coefficients of absorption. When thick layers of radioactive material are used, the β-particles from the various depths emerge with various velocities. In order to avoid these complications, the active material used was always in the form of a very thin layer deposited on a very thin aluminium leaf, whose absorption or scattering effects were negligible.

Scattering.

The β-particles from a uniform thin layer of radioactive material radiate equally in all directions. The measurement of the absorption by thin sheets is generally carried out by placing the radioactive matter some distance below an ordinary β-ray electroscope, and by placing the absorbing sheets at some distance above the active matter, so that only the more or less parallel rays normal to the sheets are considered. If the absorbing matter is some distance below the opening in the electroscope, the scattering observed by Crowther* produces a steeper incline in the initial portion of the absorption curve than would be expected from the latter portion of the curve. If, however, the thin absorbing

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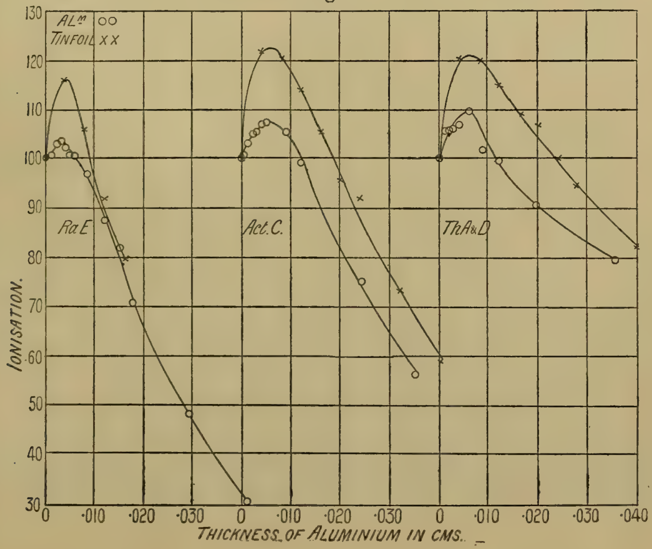
* J. A. Crowther, Proc. Roy. Soc., A. vol. lxxx. p. 186 (1908).

foils are placed directly on top of the thin radioactive material, and this is placed at some distance below the electroscope, an entirely different initial portion of the curve is obtained. This is clearly shown by the following experiments. Table I. and the corresponding curves in fig. 1 show the results.

TABLE I.

Aluminium in mms.	Ionization.			Tinfoil equivalent in mms. of Al.	Ionization.		
	Ra E.	Act C.	Th A+D.		Ra E.	Act C.	Th A+D.
0·0000	100·0	100·0	100·0	0·00	100·0	100·0	100·0
·0025	100·0	101·3	100·1	·04	116·3	121·8	120·3
·0050	100·3	...	...	·08	106·0	120·5	119·8
·010	100·8	103·0	105·8	·12	92·0	114·0	114·9
·020	103·3	105·0	105·9	·16	79·9	105·4	109·1
·030	103·7	105·5	106·0	·20	...	95·7	106·9
·035	102·3	...	...	·24	...	91·8	100·0
·040	...	106·9	107·0	·28	...	...	94·4
·045	100·9	...	...	·32	...	73·2	...
·050	...	107·4	109·8	·40	...	58·8	82·0
·059	100·8	...	...	·52	...	...	67·4
·090	97·1	105·5	101·6	·64	...	...	57·8
·120	87·5	99·0	99·4				
·150	82·0	...	...				
·177	71·0	...	...				
·236	...	75·0	90·6				
·295	48·1	...	...				
·354	...	56·1	79·4				
·413	30·8						

Fig. 1.



The first column gives the thickness of the absorbing layers of aluminium placed directly on top of the thin active layer. The second, third, and fourth columns give the ionization observed in the electroscope. The ionization, when no absorbing matter was on top of the active material, is taken as 100. The remaining columns give similar results when tinfoil was used for which the equivalent absorbing thickness of aluminium is given. This equivalent value of tinfoil in terms of aluminium was found from the latter portions of the absorption curves, where, as will be seen from later work, the absorption curves are similar in form. Several radioactive materials were used in this determination with very similar results.

It should be stated here that the opening of the electroscope was covered with a considerable thickness of mica and tinfoil, so that the very easily absorbed radiations are not effective. It will be noticed that the initial portions of the curves rise to a maximum before absorption becomes at all obvious. Furthermore, the percentage increase is greater when tinfoil is used instead of aluminium. For a given source of β rays, the maximum is reached for equivalent thicknesses of tinfoil and aluminium, but this maximum shifts to the right on using more penetrating β rays. The observed effect is therefore a function of both the absorbing material and the velocity of the β-particles. When the absorbing foils were placed at some distance above the active material, the maximum decreased in magnitude with the increase of the distance until finally the reverse effect observed by Crowther showed itself. By placing a perforated diaphragm above the active matter the maximum decreased in magnitude with the decrease of the size of the opening.

These experiments show that the initial rise to a maximum is undoubtedly due to the scattering of the β-particles by the thin absorbing foils. In order that scattering may be complete, the β-particles must pass through a definite thickness of the absorbent. In the experiments described the radiation is equal in all directions. Those particles which strike the absorbent normally are scattered less than the oblique ones, provided the absorbing layer has a thickness smaller than that required for complete scattering. Consequently, the oblique rays, which did not reach the electroscope when no absorbing matter was placed over the active material, become scattered when a thin foil is so placed, the degree of scattering depending on the thickness traversed, and therefore on the obliquity of the rays. These scattered β-particles reach the electroscope in numbers sufficiently large to more than compensate for the loss suffered by the normal rays due to absorption, reflexion, and slight side scattering.

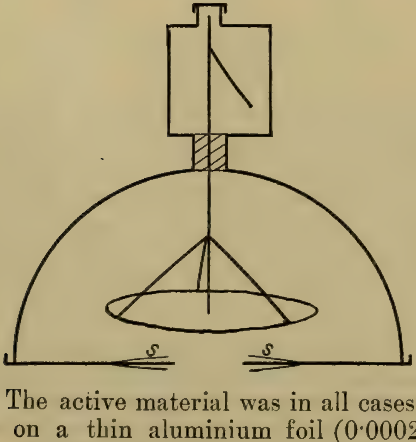
When a thick layer of radioactive material was used, *e. g.* uranium oxide, the effect described was not observed owing to the fact that complete scattering took place within the material itself except for the uppermost layer. The radiation from the latter was relatively too weak to produce an observable effect.

It is clear, therefore, that scattering may produce a rise in the initial portion of absorption curves as well as a steep incline, or no observable effect, depending entirely on the experimental arrangements. In order to obviate the effect of the scattering of the β-particles on the initial portion of the absorption curve, the absorbing screens should be placed directly against the opening of the electroscope, in which case none of the scattered β-particles will be lost.

Apparatus.

In the ordinary cylindrical or rectangular shaped ionization vessels, the β-particles do not have equal paths, and consequently do not produce equal numbers of ions within the vessel. For this reason it was decided to use a hemispherical ionization vessel in the following investigation. A copper hemisphere, 30 cms. in diameter, was used for this purpose, and an appropriate electrode and electroscope were constructed as shown in fig. 2. The bottom of the ionization vessel was removable. The active material was in all cases deposited as a thin layer on a thin aluminium foil (0·00025 cm.), and

Fig. 2.



this was in turn attached to a sheet of mica or aluminium of a thickness slightly greater than would be necessary to stop all the α-rays which might be emitted by the active material. This sheet was then placed inside the ionization vessel, active side downward and over the central opening of the cover, to which it was held by means of springs. The absorbing sheets were also placed on the inside and were also held in position by springs. The change of capacity produced by the slight elevation of a large number of absorbing sheets was found to be negligible in the large vessel. The capacity of the instrument was about 10 E.S. units. Care was taken to obtain saturation in all the experiments.

With this arrangement the β-particles have the radius of the vessel for their path, and all the scattered rays become effective. Since, however, the β-particles after passing through matter have their velocity slightly decreased *, then, if the ionization changes considerably with the velocity, the oblique rays will be affected more than the normal rays. In addition, with plane absorbing sheets, the oblique rays are more absorbed than the normal rays, and this should result in a slight drop in the initial portion of the absorption curve. Experiments were tried with more or less normal rays, but the absorption curves were nearly identical with those obtained when radiations in all directions were used.

In some of the experiments, the interior of the vessel was lined with a thick cardboard covered with a conducting paper. The result was a decrease of about 20 per cent. of the ionization due to the fact that multiple reflexion of the β-particles is less from cardboard than from copper.

Effect of reflected β-particles on the absorption coefficient.

The present form of the apparatus was well adapted for the investigation of the amount of reflexion * of the β-particles by any substance, and also for the investigation of the effect of the reflected β-particles † on the absorption coefficient. When air was underneath the thin aluminium foil on which the active matter was deposited, the coefficient of absorption was always found to be smaller than when a reflecting substance was placed under, and it increased with the atomic

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* W. Wilson, *loc. cit.*

† The terms "reflexion" and "reflected β-particles or rays" are used for convenience only. By "reflected β-particles" is meant the β-particles which entering the substance, conveniently called the "reflector," are deflected in their course by collision with the atoms of the substance so that they emerge again as diffusely scattered β-particles.

weight of the reflector. When a differential curve was plotted, which would show the absorption of the reflected rays alone, the coefficient of absorption for the reflected rays was considerably greater than for the incident rays. For example, in the case of the β rays from Ra E, when air was underneath, the coefficient of absorption $\mu=42\cdot4$ (cms $)^{-1}$; when lead was underneath $\mu=44\cdot8$, while the differential curve gave for the reflected rays $\mu=51\cdot0$ cms.$^{-1}$ for aluminium. Schmidt* had already drawn attention to this fact.

Table II. gives the values of the coefficients of absorption in terms of cms. of Al for the β-particles from Ra E, Act C, Th D, and Ra C, when different substances are placed under the active material.

Table II.

Substance underneath.	Coefficients of Absorption.			
	Ra E.	Act C.	Th D.	Ra C.
Air	42·4	27·6	15·7	13·0
C	43·0	28·3	16·1	13·2
Al	43·3	28·5	16·3	13·4
S	43·8	28·9	16·4	13·6
Fe	44·3	29·2	16·4	13·6
Ni	44·3	29·3	...	13·9
Cu	44·4	29·3	16·4	13·8
Zn	44·4	29·5	...	14·0
Ag	44·6	30·1	...	14·2
Sn	44·7	30·2	...	14·3
Pt	44·8	30·4	...	14·7
Au	44·8	30·4	16·7	14·7
Pb	44·8	30·4	16·7	14·7
Bi	44·8	30·4	...	14·7

It will be observed that in all cases the absorption coefficients are greater when a substance of greater atomic weight is placed underneath. The value for air underneath would apparently be the value of μ for the incident rays. It follows from this that the average velocity of the β-particles is decreased by reflexion.

Since the β-particles are reflected by matter, it is obvious that the absorbing matter above the active material will reflect downwards a certain fraction of the incident radiation, the amount of which will depend on the velocity of the rays themselves (as will be shown later) and on the thickness and

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* H. W. Schmidt, *loc. cit.*

the atomic weight of the absorbing element. If air is underneath, the β-particles reflected by the absorbing sheets do not re-enter the ionization vessel in appreciable amount. As a result, the initial portion of the absorption curve under these conditions will suffer a drop not due to absorption alone but due to reflexion as well. This effect is quite noticeable, as may be seen from Table III. and the curves *b* and *c* in fig. 3, where aluminium and tinfoil were used respectively as the absorbing matter, air being underneath the active material in both cases. Evidently, to obtain a more accurate absorption curve, the same thickness of the material used for absorption should be placed under the thin radioactive layer as is placed above it, in which case the loss of the β-particles by reflexion by the absorbing layers is compensated by the reflexion into the ionization chamber by the layers underneath. Column *a*, Table III., and curve *a*, fig. 3 (p. 857), show the results when aluminium is so used for the absorption of the β-particles from Ra E.

Table III.

Absorption of the β-particles from Ra D + E.

a=Aluminium as absorbing substance; same number of layers underneath as used for absorption.
b=Aluminium as absorbing substance; air underneath.
c=Tinfoil as absorbing substance; air underneath.

Aluminium in mms.	*a*.	*b*.	Tinfoil in equivalent value of mms. Al.	*c*.
0·059	100·9	100·0	0·059	100·0
·118	65·9	60·7	·099	65·5
·177	46·3	44·4	·139	49·4
·236	34·6	33·9	·179	40·0
·295	25·7	25·4	·219	32·5
·354	19·4	19·3	·299	22·8
·472	11·6	11·55	·339	19·4
·590	6·70	6·97	·459	11·55
·708	4·10	4·51	·599	7·24
·826	2·41	2·41	·744	3·11
·944	1·52	1·60	·870	1·87
1·062	0·80	0·84	·939	1·38

The coefficients of absorption of the β-particles from Ra D, Th A, Ra B, Ra E, Act C, Th D, and Ra C, obtained in this manner, are given in Table IV.

Fig. 3.

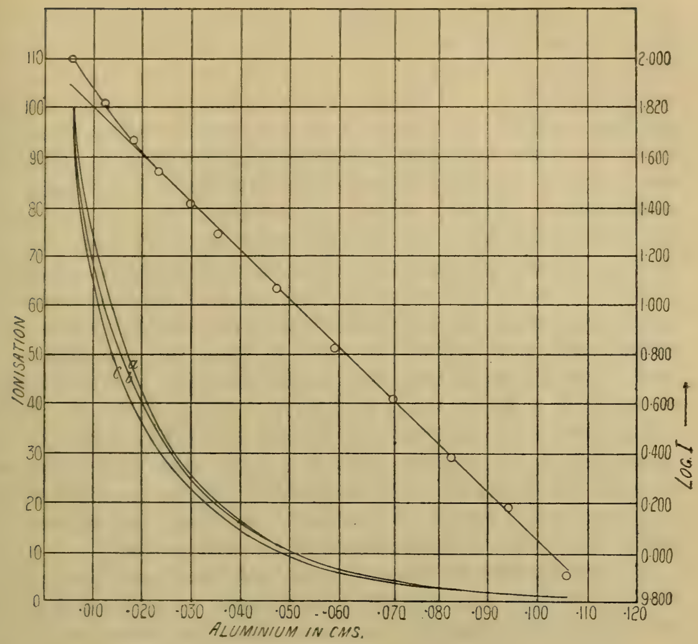

TABLE IV.

Coefficients of Absorption in cms. of Al.

Ra D (?).	Th A.	Ra B.	Ra E.	Act C.	Th D.	Ra C.
130	111·0	75·0	43·3	28·5	16·3	13·5

The coefficient of absorption of the β-particles from RaB was determined by using RaB obtained initially pure by recoil from radium A, as well as by difference method, while in the case of Th A and Ra D (?) the difference method alone was used. Act C was also obtained by the recoil method, but in some determinations the actinium active deposit was used.

When the logarithm of the ionization given in column *a*, Table III. is plotted against the thickness of aluminium we still observe an initial drop. This must be attributed to weak radiations possibly belonging to Ra D.

In the case of Ra E, Act C, and Th D absorption curves, it is found that down to about 5 per cent. of the initial activity, the logarithm of the ionization when plotted against the thickness of the absorbing material gives a straight line. The conclusion generally drawn from such a result is that the absorption follows an exponential law, and that the rays are homogeneous. This, however, should be done with due caution, for the logarithm of the ionization changes slowly with the ionization, and a straight line would be obtained when the absorption follows the exponential law only approximately. This is clearly illustrated when we consider the differential curve for the reflected rays, say from lead, in the case of any of the above mentioned radioactive materials. For Ra E rays, for example, after the soft rays are absorbed we get a straight line with the value of $\mu=42{\cdot}4$ when air is underneath, a straight line with a value of $\mu=44{\cdot}8$ when lead is underneath, and a straight line for the differential curve with a value of $\mu=51{\cdot}0$ cms.$^{-1}$ Al. Now, the differential curve is obtained by taking the differences of two exponentials, supposing they are such, and this difference cannot, therefore, be an exponential; but on account of the comparatively small differences in the exponents the differential curve approximates to an exponential.

It must further be remembered that the rays after passing through matter are scattered and their velocity is changed, and while the β-particles of one velocity predominate there are, however, β-particles of smaller and greater velocities[*] present as well, and a distribution of velocities of this kind may be the one which is required for such an approximation to the exponential law as is generally obtained.

Reflexion of the β-particles of different velocities.

It was shown above that the reflexion of the β-particles is important in the study of the absorption curves. McClelland[†] and Schmidt[‡] have shown that elements of higher atomic weight reflect a larger percentage of the incident β-particles than the elements of lower atomic weight. In the course of this investigation it was noticed that the β-particles from Ra E and Act C were not reflected equally readily by the same substance. This suggested that the velocity of the β-particles plays an important rôle in the problem of reflected rays. Systematic experiments were therefore carried out to study the amount of reflexion of the β-particles from Ra E and the

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[*] W. Wilson, *loc. cit.*

[†] J. McClelland, Sci. Trans. Roy. Dublin Soc. ix. pts. 1 & 2, pp. 1 & (1906).

[‡] H. W. Schmidt, *Jahrbuch der Radioaktivität und Elektronik*, iv. p. 451 (1908).

active deposits from actinium, thorium, and radium emanations by various substances. The apparatus used was the same as the one used in the absorption experiments. The active material was deposited on a thin aluminium leaf (0·00025 cm.), and this was attached to a piece of mica or aluminium of sufficient thickness to stop all the α-particles and yet not diminish the β-ray activity to any great extent. The plate was then fastened on the inside of the cover of the ionization vessel while the reflectors were held by springs on the outside. Readings were taken by having air underneath the active material, and then by placing the reflecting substance underneath. The difference in the ionization in the two cases divided by the ionization when air was underneath gave the percentage of reflexion. The reflected rays being somewhat softer than the primary rays would, consequently, be absorbed more by the mica or the aluminium than the primary rays, and a knowledge of the values of μ (Table II.) is necessary to correct for this difference. The results of the investigation are given in Table V. (p. 860).

The numbers in the first column for each kind of rays give the mean of a large number of observations under the actual conditions, the thickness of the mica or aluminium sheet being given, while the numbers in the second column are the corrected values. The reflector was of sufficient thickness to produce complete absorption.

It will be noticed that the β-particles from the actinium active deposit are reflected in greater proportion than those from Ra E, and that in the case when Th D predominates over Th A the percentage of reflected β-particles is greater than in the case when Th A and Th D are of about equal importance, so far as ionization is concerned. The β-particles from Ra B show a still smaller percentage of reflexion than those from Ra E. In these experiments the radium B was obtained by recoil from radium A by exposure in a strong field for a few seconds to a large quantity of active deposit, and measurements were made as rapidly as possible. Since radium B changes quickly into radium C and the latter emits β-particles of higher velocity, the percentage of reflected rays was found to increase with time, *i. e.* with the quantity of radium C present.

These results show conclusively that for the β-particles whose coefficients of absorption lie between 75 and about 20 cms.$^{-1}$ Al, the percentage of reflected rays increases with the decrease of the coefficient of absorption, *i.e.* with increase of the velocity of the β-particles. When more absorbing aluminium was placed in the path of the rays from the active

TABLE V.

		Ra E.		Act C.		Thorium active deposit,				Radium active deposit.						
Atomic weight.	Reflector.	Observed. Mica =·004 cm.	Corr,	Obs. Mica= ·004 cm.	Corr.	Obs. Mica = ·0045 cm.	Corr.	Obs. Al = ·0127 cm.	Corr.	Obs. Al = ·00445 cm.	Corr.	Obs. Al = ·0118 cm.	Corr.	Obs. Al = ·0295 cm.	Corr.	Ra B. Al = ·0059.
208·5	Bi	70·5	70·9	80·1	81·0	65·8	66·4	78·3	79·6	77·0	77·8	81·0	82·6			
206·9	Pb	69·6	70·2	79·1	80·0	64·8	65·3	77·4	78·6	74·2	74·9	80·0	81·5	70·4	74·0	59·0
197·2	Au	67·4	67·8	77·9	78·7	64·2	64·7	75·7	76·9	...	...	77·0	78·5	...	...	
194·8	Pt	67·3	67·7	76·8	77·6	...	...	75·6	76·7	...	...	76·8	78·2	...	...	
119·0	Sn	62·1	62·5	69·0	69·7	57·0	57·4	67·1	68·1	70·0	70·7	66·0	67·1	...	...	
107·9	Ag	57·0	57·4	62·9	63·5	53·1	53·5	61·7	62·6	...	...	66·5	67·6	42·8	44·9	
65·4	Zn	45·2	45·5	52·3	52·6	42·9	43·2	49·1	49·9	52·6	53·0	58·6	59·5	43·5	45·1	
63·6	Cu	44·4	44·7	51·6	51·9	42·0	42·3	46·5	47·1	50·9	51·3	52·1	52·9	39·8	41·7	
58·7	Ni	43·2	43·5	47·8	48·0	40·2	40·6	45·1	45·8	...	...	46·3	47·0	37·5	39·3	
55·9	Fe	41·0	41·2	46·9	47·1	37·6	37·8	42·4	44·7	48·2	48·6	45·6	46·2	...	...	
32·1	S	31·9	32·1	40·0	40·1	29·5	29·7	34·1	34·5	35·8	36·1	30·0	30·4	28·8	30·2	
27·1	Al	29·8	30·0	38·2	38·3	28·6	28·7	30·4	31·9	...	...	...	...	18·4	19·2	
12·0	C	17·0	17·1	27·3	27·4	17·7	17·8	20·9	21·1	...	...	24·0	24·3	12·0	12·5	
	Brass	44·9	...	52·0	...	42·0	...	48·6								
	Glass	27·8	...	31·0	...	26·2	...	35·9								
	Ebonite ...	22·6	...	...	...	22·8	...	32·4								
	Pine wood.	16·0	...	...	...	...	...	18·4								
	Mica	...	...	...	...	23·0	...									

deposits of thorium or of radium emanation, the percentage of the reflected β-particles rose to a maximum but finally decreased. The results with the thorium active deposit are given in Table VI. and shown graphically in fig. 4.

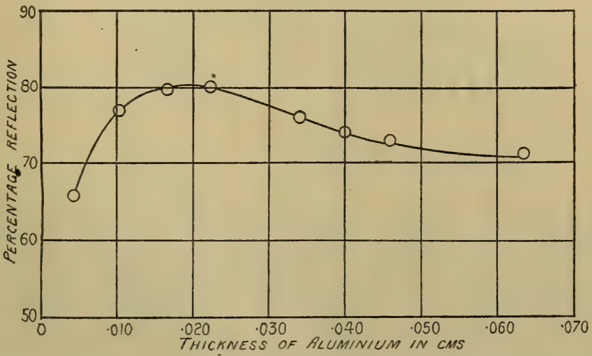
Table VI.

Thorium active deposit.

Aluminium in mms.	Percentage of reflected β-particles.
0·045	65·3
·104	77·0
·163	79·6
·222	80·0
·340	76·0
·399	74·0
·458	73·0
·635	71·0

The first column gives the absorbing aluminium in mms., and the second column gives the percentage of reflected β-particles.

Fig. 4.



This decrease may be due to one of two possible factors, viz., either the softer reflected rays are absorbed more than is accounted for by the correction or the amount of reflexion, as measured by the ionization, increases with the velocity of the β-particles only up to a certain velocity, after which it decreases again. Since this investigation deals with the heterogeneous rays from radioactive bodies, and not with the pure rays of any one velocity, this point cannot be answered here definitely. Investigation of this special phase of the problem is, however, now in progress (see following paper by Kovarik and W. Wilson).

Multiple Reflexion.

Since the β-particles are reflected from a substance into which they penetrate, the reflected rays should in turn be reflected if a substance is placed in their path. Suppose we have two parallel plates of lead and β-particles of the type pair Ra E, say, to be emitted from the lower plate. Let us also suppose the velocity after reflexion to remain constant, and consequently the percentage of reflexion and the ionization of the particles involved in multiple reflexion to be constant also. The following calculation then shows what the ionization due to multiple reflexion should be.

Let I represent the ionization due to the incident rays and ρ represent the percentage of reflexion. Then for the rays passing upwards the ionization is equal to

$$\mathrm{I}+\rho\mathrm{I}+\rho^2\mathrm{I}+\rho^3\mathrm{I}+\ \dots\ \&\mathrm{c.}$$

and for the rays initially passing downwards, after reflexion into the ionization chamber

$$\rho\mathrm{I}+\rho^2\mathrm{I}+\rho^3\mathrm{I}+\ \dots\ \&\mathrm{c.}$$

giving a total ionization of

$$\begin{aligned}&\mathrm{I}+2\rho\mathrm{I}(1+\rho+\rho^2+\rho^3+\ \dots\ \&\mathrm{c.})\\ &=\mathrm{I}\left[1+\frac{2\rho}{1-\rho}\right]\\ &=100\left[1+\frac{2\times 70{\cdot}9}{29{\cdot}1}\right],\end{aligned}$$

$=587$ per cent. of the ionization due to the incident rays; or that due to multiple reflexion alone is 487 per cent. The numbers substituted are obtained from Table V.

Since the reflected particles have a smaller velocity than the incident, and the amount of reflexion decreases with decreasing velocity, it follows that the above ratio must be too high, unless the variation of the ionization with the velocity is very marked. In order to test this point and to see how the multiple reflexion varies with different reflectors and with rays of different velocities, a special apparatus was constructed. It was then found experimentally for the Ra E radiation that the multiple reflexion was 236 per cent. of the incident radiation, measured by the ionization. This seems to justify the conclusion that the rays after the first reflexion are not as readily reflected. To see what the average value of the reflexion percentage is after the first reflexion, we have, calling x the percentage of reflected rays after the first, the series

$$\begin{aligned} & \mathrm{I}+2\rho\mathrm{I}+2\rho x\mathrm{I}+2\rho x^2\mathrm{I}+\ \ldots\ \&\text{c.} \\ & =\mathrm{I}[1+2\rho(1+x+x^2+x^3+\ \ldots\ \&\text{c.})] \\ & =\mathrm{I}\left[1+\frac{2\rho}{1-x}\right], \end{aligned}$$

or

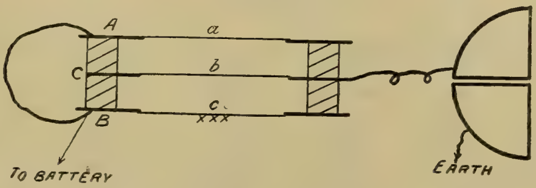
$$336=100\left[1+\frac{2\times 70{\cdot}9}{1-x}\right],$$

from which $x=40$ per cent.

Hence the percentage of reflected rays drops from 70·9 for the first reflexion to an average value of 40 for the following reflexions. This indicates that the slower β rays are less easily reflected than the swifter, unless the variation of the ionization with the velocity is large.

The apparatus used in the multiple reflexion experiments consisted virtually of two ionization chambers. The parallel plates A and B (fig. 5) were connected together and to a source of potential and had equal size openings a and b of 4 cms. diameter; C was another plate with a little larger opening c and was separated from A and B by means of sulphur. C acted as an electrode, and was connected to a quadrant electrometer. a and b were covered with very thin aluminium foils so that the β-particles could readily pass through them without suffering much in absorption or reflexion. The active material attached to a piece of mica or aluminium to absorb the α-rays was placed at c. The distance between A and B was varied from 1 mm. to 1 cm. in order to see if the change of the solid angle of the issuing rays within the present size vessel produced variations in the multiple reflexion. Between 1 mm. and 3 mm. the readings were concordant, but with a greater distance the ratio for the multiple reflexion to the initial ionization decreased. Hence the smaller distances were used in these experiments.

Fig. 5.



Readings were taken by measuring the ionization produced (1) when the rays from *c* were allowed to pass through *a* and *b*, (2) when the rays were reflected by the reflector placed over *a*, (3) when the rays below *c* were reflected upwards by placing the reflecting substance under *c*, (4) when the rays were multiply reflected by placing the reflectors over *a* and under *c*.

When the substance was over *a* the incident rays were reflected downward in a diffuse manner, and striking the aluminium (·0059 cm.) over the active material become to some extent again reflected, &c. The readings in (2) were therefore always somewhat higher than in (3), which case (except for slight multiple reflexion from the interior of the chamber, amounting to about 3 per cent.) corresponds to the case when reflexion was studied with the hemispherical ionization vessel. Correcting (2) for reflexion and (3) for the absorption and slight multiple reflexion, the two readings always agreed.

The results of these experiments for the rays from Ra E, using various substances as reflectors, are given in Table VII.

Table VII.

Reflecting substance.	Initial ioniza-tion.	Ionization: reflector on top.	Ionization: reflector under.	Ionization: reflector on top and below.	Multiple reflexion alone.
Pb	100	182·0	172·6	336·0	236·0
Pt	,,	187·2	170·0	337·5	237·5
Sn	,,	173·0	170·5	313·0	213·0
Ag	,,	173·4	156·8	279·0	179·0
Zn	,,	157·5	150·8	236·0	136·0
Cu	,,	160·0	149·6	233·0	133·0
Ni	,,	154·5	141·4	224·2	124·2
Fe	,,	150·8	147·0	218·0	118·0
S	,,	143·2	135·7	189·0	89·0
Al	,,	138·0	131·5	171·7	71·7
C	,,	121·5	121·0	146·0	46·0
Cardboard	,,	122·5	119·0	141·2	41·2

The first column gives the substance used for reflecting the β-particles. In the following four columns are the values of the ionization obtained corresponding to the readings taken as given above, the ionization for the incident rays being taken as 100. The last column gives the ionization due to multiple reflexion alone.

It will be observed that the substances of higher atomic weight give larger values for the multiple reflexion (Pt for some reason gives slightly higher value than Pb) than the substances of lower atomic weight.

Experiments were next performed by using various radioactive substances as the sources of β-rays of different velocities but using lead in all cases as the reflector. The results are given in Table VIII.

TABLE VIII.

Ionization due to multiple reflexion of β-particles of various penetrating powers.

Ra E.	Act C.	Th A+D.		Ra B+C.	Ra C.
		Th A=Th D.	Th D=90 per ct.		
236·0	250·0	74·0	225·0	243·0	202·0

The numbers in the various columns give the percentages of ionization due to multiple reflexion alone. The multiple reflexion increased in value for the more penetrating rays, but apparently reaches a maximum and then begins to decrease again. This agrees with the previous observations.

Conclusions.

(1) Scattering of the β-particles may produce a rise in the initial portion of the absorption curve under certain conditions, and a steep incline under other conditions. The effect of this scattering appears to be a function of the velocity.

(2) In measurements of absorption the absorbing material should be placed directly against the opening of the electroscope in order to avoid errors due to scattering.

(3) The coefficient of absorption of the β-particles from thin layers varies with the substance underneath the active material, being greater for elements of greater atomic weight.

(4) To avoid the steep incline in the initial portion of the absorption curve caused by reflexion of the β-particles by the absorbing layers, it is necessary to place underneath the thin active layer as many absorbing sheets as above.

(5) The percentage of reflexion, measured by the ionization method, of the β-particles from thin active layers by any one substance is a function of the velocity, and for rays whose

coefficients of absorption by aluminium lie between 75 and about 20 (cms.)$^{-1}$ it is greater for the rays of greater velocity; for the very penetrating rays the percentage decreases again.

(6) The percentage of reflected β-particles is greater for the reflectors of greater atomic weight.

(7) By multiple reflexion the ionization may be increased from 100 to 350. The multiple reflexion changes in value with the atomic weight of the reflector, and the velocity of the β-particles in the same manner as the single reflexion.

These experiments were suggested by Professor Rutherford, to whom I wish to express my deep gratitude for his valuable suggestions, attention, and the permission to work in his laboratory.

Physical Laboratory,
Victoria University of Manchester.
July 4, 1910.

XCIV. *On the Reflexion of Homogeneous β-Particles of Different Velocities.* *By* Alois F. Kovarik, *Ph.D.*, *and* W. Wilson, *M.Sc.*[*]

IN the preceding paper by one of us it was shown that the ratio of the number of β-particles reflected from a sheet of matter to the number impinging upon it increased, within certain limits, with the penetrating power of the rays. This result was found for the heterogeneous rays emitted by radioactive bodies. The following experiments were made to determine the variation of this ratio for approximately homogeneous rays of different velocities. Such rays were sorted out by means of a magnetic field.

The apparatus used is shown in fig. 1. The rays were emitted by the active deposit in equilibrium with radium emanation, corresponding to about 30 mmg. of radium, contained in the bulb A. They entered the magnetic field B and described circular paths passing through the hole R and the tube S into an ionization vessel. The ionization vessel consisted of three parallel leaves of thin aluminium foil on rigid frames, 10 cms. × 10 cms.; the outer two metallically connected together were about one centimetre apart; the inner one was separated from the outer two by means of sulphur, and it was connected by a protected wire to the gold-leaf system of a small electroscope E by means of which the ionization in the vessel was measured. The tube S was

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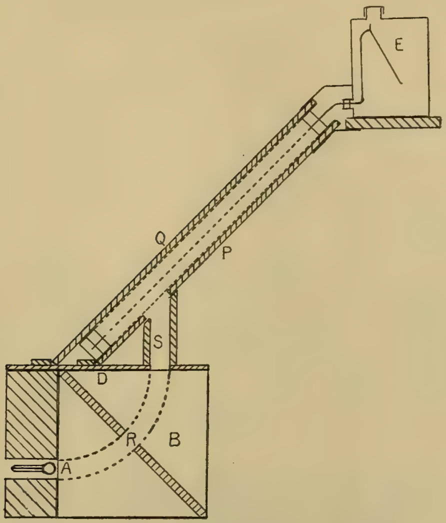
[*] Communicated by Prof. E. Rutherford, F.R.S.

made of soft iron in order to protect the rays passing through it from the magnetic field, and thus prevent their deflexion to the sides. The ionization vessel rested on a plate P of the substance used for reflexion, which had a hole cut in it corresponding to the hole in S. The plate P could be turned about the end D by means of an arrangement not shown in the figure, so that any desired angle with the horizontal could be obtained. A change in the inclination necessarily involved also a change of the tube S. A plate of the substance used as reflector could be placed so as to cover the upper side of the ionization vessel as shown by Q. To determine the ionization by the γ rays alone, a sheet of lead of sufficient thickness to absorb all the β-particles was placed between the pole-pieces of the magnet so as to cover the hole R. In the experiments with different reflecting substances the plates P and Q were of the same substance. It was found necessary to keep the plate P always in position in order to reduce the effect of scattered radiation from various parts of the apparatus.

Fig. 1.



During an experiment on the reflexion of the β-particles of any velocity the following readings were taken in the order given, and in the reverse order, repeating many times and using the mean values:

(1) γ-ray effect, Q in position;
(2) $\beta+\gamma$-ray effect, Q in position;
(3) $\beta+\gamma$-ray effect, Q taken off;
(4) γ-ray effect, Q taken off.

Subtracting (1) from (2) we obtain the ionization due to multiple reflexion of the β-particles plus the initial ionization; subtracting (4) from (3) we obtain the initial ionization of the incident β rays alone. The difference of these two values divided by the latter gives a ratio which is taken as a measure of the reflective power of the substance for the β-particles of the velocity under consideration. Owing to the fact that P had to be always in position and that some reflexion must occur in the ionization chamber even when Q is absent, this ratio is of necessity somewhat low, yet, the conditions being the same for rays of all velocities, the change of this ratio indicates the changes in the reflexion of the β-particles of different velocities.

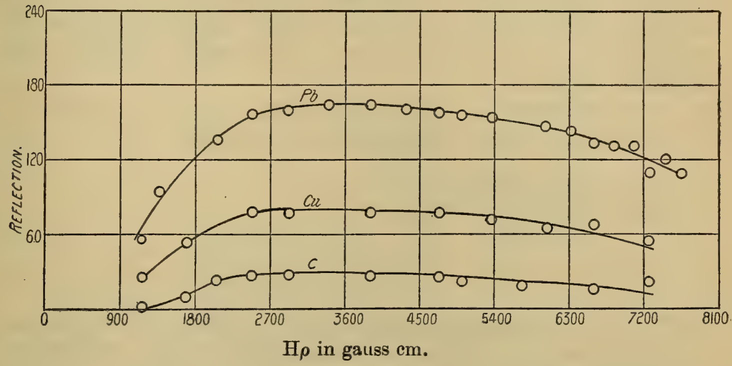
Experiments were made with lead, copper, and carbon. The β-particles considered were those between the values $H\rho=1164$ and $H\rho=7660$ gauss cm. The results obtained when the angle of inclination was 45° are in Table I. and plotted in the curves of fig. 2.

TABLE I.—Ionization vessel inclined 45° to the horizontal.

$H\rho$ in gauss cm.	Ratio of the ionization due to multiple reflexion alone to the ionization of the incident rays.			$\frac{\text{Pb}}{\text{Cu}}$ (from curves).
	Pb.	Cu.	C.	
1164	0·56	0·25	0·02	2·56
1372	0·94	...	...	2·38
1700	...	0·53	0·10	2·25
2072	1·36	...	0·23	2·08
2480	1·57	0·78	0·26	1·91
2920	1·60	0·77	0·27	2·04
3400	1·64	...	...	2·04
3900	1·64	0·77	0·26	2·08
4340	1·60	...	...	2·05
4720	1·58	0·77	0·25	2·10
5000	1·56	...	0·22	2·12
5380	1·53	0·71	...	2·12
5720	...	...	0·18	...
6040	1·46	0·64	...	2·12
6320	1·42	...	...	2·22
6600	1·33	0·67	0·16	2·18
6850	1·31	...	...	2·11
7080	1·31	...	...	2·29
7280	1·15	0·64	0·21	2·30
7480	1·20	...	...	2·34
7660	1·08	...	...	2·36
				2·18 mean

The first column gives the values of Hρ. The following three columns give the ratio of the ionization produced by multiple reflexion to the ionization produced by the incident rays for lead, copper, and carbon respectively. The last column gives the ratio of the values for lead and copper as obtained from the smooth curves. This ratio is roughly constant, indicating that the changes of reflexion with the velocity are proportional for the two substances. The experiments with carbon were difficult on account of its weak reflecting power, and the results are consequently subject to greater errors than in the case of the other two substances. The experiments with an angle of 30° for the inclination of the ionization vessel with the horizontal were tried with lead only, and the results were materially the same as for 45° inclination. For the very slowly and very rapidly moving β-particles the experimental errors are greater on account of the fact that the β-ray effect is small compared with the γ-ray effect, since the distribution of the number of β-particles with the velocity gives a maximum and decreases quite rapidly on each side. This accounts for the irregularity of the observations at both extremities of the smooth curve.

Fig. 2.



The results here obtained fully confirm the results of the investigation with the heterogeneous rays from radioactive bodies as given in the preceding paper. It will be observed that the diffusely reflected radiation as measured by the ionization rises rapidly to a maximum and then slowly begins to fall. If the β-particles were reflected with the same velocity with which they impinge on the matter, or if the ionization did not change materially with the velocity, then the rise and fall in the curve would have to be explained by supposing the number of β-particles reflected to increase with the velocity up to a certain value and then decrease again. Since, however, the ionization produced by β-particles of different velocities may play an important part in the results obtained, a satisfactory explanation of this phenomenon cannot be arrived at until we know definitely the variation of the ionization due to β-particles moving with different velocities.

In conclusion we wish to express our best thanks to Prof. Rutherford for suggesting this research.

Physical Laboratory,
Victoria University of Manchester.
July 25, 1910.

XCV. *The Heterogeneity of the β Rays from a Thick Layer of Radium E.*

By J. A. Gray, *B.Sc.*, 1851 *Exhibition Scholar, Melbourne University, and* W. Wilson, *M.Sc., Hon. Research Fellow, Manchester University*[*].

The law of absorption of β rays by matter has lately been the cause of some discussion. Until the experiments of W. Wilson[†], it had generally been assumed that β rays absorbed exponentially by aluminium were homogeneous. It was shown, however, that the coefficient of absorption of approximately homogeneous β rays rapidly increased with the thickness of matter traversed, which suggests that the rays experience a diminution in velocity as they pass through the aluminium. Crowther[‡] obtained a similar result by the same method.

The decrease in velocity indicated by these experiments has been determined directly[§]. It follows as a necessary consequence of these results that β rays which are absorbed exponentially by aluminium are not homogeneous.

Recently, however, v. Baeyer and Hahn[‖], using a photographic method. have shown that the β rays from several radioactive products initially possess a considerable degree of homogeneity. We have no definite evidence so far that the

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[*] Communicated by Prof. E. Rutherford, F.R.S.

[†] Wilson, Proc. Roy. Soc., A. lxxxii. 1909, p. 612.

[‡] Crowther, Proc. Camb. Phil. Soc. xv. pt. v. p. 442.

[§] Wilson, Proc. Roy. Soc., A. lxxxiv. 1910, p. 141.

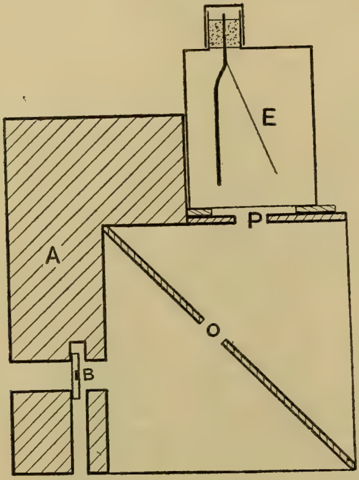
[‖] v. Baeyer & Hahn, *Phys. Zeit.* xi. 1910, p. 488.

rays from such thin layers as they used are absorbed according to an exponential law.

Gray * by the same method showed that the β rays from a thick layer of radium E are distinctly heterogeneous, although they are absorbed according to an exponential law by aluminium. In view of the experiments of v. Baeyer and Hahn the following experiments were performed.

The apparatus is shown in fig. 1 and is similar to that used by Wilson (*loc. cit.*).

Fig. 1.



The rays from the radium E which was placed at B could pass through a hole in a lead block A and into a magnetic field perpendicular to the plane of the diagram. They were bent round in circular paths and passed through holes O and P in lead screens into an electroscope E. The mean radius of the path of the rays was 4 cm. and the diameters of the holes O and P ·8 cm. The ionization in the electroscope was determined for several strengths of the magnetic field, and the results obtained are shown in fig. 2 *a*, where the ionization in the electroscope is plotted against the product of the field strength and the radius of curvature of the path of the rays. If the rays were homogeneous and the holes O and P and the source infinitely small, we should only get ionization in the electroscope for one definite strength of field. Experimentally however, even if the

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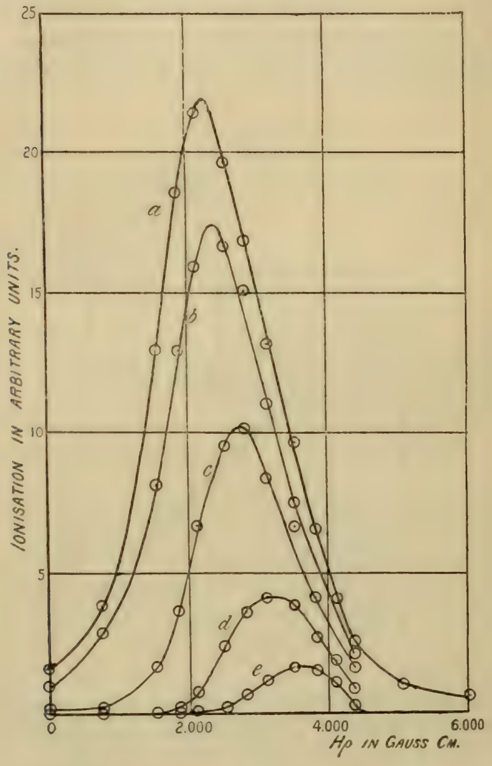
* Gray, Proc. Roy. Soc., A. lxxxiv. 1910, p. 136.

rays were homogeneous we should get a curve somewhat similar to that shown, on account of the necessarily finite size of the holes O and P. The following test of the homogeneity of the rays was therefore applied. A sheet of aluminium of known thickness was placed in the path of the rays just underneath the electroscope, which was about 2 mm. above the hole P, and the experiment repeated. Now if the rays are heterogeneous, those which enter the electroscope with the higher magnetic fields should be less easily absorbed than those which enter with the lower. The maximum point should therefore move to the higher fields when sheets of aluminium are placed under the electroscope. That this is the case is shown unmistakably by the curves of fig. 2, *a*, *b*, *c*, *d*, *e*, which are plotted from the results obtained with 0, ·067, ·245, ·489, ·731 mm. of aluminium respectively under the electroscope. If, on the other hand,

Fig. 2.



the rays were homogeneous there would be no such change, since for any strength of field the percentage change in ionization would be the same for the same absorbing screen.

The change in the position of the maximum is quite marked, being at $H\rho = 2{,}400$ in curve *a*, and at $H\rho = 3{,}650$ in curve *e*.

It will be noticed that the rays which produced the maximum ionization when no aluminium was placed under the electroscope are practically all absorbed by a thickness of ·73 mm. Al, while for rays corresponding to the higher fields appreciable quantities are still transmitted.

In these experiments the bottom of the electroscope was closed by a sheet of tinfoil so that the maximum point even with no aluminium under the electroscope occurs at a rather higher field than it would if no matter whatever were placed in the path of the rays. An experiment was therefore made with a dutch-metal leaf closing the bottom of the electroscope, and the maximum point, which was carefully determined, was found to occur for a value of Hρ 2,200 gauss cm.

This value is in very good agreement with those obtained by Schmidt* 2,200 and Gray 2,300. Experiments made with tin as absorbing medium gave the same type of result.

Absorption curves were taken for rays corresponding to various field strengths and are shown in fig. 3, curves *a*, *b* and *d*, in which the log of the ionization in arbitrary units is plotted against the thickness of absorbing material. The curves are for rays corresponding to $H\rho = 3{,}200$, 2,400, and 1620 gauss cm. respectively. It will be seen that the different pencils of rays have very different penetrating powers, the initial absorption coefficients being 13·0, 22·2, and 62·5 cm.^{-1} for curves *a*, *b*, and *d* respectively.

It is especially significant that bundles of rays forming *a large percentage of the whole* can be separated out which have *initial absorption coefficients much less than that of the whole beam.* If homogeneous rays were absorbed according to an exponential law the absorption coefficient of the whole beam would continually decrease, which is not found to be the case.

The source of radium E was a thick layer of radium D, so that any soft rays are practically all absorbed in the material. As a further precaution the active material was covered with ·1 mm. of aluminium.

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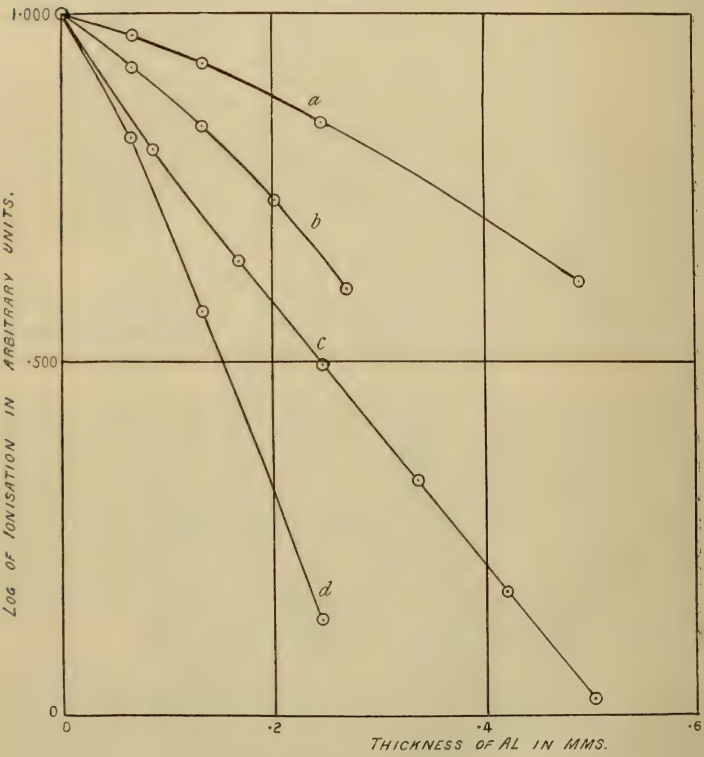
* Schmidt, *Phys. Zeit.* viii. 1907, p. 361.

That the type of absorption curve obtained for homogeneous rays was not due to the arrangement of apparatus was shown as follows. The radium E was placed 6 cms. below the hole P and an absorption curve of the whole bundle of rays taken. The result obtained is shown in fig. 3 curve *c*. The curve is exponential, showing that the apparatus used has no effect on the absorption curves and the absorption coefficient found 42·8 cm.$^{-1}$ is in very good agreement with the results obtained by other observers. The initial drop is due to scattering of the rays and not to the presence of any soft radiation, since the same percentage drop is obtained if various thicknesses of aluminium are placed directly over the radium E and the absorption curve again taken.

Fig. 3.



Conclusion.

It has been shown above that from a pencil of β rays which is absorbed by aluminium according to an exponential law, rays of widely different penetrating powers can be separated out. It follows, therefore, that absorption of β rays according to an exponential law is no criterion of homogeneity. The experiments confirm the results obtained by Gray by the photographic method.

We wish to express our best thanks to Prof. Rutherford for the kind interest he has taken in this research.

Physical Laboratories,
The University, Manchester.
Aug. 19th, 1910.

XCVI. *The Deflexion by an Electrostatic Field of Radium B on Recoil from Radium A.*

By SIDNEY RUSS, *D.Sc.*, *and* WALTER MAKOWER, *M.A.*, *D.Sc.*[*]

Introduction.

IN a previous paper[†] an account was given of some attempts made to determine whether radium C is electrically charged when it recoils from radium B; but the experiments made for this purpose failed to reveal any such charge. The formation of radium C from radium B is accompanied only by the emission of β-particles, and it was thought that a transformation involving the expulsion of an α-particle might afford a more satisfactory case for investigation. Experiments were therefore undertaken on the recoil of radium B from radium A. In this transformation the atom of radium B should be negatively charged after recoil, if the process is accompanied simply by the expulsion of an α-particle, as is usually supposed. If, however, there is a simultaneous evolution of β-particles, the recoiling atom might be electrically neutral or even positively charged. It will be remembered that radium A on formation from the emanation in air at atmospheric pressure does in fact acquire a positive charge, so that it is concentrated on the negative electrode when the emanation is subjected to an electric field[‡]. The following experiments were made with the object of determining whether the radium B is charged when

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[*] Communicated by the Authors.

[†] Makower and Russ, Phil. Mag. Jan. 1910.

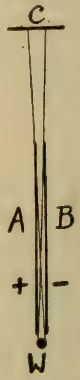
[‡] Rutherford, Phil. Mag. Feb. 1900.

recoils and, if so, its sign; the magnitude of the deflexion of the recoiling atoms by an electric field has also been determined. A great number of experiments has been made by different methods, which show that the "recoil-atoms"[*] of radium B are positively charged. The process of the formation of radium B from radium A would therefore seem to be accompanied by the expulsion of β rays as well as α rays, though the speed of the former may be too small to allow of their detection by ordinary methods.

Preliminary Experiments.

In the earlier experiments, two insulated brass plates 3·5 centimetres long and 1·7 centimetres wide were mounted at a distance of one millimetre apart inside a glass vessel which could be rapidly exhausted to a high vacuum. A platinum wire was exposed to radium emanation for about ten minutes to obtain as much radium A on it as possible and then transferred to a tube which could be quickly exhausted, contained in a furnace at about 400° C. It was found that the emanation adhering to the wire could in this way be completely removed. The wire was then mounted at W, as shown in fig. 1, so that the "recoil-stream" from it was projected symmetrically between the two plates A and B. An electric field could be applied by connecting the two plates respectively to the two terminals of a storage battery by leads sealed through the glass vessel.

Fig. 1.



After ten minutes' exposure *in vacuo* the plates were removed from the vessel and the distribution of activity on each tested by mounting them in turn on a movable platform, and bringing successive strips of the plates under a rectangular window 3 centimetres long and 3 millimetres wide, cut in the base of an electroscope and closed by an aluminium leaf. The α and β radiation from the section of the plate just under the window could thus enter the electroscope, but the radiation from the rest of the plates was prevented by lead screens from contributing to the ionization inside the electroscope. From such measurements the number of "recoil-atoms" projected from the active wire on to the different portions of the plates could be compared. A measure of those undeflected by the electric

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[*] We propose to use this term for brevity, to denote the matter which recoils as the result of a radioactive process.

field was obtained by testing the cross-piece C in a similar manner.

The results of a series of experiments made in this way with different voltages between the plates led us to believe that at least some of the "recoil-atoms" of radium B projected from the wire were positively charged.

To test the correctness of this conclusion with certainty the following experiments were made.

Direct Determination of the Quantity of Radium B deflected by an Electric Field.

The active wire W (fig. 2) was placed symmetrically between two pairs of plates 1·4 millimetres apart and 4 centimetres long adjusted to be in line with each other and contained in a glass vessel which could be evacuated as in the previous experiments. The "recoil-stream" from the wire W was thus projected through the gaps between the two pairs of plates, and fell upon the cross-pieces A and B. Between one pair of plates an electric field was maintained, while the other plates were kept at the same potential. If the "recoil-stream" were charged on leaving the wire, it would be deflected by the electric field, and the plate B should therefore receive less activity than A. Since the radium A on the wire might not have been deposited uniformly by exposure to the emanation, the wire was kept constantly rotated by attaching it to a ground-glass stopper turned by hand and fitted into the containing vessel. After an exposure of ten minutes *in vacuo* to the radiation of the wire, the two cross-pieces A and B were removed and tested by an α-ray electroscope.

Fig. 2.

The number of "recoil-atoms" reaching the plate A through the uncharged plates was always found to be greater than the number reaching B through the electric field. The reduction in the number reaching B depended on the field-strength, being greater the greater the field applied; but although the quantity of radium B reaching the cross-piece B was reduced in this way by the field between the plates, some activity was always found there even with the greatest field used, indicating that part of the "recoil-stream" projected from the wire was undeflected. In view of some subsequent experiments on the magnetic deflexion of radium B it seems probable that this undeflected portion was deposited on the strip during the exhaustion of the apparatus ; owing to the large electric fields used, it was not possible to apply the voltage until the evacuation was almost complete. The fraction of the "recoil-atoms" deflected by the electric field with different voltages between the plates can be seen from Table I.

Table I.

Voltages between plates.	Activity on cross-piece A.	Activity on cross-piece B.
0	100	98
340	100	69·5
340	100	68·5
1110	100	50
1180	100	38

Magnitude of the Electric Deflexion.

Having established that the "recoil-stream" in a high vacuum is deviated by an electric field, it remained to determine the magnitude of the effect, to see whether the observed deflexion is in agreement with that calculated on the following simple assumptions. Since radium B is formed from radium after three successive stages, at each of which an α particle is evolved, then since the atomic weight of radium is 226 and that of helium 3·96, the atomic weight of radium B should be 214 according to this view. Taking this value, then, if the velocity of the α particle from radium A is taken as $1{\cdot}77 \times 10^9$ centimetres per second*, we obtain from the equation of momentum the value $3{\cdot}27 \times 10^7$ centimetres per second for the velocity of the "recoil-atoms" of radium B. Assuming, further, that the atoms of radium B on recoil each carry with them $4{\cdot}65 \times 10^{-10}$ electrostatic unit (the charge carried by the hydrogen ion in electrolysis), it is easy to calculate the radius of curvature of the particles when passing through an electrostatic field applied at right angles to the direction in which they are travelling.

A number of experiments made to measure the magnitude of the deflexion of the "recoil-atoms" of radium B in an

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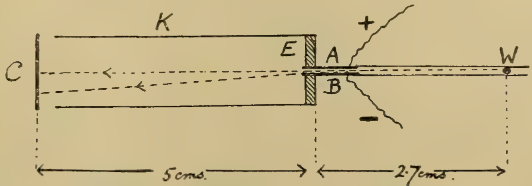
* Rutherford, Phil. Mag. Oct. 1906.

electric field gave inconclusive results; for it was found that surfaces, even though situated so that they could receive no direct radiation from a source of radium A, became active. It is unnecessary here to enter into a discussion of the mechanism by which this occurs.

It thus appeared that no reliable results could be obtained unless the possibility was excluded of much active matter reaching the receiver by methods other than direct radiation. The apparatus shown in fig. 3 was therefore designed to obviate this trouble.

Fig. 3.

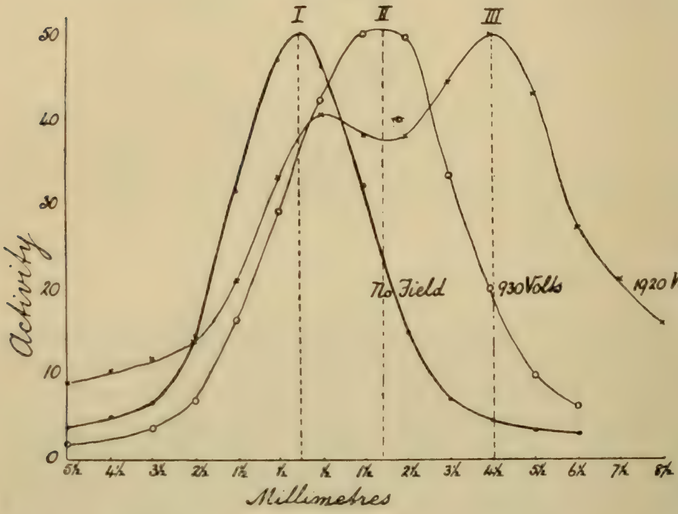


The wire W was mounted between two parallel mica strips 2 centimetres long, coated with copper plates kept at the same potential. The "recoil-stream" from the wire passed from the region between the two copper plates where no electric field existed into the space between the two parallel brass plates A and B, 9·4 millimetres long, between which a difference of potential was maintained. The plates A and B fitted into the ebonite plug E and were 1·17 millimetres apart. The copper cylinder K, which was 4·5 centimetres long and fitted over the ebonite plug E, prevented the "recoil-stream" from being subjected to an electric field after leaving the space between the plates A and B. The "recoil-stream" subsequently fell on a brass strip C, 2 centimetres long, situated 5 millimetres from the end of the copper tube.

To carry out an experiment the wire W was exposed to a large quantity of emanation for ten minutes, transferred to a vessel at 400° C. which could be quickly evacuated to remove adhering emanation, and then mounted as shown in fig. 3. The whole apparatus just described was contained in a glass tube which could be exhausted to a pressure of about 1/300 millimetre of mercury within two minutes, after which the electric field could be applied between the plates A and B without fear of a discharge taking place through the residual gas in the tube. The difference of potential between A and B was determined by a direct-reading electrostatic voltmeter. After an exposure of ten minutes to the "recoil-stream" from the wire, the distribution of activity over the strip was tested in a manner similar to that described for the preliminary experiments, except that the width of the aluminium window in the base of the α-ray electroscope was reduced from 3 millimetres to 1 millimetre.

The distribution of activity on the strip is shown in fig. 4 for three typical cases when no field was applied between the plates and with 930 and 1920 volts respectively. To show that there was no lack of symmetry in the disposition of the apparatus, measurements were also made with the field reversed. The results so obtained were in substantial agreement with those shown in the diagram.

Fig. 4.



It will be seen that with no field the activity of the strip exhibited a well-marked maximum at its middle, while the activity fell off rapidly and symmetrically on either side. With 930 volts the point of maximum activity was displaced 2 millimetres, but the distribution was no longer symmetrical about the maximum. With 1920 volts the curve of distribution showed two maxima, one near the centre of the strip and the other about 4 millimetres from the centre.

It is not clear what is the cause of these two maxima, but one maximum always occurred at the middle of the plate and was therefore due to "recoil-atoms" which probably for the reason already suggested, reached the plate without being deflected. The distance between the two maxima was taken as a measure of the deflexion of the "recoil-stream" while passing through the electric field. Although this procedure does not give accurate values, it serves to show the order of magnitude of the deflexion.

TABLE II.

Voltage between plates.	Displacement of maximum observed, in millimetres.	Displacement of maximum calculated, in millimetres.
930	2·0	1·62
1680	3·9	2·94
1860	4·5 *	3·25
1890	4·0	3·31
1920	4·1	3·36

* In this case the readings were small and correspondingly more uncertain than in the other experiments.

If the velocity of the "recoil-atoms" of radium B is assumed to be $3{\cdot}27 \times 10^7$ centimetres per second, as calculated on p. 878, it is possible to deduce the deflexion to be expected on certain simple assumptions. For the particles projected from the wire will have a parabolic path as they pass between the two charged plates, and will proceed along the tangent to the parabola at the point at which they emerge from the electric field until they ultimately strike the strip mounted to receive them. From the known dimensions of the apparatus it is a matter of no great difficulty to calculate the displacements to be expected on the strip for different voltages applied between the plates, assuming that the value of $\frac{e}{m}$ for the hydrogen ion in electrolysis is $9{\cdot}63 \times 10^3$ on the electromagnetic system, that the charge carried by the atom of radium B is the same as for the hydrogen ion in electrolysis, and that its mass is 214.

There is, however, one source of uncertainty in making the calculation; for since the length of the plates was only 9·4 millimetres, which is not very great compared with their distance apart, which was 1·17 millimetres, the field must spread out appreciably at both ends. The corrections for the end effects in cases similar to that of our experiments have been worked out by Coffin[*], and it was estimated that on this account the *effective* length of the plates in our experiments was about four per cent greater than their actual length. In the calculation the value 9·8 millimetres has therefore been taken as the length of the plates instead of their real length, 9·4 millimetres, and the numbers given in column 3 of Table II. were thus obtained.

An inspection of the calculated and experimental deflexions shows them to be of the same order of magnitude, and we may therefore conclude that if radium B carries the unit charge of electricity, its atomic weight is of the order to be expected on the disintegration theory of radioactivity.

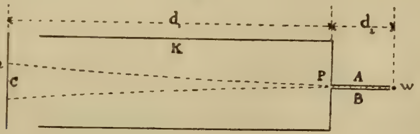
Our thanks are due to Professor Rutherford not only for supplying us with the radium emanation necessary for the experiments, but also for his interest in the work.

XCVII. *The Deflexion by a Magnetic Field of Radium B on Recoil from Radium A. By* W. MAKOWER, *M.A.*, *D.Sc.*, *and* E. J. EVANS, *B.Sc.*[†]

[Plate XVIII.]

IT has been shown by Russ and Makower[‡] that radium B is positively charged when it recoils from radium A and that the "recoil-atoms" can be deflected by an electric field. Some experiments have lately been made to measure the deflexion suffered by the radium B when it passes through a strong magnetic field. For this purpose a powerful electromagnet was constructed[§] capable of giving 10,000 lines per square centimetre over an area 9 cm. by 5 cm., with the poles 2 cm. apart. A glass tube of 2 cm. external diameter containing the apparatus shown in fig. 1 was placed in this gap between the poles; the glass vessel could be rapidly

Fig. 1.



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[*] Coffin, Proceedings American Academy, xxxix. No. 19, 1903.

[†] Communicated by the Authors.

[‡] Russ and Makower, Phil. Mag. *supra*, p. 875.

[§] We are indebted to Dr. R. Beattie for designing and supervising the construction of this magnet.

evacuated when required. The wire W, of diameter 0·5 mm., coated with radium A by exposure to the emanation for ten minutes, was placed at the end of the aperture between the two metal plates A, B, 1 cm. long and 0·5 mm. apart. The "recoil-stream" from W passed through this aperture and fell upon the plate C. The metal tube K served to prevent disturbances by stray electric charges on the glass of the containing vessel. In its path of 7·1 cms. from W to C, the recoil-stream was exposed to a uniform magnetic field.

To carry out an experiment the active wire W was mounted in the position shown in fig. 1, the glass tube was evacuated as quickly as possible, the magnetic field applied and the recoil-stream from W allowed to pass between the plates A and B and fall upon the metal strip C. The distribution of the activity on the plate C was subsequently measured in exactly the same manner as in the experiments on the electrostatic deflexion by means of an α-ray electroscope. To obtain the magnitude of the deflexion suffered by the radium B while passing through the magnetic field, two experiments were performed, one as described and a second one with the field reversed. The distribution of activity over the plate in these two experiments is shown in Pl. XVIII. fig. 2, curves I. and II. respectively. Now it had been shown by other experiments that the strip C and wire W could be removed and replaced very nearly in the same position, so that the distance between the positions of maximum activity in the two experiments just described, gives twice the deflexion suffered by the recoil-stream in each experiment. It will be seen from fig. 2 that the distance between the two maxima is ·645 cm. The paths of the recoil-streams are circles and the positions of maximum activity Q and R on the strip C are due to matter projected from W describing circular paths passing through WPQ and WRP respectively. If $PC=d_1$ and $WP=d_2$, then if $QR=d$ and ρ is the radius of curvature of the path of the rays, we have that

$$d\rho=d_1\ (d_1+d_2).$$

Since $d_1=6{\cdot}1$ cm. and $d_2=1$ cm., it follows that

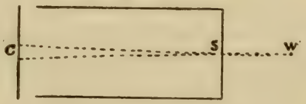
$$\rho=67{\cdot}2 \text{ cm.}$$

Since for the experiments described the strength of the magnetic field was 10,800 gauss we have, with the ordinary notation, that

$$\frac{mv}{e}=\mathrm{H}\rho=7{\cdot}26\times 10^5.$$

The method of finding Hρ just described is, however, open to certain objections, for it is necessary to make two separate experiments with a direct and reversed magnetic field in order to obtain the deflexion suffered by the recoil-streams. A further disadvantage is that a somewhat large aperture of width, 0·5 mm., was used. Some other experiments were therefore made as follows with a narrower slit and finer wire. The apparatus used is shown in fig. 3.

Fig. 3.



An active wire W of diameter 0·3 mm. was mounted as shown in the figure, 1·25 cm. from the slit S which was 3·6 cm. from the strip C placed to receive the recoil-atoms. The whole apparatus was enclosed as before in a glass vessel which could be quickly evacuated and placed between the poles of the electromagnet. The wire W was fixed in position, the field applied and the glass vessel quickly evacuated, and the radium B recoiling from the radium A on the wire allowed to fall on the plate for three minutes. The field was then reversed and the recoil allowed to proceed for another seven minutes until the radium A on the wire had decayed to an inappreciable quantity. The strip C was then removed and placed on a photographic plate in the dark. The radium B distributed over the strip would itself have little or no effect on the photographic plate, but as it decayed radium C was produced *in situ*, and this by reason of the rays given out by it made an impression on the plate which could be developed in the ordinary way. The result of this experiment is shown in fig. 4 (Pl. XVIII.). The two bands on the plate are due to the radium B reaching the plate with the direct and reversed magnetic fields respectively. It will be noticed that the bands are of considerable width and their edges not sharp, indicating that the particles of radium B on reaching the metallic strip are scattered before being stopped. That this should be so was to be expected considering the relatively low velocity with which the particle must travel. In spite of this scattering, however, it is possible to measure the distance between the middles of the two bands with reasonable accuracy by the method of projecting an image of the photograph on to a screen by means of a lantern and measuring the magnification thus produced in a manner similar to that adopted by Rutherford in his experiment on the magnetic deflexion of the α-particles *.

The distance between the bands was in this way found to be 2·86 mm. Since $d_1=3{\cdot}6$ and $d_2=4{\cdot}85$ we have as above

$$\rho=61,$$

and since the field was 10,700 gauss, we have

$$\frac{mv}{e}=\mathrm{H}\rho=6{\cdot}52\times10^5.$$

This value is certainly more reliable than that obtained by the first method described above, and is in fair agreement with it.

It is of interest to compare the value of Hρ obtained with that to be theoretically expected. Now the momentum of the recoil-atom of radium B which is produced on the emission of an α-particle from radium A must be the same as the momentum of this α-particle, since an atom of radium A gives out only one α-particle when it is transformed into radium B. It therefore follows that if the charge carried by radium B on recoil is the same as that carried by an α-particle, the value of Hρ for the radium B should be the same as for the α-particle from radium A. Now it has been shown by Rutherford † that the value of Hρ of this α-particle is $3{\cdot}48\times10^5$ or nearly half that for the recoil-atom of radium B. It therefore appears that the charge carried by the radium B is half that on an α-particle, or, in other words, the atom of radium B carries with it the same charge as the hydrogen ion in electrolysis; for it is known that the α-particle is associated with twice that charge ‡.

Although the experimental values so far obtained are not of very great accuracy, it is possible to calculate from the electric and magnetic deflexions of radium B the velocity of these particles and the value of $\frac{e}{m}$. Since the charge carried by the particles has been shown to be the same as that carried by the hydrogen ion in electrolysis, a knowledge of the latter quantity gives the atomic weight of radium B.

Taking the path of the particles in an electric field as approximately circular, from the experiments of Russ and Makower we have that with a field of 16,250 volts per

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* Rutherford, Phil. Mag. Aug. 1906.

† Rutherford, Phil. Mag. Aug. 1906.

‡ Rutherford and Geiger, Proc. Roy. Soc. A., vol. lxxxi. 1908.

centimetre the radius of curvature was 12·9 cm. Thus, using electromagnetic units,

$$\frac{mv^2}{e} = 2{\cdot}1 \times 10^{13},$$

and taking the result obtained from the photographic method of measuring the magnetic deflexion, we have

$$\frac{mv}{e} = 6{\cdot}5 \times 10^5.$$

Hence $v = 3{\cdot}23 \times 10^7$ centimetres per second and $\frac{e}{m} = 49{\cdot}7$.

Now since for the hydrogen ion in electrolysis $\frac{e}{m} = 9{\cdot}6 \times 10^3$ the result of these experiments gives the value for the atomic weight of radium B as 194. Considering the difficulty of the experiments this number is in good agreement with the theoretical value 214. Also it will be noticed that the velocity of the particles has very nearly the value $3{\cdot}27 \times 10^7$ centimetres per second, calculated on the assumption that the momentum of the recoil-atoms of radium B is equal to that of the α-particle causing it to recoil, and that the atomic weight of radium B is 214.

It is with pleasure that we take this opportunity of thanking Professor Rutherford for the facilities he has afforded us for carrying out these experiments in his laboratory and also for many valuable suggestions during the course of the work.

XCVIII. *Groove-Form and Energy Distribution of Diffraction Gratings.* By AUGUSTUS TROWBRIDGE, *Professor of Physics, Princeton University, and* R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University**.

PRACTICALLY no rigorous investigation has ever been made of the distribution of energy among the spectra of different orders formed by a diffraction grating, as a function of the wave-length of the light and the form of the grooves. The chief obstacle in the way of such a study is the difficulty of obtaining an exact knowledge of the nature of the furrow cut by a diamond point upon a surface of glass or speculum metal. Microscopical examination teaches us very little or nothing in the case of such fine markings, and it is not safe to infer that the groove will conform at all to the ruling point.

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* Communicated by the Authors.

It occurred to one of us that a promising method of attack would be to stamp or rule gratings with such wide grooves that their form could be determined with certainty, and then investigate the energy distribution among the spectra with very long heat-waves, *i. e.* with "residual rays" of various wave-lengths.

The manufacture of these echelette gratings, and their behaviour with visible light, have been described in a preceding paper *.

The investigation was made with the large vacuum spectro-bolometer described in a previous paper by one of the present writers †. The gratings were mounted on the table of the instrument, and the slit illuminated with the radiant energy in question. Two groups of rays were used in the investigation, the residual rays from quartz with a mean wave-length of 8·6 μ and the CO_2 radiation from a Bunsen flame, with a wave-length of 4·3 μ or about half as great as that of the quartz rays. The smallest grating constant used was 0·0123 mm., or seven times the width of the grooves on the gratings ruled on Rowland's first machine, the largest, ·05 mm. It is evident that when these gratings are used with the long heat-waves above referred to, the ratio of the grating constant to the wave-length is about the same as that which obtains in the case of visible light and the optical gratings in common use. The nature of the ruled surface of the echelette gratings used in the present investigation, and the method by which it was studied, have been described in the previous paper.

In order to make a thoroughly satisfactory study of the distribution of the energy it would be advisable to keep the angle of incidence fixed (for example normal) and swing the bolometer or thermopile through the spectra. With the instrument at our disposal at the present time this was impossible, and it was necessary to make the spectra pass across the bolometer by rotating the grating. This complicates the discussion of the results in no small degree, for the energy distribution varies with the angle of incidence, as can be seen easily with an ordinary grating. We have, however, already obtained results which are in qualitative agreement with theory, and which show that the method is admirably adapted to the experimental investigation of the problem. We shall, in the present treatment, discuss the results by the Fresnel method, considering the interference between secondary wavelets originating on the surface of the

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* *Supra*, p. 770.

† *Supra*, p. 768.

wave-fronts reflected from the oblique edges of the grooves. As Lord Rayleigh has pointed out, this method holds only when the width of the groove considerably exceeds the wave-length of the light.

In the present case, with our closest ruling, the groove-width was 1·5 times the wave-length of our longest waves, and it appears probable that in this case we are very near, if not beyond the point, at which we may safely employ the Fresnel treatment.

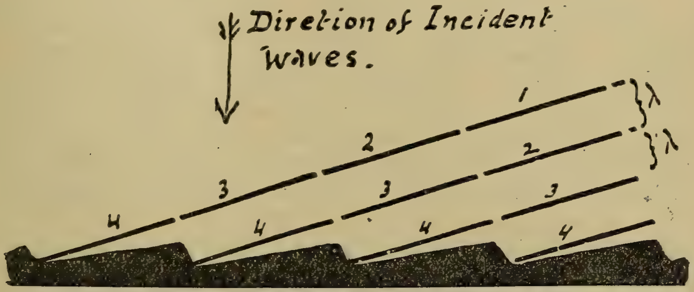
In continuing the work it is our intention to employ waves of continually increasing wave-length, until the point is reached at which the spectra disappear entirely, which will give us the complete experimental solution of each case.

In the case of the echelette grating the conditions are quite different from those which obtain in the case of the gratings usually considered, which act by opacity. For a wire grating, or a reflecting grating made by ruling black lines on a reflecting surface, the spectra of even order fall out when the widths of the operative and inoperative elements are equal. In the case of the echelette grating, practically the whole surface is operative, and if we place the eye, or better the objective of a microscope (focussed upon the grooves in the direction of a spectrum) we see a uniform blaze of light illuminating the entire surface. This means that the widths of the reflected elements of the wave-front are twice as wide as in the case of a grating of the opaque type having the same constant.

Now in a grating of this type the spectra of even order disappear when $a=b$, as a result of the circumstance that in the directions of these spectra each diffracted wave front is *self destructive*, i. e. these directions are the directions of Fraunhofer's minima of the first class, namely such as will make the path difference between the disturbances coming from the two edges of each reflecting element equal to the wave-length of light. In the case of the reflecting grating with its opaque strips, if we widen the reflecting strips and narrow the opaque ones, keeping the constant the same, the direction of the first class minima will move in towards the first order spectra, which will disappear when the opaque strips become infinitely narrow. The same thing, however, holds for all the other spectra, for as we widen the reflecting strip the first class minima draw closer together, coinciding with the spectra of the second class (grating spectra) in the limiting case of opaque lines infinitely narrow. If, however, we *narrow* the reflecting strips, keeping the grating space constant, the first class minima move out and presently the spectra of the third and sixth orders disappear.

Going back now to the echelette grating we find that in the ideal case, in which the reflected fronts build up an unbroken surface (*i. e.* with no inoperative or dark regions between them) we should expect all of the light in one spectrum, namely the one lying in the direction in which the reflected wave-fronts are travelling, the case being analogous to the reflecting grating with infinitely narrow opaque lines, except that in this case we find the light in a spectrum instead of in the central image. We must remember, however, that in this case we have chopped up the wave-front into linear strips, and that our reflected wave-front is built up of strips obtained from successive waves, as can be seen from fig. 1, in which we have the reflexion of a train of four waves, numbered 1, 2, 3, and 4 from the echelette grooves. It is very questionable whether the upper wave-front 4, 3, 2, 1, will behave as a plane-wave, *i. e.* travel out without diffraction, for each one of the elements of which it is composed has had to travel one or more wave-lengths before uniting with its neighbour.

Fig. 1.



This is a question, however, which can be best answered by experiment. In the paper on the Echelette grating the opinion was expressed that a concentration of light could not be obtained in a region narrower than that covered by the diffraction range from a single reflecting element*. Further consideration shows that this is not the case, for in the ideal case shown in fig. 1 the maxima of the first class coincide in position with the minima of the second class, and *vice versa*. In the case figured the reflected waves are travelling in the direction of the first order spectrum, and the path-difference between the successive elementary wave-fronts is λ.

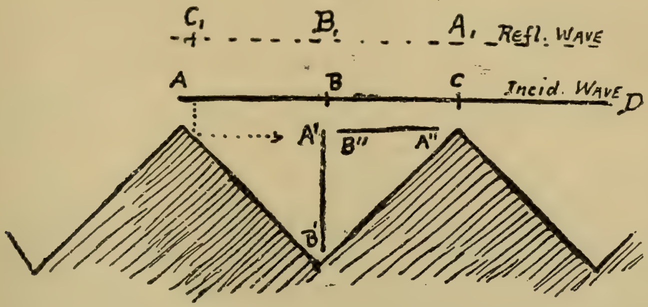
* *Supra*, p. 777.

Neglecting the probable disturbances in phase continuity resulting from the breaking up of the wave into narrow strips, we should expect all of the energy in the first order spectrum. If, however, we work with waves twice as long, the path-difference will be $\frac{\lambda}{2}$ instead of λ and we should find the energy about equally divided between the central image and the first order spectrum, which in this case will lie well to the left of the direction in which the reflected waves start. Grating No. 8, which will be described presently, comes the nearest to fulfilling these conditions of any thus far examined. With waves $4{\cdot}3\,\mu$ in length the first order spectrum lies nearly in the direction of the reflected waves, and contains 70 per cent. of the energy. With the "Reststrahlen" from quartz ($\lambda = 8{\cdot}6$) we have 34 per cent. in the first order spectrum and 66 per cent. in the central image. The preponderance in the central image is due to the fact that the "oblique image" (direction of reflexion) lies nearer to the central image than the first order spectrum for $8{\cdot}6\,\mu$.

A large number of gratings have been examined and the work is not yet completed. For a complete solution of each case, it is necessary to know whether any of the original flat surface has been left between the grooves. This is often the case with the coarser rulings, and results in the formation of strong central images when the gratings are examined with visible light. Each grating element may thus consist of three strips, the two edges of the groove and the flat portion between. Thus far, but a single type of groove has been tried, viz. the one ruled by the 120° carborundum crystal. The angle at which the crystal was mounted with respect to the surface has, however, been varied over a wide range, as well as the depth of the groove, &c. Other types of grooves will be investigated with a view of finding the one best suited for work in the infra-red. It seems probable that a 90° groove will be the best, as with a groove of this type one edge can be made almost inoperative, and a larger proportion of the surface brought into play. A symmetrically placed 90° groove with the light incident normally will be an interesting type to investigate, for in this case we have a two-fold reflexion in the groove, each element of the plane wave being broken into two, which are turned end to end and reunited, as can be seen by constructing the reflected rays for a surface of this nature. A 90° double mirror has the property of returning a twice-reflected ray back to its source, regardless of its direction, provided it cross the groove in a direction perpendicular to the groove.

In fig. 2 let AB be a portion of the plane wave AD incident upon the grooved surface. After the first reflexion it

Fig. 2.



will occupy the position A′B′, and after the second A″B″. The portion BC will be reversed in the same way, and the two portions will unite into the wave $C_1B_1A_1$. It seems, therefore, as if a surface of this nature would not interfere with the constancy of the phase along the wave-front, notwithstanding the fact that the wave has been chopped to pieces, and the pieces made to change places. This being the case, it appears as if we should have no diffraction spectra at all, in spite of the deep furrows.

Just how a surface ruled with grooves of this type, with perfectly smooth reflecting sides meeting in a sharp edge, would behave is perhaps open to question. Whether a wave can be broken up into paired strips, reversed, and reunited into a plane wave without suffering diffraction, is a question which can probably be answered only by experiment. It seems possible that many of the anomalies exhibited by reflecting gratings can be explained by a two-fold or even multiple reflexion from the groove. It is doubtful, however, if multiple reflexions can be considered as taking place in a groove commensurable in size with the wave-length. The investigation of gratings of this type will be taken up later. The present paper deals only with the behaviour of the 120° groove.

We will now take up the individual behaviour of the gratings which have been investigated up to the present time.

The arrangement of the apparatus was as follows :—The light from a Nernst filament, rendered parallel by a concave mirror, was reflected from three large polished surfaces of quartz and focussed upon the slit of the vacuum spectro-bolometer by a second concave mirror. The diffraction spectra were caused to pass across the bolometer strip by revolving the grating, which made the incidence angle vary, and necessitated the use of the formula for fixed telescope and collimator and rotating grating. Each grating was studied with the quartz residual rays, and with the CO_2 radiations, and the curves representing intensity distribution plotted. The areas of the curves were measured with a planimeter to determine the total energy in each spectrum. The "central image" curve was always very much higher than any spectrum curve, but owing to its narrowness frequently contained much less energy; in other words, we cannot take the deflexion at the central image, and in a given spectrum, as a measure of the energy distribution, since the radiation is not monochromatic. The curves were plotted on large sheets of coordinate paper, and cannot be reproduced very well, even on a greatly reduced scale. It has seemed best, therefore, to make a small chart, showing in a rather qualitative manner the positions and magnitudes of the spectra of different orders, obtained with each grating. Dotted lines represent the CO_2 radiation (wave-length 4·3), solid lines the quartz rays (wave-length 8·6). To save space the central image curve, the height of which is sometimes 70 or 80 times the width at the base, is shown on a much smaller scale.

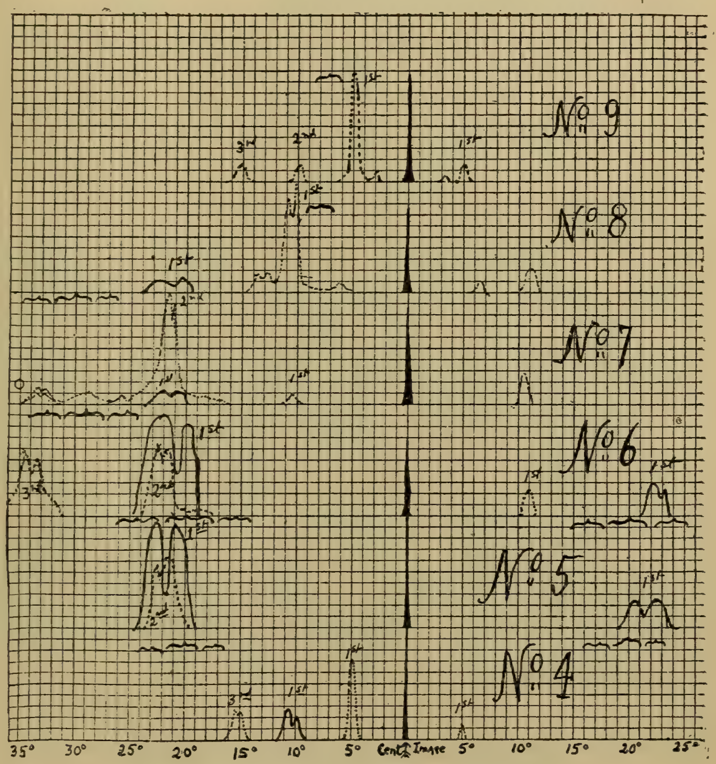
We will now take up the gratings individually.

Grating No. 4. Constant, 0·0265.

This grating was ruled on Rowland's oldest machine fitted with a 15-tooth cam. The constant is therefore 15 times as large as that of the usual gratings. The reflecting planes made angles of 20°·5 and 27°·5 with the original surface. Examination with the microscope, by the red and green light method, described in the paper on the echelette grating, showed that both reflecting surfaces were good, and that the grooves were separated by strips of the original surface, which appeared black under the microscope, and were of such a width that the 27°·5 edge (red) plus the black strip, was equal to the width of the 20°·5 edge (green), a matter of importance in connexion with the disappearance of the second order spectrum. The grating upon the whole is neither a very satisfactory nor an interesting one. It concentrates light both to the right and left of the central image, giving the brilliant spectra of the first class alluded to in the previous paper, at angles of 40° and 55° for normal incidence. In each case the important thing to determine is the position of the heat-ray spectra with respect to the blaze of light

(1st class spectra) reflected by the oblique edges of the grooves. If one edge of the groove makes an angle of 20° with the original surface, and the light is incident normally, the blaze of light, or the oblique image as we will term it hereafter, is seen at an angle of 40°. In the case of the spectrometer readings, it will be found 20° from the central image, since, when the grating turns with the circle through a given angle, the ray turns through the double angle. The angular position of the oblique image on our chart (fig. 3) is therefore given by the angle of the edge of the groove. It has been indicated by brackets. In the case of very coarse rulings it is merely an image of the source, but slightly diffused by diffraction; with the finer rulings we have the broad maxima and minima of the first class (the positions of the superposed patterns due to the individual reflecting strips or the so-called oblique images, are indicated by brackets in fig. 3).

Fig. 3.



In the case of grating No. 4, the heat-ray spectra were found between the oblique image and the true central image, as will be seen from the chart. The explanation of this is not clear and it seems probable that some grave mistake was made in its examination.

It will be necessary to repeat the observations with this grating, for no spectra were found to the right of the central image, with the exception of a very weak one of the first order, with the CO_2 rays, and we should expect strong ones in the position of the oblique image at 27°·5.

The distribution of intensity was as follows:—

Total area of central image and spectra...	100
Quartz rays, first order, left	36
Central image..................	64
CO_2 rays, first order, left	32
third ,, ,, ...	12
Central image..................	46

The absence of the second order with the CO_2 rays probably results from the circumstance that the widths of the reflecting edges are equal to the inoperative surface between them. There are therefore gaps between the reflected wavelets as in the case of a wire grating for which $a=b$, and the spectrum of two orders higher or lower than the one in the direction in which the waves travel will fall out, *i. e.* the waves are self-destructive in these directions. The oblique image lies in the direction of the 4th order spectrum for the CO_2 rays, consequently the 2nd order should be absent as was found to be the case. It is interesting to see that with quartz rays we have a strong first order spectrum at this point. Our failure to find a strong 2nd order spectrum for quartz rays, and 4th order for CO_2 rays, in the direction of the oblique image probably resulted from our failure to rotate the grating sufficiently to bring this region upon the bolometer.

Grating No. 5. Constant, 0·0123 mm.

Angle of reflecting planes, 22° and 30°. Microscopical examination showed that the 30° planes were very poor reflectors; they appeared covered with dark patches, showing that the surface was very ragged and there was no oblique image to the right of the central image, which was wholly absent with visible light. With the heat rays the intensity distribution was as follows:—

Quartz Rays.		CO$_2$ Rays.	
First order, left ...	63	Second order, left	46
„ „ right ...	7	Central image ...	54
Central image	30		

In this case the slit width was 0·5 mm., and the width of the bolometer strip was 0·5 mm., so that the resolving power was high. The deflexions of the galvanometer could be repeated with an error of less than 1 mm. (with total deflexions of 35 mm.).

The first order spectrum for the quartz rays falls exactly in the direction of the oblique image, and contains 63 per cent. of the energy. With visible light there is scarcely a trace of any central image, practically all of the light going into the oblique image, yet with the heat-rays we find the central image quite strong. This is what we should expect, for the heat-rays are diffracted by the edges of the grooves to the same extent as are light-waves by an ordinary optical grating, and the concentration is not complete even when the direction of a spectrum coincides with that of the oblique image.

With the CO$_2$ rays the first order spectra are absent. This is in agreement with theory, for if we draw the reflected wave-fronts moving off at an angle of 44°, and make their width such as would obtain with a grating constant of ·0123 and angles such as specified, we find that if we reduce their width a trifle the path-difference between the disturbances coming from their edges, in the direction of the first order spectrum, is exactly λ.

We should, however, expect the central image to very nearly disappear from the same circumstance, for in this case the path-difference will be 2λ. Its appearance is probably due to the circumstance that the ideal condition of fig. 1 is not fulfilled, *i. e.* there is a narrow dark region between the reflected wave-fronts. We have moreover disturbances from the other edges of the groove which have not been taken into account.

Grating No. 6. Constant, ·0123 mm.

Angles of Reflecting Planes, 18° and 29°.

The 18° edge was bad, showing little reflexion with visible light. The oblique image had a blue central maximum, bordered by red and yellow maxima. This peculiarity has been discussed in the previous paper, and was found to result from the circumstance that the 29° edge was double. The intensity distribution was as follows:—

Quartz Rays.		CO$_2$ Rays.	
Central image	17	Central image......	16·8
First order, left ...	57	2nd order, left ...	37
„ „ right ...	26	3rd „ „ ...	39
		1st „ right ...	7·2

The oblique image lies at 29° to the left, midway between the 2nd and 3rd order spectra of the CO$_2$ rays, consequently they contain very nearly the same amount of energy. The first order to the left is absent, but it is present on the right-hand side, though feeble.

The quartz rays show a remarkable concentration in the first order spectrum which contains 57 per cent. of the total energy. With the CO$_2$ rays we again find concentration owing to shorter wave-lengths, for the two spectra, which lie symmetrically to the right and left of the oblique image, contain together 76 per cent. of the energy.

Grating No. 7. Constant, ·0123 mm.

Angle of Planes, 30° and 20°.

The 20° planes were rough, reflected poorly, and gave no oblique image. The 30° planes were excellent, and there was no visible central image. The intensity distribution was as follows:—

Quartz Rays.		CO$_2$ Rays.	
Central image ...	52	1st order, left ...	2
First order	48	„ „ right...	6
		2nd „ left ...	63
		3rd „ „ ...	6
		Central image ...	23

Here again we have the first order spectra practically absent for the CO$_2$ rays, while the second order contains 63 per cent. of the total energy, the largest thus far obtained. The third spectrum in this case is very weak.

With grating No. 6 the 2nd and 3rd order spectra were of equal intensity, yet there is very little difference between the gratings when examined optically, except the very inferior reflecting power of the 20° planes in the case of No. 7. Owing to the powerful concentration of the energy in the 2nd order spectrum, fainter outlying parts of the CO$_2$ band appear reaching nearly to the 3rd order spectrum of the strong portion.

Grating No. 8. Constant, ·0123 mm.
Angle of Planes, 8°.

In this case the angle of the reflecting planes is so small that the maxima and minima of the oblique image meet the grating spectra to the left of the central image. These grating spectra and the central image are strong, and the colour distribution is most remarkable. The spectrum of the 3rd order, for example, may contain only green light, while another contains only red and blue, as shown by a coloured plate in the forthcoming edition of 'Physical Optics' (Wood's).

The intensity distribution with the heat-rays is as follows:—

Quartz Rays.		CO_2 Rays.	
Central image ...	66	Central image ...	22
1st order, left ...	34	1st order, left ...	70
		,, ,, right ...	8

In this case we find, for the CO_2 rays, the second order absent, and a very strong first order, which lies very near the point towards which the energy is thrown by the 8° reflecting planes. As in the previous case, the CO_2 band appears wide and distinctly resolved into a double band at the centre. The oblique image lies nearer to the central image than the first order spectrum for the quartz rays, consequently it receives the larger portion of the energy.

This grating has been already discussed in connexion with the theory.

Grating No. 9. Constant ·0265 mm.

The angle of the reflecting planes was very small, about 6°, and most of the energy appears in the first order spectrum from the CO_2 rays, which were the only ones used in this case.

The distribution of intensity was as follows :—

First order, left	40
Second ,, ,, ...	9
Third ,, ,, ...	10
Central image	32
First order, right	9

Here again we have concentration of energy in the first order spectrum as a result of the small angle of the reflecting planes.

Summary of Results.

The results obtained thus far appear to be in excellent agreement with theory, and indicate that the method gives reliable experimental data regarding the distribution of energy as a function of the groove form. It indicates that diffraction of the radiation from the reflecting planes prevents us from concentrating all of the energy in a single spectrum, but that with a properly sloped edge we can utilize as much as 70 per cent. of the energy.

This paper is intended only as a preliminary communication, and the investigation of grooves of other forms will be taken up next. A more exact knowledge of the precise nature of the ruled surface is desired, and preliminary experiments have shown that it can be obtained by making sections with a microtome of celluloid casts of the surface. These combined with the microscopical examination with red and green light, and spectrometer determinations of the groove angles, will give us a very complete idea of the furrow.

In the future it is planned to use more homogeneous radiation, by spectral decomposition of white light with a rock-salt apparatus, and study each grating with a wider range of wave-lengths. This will enable us to pass by gradual stages from the energy distribution obtained with the quartz-rays to that obtained with the CO_2 radiation.

XCIX. *Note on Infra-Red Investigations with the Echelette Grating. By* AUGUSTUS TROWBRIDGE, *Professor of Physics, Princeton University, and* R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University**.

IN the preceding paper we have reported a preliminary study of the distribution of intensity among the spectra of different orders furnished by the echelette grating. In the present note we propose to show that these gratings give us the highest resolving power that has yet been brought to bear upon the remote infra-red region of the spectrum. The form of the intensity curve of the "Reststrahlen" reflected from quartz, discovered by Rubens and Nichols, is shown in fig. 1, *a*, which is from a figure given by Coblentz. The longer wave-length maximum is considerably higher than the short wave-length one, and the minimum between is very shallow. A curve of practically the same form has been obtained in all other investigations. In fig. 1, *b* is shown the curve obtained with the echelette grating. The maxima are

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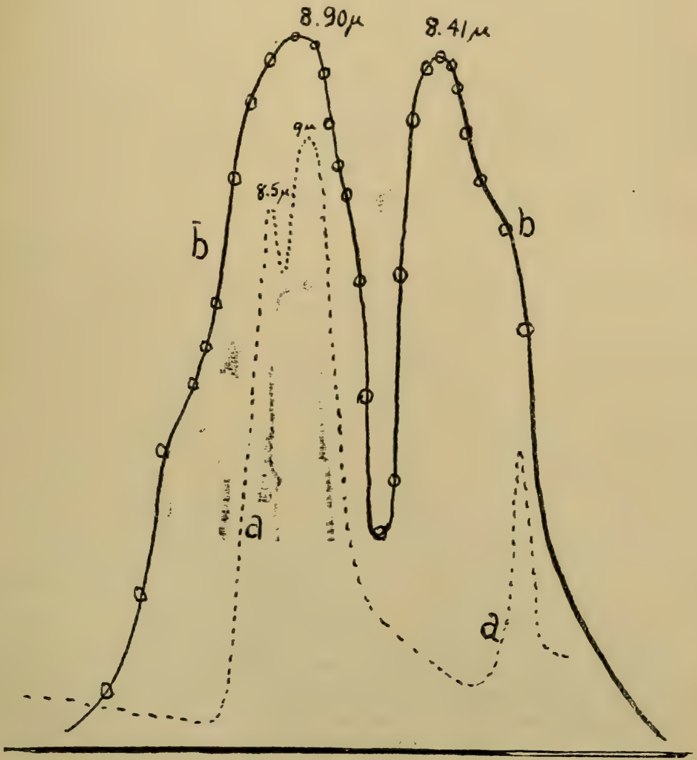
* Communicated by the Authors.

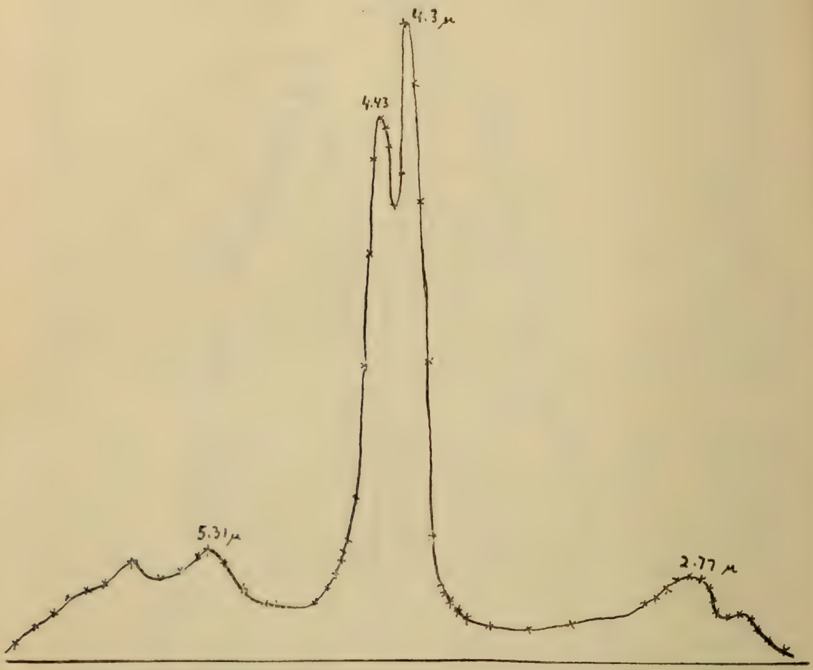
practically of the same height, and the minimum between them has an intensity of only about 1/3 that of the maxima : in other words, it is very much deeper than when observed with a rock-salt prism. The slit width was only half a millimetre, and the width of the bolometer strip was the same. This type of curve was obtained with all of the gratings The maximum at 13, figured by Coblentz, who worked with a single reflexion only, did not appear in our work, as it was lost by the threefold reflexion which we employed. The curve obtained with the radiations of CO from the Bunsen flame is shown in fig. 2. There is distinct resolution of the band into a double band in the case of every curve obtained. In addition to the strong band at 4·3 there are weaker maxima to the right and left. The curve figured was obtained with grating No. 8.

Fig. 1.



The wave-lengths of the maxima of the bands for the quartz rays and the radiations from the flame have been very carefully determined. The angle between the collimating mirrors of the vacuum spectrometer were determined, and the formula for fixed collimator and telescope and revolving grating. In the case of the quartz rays the following values were obtained :—

Fig. 2.



	8·42	8·90
	8·42	8·99
	8·40	8·80
	8·36	8·90
	8·49	8·90
Mean ...	8·41μ	8·90μ

For the flame radiations the following values were found for the three maxima, 4·2μ, 4·4μ, 4·5μ (these values were obtained from calculations made both from the second and third order spectra of grating No. 6). With grating No. 5 the values of the two brightest maxima were 4·32μ and 4·43μ.

Previous work on CO_2 is as follows. Julius finds bands at 2·8 and 4·4. Rubens and Aschkinass find, in addition, a weak at 14·1. Water vapour has a band at 5·4. The small maximum which we find at 2·84 is undoubtedly a first order maximum on the concentration side which Julius located at 2·8. The two large maxima at 4·41 and 4·51 are first order spectra of the Julius band, found at 4·4, which he failed to resolve but which was distinctly resolved in the present case. The small band at 5·37 is probably first order for the water-vapour band which Rubens and Aschkinass found, while the other small band may be a first order band at 5·77 (due to ?), or more probably a second order of the band at 2·84. If this be so, its wave-length in second order figures ought to be 2·89.

No very great effort was made to get the highest resolution possible, and the results given are to be regarded rather as a by-product of the other investigation.

It is interesting to compare the dispersion of the gratings with that of rock-salt and fluorite prisms :—

In the interval 4μ to 5μ in the spectrum furnished by a rock-salt prism, the difference in angles of minimum deviation is 0° 15′ of arc. This means 7′·5 of arc change in the setting of the Wadsworth prism-mirror combination. In the grating spectrum grating of No. 8, 13′ of arc corresponds to $0{\cdot}1\mu$, or 1μ would correspond to about 130′ of arc. Our dispersion therefore near the CO_2 band is nearly 17 times that of a 60° rock-salt prism in the same region. This region is about the worst part of the rock-salt spectrum, on account of the flatness of the dispersion curve at this point. The dispersion of a 60° fluorite prism is apparently 4 times that of a salt prism between 4μ and 5μ; therefore our dispersion is about 4 times that of fluorite in this region. Near the quartz bands with grating No. 5 we have about 150′ of arc to 1μ, while with a 60° rock-salt prism there are 27′ of arc to 1μ. Here then we have 5·4 times the dispersion of a standard 60° salt prism.

Further investigations with the gratings will be made in the near future.

C. *On Molecular Attraction.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

IN a paper published in the October number of the Philosophical Magazine, Mr. Mills gives a *résumé* of some of his work on molecular attraction. May I be permitted to call attention to some points in connexion with the subject.

It can be strictly shown mathematically that it is impossible to determine completely the law of attraction between molecules from latent heat data, or in other words the law deduced should contain an arbitrary function of the distance of separation of the molecules and the temperature. It follows therefore that if we assume a certain law of attraction and deduce from it a formula for the latent heat and find that it fits the facts, it does not therefore follow that the law assumed is correct. In fact an infinite number of different laws can be obtained, each of which gives a formula for the latent heat agreeing with the facts. It is owing to this that different investigators have obtained different laws for the attractions between molecules. Attention was drawn to this point in a paper read before the Sheffield Meeting of the British Association. A demonstration of the result stated cannot be given here, and I therefore beg to refer to a paper on the subject which will be published in this journal shortly.

That we may deduce from latent heat data more laws than one, can be shown by an example. Assuming that the attraction between two molecules varies inversely as the square of their distance of separation, Mills obtained for the latent heat the formula $A(\rho_1^{1/3}-\rho_2^{1/3})$, where A is a constant and ρ_1, ρ_2 denote the densities of the liquid and vapour respectively. Now if we assume that the attraction varies inversely as the seventh power of the distance, we obtain the formula $B(\rho_1^2-\rho_2^2)$ for the latent heat, where B is a constant, and this also agrees well with the facts ("Equation of State," Phil. Mag., *supra*, pp. 678 *et seq.*). We may therefore with equal justice assume that the attraction obeys the latter law.

Further, it can be shown independently of the above considerations that the law of Mills cannot possibly account for the latent heat of evaporation, etc. According to Mills the attraction between two molecules is $\frac{K}{z^2}$, where z is their distance of separation and K a constant. The heat of evaporation of a molecule may be taken as the energy expended in bringing it from the interior of a large mass of liquid to an infinite distance from the liquid; for which I have given a general formula, Phil. Mag. May 1910, p. 801.

Substituting $\frac{K}{z^2}$ for $\phi(z)(\Sigma\sqrt{m_1})^2$ in the formula we obtain

$$L=\frac{K}{m^{4/3}}(\rho_1^{1/3}-\rho_2^{1/3})\,2{\cdot}96,$$

where m is the mass of a molecule and L the internal latent heat in ergs. In the case of ether at 273° this gives $K=8{\cdot}9\times10^{-21}$ dyne, K being the attraction between the molecules unit distance apart. Now the gravitational attraction obeys the inverse square law, and its value for two ether molecules separated by unit distance should therefore be equal to the above value of K. The former quantity is equal to $1{\cdot}84 \times 10^{-52}$ dyne, which is much smaller than the latter; and this law cannot therefore account for the latent heat of evaporation. Apart from molecular attraction considerations the latent heat formula given by Mills is, however, of great interest.

To be on safe ground the law deduced from latent heat data must contain an arbitrary function. But still the law may give some valuable information, for we might be able to prove that the arbitrary function cannot include some of the known parts of the law obtained, and these parts may bring out some important properties, and these must be true.

Yours faithfully,

Cambridge, Oct. 5, 1910. R. KLEEMAN.

CI. *Note on the Electricity of Mercury-falls and on very large Ions.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

REFERRING to the paper by Mr. Lonsdale in your September number, on the "Ionization produced by the Splashing of Mercury," I may perhaps mention to your readers, that Mr. Lonsdale's results, which are certainly of great interest, are, however, not so new as may seem. Most of these results, including the large excess of the one kind of carriers (ions), the small velocity of these carriers, the influence of the surface of impact, are to be found in two elaborate papers by A. Becker, published in the *Annalen der Physik*, vol. xxix. p. 909, in 1909, and vol. xxxi. p. 98, in 1910, "Ueber Quecksilberfall elektricität" ("On the Electricity of Mercury-falls"). Prof. Becker shows there also, that the smallest impurities of the mercury are of great influence, and he comes to employ very-carefully purified mercury. Moreover, in the same papers there are also to be found experiments with several amalgams and in other gases than air (H_2, CO_2), and the surface of impact is also further varied.

As to the last point in Mr. Lonsdale's summary of results, viz. the appearance of "neutral doublets," reference may be made to the paper by K. Kähler (*Ann. d. Phys.* vol. xii. 1903), who found quite the same appearance of new carriers of electricity in the air from waterfalls which had already passed an electric field and was therefore expected to be free from carriers. According to the state of knowledge at that time, Mr. Kähler interpreted his result as "radioactive property of the air from waterfalls." Later on, we were not able to reproduce this unexpected reappearance of new carriers (*cf.* Aselmann, *Ann. d. Phys.* vol. xix. 1906), and this is quite in agreement with Mr. Lonsdale's statement, that something not yet known seems necessary to produce this result.

I may perhaps also mention here one of our more recent results bearing on the subject (P. Lenard and C. Ramsauer, Heidelberg Acad. of Sciences, 1910; also mentioned by C. Ramsauer at the Rad. Congress at Brussels), namely, that the smallest traces of water vapour, and perhaps also other vapours, are of great influence on the size of the carriers (ions) in gases—even at atmospheric pressure,—the carriers becoming very large when traces of such vapours are present. We have found this with carriers produced by ultra-violet light. The usual drying of the air by phosphoric acid is not sufficient to reduce the carriers to their smallest size; they became much smaller, if previous cooling to −70° C. was employed to purify the air. It may therefore be expected, that the large carriers from mercury-falls contain also many molecules of the liquid (mercury).

Yours very sincerely,
P. LENARD.

Physical Laboratory of the
University, Heidelberg,
Sept. 26, 1910.

CII. *On the Statistical Theory of Radiation.*

To the Editors of the Philosophical Magazine.

McGill University, Montreal,
Sept. 6, 1910.

GENTLEMEN,—

IN the Philosophical Magazine for August (p. 350) Sir J. Larmor gives reasons for supposing that my conclusion, that his modification of Planck's theory of natural radiation does not evade the main difficulty that an atomic constitution of radiation must be implied, need not follow.

Sir J. Larmor states that on his theory k need not be equal to the gas constant for one molecule but is indeterminate. To make this clear it ought to be shown that the calculations of k given by Boltzmann, Planck, and others can be modified so as to leave k indeterminate. This I think has not yet been done, and until it has been done the conclusion that k must have a definite value cannot be regarded as disposed of. The only reason why Planck was obliged to introduce the idea of finite elements of energy was that he found the only possible value of k to be that of the gas constant for one molecule.

Yours very truly,
HAROLD A. WILSON.

FIG. 2.

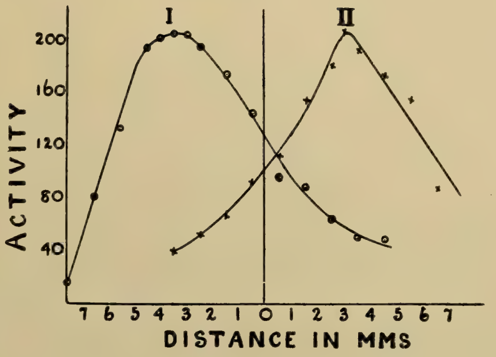
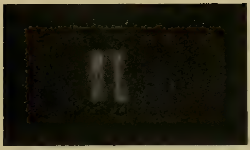

I
II
200
160
120
80
40
ACTIVITY
7 6 5 4 3 2 1 0 1 2 3 4 5 6 7
DISTANCE IN MMS

FIG. 4.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

DECEMBER 1910.

CIII. *The Attraction Constant of a Molecule of a Substance and its Chemical Properties. By* R. D. KLEEMAN, *D.Sc., B.A., Mackinnon Student of the Royal Society* *.

FROM the surface-tension of liquids and the latent heat of evaporation the writer † has deduced the nature of the law of attraction between molecules which gives rise to these properties of liquids. It follows from the nature of surface-tension and the heat of evaporation that the law obtained does not necessarily apply to distances between the attracting molecules less than the distance of separation of molecules in the liquid state. Molecules and atoms may approach much nearer to one another than this distance, as happens for example in the polymerization of molecules and the combination of atoms to form a molecule. It is not impossible, therefore, that another force of attraction of a different nature exists besides that brought out by the above investigation, which operates effectively only when the distance of the attracting molecules or atoms is less than the distance of separation of molecules in the liquid state. Such a force of attraction, if it exists, would assist in producing chemical combination. It seems improbable, however, that any other force of attraction should exist than that which gives rise to surface-tension, and that this is therefore the force tending to produce chemical combination. Whether that is so or not

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* Communicated by the Author; some of the results in this paper have been given in a paper read before the Meeting of the British Association in Sheffield this year.

† Phil. Mag. May 1910, pp. 783-809.

cannot be tested directly. There is some indirect evidence, however, supporting this supposition. Thus the attraction constant $\Sigma\sqrt{m_1}$, denoting the sum of the square roots of the atomic weights of the atoms of a molecule in the law of attraction $\frac{K}{z^5}(\Sigma\sqrt{m_1})^2$ between molecules of the same kind, may be replaced by Σv, the sum of the maximum valencies of the atoms of a molecule. The quantity K in the above expression is the same for all substances at corresponding temperatures, and may therefore be a function of the ratio of the temperature of the molecules to the critical temperature, and the ratio of z—the distance of separation of the molecules—to their distance of separation at the critical temperature. Its correct form was not indicated by the investigation mentioned: a later investigation * showed, however, that it must be principally a function of the temperature.

If the force of attraction producing chemical combination is that given by the above law, we should expect that further relations of the quantity $\Sigma\sqrt{m_1}$ of a substance with its chemical properties exist. The object of this paper is to point out some relations of this kind. These constitute further indirect evidence that the above law of attraction is the only one operating when chemical combination takes place.

The quantity $\frac{T}{\Sigma\sqrt{m_1}}$ of substances, where T denotes a given corresponding temperature, is of the greatest importance as its properties run parallel with the chemical properties of the substances. This parallelism appears in many ways. Thus the value of $\frac{T}{\Sigma\sqrt{m_1}}$ for a substance and its substitution products is approximately a constant, but varies considerably from one set of substances to another. This is shown by Tables I. and II., using the critical temperatures † of substances, which by definition are corresponding temperatures. The tables contain also for comparison the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ for a number of other substances which are not substitution products. The constancy of $\frac{T_c}{\Sigma\sqrt{m_1}}$ is better in some sets of substances than in others. It is probable that a deviation of $\frac{T_c}{\Sigma\sqrt{m_1}}$ from constancy in a set of substances indicates a

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* Phil. Mag. Oct. 1910, p. 665.

† They were taken from Landolt and Börnstein's Tables, 5th edition.

TABLE I.

Name of substance.		Tc.	$\Sigma\sqrt{m_1}$.	$\frac{T_c}{\Sigma\sqrt{m_1}}$.
Methane,	$CH_3.H$	191·2	4·46	25·63
Methyl fluoride,	CH_3F	317·9	10·82	28·62
Methyl chloride,	CH_3Cl	414·5	12·42	32·61
Methyl bromide,	CH_3Br	467	15·40	29·80
Methyl iodide,	CH_3I	528	17·73	29·29
Amyl chloride,	$C_5H_{11}Cl$	552	24·26	16·11
Amyl bromide,	$C_5H_{11}Br$	580	27·24	15·57
Hydrochloric acid,	HCl	324·3	6·96	46·59
Hydrobromic acid,	HBr	364·3	9·94	36·65
Hydriodic acid,	HI	423·4	12·27	34·53
Ethane,	$C_2H_5.H$	308	13·92	22·13
Ethyl chloride,	C_2H_5Cl	455·5	17·88	25·39
Ethyl bromide,	C_2H_5Br	499	20·86	23·92
Ethyl iodide,	C_2H_5I	554	23·19	23·89
Phosphorous chloride,	PCl_3	558·5	17·49	31·94
Arsenic chloride,	$AsCl_3$	629	20·58	30·57
Methyl acetate,	$C_3H_6O_2$	505·9	24·38	20·75
Ethyl formate	,,	503	,,	20·64

Name of substance.		Tc.	$\Sigma\sqrt{m_1}$.	$\frac{T_c}{\Sigma\sqrt{m_1}}$.
Stannic chloride,	$SnCl_4$	591·7	34·70	17·05
Titanic chloride,	$TiCl_4$	631	30·71	20·06
Silicic chloride,	$SiCl_4$	503	29·16	17·27
Carbon tetrachloride,	CCl_4	556·2	27·30	20·37
Ethylene bromide,	$C_2H_4Br_2$	582·8	28·80	48·58
Chloride of ethyl,	$C_2H_4Cl_2$	561·4	22·84	59·17
Chloraldehyde,	$C_2H_4Cl_2$	523	22·84	55·61
Propyl acetate,	$C_5H_{10}O_2$	549·2	35·30	15·56
Ethyl propionate	,,	545·4	,,	15·45
Methyl butyrate	,,	551	,,	15·61
Methyl isobutyrate	,,	540·5	,,	15·31
Isobutyl formate	,,	551·2	,,	15·63
Isobutyl propionate,	$C_7H_{14}O_2$	591·7	46·22	12·80
Propyl butyrate	,,	599·6	,,	12·97
Propyl isobutyrate	,,	589	,,	12·75
Ethyl valerianate	,,	570	,,	12·33
Sulphur dioxide,	SO_2	428·4	13·66	31·36
Carbon dioxide,	CO_2	404·1	11·46	35·26

TABLE II.

Name of substance.	T_c.	ρ_c.	p_c.	L.	m.	$\Sigma\sqrt{m_1}$.	$\frac{T_c}{\Sigma\sqrt{m_1}}$.	$\frac{v_c}{(\Sigma\sqrt{m_1})^{3/4}}$.	$\frac{p_c}{(\Sigma\sqrt{m_1})^{1/4}}$.	$\frac{Lm}{\Sigma\sqrt{m_1}}$.
Benzene, $CH_5.H$.	561·5	·3045	47·89	81·73	78	26·76	20·68	21·77	21·05	238·3
Fluorbenzene, CH_5F ...	559·5	·3541	44·62	69·71	96·09	30·12	18·58	21·11	19·04	222·4
Chlorobenzene, CH_5Cl...	633	·3654	44·62	65·88	112·5	31·72	19·95	23·03	18·80	233·5
Bromobenzene, CH_5Br...	670	·4853	44·62	48·84	157	34·70	19·32	22·63	18·39	221·0
Iodobenzene, CH_5I ...	721	·5814	44·62	40·79	203·9	37·03	19·47	23·36	18·09	224·7
Methyl formate, $C_2H_4O_2$...	487	·3489	56·62	92·85	60	18·92	25·79	18·95	48·27	294·3
Propyl formate, $C_4H_8O_2$...	533·8	·305	42·7	78·35	88	29·84	17·88	22·60	18·27	231·1
Ethyl acetate ,, ...	522·5	·2993	39·65	78·61	,,	,,	17·51	23·03	16·96	232·1
Methyl propionate ,, ...	528·7	·300	39·88	79·72	,,	,,	17·72	22·98	17·02	235·2
Ethyl butyrate, $C_6H_{12}O_2$...	565·8	·276	30·24	......	......	40·76	13·88	26·06	11·97	......
Ethyl isobutyrate ,, ...	553·4	·276	30·13	......	......	,,	13·57	26·06	11·92	......
Isobutyl acetate ,, ...	561·3	·281	31·40	......	......	,,	13·77	26·19	12·43	......
Methyl valerianate ,, ...	566·7	·279	31·50	......	......	,,	13·90	25·78	12·47	......
Amyl formate ,, ...	575·6	·282	34·12	......	......	,,	14·13	25·51	13·51	......

departure from the normal chemical behaviour of the set. The grouping is however, very marked, the change in the value of $\frac{T_c}{\Sigma\sqrt{m_1}}$ as we pass from one group to another being usually greater than the deviations from constancy of the values of one group.

The values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ for SO_2 and CO_2 are approximately equal to one another; they behave as if both are substitution products of some primary compound. It may be noted that they are formed in a similar way, viz. by the burning of carbon or sulphur in oxygen.

A number of expressions involving other quantities than the temperature can be deduced which possess the same property as $\frac{T}{\Sigma\sqrt{m_1}}$. The expressions can be deduced by means of the relations

$$T = H^2\left(\frac{\rho}{m}\right)^{4/3}(\Sigma\sqrt{m_1})^2, \quad . \quad . \quad . \quad . \quad (a)$$

$$\lambda = \kappa''\left(\frac{\rho}{m}\right)^{2}(\Sigma\sqrt{m_1})^2, \quad . \quad . \quad . \quad . \quad . \quad (b)$$

$$L = \frac{B^2}{m}\left(\frac{\rho}{m}\right)^{4/3}(\Sigma\sqrt{m_1})^2, \quad . \quad . \quad . \quad . \quad (c)$$

$$p = M^2\left(\frac{\rho}{m}\right)^{7/3}(\Sigma\sqrt{m_1})^2, \quad . \quad . \quad . \quad . \quad (d)$$

given by the writer, where p, L, λ denote the pressure of the saturated vapour, the latent heat, and the surface-tension of a liquid at the temperature T, and H, κ'', B, M are constants which have the same values for all liquids at corresponding temperatures, ρ denotes the density of the liquid and m its molecular weight.

Let us write

$$P = \frac{T}{\Sigma\sqrt{m_1}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

By means of equations (a) and (1) we obtain

$$P = H^2\left(\frac{\rho}{m}\right)^{4/3}\Sigma\sqrt{m_1},$$

or

$$\frac{H^{3/2}}{P^{3/4}} = \frac{m}{\rho}\frac{1}{(\Sigma\sqrt{m_1})^{3/4}} = \frac{v}{(\Sigma\sqrt{m_1})^{3/4}}, \quad . \quad . \quad . \quad (2)$$

where v denotes the molecular volume of a molecule.

Now at corresponding temperatures H is the same for all liquids, and P is constant for a compound and its substitution products. The quantity $\frac{v}{(\Sigma\sqrt{m_1})^{3/4}}$ will therefore be constant for a compound and its substitution products at corresponding temperatures. The ninth column of Table II. bears this out for the critical molecular volumes of a set of substances.

By means of equations (2) and (*b*) we obtain

$$\lambda=\frac{\mathrm{P}^{3/2}\kappa''}{\mathrm{H}^3}(\Sigma\sqrt{m_1})^{1/2} \quad\text{or}\quad \frac{\lambda}{(\Sigma\sqrt{m_1})^{1/2}}=\frac{\mathrm{P}^{3/2}\kappa''}{\mathrm{H}^3}. \quad . \quad (3)$$

Thus $\frac{\gamma}{(\Sigma\sqrt{m_1})^{1/2}}$ is constant for a compound and its substitution products at corresponding temperatures.

Since $\frac{\mathrm{E}}{\gamma}$ = constant for corresponding states, where E denotes the potential energy of the surface film of a liquid, we have that $\frac{\mathrm{E}}{(\Sigma\sqrt{m_1})^{1/2}}$ is constant under the same conditions.

From equations (*c*) and (2) we have

$$\mathrm{L}=\frac{\mathrm{B}^2\mathrm{P}\Sigma\sqrt{m_1}}{\mathrm{H}^2 m}, \quad\text{or}\quad \frac{\mathrm{L}_1}{\Sigma\sqrt{m_1}}=\frac{\mathrm{B}^2\mathrm{P}}{\mathrm{H}^2}, \quad . \quad . \quad (4)$$

where $\mathrm{L}m=\mathrm{L}_1$ and is the molecular internal heat of evaporation of a liquid. The quantity $\frac{\mathrm{L}_1}{\Sigma\sqrt{m_1}}$ is thus constant under the same conditions as the above quantities. This is shown by the last column of Table II. The internal latent heats used relate to 2/3 of the critical temperature; they have been calculated from the tables of latent heat given by Mills *.

From equations (*c*) and (2) we have

$$p=\frac{\mathrm{M}^2\mathrm{P}^{7/4}}{\mathrm{H}^{7/2}}(\Sigma\sqrt{m_1})^{1/4}, \quad\text{or}\quad \frac{p}{(\Sigma\sqrt{m_1})^{1/4}}=\frac{\mathrm{M}^2\mathrm{P}^{7/4}}{\mathrm{H}^{7/2}}. \quad . \quad (5)$$

Thus $\frac{p}{(\Sigma\sqrt{m_1})^{1/4}}$ is constant under the same conditions as the quantities discussed above. This is borne out by the tenth column of Table II., using the critical pressures of the substances. Since the exponent in $(\Sigma\sqrt{m_1})^{1/4}$ is $\frac{1}{4}$ the value

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* Journ. of Phys. Chem. vol. viii. p. 405 (1904).

of this expression will not vary much from one substance to another; and the critical pressures will therefore not vary much in the case of a compound and its substitution products.

We have then that the values of each of the simple expressions $\frac{T}{\Sigma\sqrt{m_1}}$, $\frac{v}{(\Sigma\sqrt{m_1})^{3/4}}$, $\frac{\lambda}{(\Sigma\sqrt{m_1})^{1/2}}$, $\frac{E}{(\Sigma\sqrt{m_1})^{1/2}}$, $\frac{L_1}{\Sigma\sqrt{m_1}}$, $\frac{p}{(\Sigma\sqrt{m_1})^{1/4}}$ are constant for a compound and its substitution products at corresponding temperatures.

Any function of these quantities will possess the same properties. It is of interest to note that the form of the function may be such that $\Sigma\sqrt{m_1}$ does not appear in it.

Further chemical properties of the quantity $\frac{T_c}{\Sigma\sqrt{m_1}}$ will now be discussed. The chemical compounds considered will be taken in groups according to their chemical properties.

Esters.

The values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ for each set of isomers of the esters are practically the same, as will be seen from Tables I. and II. In comparing the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ we may therefore take the mean of the values of each set. These mean values are contained in Table III. (p. 912).

The chemical formula for the esters may be written $2O+\alpha(C+2H)$, where α denotes an integer. Now it was found that the value of $\frac{T_c}{\Sigma\sqrt{m_1}}$ may be expressed by the equation

$$A_1-\{2O+\alpha(C+2H)\}=(A_1-2O)-\alpha(C+2H)=\frac{T_c}{\Sigma\sqrt{m_1}},$$

where A_1 is a constant, and H, C, O have the same value for each compound. The values of (A_1-2O) and $(C+2H)$ were determined from the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ by the method of least squares, and found to be equal to 29 and 2·51 respectively. By means of these quantities the value of the left-hand side of the above equation was calculated for each ester, the result being given in the last column of Table III. It will be seen that the agreement with the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ is fairly good.

TABLE III.

Substance.	T_c.	$\Sigma\sqrt{m_1}$.	$\frac{T_c}{\Sigma\sqrt{m_1}}$.	(A_1-2O) $-\alpha(C+2H)$.
M. formate, $C_2H_4O_2$	487	18·92	25·79	24·98
Mean of type $C_3H_6O_2$	504·4	24·38	20·69	21·47
,, ,, $C_4H_8O_2$	528·3	29·84	17·70	18·96
,, ,, $C_5H_{10}O_2$	547·5	35·30	15·51	16·45
,, ,, $C_6H_{12}O_2$	564·5	40·76	13·85	13·94
,, ,, $C_7H_{14}O_2$	587·6	46·22	12·71	11·43

Acids.

The chemical formula for the acids contained in Table IV. may be written $2O+\alpha(C+2H)$, where a denotes an integer, and is thus the same as that of the esters. This expression may be connected with $\frac{T_c}{\Sigma\sqrt{m_1}}$ by an equation similar to

TABLE IV.

Substance.	T_c.	$\Sigma\sqrt{m_1}$.	$\frac{T_c}{\Sigma\sqrt{m_1}}$.	(A_2-2O) $-\alpha(C+2H)$.
Butyric acid, $C_4H_8O_2$	611	29·84	20·47	20·14
Acetic acid, $C_2H_4O_2$	594·5	18·92	31·42	31·22
Propionic acid, $C_3H_6O_2$	612·9	24·38	25·14	25·68

that obtained in the case of the esters; that is, we may write

$$A_2-(2O+\alpha(C+2H))=(A_2-2O)-\alpha(C+2H)=\frac{T_c}{\Sigma\sqrt{m_1}},$$

where A_2 is a constant. The values of (A_2-2O) and $(C+2H)$ are, however, much larger than the values of the corresponding quantities of the esters. Thus it was found by means of the method of least squares that

$$(A_2-2O) = 42·3 \quad \text{and} \quad (C+2H) = 5·54,$$

values which are about double the corresponding values for the esters. The value of the left-hand side of the above equation was calculated for each acid by means of these quantities, and a fair agreement with the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ obtained.

Nitriles.

The chemical formula for the nitriles contained in Table V. may be written $N+\alpha C+\beta H$, where α and β denote integers. It can be connected with the value of $\frac{T_c}{\Sigma\sqrt{m_1}}$ in a similar way as before; that is, we may write

$$A_3-(N+\alpha C+\beta H)=(A_3-N)-\alpha C-\beta H=\frac{T_c}{\Sigma\sqrt{m_1}}.$$

The values of (A_3-N), C, and H were calculated by the method of least squares from the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ in the table, giving 43·42, 2·051, and 1·339 respectively. Using these values, the values of the left-hand side of the above equation was calculated for the nitriles in the table. The agreement with the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ is fairly good.

Table V.

Substance.	T_c.	$\Sigma\sqrt{m_1}$.	$\frac{T_c}{\Sigma\sqrt{m_1}}$.	(A_3-N) $-\alpha C-\beta H$.
Acetone nitrile, C_2H_3N	543·2	13·67	37·74	35·30
Benzonitrile, C_7H_5N	699·2	32·97	21·20	22·37
Butyronitrile, C_4H_7N	582·1	24·59	23·67	25·84
Capronitrile, $C_6H_{11}N$	621·8	35·51	17·52	16·39
Propionitrile, C_3H_5N	558·1	19·13	29·20	30·57
Toluylnitrile, C_8H_7N	723	38·43	18·81	17·64

The deviations from exact agreement that occur are greater than the experimental error that can occur in the determination of the critical temperatures. The lack of the quantity

$\frac{T}{\Sigma\sqrt{m_1}}$ being exactly additive, probably indicates certain deviations in chemical properties of the substances.

The values of H and C, it should be noticed, increase with increase of atomic weight.

Ethers.

The chemical equation for the ethers contained in Table VI. may be written $\alpha C+\beta H+O$, where α and β are integers. From what has gone before we should expect that there exists a relation of the form

$$A_4-\alpha C-\beta H-O=(A_4-O)-\alpha C-\beta H=\frac{T_c}{\Sigma\sqrt{m_1}}.$$

The values of (A_4-O), C, and H, determined from the four ethers, are 34·87, −·277, and 1·959 respectively. The values of the left-hand side of the latter equation calculated by means of these quantities are given in the fifth column of the table, and agree fairly well with the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$. The values obtained for H and C decrease algebraically with increase of atomic weight. The opposite occurs, we have seen, when H and C occur in the equation for the nitriles.

Table VI.

Substance.	T_c.	$\Sigma\sqrt{m_1}$.	$\frac{T_c}{\Sigma\sqrt{m_1}}$.	(A_4-O) $-\alpha C-\beta H$.	(A_5-O) $-(C+2H)$.
Allyl ethyl ether, $C_5H_{10}O$ ...	518	31·30	16·55	16·66	
Methyl ethyl ether, C_3H_8O ...	440·7	22·38	19·70	20·03	20·07
Methyl ether, ... C_2H_6O ...	402·6	16·92	23·79	23·67	23·60
Ethyl oxide, ... $C_4H_{10}O$ ...	465·6	27·84	16·73	16·29	16·55

The chemical equation for the three ethers at the end of the table may be written $O+\alpha(C+2H)$, and we have accordingly $(A_5-O)-\alpha(C+2H)=\frac{T_c}{\Sigma\sqrt{m_1}}$, where A_5 is a constant. The values of (A_5-O) and $(C+2H)$ were found to be equal to 30·64 and 3·522 respectively. The values of the left-hand side of the above equation calculated by means of these quantities will be seen to agree well with the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$.

The value of the expression $(C+2H)$ obtained by substituting for H and C their values is 3·64, which is approximately equal to 3·52 the value of $(C+2H)$ just obtained in a different way.

Amines.

The chemical formula for the three primary amines in Table VII. may be written $N+3H+\alpha(C+2H)$ where α is an integer. We would therefore expect the value of $\frac{T_c}{\Sigma\sqrt{m_1}}$ to be given by the equation

$$A_6-(N+3H+\alpha(C+2H))=(A_6-N-3H)-\alpha(C+2H)=\frac{T_c}{\Sigma\sqrt{m_1}},$$

where A_6 is some constant. It was found in the same way as before that $(A_6-N-3H)=41{\cdot}27$ and $(C+2H)=7{\cdot}01$. By means of these values the left hand-side of the above equation was evaluated for each of the three primary amines in the table, giving a good agreement with the corresponding values of $\frac{T_c}{\Sigma\sqrt{m_1}}$.

TABLE VII.

Substance.	T_c.	$\Sigma\sqrt{m_1}$.	$\frac{T_c}{\Sigma\sqrt{m_1}}$.	$(A_6-N-3H)-\alpha(C+2H)$.
Ethylamine, C_2H_7N ……	450	17·67	25·48	27·25
Methylamine, CH_5N ……	428	12·21	35·05	34·26
Propylamine, CHN………	491	23·13	21·21	20·24
Diethylamine, $C_4H_{11}N$……	489	28·59	17·10	18·57
Dimethylamine, C_2H_7N ……	436	17·67	24·68	23·81
Dipropylamine, $C_6H_{15}N$……	550	39·51	13·92	13·33
Triethylamine, $C_6H_{15}N$……	532	39·51	13·47	13·47
Trimethylamine, C_3H_9N ……	433·5	23 13	23·06	23·06
Pyridin, ……… C_5H_5N ……	617·2	26·05	23·69	25·09

The chemical equation for the three secondary amines in the table is the same as the above, and the value of $\frac{T_c}{\Sigma\sqrt{m_1}}$ we would therefore expect to be given by an equation of the above form. The values of (A_6-N-3H) and $(C+2H)$ for the secondary amines were found to be equal to 29·05 and 2·62 respectively. These values, it will be noticed, differ considerably from those found for the primary amines. A fair agreement of the left-hand side of the above equation with the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ is also obtained in the case of the secondary amines.

The chemical equation for the two tertiary amines in Table VII. is the same as for the primary amines, and is therefore connected with $\frac{T_c}{\Sigma\sqrt{m_1}}$ by an equation similar to the above. It was found that $(A_6-N-3H)=32·61$ and $(C+2H)=3·19$. These values are very nearly equal to those obtained for the secondary amines.

The chemical equation for the anilines in Table VIII. is $N-5H+\alpha(C+2H)$, where α is an integer. The equation for $\frac{T_c}{\Sigma\sqrt{m_1}}$ we would therefore expect to be

$$A_7-(N-5H+\alpha(C+2H))=(A_7-N+5H)-\alpha(C+2H)=\frac{T_c}{\Sigma\sqrt{m_1}}.$$

The values of (A_7-N+5H) and $(C+2H)$ were calculated from the three anilines in the table by the method of least squares and found to be equal to 39·79 and 2·94 respectively, and these values then used to calculate the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$. The agreement between the values thus obtained and those obtained directly is very good.

TABLE VIII.

Substance.	T_c.	$\Sigma\sqrt{m_1}$.	$\frac{T_c}{\Sigma\sqrt{m_1}}$	$(A_7-N+5H)-\alpha(C+2H)$.
Aniline, ... C_6H_7N	698·6	31·51	22·18	22·15
Ethyl aniline, $C_8H_{11}N$	698·4	42·43	16·46	16·27
Methyl aniline, C_7H_9N	701·6	36·97	18·98	19·21

The organic alkali pyridin, whose value of $\frac{T_c}{\Sigma\sqrt{m_1}}$ is given in Table VII., is usually classed with the tertiary amines.

Its chemical formula is the same as that of the anilines, and we may therefore suppose the above equation for the anilines to apply also to pyridin. It is of interest that the value of $\frac{T_c}{\Sigma\sqrt{m_1}}$ for pyridin is approximately given by the above equation, using the values of (A_7-N+5H) and $(C+2H)$ found for the anilines. The value obtained in this way is 25·09, which is approximately equal to 23·69, the value given in Table VII.

Alcohols.

The chemical formula for each of the two sets of alcohols in Table IX. is $O+2H+\alpha(C+2H)$, where α is an integer. We would therefore expect that

$$A_8-(O+2H+\alpha(C+2H))=(A_8-O-2H)-\alpha(C+2H)=\frac{T_c}{\Sigma\sqrt{m_1}}.$$

From the first set we obtain $(A_8-O-2H)=30·58$, and $(C+2H)=2·635$, giving a fair agreement of the calculated values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ with those obtained directly.

From the second set we obtain $(A_8-O-2H)=30·08$ and $(C+2H)=2·29$. These values do not differ much from those found for the first set. The agreement between the calculated values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ and those obtained directly is very good.

TABLE IX.

Substance,	T_c.	$\Sigma\sqrt{m_1}$.	$\frac{T_c}{\Sigma\sqrt{m_1}}$.	$(A_8-O-2H)-\alpha(C+2H)$.
Isoamyl alcohol	579·6	33·30	17·41	17·40
Isobutyl alcohol	561·3	27·84	20·17	20·04
Isopropyl alcohol	507·6	22 38	22·69	22·68
Amyl alcohol	621	33·30	18·65	18·53
Butyl alcohol.....................	560 1	27·84	20·12	20·92
Propyl alcohol	536·7	22·38	23·99	23·21

The values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ for methyl and ethyl alcohol are respectively 44·14 and 30·53. These alcohols do not fit in with the second set, though belonging to it. Using the values of (A_8-O-2H) and $(C+2H)$ found for the second set of alcohols in Table IX., we obtain for the calculated values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ respectively the numbers 27·95 and 25·31, which we see differ considerably from those obtained directly. The reason for the disagreement appears to be that these two alcohols are polymerized at ordinary temperatures, which gives rise to a displacement of the critical temperature. The writer has shown that the liquids which we know (from surface-tension and other considerations) to be polymerized, usually do not fit in with the critical constant relations that apply to normal liquids. The polymerization of a liquid at ordinary temperatures may thus affect the critical constants although there may be no polymerization in the critical state.

Sulphur Compounds.

The sulphur compounds in Table X. are too diverse in character to admit of being divided into groups the members of each of which are connected by a simple relation. The following relations may, however, be noticed. The chemical formula for the first six compounds is $S+2H+\alpha(C+2H)$, where α is an integer. We may therefore suppose that there exists the relation

$$A_9-(S+2H+\alpha(C+2H))=(A_9-S-2H)-\alpha(C+2H)=\frac{T_c}{\Sigma\sqrt{m_1}}.$$

Now, if we suppose that the value of (A_9-S-2H) and $(C+2H)$ is the same for ethyl methyl sulphide and ethyl sulphide we get, by subtracting one from the other, that $(C+2H)=3·25$. If we suppose the values of these quantities are the same for ethyl sulphide (one of the former compounds) and methyl sulphide, we get $(C+2H)=6·47$. This value is almost exactly double the former. Again, if we suppose that these quantities have the same values for ethyl and isoamyl sulphydrate we get $(C+2H)=3·23$, which is almost exactly half the previous value. And if these quantities have the same value for ethyl and isoamyl sulphide (which correspond to the sulphydrates) we obtain $(C+2H)=1·37$, which is much smaller than the value obtained in the case of the sulphydrates.

When the critical constants for a larger number of sulphur compounds are available some systematic relations should be possible of being discovered by the help of which the compounds might be classified into sets.

TABLE X.

Substance.		Tc.	$\Sigma \sqrt{m_1}$.	$\frac{T_c}{\Sigma \sqrt{m_1}}$.
Ethyl methyl sulphide,	C_3H_8S	532·7	24·04	22·16
Ethyl sulphide,	$C_4H_{10}S$	557·7	29·50	18·91
Methyl sulphide,	C_2H_6S	592	18·58	31·85
Ethyl sulphydrate.	C_2H_6S	501	18·58	26·96
Isoamyl sulphydrate,	$C_5H_{12}S$	603·9	34·96	17·27
Isoamyl sulphide,	$C_{10}H_{22}S$.........	664·2	62·26	10·67
Allyl sulphide,	$C_6H_{10}S$	653·4	36·42	17·95
Ethyl disulphide,	$C_7H_{10}S_2$.........	441·9	35·16	12·57

Hydrocarbons.

Table XI. contains the values of $\frac{T_c}{\Sigma \sqrt{m_1}}$ of a number of paraffins and benzenes. The chemical formula may be written $2H + \alpha(C + H)$. Let us suppose that

$$(A_{10} - 2H) - \alpha(C + 2H) = \frac{T_c}{\Sigma \sqrt{m_1}},$$

and that the values of the quantities in this equation are the same for each paraffin. Subtracting each value of $\frac{T_c}{\Sigma \sqrt{m_1}}$ from the one preceding it we obtain the values 3·50, 2 00, 2·04, 1·43, 1·22, 92 for $(C + 2H)$. They are not equal

TABLE XI.

Substance.	Tc.	$\Sigma \sqrt{m_1}$.	$\frac{T_c}{\Sigma \sqrt{m_1}}$.	Substance.	Tc.	$\Sigma \sqrt{m_1}$.	$\frac{T_c}{\Sigma \sqrt{m_1}}$.
Methane, CH_4 ...	191·2	7·46	25·63	Heptane...C_7H_{16}	539·9	40·32	13·39
Ethane, C_2H_6...	308	13·92	22·13	Octane ...C_8H_{18}	569·4	45·68	12·47
Propane, C_3H_8...	370	18·38	20·13	Benzene ...C_6H_6	553·6	26·76	20·68
Pentane, C_5H_{12}	470·2	29·23	16·04	Ethyl benzene, C_8H_{10}	619 4	37·68	16·82
Hexane, C_6H_{14}	507·8	34·76	14·61	Propyl benzene, C_9H_{12}	599 6	43·14	13·90

to one another, but decrease in value with the complexity of the molecules considered, showing that the quantities A_{10}. C, H, have not the same value for each paraffin. This applies also to the benzenes in the table. It does not seem possible to draw any further conclusions from the values of $\frac{T_c}{\Sigma\sqrt{m_1}}$ in the table.

It will in general be found that if the molecules of a compound contain the same atoms as the molecules of another compound and in addition to these one or more atoms of any kind, the value of $\frac{T_c}{\Sigma\sqrt{m_1}}$ of the former compound is always smaller than that of the latter.

General Remarks.

The values of $\frac{T}{\Sigma\sqrt{m_1}}$ or P of substances, where T denotes a corresponding temperature, may be expressed in terms of other quantities. Thus from equations (1), (2), (3), (4), and (5) we have

$$P=\frac{T}{\Sigma\sqrt{m_1}},\quad P=H^2\left(\frac{\rho}{m}\right)^{4/3}.\Sigma\sqrt{m_1},\quad P=\frac{H^2}{\kappa''^{2/3}}\frac{\gamma^{2/3}}{(\Sigma\sqrt{m_1})^{1/3}},$$

$$P=\frac{H^2}{B^2}\cdot\frac{L_1}{\Sigma\sqrt{m_1}},\quad P=\frac{H^2}{M^{8/7}}\frac{p^{4/7}}{(\Sigma\sqrt{m_1})^{1/7}}.$$

At corresponding states each of the quantities $\left(\frac{\rho}{m}\right)^{4/3}\Sigma\sqrt{m_1}$, $\frac{\gamma^{2/3}}{(\Sigma\sqrt{m_1})^{1/3}}$, $\frac{L_1}{(\Sigma\sqrt{m_1})}$, $\frac{p^{4/7}}{(\Sigma\sqrt{m_1})^{1/7}}$, is equal to P multiplied by a constant which is the same for each substance, and these quantities therefore possess the same properties as $\frac{T}{\Sigma\sqrt{m_1}}$. The theory of corresponding states is, however, only approximately true, and the properties of these quantities may therefore not appear so marked as those of $\frac{T_c}{\Sigma\sqrt{m_1}}$.

The properties of the quantity $\frac{T}{\Sigma\sqrt{m_1}}$ or P of substances, we have seen, usually run parallel with the chemical properties. One of these, stated in general terms, is, if $\phi(H, C, O, \ldots)$ denotes the general chemical formula for a group of substances linked together by chemical properties, then the equation $A-\phi(H, C, O, \ldots)=\frac{T}{\Sigma\sqrt{m_1}}$, where A is a constant, applies to all the substances. The various results obtained indicate the lines along which chemical compounds may be classified according to their physical properties. They would also be of use in aiding the classification from a purely chemical point of view in pointing out the existence of chemical relations. Thus if it is found that certain relations connect the values of $\frac{T}{\Sigma\sqrt{m_1}}$ of certain chemical compounds, we might expect that some corresponding chemical relations exist. The determination of the critical constants of chemical compounds, especially the critical temperature, becomes therefore of great importance. A more complete list of the critical constants than the one at present available may lead to the discovery of a number of other properties of the quantity $\frac{T}{\Sigma\sqrt{m_1}}$ corresponding to certain chemical properties, besides those given in this paper.

There appears no obvious reason why the quantity $\frac{T_c}{\Sigma\sqrt{m_1}}$ of a substance should be so closely connected with its chemical properties. We may state this quantity in a different way, but that hardly throws any light on the subject. The kinetic energy of a molecule is proportional to the temperature, and we may therefore define this quantity as the ratio of the kinetic energy of a molecule at the critical temperature to its chemical attraction at a given distance.

Further relations of the quantity with physical and chemical quantities will be given in subsequent papers. A comparison of the various results obtained will probably lead to a definite explanation why the properties of this quantity run parallel with the chemical properties.

Cambridge, July 20, 1910.

CIV. *Primary and Secondary γ Rays.*

By D. C. H. Florance, *M.A.*, *M.Sc.*[*]

WHEN γ-rays strike a body it is well known that a secondary radiation is produced. Part consists of a corpuscular radiation similar in character to β-rays; and part consists of a very penetrating radiation similar in character to the primary γ-rays. Eve[†] first proved that these penetrating secondary rays were of the γ-ray type. Kleeman[‡]

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[*] Communicated by Prof. E. Rutherford, F.R.S.

[†] Phil. Mag. Dec. 1904.

[‡] Phil. Mag. May 1908.

examined closely the radiations from various metals, and from his results concluded that the primary and secondary γ-rays could be divided into several homogeneous groups. Madsen*, by a study of the "emergent" radiation, *i. e.* the radiation emitted from a screen in the direction of the primary γ rays, divided the primary radiation into two homogeneous groups. One was "hard" or very penetrating, and the other a soft group or one easily absorbed. He has shown that there exists a marked lack of symmetry in the quantity of secondary radiation emitted from the two sides of the plate, and in some cases a considerable difference in the penetrating power of the radiation. He considers that this secondary radiation is derived from the primary by a scattering process.

The question of the distribution and character of the secondary γ-rays is very complicated, and although a large amount of work has been done, many points still remain to be settled. It is of great importance, for example, to settle whether the secondary radiation of the γ-ray type is merely part of the primary rays which have been scattered in their passage through matter, or is a true secondary radiation excited by the passage of the γ-rays through matter. In the latter case, it is to be expected that the secondary γ-rays would differ in quality from the primary. One of the main difficulties of the subject is the apparent complexity of the primary γ-rays, to which attention has been drawn by Eve, Kleeman, and Madsen. Soddy has found under special conditions that the γ-rays from radium are absorbed according to an exponential law, and has concluded consequently that the radiations are homogeneous. This view is, however, difficult to reconcile with the evidence obtained by a study of the secondary γ-rays †.

The following experiments were undertaken to see if any conclusive evidence could be obtained to settle between these hypotheses. The results given in this paper extend and somewhat modify those obtained by Madsen. The γ-rays appear to be entirely heterogeneous, and the terms "hard" and "soft" can only be used for convenience and not to denote two distinct groups of homogeneous rays.

The paper consists of two parts:—

I. A short investigation of the initial absorption of γ-rays by lead under ordinary experimental conditions.

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* Phil. Mag. March 1909.

† Note recent letters: Kleeman, Phil. Mag. July 1910; Soddy, Phil. Mag. August 1910.

II. Secondary γ radiation.
- (1) The distribution of secondary γ radiation :
  - (*a*) produced by different thicknesses of the same material ;
  - (*b*) produced by different materials.
- (2) The quality of the secondary γ radiation. The variation of quality with
  - (*a*) Position of electroscope.
  - (*b*) Material of radiator.
  - (*c*) Thickness of radiator.
  - (*d*) Area of radiator.
  - (*e*) Screening of radium.
- (3) A discussion of the question whether the secondary γ-rays are true secondary rays or scattered primary rays.

I. INITIAL ABSORPTION OF γ RAYS.

When γ-rays are absorbed by a substance such as lead it has been observed by most experimenters that the coefficient of absorption decreases with an increase in thickness of the absorbing material. This has been generally explained by assuming the original radiation to be heterogeneous, and consequently the softer radiation to be cut out more in proportion than the harder radiation. That the γ-rays from radium are heterogeneous is no doubt true, but the above assumption requires modification to explain all the cases that are likely to arise. Observers do not agree in the exact values to be assigned for the initial absorption of γ-rays. A few experiments were performed to see what was the reason of this divergence.

Apparatus.

The electroscope was of lead, 3 mm. thick and 7 cm. cube. The top, bottom, and the two sides of the electroscope containing the windows were surrounded in lead about 1 cm. thick. The face through which the γ-rays penetrated was 3 mm. thick. A screen of lead ·7 cm. could be used to test the quality of the radiation. The quality is determined by calculating λ the absorption coefficient of this ·7 cm. of lead from the relation $I_t = I_0 e^{-\lambda t}$, where I_0 is the leak in the electroscope before the lead screen is placed in position. The electroscope was supported on an iron pipe about $1\frac{1}{4}$ inches in diameter. The radium was placed near the edge of a table, and in some cases the lead screen was supported by string from a board overhead. Thus care was taken to prevent secondary radiation from surrounding bodies. In these experiments the leak of the electroscope was fairly large, and no difference was observed when the small glass windows were screened by lead.

Radium (20 mgrs. Ra) was placed 56 cms. from the electroscope. The absorption coefficient was measured for narrow pieces of lead ·172 cm. thick placed against the radium. The length, breadth, and thickness were (11 × 3·5 × ·172)cm.

	Thickness of Screen.			
Thickness	·0 ·172 cm.	·516 ·684 cm.	·854 1·04 cm.	1·38 1·55 cm.
λ	·99	·70	·65	·58

From this experiment it would seem that the lead screen simply cut out the less penetrating γ-rays.

Compare these results with those obtained by other investigators.

McClelland[*]...	Thickness	·8 1·05 cm.	1·05 1·3 cm.	1·3 1·8 cm.	1·8 2·3 cm.
	λ	64	·56	·48	·44
Tuomikoski[†]...	Thickness	·4 1·0 cm.	1·0 2·2	2·2 5·4	5·4 12·0
	λ	·70	·58	·52	·50
Eve[‡]	Thickness	·64 1·21 cm.	1·21 1·79	1·79 2·36	2·4 3·0
	λ	·57	·56	·46	·46

As we have seen, Soddy has concluded that the true value for the absorption coefficient right from the initial stage should be λ = ·50.

A glance at the above results shows discrepancies much too large to be ascribed to experimental errors.

The radium still in the same position is surrounded with lead. A piece (11 × 5 × 1·4) cm. is placed directly in front of the radium and lead 1·5 cm. thick placed at the side.

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[*] Phil. Mag. July 1904.

[†] *Phys. Zeit.* June 1909.

[‡] Phil. Mag. April 1906.

The absorption coefficient is now determined for a screen of lead (11 × 11 × ·7) cm., when it is placed against the lead screen in front of the radium; and secondly, when it is placed against the electroscope.

·7 cm. against the lead screen $\lambda = {\cdot}50$
·7 ,, ,, ,, electroscope $\lambda = {\cdot}55$.

This effect seemed to be caused by the secondary radiation emitted by the screen.

A narrow screen 3·4 cm. wide and 1·3 cm. thick is placed in front of the radium. A lead screen (13 × 13 × 1·1) cm. is divided into three strips. One of these narrow strips is placed against the lead screen in front of the radium, and the coefficient of absorption is thus determined.

The apparent absorption coefficient $\lambda = {\cdot}51$. The two other strips are now added to continue the plate, and for this large plate $\lambda = {\cdot}46$. The side portions of the screen which are added in this latter case do not cut off any of the direct primary radiation from the electroscope. They add, however, the secondary radiation due to the passage of the primary radiation. Hence the area of the absorbing screen will modify the value of the coefficient of absorption. Experiments also show that bodies in the neighbourhood, from which a secondary radiation can be produced, will cause a variation in the value of results. The secondary radiation from the air due to the passage of the primary radiation would most probably be very small.

Importance of secondary γ-rays in the measurement of the absorption coefficient of primary γ-rays.

The radium is kept in a constant position 80 cm. from the electroscope. A large screen (20 × 20 × 1·01) cm. can be placed in any position between the radium and electroscope. A lead screen ·7 cm. thick is placed against the electroscope to test the quality of the radiation.

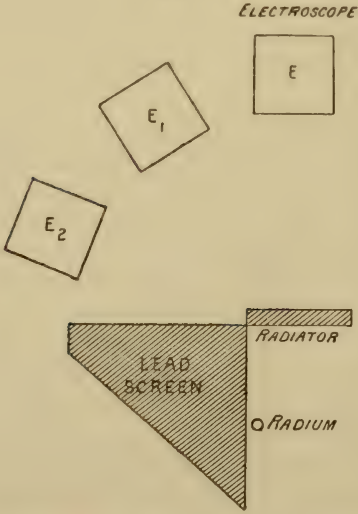
Position of large screen ...	Position I.	Position II.	Position III.
Distance from electroscope...	77·5 cm.	66 cm.	1 cm.
No screen against electroscope	5·05 div./min.	4·65 div./min.	4·29 div./min.
Screen against electroscope...	3·26 div./min.	3·17 div./min.	2·82 div./min.
Absorption coefficient	$\lambda = {\cdot}62$	$\lambda = {\cdot}54$	$\lambda = {\cdot}60$

It will be seen that the magnitude of the leak and also the absorption coefficient of the radiation change considerably with the position of the screen. In position I. the large screen does more than cut out the direct radiation--it adds the secondary radiation scattered from all parts of its volume. This quantity will decrease as the solid angle subtended by the screen at the radium decreases. On the other hand, as the screen approaches the electroscope it would be expected that the secondary radiation emitted would have an increased effect. Results point to the general conclusion that the production of the secondary radiation is the chief cause for the variation in the value of the absorption coefficient determined under different experimental conditions. The initial rapid change of the absorption coefficient is no doubt due to the rapid absorption of the soft portion of the primary radiation.

In connexion with the secondary γ-rays a few experiments were performed to test the quality and the amount of the primary γ-rays passing through various materials.

In this case a lead electroscope ·6 cm. thick was used. The thickness of absorbing screen was ·624 cm. of lead, which was placed against the electroscope. The 20 mgrs. of radium was surrounded by ·208 cm. of lead. (See fig. 1.)

Fig. 1.



E is the electroscope in the position of direct radiation.

E_1 and E_2 are positions of the electroscope for the measurement of secondary radiation.

The radium cannot be placed symmetrically as regards the radiator as it is required to have E_1 as near the position E as possible without intercepting the direct radiation.

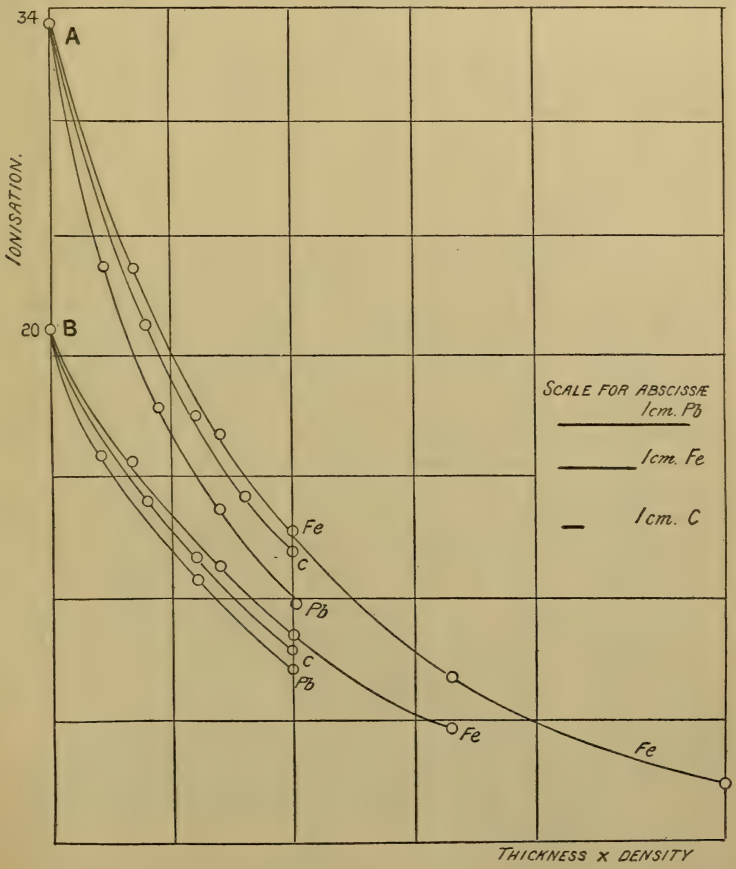
The different radiators are supported by string.

No radiator	$\lambda = \cdot 71$
5 cms. of carbon	$\lambda = \cdot 68$
10 cms. of carbon	$\lambda = \cdot 65$
2 cms. of iron	$\lambda = \cdot 65$
5 cms. of iron	$\lambda = \cdot 59$
·416 cm. of lead	$\lambda = \cdot 625$

The area of the radiator is constant (11 × 11) cm. Each radiator has had, therefore, a hardening effect. It will be shown later that the relative values of these absorption coefficients remain the same for each position of the electroscope.

Consider now the amount which passes through these radiators. In fig. 2 are plotted the curves showing the

Fig. 2.



Group A shows absorption of the direct γ rays through different thicknesses of three radiators. Side of electroscope is 6 mm. thick.

Group B, side of electroscope is 12 mm. thick.

relation between thickness of radiator × the density, and the amount of radiation passing through as measured by the electroscope in scale-divisions per minute. It will be noticed that the curve for carbon falls between those for iron and lead. This is unexpected, but it may be due to the fact that the radiation has to pass through the side of an electroscope 6 mm. thick, which would cut out the radiations emitted from different radiators in a varying degree. The second group of curves shows the effect of placing 6·24 mm. of lead against the electroscope. The initial drop is not so great in this case. For equal weights per unit area the amount of radiation passing through varies for different substances.

A comparison in the following table is made of the quantities passing through different radiators which give the same coefficient of absorption when examined by lead.

Radiator.	Thickness.	Mass per unit area in grs.	Quantity.	λ.
Carbon ...	10 cm.	22	14	·65
Iron	2 cm.	14·7	17	·65
Lead	·25 cm.	2·8	26	·65

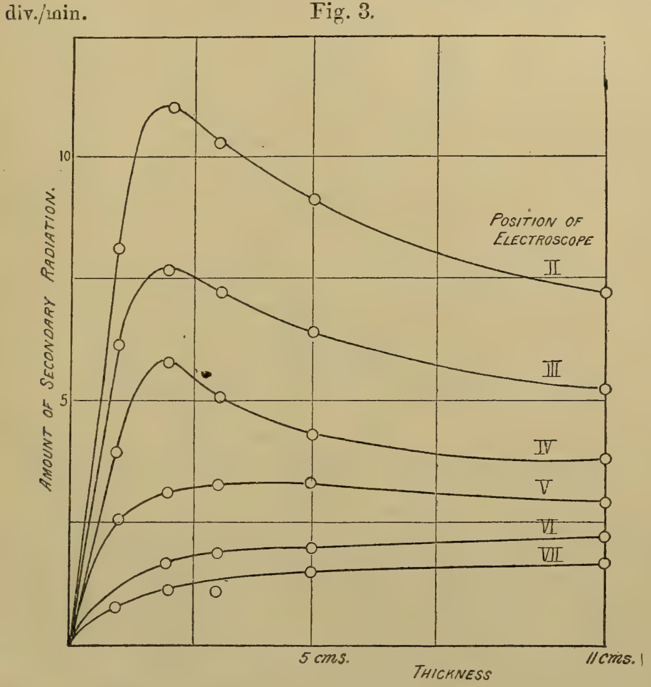
A greater amount of the primary radiation passes through the lead than through the carbon, yet the absorption coefficient is the same in both cases. There is no difficulty in explaining this if we assume that the γ-rays of radium are heterogeneous. For the sake of clearness consider the γ-rays divided into a hard and a soft group. Probably the soft group is in excess of the hard group. The results of experiments in the second part of this paper show that there is more scattering in a substance like carbon than in lead. The relative amount of scattering and of absorption of the two groups will most likely vary according to the material of the radiator. It is well known that lead cuts out a soft radiation much more rapidly than does a similar weight of iron. Therefore, when the primary radiation strikes the lead radiator, the softer portion will be cut out much more in proportion to the harder than in the case of the carbon radiator. If a radiator produces a scattering of the primary radiation, then the sorting out process will be simply a difference in degree for the two groups by different radiators. There is no need to suppose there has been a change in type of the primary radiation.

II. Secondary γ Rays.

(1) *The Distribution of Secondary γ Radiation.*

Apparatus.—The electroscope was of lead 3 mm. thick and 7 cm. cube. In the first experiments, it was supported on a wooden arm which could be revolved so that the electroscope moved round the arc of a circle of radius 25 cm. The centre of this circle was approximately the centre of the radiator. The radium, about 300 mgrs.* of $RaBr_2$, was contained in a platinum vessel, and the electroscope was screened from the direct radiation by a mass of lead. The arrangement was similar to that shown in fig. 1. The radiator consisted of iron plates 11·1 cm. square. The electroscope was turned into the different positions, and the readings taken with and without the radiator. Seven positions of the electroscope are taken; the first one measures the direct radiation and the last one the secondary radiation at right angles to this. The other positions are intermediate.

Fig. 3.



Relation between amount of secondary radiation and thickness of iron radiator.

In fig. 3 curves are plotted showing the effect of varying

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* This was kindly lent for the purpose by Professor Rutherford. It was sealed up in order to determine the rate of production of helium from it.

the thickness of radiator from 1·05 cm. to 11 cm. for each position of the electroscope round a quadrant of a circle.

Eve has shown (Phil. Mag. Dec. 1904) that for an increase in thickness of radiator, the emergent secondary γ radiation increases rapidly till it reaches a maximum, and then it decreases. The curve thus obtained can be expressed mathematically by the difference of two exponentials. Madsen (Phil. Mag. March 1909) has shown the same effect. The "incident" secondary γ radiation, *i. e.* the radiation turned back in its path, has also been shown to be represented by an expression $K(1-e^{-\lambda_2 d})$, where K is a constant, λ_2 the coefficient of absorption of this secondary radiation, and d the thickness of the plate. Experimenters in attacking this problem have kept their ionization vessel in one position and have made it large to obtain the greatest secondary effect. With 300 mgrs. of $RaBr_2$ there was sufficient secondary radiation to allow measurements to be made with a small electroscope and to be carried out round the arc of a circle. Hence it was found that instead of a sharp line of demarcation between the emergent and incident secondary γ radiation, the one gradually changed into the other. Curves illustrating this would change in form from that represented by $(e^{-\lambda d}-e^{-\lambda_1 d})$ to $(1-e^{-\lambda_2 d})$.

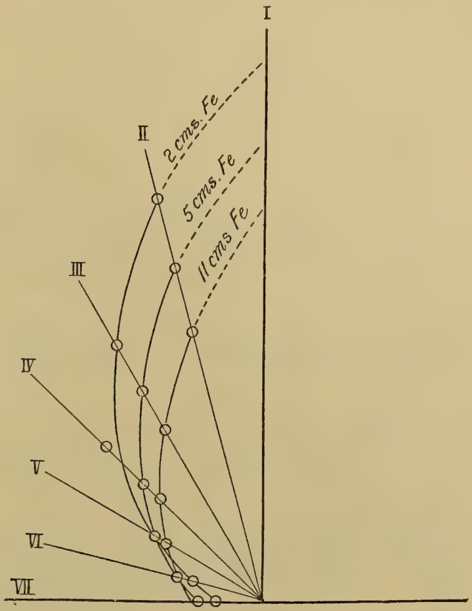
Considering the complexity of the radiation and the imperfections of experimental arrangements, it is not to be expected that there would be any simple mathematical relation between the quantities measured; and the equations proposed by former experimenters are certainly inadequate.

Relation between the amount of secondary radiation and position of electroscope for certain thicknesses of radiator (fig. 4).

In these curves for each thickness of radiator the amount of secondary radiation is plotted radially. By continuing the curves an approximation can be obtained of the amount of the secondary radiation which passes through in the direction of the primary radiation, and also of the amount of "incident" secondary radiation. A similar approximation can be obtained from fig. 3.

It is important to notice that a considerable portion of the total γ radiation striking the radiator is converted into secondary. For instance, the leak in the electroscope when there is no radiator is 215 div./min. The leak when there is a radiator of iron 2·1 cm. thick is 103 div./min. When the electroscope is in a position just outside the direct radiation the leak is 11 div./min. With the present arrangement it is difficult to determine the total quantity of secondary radiation even approximately; but by integrating over the distributed curves there appears to be about 20 to 30 per cent. of the ionization due to the secondary radiation emitted from the radiator.

Fig. 4.



Curves showing relation between position of electroscope and the amount of secondary radiation when the thickness is constant for each curve.

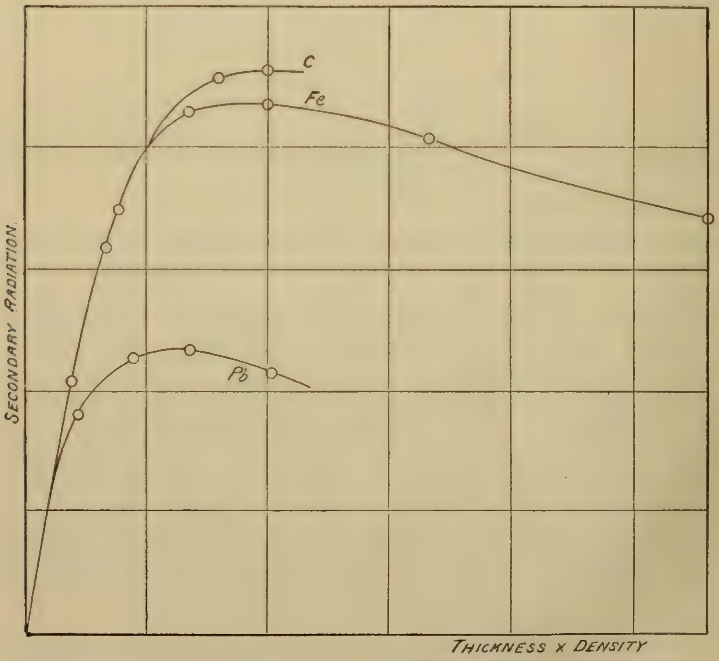
A study of the curves shows that as the thickness of radiator increases the point A will approach 0 more rapidly than the points on the radial lines. It is not desirable at present to attempt to attach much meaning to the exact form of these curves, as it is possible that the shape would vary with the arrangement of the apparatus. The radium could not be placed symmetrically with respect to the radiator, but had to be placed against the lead screen. The gradual change in volume of the radiator due to a change in thickness from 1·05 to 11 cm. undoubtedly has a disturbing influence.

It was thought possible that these results might be affected by secondary radiation from surrounding bodies, quite apart from the radiator itself. To test this point and to examine the quantity of radiation produced by different radiators the apparatus was set up afresh. A new electroscope was made of similar dimensions to the original one, but the thickness of the sides was 6 mm. A lead screen was also made for the small glass windows and a lead cap for the ebonite support of the leaf system. The electroscope was supported on an iron pipe so that it could be turned round an arc of a circle. The radium (20 mgrs.) was surrounded by 2·08 mm. of lead. The radiators were supported by string from a beam overhead, so that secondary radiation from surrounding bodies was reduced to a minimum. The arrangement is the same as shown in fig. 1.

The direct radiation was first measured through the various radiators. The results were plotted with the ionizations in the electroscope as ordinates and the weight per unit area as abscissæ. These curves (fig. 2) have already been referred to.

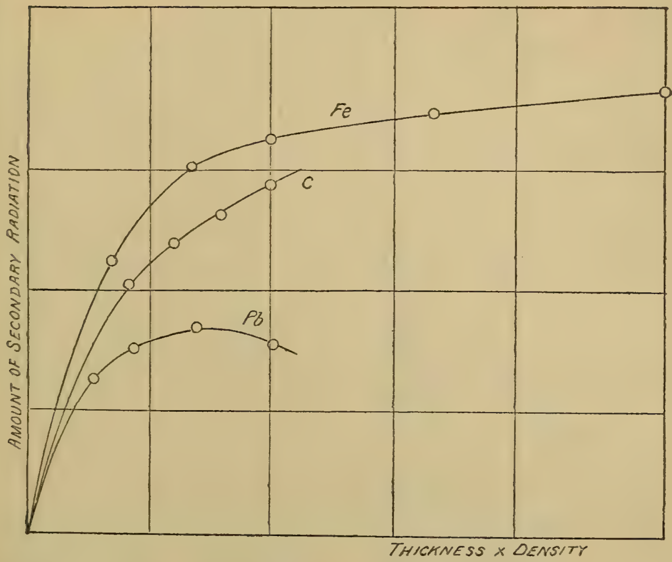
To examine the secondary radiation two definite positions were taken and the results plotted in figs. 5 and 6.

Fig. 5.



Electroscope turned through angle 25°. Comparison of amount of secondary radiation for different thicknesses of different materials.

Fig. 6.



Electroscope at an angle 55°. Comparison of amount of secondary radiation for different thicknesses of different materials.

Position I. The angle between the normal position and this position is approximately 25°. The carbon radiator produces more secondary radiation than does iron or lead.

Position II. The angle is approximately 55°. In this case the curve for carbon has fallen below that for iron, and even after 12·5 cm. of carbon the maximum amount of secondary radiation had not been reached. Lead reaches its maximum value and then decreases.

A quantitative relation between the amounts of secondary radiation emitted by different radiators was looked for, but no evidence of such a relation has been discovered. The absorbing action of the 6 mm. side of the electroscope would tend to mask any relation. It seemed probable, too, that variations in the amount of secondary radiation would be produced according to the experimental arrangement. In the present case, the volume of a certain weight of lead differed greatly from a similar weight of carbon.

This is borne out by the result of a special experiment. For example, five sheets of lead were spaced out over a distance of 8 cm. They were held together by four thin brass rods so that they could be easily suspended in position, and thus they corresponded to the condition in which the large blocks of carbon were used. These readings were compared with those obtained with five similar sheets of lead tied together. For the direct radiation, the rate of leak was 2 per cent. greater in the case of the lead fastened closely together. But as the electroscope was turned round the secondary radiation from the radiator occupying the large volume produced a leak as much as 20 per cent. greater than that produced from the lead when tied together. This is what might have been expected, as the secondary radiation instead of getting absorbed has in the one case a chance of escaping, and this is more marked the further the electroscope is moved from the direct line of radiation. In the present arrangement, where the radius of the arc is about 22 cm., the large volume of a radiator such as carbon may not give results comparable with those obtained for 1 cm. thick of lead.

(2) *The Quality of the Secondary γ Radiation.*

The apparatus, as previously explained, was set up so as to reduce to a minimum the secondary radiation except that due to the radiator itself. A lead screen 3 mm. thick was placed over the window so as to avoid any constant radiation that might get through them. The electroscope was in such a position, therefore, that when the radiator was placed in position none of the original radiation entering the electroscope was stopped; but there was simply an increased leak in the electroscope due to the secondary radiation produced by the radiator.

The quality or the penetrating power of the radiation was measured by placing a screen 6·24 mm. of lead against the side of the electroscope, which was 6 mm. thick. Readings were taken without the radiator, first without the lead screen, secondly with the lead screen; then similar readings with the radiator. A large number of readings were taken, and the mean value is given. In these experiments radium emanation was generally used as a source of γ-rays and a suitable correction was made for its decay.

The first table shows clearly that for all radiators the secondary γ radiation gradually becomes softer as the electroscope is moved further away from the normal position; and that an increase in thickness of radiation hardens both the primary and the secondary. The ratio of the absorption coefficients for any two metals or for different thicknesses of one metal keeps constant for each position of the electroscope.

For example, the quality of the direct radiation passing

Relation between coefficients of absorption of the secondary γ radiation.

The area of each radiator is (11·1 × 11·1) cm.

Radiator.	Direct radiation.	Electroscope at angle 25°.	Electroscope at angle 55°.
	The coefficient of absorption is	The coefficient of absorption is	The coefficient of absorption is
5 cm. carbon .	=·68	=1·20	=1·77
10 cm. carbon .	=·65	=1·18	=1·70
2·2 cm. iron ...	=·65	=1·17	=1·68
5 cm. iron ...	=·59	=1·05	=1·55
·416 cm. lead .	=·625	=1·11	=1·65

Effect of area of radiator.

Radiator.	Area.	Electroscope at angle 80°.
2·2 cm. of iron ...	(11·1 × 11·1) cm.	λ=1·82
2·2 cm. of iron ...	(22 × 22) cm.	λ=1·96

through 2 cm. of iron is the same as that passing through 10 cm. of carbon. For any position of the electroscope this equality of ratio seems to hold true. This points to the conclusion that the secondary radiation is the primary radiation scattered. If the radiation was a true secondary radiation it would be expected that the quality would depend on the material.

In the second table it is shown that an increase in area of the radiator causes the secondary radiation to become softer. This is no doubt due to the fact that as the area increases, a more oblique secondary radiation will come from the radiator.

Effect of Screens round Radium.

Experiments were made to examine the effect of different screens round the radium. The electroscope was 3 mm. thick, and 8·75 mm. of lead was used as an absorbing screen.

Radiator.	Thickness.	Radium unscreened.	Screened.
Carbon	10 cm.	λ=2·68	λ=2·37
Lead	2·5 cm.	λ=1 60	λ=1·40

Two narrow blocks of lead, each 1·5 cm. thick, were used as screens to the 300 mgrs. of $RaBr_2$. The position of the electroscope was at right angles to the normal.

From the table it is seen that the screen has a hardening effect. Similarly it was shown that any other screen always had a hardening effect. The ratio of the absorption coefficients remains the same for each radiator, and the results go to show that this ratio keeps constant for each position of the electroscope.

Lead has always been used as the absorbing screen in these experiments, as the changes in coefficient of absorption are much more marked than with any of the lighter substances. Yet similar results are given for screens of iron or zinc. It is well known that lead will cut out the soft radiation to a much greater extent than iron. This holds for the secondary γ-rays as well as for the primary.

Radiator.	·875 cm. of Pb.	1·05 cm. of Fe.	·875 cm. of Pb.	1·05 cm. of Fe.
10 cm. of C ...	$\lambda_{Pb}=\cdot 70$	$\lambda_{Fe}=\cdot 28$	$\lambda_{Pb}=2\cdot 68$	$\lambda_{Fe}=\cdot 56$
2·5 cm. of Pb ...	$\lambda_{Pb}=\cdot 46$	$\lambda_{Fe}=\cdot 24$	$\lambda_{Pb}=1\cdot 60$	$\lambda_{Fe}=\cdot 49$
	Direct Radiation.		Electroscope turned through 90°.	

The absorption coefficient is first determined for ·875 cm. of lead, then for 1·05 cm. of iron. Hence, while the absorption coefficient of the radiation changes from ·70 to 2·68 when measured by ·875 cm. of lead, it only changes from ·28 to ·56 in the case of iron. Carbon shows this effect to a less extent than iron.

All metals will send out a radiation of the same quality provided the right thickness of radiator is used.

Incident secondary γ-rays.

A few experiments were carried out on the radiation emitted from the surface of the plate against which the primary rays strike. This radiation from iron and lead was softer than the emergent secondary radiation. This suggests that the softest radiation is most scattered. This incident radiation is similar in type to the emergent secondary and to the primary radiation.

Summary.

(1) Secondary γ-rays are emitted from both sides of a plate exposed to γ-rays. The "incident" secondary is in all cases softer than the "emergent" secondary. There is, moreover, a gradual change from the quality of the primary to that of the secondary emergent, and then to that of the secondary incident. The quality therefore depends on the position of the electroscope.

(2) An increase in area of the radiator softens the secondary radiation, *i. e.* the quality depends on area of radiator.

(3) An increase in thickness of the radiator produces a hardening of the primary and of the secondary emergent radiation. The quality depends on thickness of radiator.

(4) For radiators of different material the quality varies. But if the right thickness for each radiator is chosen, then the quality of the primary and secondary radiation is independent of the material of radiator. With any two radiators the ratio of the absorption coefficients keeps approximately constant for any position of the electroscope.

(5) The effect of screening the radium is to harden the secondary. The screen seems to harden the secondary radiation from carbon in the same proportion as it hardens the secondary from lead. This hardening is also proportional to the hardening of the primary as measured by the absorption coefficient.

(6) The secondary radiation is heterogeneous, and this supports the view that the primary radiation is heterogeneous.

(7) There is a gradual decrease in the quantity of secondary γ radiation from that which emerges from the radiator in the direction of the original radiation to that which is returned in the reverse direction.

(8) The curves showing the relation between quantity of secondary radiation and thickness of radiator change gradually in form for each successive position of the electroscope round the arc of a circle.

(9) The lighter materials produce more secondary γ radiation than the heavier materials. A greater weight, however, is required of the lighter materials before the maximum amount is reached.

Discussion of the Results.

In the foregoing results there is nothing to suggest that the secondary γ radiation is a true secondary excited in the material of the radiator by a transformation of the primary rays. In such a case it would be expected that each element would give out a characteristic radiation. Experiments show that with proper conditions every substance can be so chosen as to give a similar type of radiation. It is important to notice that Bragg and Madsen (Phil. Mag. Oct. 1908) have shown that the character of the β radiation caused by γ-rays is independent of the atom in which it arises, and depends solely on the nature of the γ-rays to which it is due. The present investigation shows that this is also true for the secondary γ radiation.

The quality of the secondary γ radiation shows no sudden change from that of the primary. There is simply a gradual softening the more the secondary radiation is deflected from its original direction. The gradual softening is the same for every radiator. Other investigators have shown that β-rays are scattered in their passage through matter. The scattering of γ rays appears to be analogous to the scattering of β-rays. The primary γ-rays possess a wide range of penetrating power. The softening of the secondary radiation that has been observed is the result of this heterogeneity of the primary rays. The softer radiation is more scattered than the harder radiation; as the radiator is increased in thickness more of the harder gets turned aside, and in consequence we get both the hardening of the primary and of the secondary. The hardening is due in the one case to the cutting out of the softer radiation, and in the case of the secondary to the addition of a more penetrating scattered radiation. There is no evidence of selective absorption. The production of this secondary γ radiation is undoubtedly a scattering effect, as Madsen had concluded from previous experiments.

I desire to thank Professor Rutherford for the use of large quantities of radium and of radium emanation, and also for his suggestions in the course of this work.

Physical Laboratories, Manchester.

CV. *The Approximate Calculation of Bessel Functions of Imaginary Argument.* *By* J. W. Nicholson, *M.A.*, *D.Sc.*[*]

IN the British Association Report for 1908, some formulæ were given suitable for the rapid tabulation of Bessel functions whose argument is purely imaginary and large, and whose order may be of any magnitude. The same results apply if the order is large, and the argument of any magnitude. A proof was not appended, and the object of the

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[*] Communicated by the Author.

present note is to supply a short proof. The corresponding formulæ for functions of real argument have been very completely dealt with in a series of papers in the Philosophical Magazine[*]. The asymptotic expansions of functions of imaginary argument present only one type instead of the three in the case of real argument, and their treatment can therefore be given briefly. It is most conveniently deduced as a special case of that of the general associated Legendre functions $P_n^m(\mu)$ and $Q_n^m(\mu)$, which has been developed in a recent paper[†].

The functions of order m and argument ιx satisfy the equation

$$\frac{d^2y}{dx^2}+\frac{1}{x}\frac{dy}{dx}-\left(1+\frac{m^2}{x^2}\right)y=0, \quad . \quad . \quad . \quad (1)$$

where x is itself real, and they are usually defined in the forms

$$I_m(x)=\iota^{-m}J_m(\iota x)=\frac{x^m}{2^m\Gamma(\frac{1}{2})\Gamma(m+\frac{1}{2})}\int_0^\pi \cosh(x\cos\phi)\sin^{2m}\phi\, d\phi$$

$$=\frac{x^m}{2^m\Gamma(m+1)}\left\{1+\frac{x^2}{2^2\,.\,1!\,m+1}+\frac{x^4}{2^4\,.\,2!\,m+1\,.\,m+2}+\ldots\right\}(2)$$

and

$$K_m(x)=\left(\frac{x}{2}\right)^m\frac{\Gamma(\frac{1}{2})}{\Gamma(m+\frac{1}{2})}\int_0^\infty d\phi\,\sinh^{2m}\phi\, e^{-x\cosh\phi}, \quad . \quad . \quad (3)$$

the latter function vanishing exponentially when x is large.

Let $P_n^m(\mu)$, $Q_n^m(\mu)$ be the general associated Legendre functions of argument μ, degree n, and order m. A comprehensive definition of these functions for all values of these three quantities has been given by Hobson[‡]. They are the functions which, when m and n are positive integers, may be expressed in relation to the ordinary zonal harmonics $P_n(\mu)$, $Q_n(\mu)$ by the equations

$$\left.\begin{aligned}P_n^m(\mu)&=(\mu^2-1)^{\frac{1}{2}m}\,.\,d^m/d\mu^m\,.\,P_n(\mu)\\ Q_n^m(\mu)&=(\mu^2-1)^{\frac{1}{2}m}\,.\,d^m/d\mu^m\,.\,Q_n(\mu)\end{aligned}\right\}\quad . \quad . \quad (4)$$

when μ is greater than unity, the only case needed for our purpose. But in the proof contained in this paper, restriction of the order and degree to integer values is not necessary, and the final results derived for the Bessel functions are true for *any* real value of m.

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[*] Dec. 1907; Aug. 1908; July 1909; Feb. 1910.

[†] Quarterly Journal, April 1910.

[‡] Phil. Trans. 1896 A. p. 443 *et seq.*

With these definitions, a well-known formula due to Heine shows that

$$\mathrm{I}_m(x) = \underset{n=\infty}{\mathrm{Lt}}\ n^{-m}\mathrm{P}_n^m\left(\cosh\frac{x}{n}\right), \quad . \quad . \quad . \quad (5)$$

and a companion formula may be readily derived as follows :— When μ is greater than unity, and $m+\frac{1}{2}$, $n-m+1$ are positive, Hobson[*] has shown that

$$\mathrm{Q}_n^m(\mu) = \frac{e^{\iota m\pi}}{2^m}\frac{\varpi(n+m)}{\varpi(n-m)}\frac{\varpi(-\frac{1}{2})}{\varpi(m-\frac{1}{2})}(\mu^2-1)^{\frac{1}{2}m}\int_0^\infty \frac{\sinh^{2m} w\,dw}{(\mu+\sqrt{\mu^2-1}\,.\cosh w)^{n+m+1}} \quad . \quad . \quad . \quad (6)$$

where $\varpi(s)$ is Gauss' function, identical with $\Gamma(s+1)$, or if s be an integer, with $s\,!$

Write $\mu = \cosh x/n$, where n tends towards infinity. Then $(\mu^2-1)^{\frac{1}{2}m}$ tends to the value $(x/n)^m$, and $\varpi(n+m)/\varpi(n-m)$ to the value n^{2m}.

Thus

$$\underset{n=\infty}{\mathrm{Lt}}\ n^{-m}\mathrm{Q}_n^m(\mu) = \frac{e^{\iota m\pi}}{2^m}\frac{\varpi(-\frac{1}{2})}{\varpi(m-\frac{1}{2})}x^m\int_0^\infty \frac{\sinh^{2m} w\,dw}{\underset{n=\infty}{\mathrm{Lt}}\left(1+\frac{x}{n}\cosh w\right)^{n+m+1}}$$

But

$$\underset{n=\infty}{\mathrm{Lt}}\left(1+\frac{x}{n}\cosh w\right)^{n+m+1} = e^{-x\cosh w},$$

and therefore we deduce by the definition (3),

$$\mathrm{K}_m(x) = \underset{n=\infty}{\mathrm{Lt}}\ e^{-\iota m\pi}n^{-m}\mathrm{Q}_n^m\left(\cosh\frac{x}{n}\right), \quad . \quad . \quad (7)$$

which is the required companion formula to (5).

Asymptotic expansions.

It is now possible to derive the asymptotic expansions of the Bessel functions $\mathrm{I}_m(x)$ and $\mathrm{K}_m(x)$ from those of the Legendre functions. The latter will be quoted from the writer's paper[†], for the case of argument greater than unity.

Writing

$$\mathrm{P}_n^m(\mu) - e^{-\iota m\pi}\mathrm{Q}_n^m(\mu)\frac{\sin(m+n)\pi}{\pi\cos n\pi} = \left\{\frac{\varpi(n+m)}{\pi\varpi(n-m)(\mu^2-1)}\right\}^{\frac{1}{2}}\mathrm{T}^{\frac{1}{2}}e^{t}$$

$$\mathrm{Q}_n^m(\mu) = e^{\iota m\pi}\left\{\frac{\pi\varpi(n+m)}{\varpi(n-m)(\mu^2-1)}\right\}^{\frac{1}{2}}\mathrm{T}^{\frac{1}{2}}e^{-t}. \quad . \quad . \quad (8)$$

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[*] *L. c. ante*, p. 500.

[†] Quarterly Journal, April 1910, pp. 250-252.

Then if $k = m/n+\frac{1}{2}$, $\nu^2 = \mu^2-1$,

$$\mathrm{T} = (\nu^2/2n+1)\{(\nu^2+k^2)^{-\frac{1}{2}}+\lambda_3(\nu^2+k^2)^{-\frac{3}{2}}+\lambda_5(\nu^2+k^2)^{-\frac{5}{2}}+\ldots\}$$

$$\frac{t}{n+\frac{1}{2}} = \left\{1+\mu_1\frac{d}{kdk}-\frac{\mu_2}{1}\left(\frac{d}{kdk}\right)^2+\frac{\mu_3}{1\,.\,3}\left(\frac{d}{kdk}\right)^3\ldots\right\}\times$$

$$\times\left[\log\{\mu+\sqrt{\mu^2+k^2-1}\}-\tfrac{1}{2}k\log\frac{\sqrt{\mu^2+k^2-1}+k\mu}{\sqrt{\mu^2+k^2-1}-k\mu}\right.$$

$$\left.+\tfrac{1}{2}k\log\frac{1-k}{1+k}\right], \quad . \quad . \quad . \quad (9)$$

where k is less than unity, and the coefficients of types λ_r, μ_r are given by

$$\lambda_1 = 1, \qquad \lambda_3 = -\tfrac{1}{8}(4k^2-1)/(n+\tfrac{1}{2})^2-1^2,$$

$$4^2\{(n+\tfrac{1}{2})^2-2^2\}\lambda_5 = -6k^2(2-3k^2)+3(4k^2-1)(28k^2-9)/8\{(n+\tfrac{1}{2})^2-1^2\};$$

and in general

$$k^4(k^2-1)(r-2)(r-4)(r-6)\lambda_{r-6}+k^2(2-3k^2)(r-2)(r-3)(r-4)\lambda_{r-4}$$

$$+(r+2)\{k^2+3k^2(r-2)^2-(r-2)^2\}\lambda_{r-2}$$

$$+(r-1)\{4(n+\tfrac{1}{2})^2-(r-1)^2\}\lambda_r = 0, \quad . \quad (10)$$

whereas the μ's are defined by the identical relation

$$1+\mu_1\sigma+\mu_2\sigma^2+\ldots = (1+\lambda_3\sigma+\lambda_5\sigma^2+\ldots)^{-1}. \qquad (11)$$

We proceed to the limit when n is infinite and m finite, so that $k=0$. In this case,

$$\underset{n=\infty}{\mathrm{Lt}}\; n^2\lambda_3 = \frac{1}{8},$$

$$\underset{n=\infty}{\mathrm{Lt}}\; n^4\lambda_5 = \frac{1}{16}\left(\frac{27}{8}-12m^2\right),$$

and so on. In fact, these limits are the coefficients which in the notation of previous papers dealing with the Bessel functions of real argument, were denoted by

$$-\lambda_2, \quad \lambda_4, \quad -\lambda_6, \ldots$$

with m taking the place of n. Similarly, in the formula for t, $n^2\mu_1$, $n^4\mu_2$, ... must be replaced in the limit by

$$-\mu_2, \quad \mu_4, \quad -\mu_6, \ldots$$

where the μ's are now the coefficients of earlier papers *.

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* *Vide e. g.* Phil. Mag. Feb. 1910, p. 240.

In terms of the old notation, therefore, on reduction, the limiting values become

$$t = \left\{ 1 - 2\mu_2 \frac{d}{dm^2} - 2^2\mu_4 \left(\frac{d}{dm^2}\right)^2 - \ldots \right\} \times$$

$$\times \left\{ \sqrt{x^2+m^2} - \tfrac{1}{2}m \log \frac{\sqrt{x^2+m^2}+m}{\sqrt{x^2+m^2}-m} \right\}$$

$$\mathrm{T} = x\left\{ (x^2+m^2)^{-\frac{1}{2}} - \lambda_2(x^2+m^2)^{-\frac{3}{2}} + \ldots \right\} \quad . \quad . \quad . \quad (12)$$

where the coefficients are defined by

$$\lambda_2 = -\frac{1}{8}, \qquad \lambda_4 = \frac{1}{2^7}(27 - 96m^2),$$

$$\lambda_6 = \frac{1}{2^{10}}(4640m^2 - 1125 - 640m^4),$$

$$4(s+3)\lambda_{s+3} + (s+2)^3\lambda_{s+1} + 2m^2 s\,.\,(s+1)(s+2)\lambda_{s-1} + m^4 s\,.\,(s^2-4)\lambda_{s-3} = 0, \quad . \quad (13)$$

and the identity

$$1 + \mu_2 x + \mu_4 x^2 + \ldots = (1 + \lambda_2 x + \lambda_4 x^2 + \ldots)^{-1}. \quad . \quad (14)$$

The limiting forms of the substitutions (8) become

$$\underset{n=\infty}{\mathrm{Lt}}\ n^{-m}\mathrm{P}_n^m\left(\cosh\frac{x}{n}\right) = \underset{n=\infty}{\mathrm{Lt}}\ \left(\frac{\mathrm{T}}{2\pi x}\right)^{\frac{1}{2}} e^t,$$

$$\underset{n=\infty}{\mathrm{Lt}}\ n^{-m}e^{\iota m\pi}\mathrm{Q}_n^m\left(\cosh\frac{x}{n}\right) = \underset{n=\infty}{\mathrm{Lt}}\ \left(\frac{\pi\mathrm{T}}{2x}\right)^{\frac{1}{2}} e^{-t},$$

where Q_n^m has now been rejected in the first substitution, as proportional by the second to e^{-t} which is very small, for only moderate values of x^2+m^2, in comparison with e^t.

Finally, therefore, by the use of (5) and (7), we obtain the results

$$\left.\begin{aligned} \mathrm{I}_m(x) &= \left(\frac{\mathrm{T}}{2\pi x}\right)^{\frac{1}{2}} e^t \\ \mathrm{K}_m(x) &= \left(\frac{\pi\mathrm{T}}{2x}\right)^{\frac{1}{2}} e^{-t} \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where

$$\mathrm{T} = x\left\{ (x^2+m^2)^{-\frac{1}{2}} - \lambda_2(x^2+m^2)^{-\frac{3}{2}} + \lambda_4(x^2+m^2)^{-\frac{5}{2}} - \ldots \right\},$$

$$t = \left\{ 1 - \mu_2 \frac{d}{mdm} - \mu_4 \left(\frac{d}{mdm}\right)^2 \ldots \right\} \times$$

$$\times \left\{ (x^2+m^2)^{\frac{1}{2}} - \tfrac{1}{2}m \log \frac{(x^2+m^2)^{\frac{1}{2}}+m}{(x^2+m^2)^{\frac{1}{2}}-m} \right\}, \quad (16)$$

and the coefficients are given by (13, 14).

These are the formulæ given in the British Association Report.

So far as tabulation will ordinarily be required, it will be sufficient in general, even for only moderate values of x or m ($x>10$ or $m>10$) to take the first terms of T and t only, if a three-figure accuracy is required. The order of accuracy possessed by the formulæ is similar to that of the ordinary semiconvergent expression for $J_0(x)$ where x is real.

The first approximations may be written

$$\left.\begin{aligned} I_m(x) &= (2\pi x\cosh\beta)^{-\frac{1}{2}}e^{x(\cosh\beta-\beta\sinh\beta)} \\ K_m(x) &= \pi(2\pi x\cosh\beta)^{-\frac{1}{2}}e^{-x(\cosh\beta-\beta\sinh\beta)} \end{aligned}\right\}, \quad . \quad (17)$$

where β is defined by $m = x\sinh\beta$.

A useful substitution in the final formulæ has been suggested to me by Prof. Alfred Lodge. If an angle θ be chosen such that

$$x = m\tan\theta,$$

then

$$t = m(\sec\theta+\log_e\tan\tfrac{1}{2}\theta), \quad . \quad . \quad . \quad . \quad (18)$$

and this logarithm has already been exhaustively tabulated. Thus the tabulation of the Bessel functions may be performed very rapidly, and this applies also when the higher approximations are used.

CVI. *On Non-Newtonian Mechanical Systems, and Planck's Theory of Radiation.* *By* J. H. Jeans, *M.A.*, *F.R.S.*[*]

1. PLANCK'S treatment of the radiation problem, introducing as it does the conception of an indivisible atom of energy, and consequent discontinuity of motion, has led to the consideration of types of physical processes which were until recently unthought of, and are to many still unthinkable. The theory put forward by Planck would probably become acceptable to many if it could be stated physically in terms of continuous motion, or mathematically in terms of differential equations. Larmor[†] has recently made an extremely interesting suggestion as to how it might perhaps be possible to do this, but has not so far carried out the analysis necessary to determine whether his suggestion leads to a solution of the difficulty or not.

The question discussed in the present paper includes that

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[*] Communicated by the Author.

[†] Bakerian Lecture, 1909, Proc. Roy. Soc. A. vol. lxxxiii. and Phil. Mag. xx. p. 350.

raised by Larmor's suggestion and is in brief as follows:— Can any system of physical laws expressible in terms of continuous motion (or of mathematical laws expressible in terms of differential equations) be constructed such that a system of matter and æther tends to a final state in which Planck's law is obeyed? It will be found that the answer obtained is in the negative.

General Dynamical Investigation.

2. We shall assume a law of causation—namely, that the state of the system at any instant is determined by its state at the previous instant, and that this state can be specified by the values of certain definite quantities $p_1, p_2, \ldots p_n$, which we shall call the co-ordinates of the system. We shall first examine the consequences of assuming that time is continuous and that these co-ordinates vary continuously with the time.

3. If we construct an n-dimensional space, a single point in this space, namely the point whose co-ordinates are $p_1, p_2, \ldots p_n$, will represent the state of the system at any instant. A knowledge of the dynamical or kinematical laws obeyed by the system would lead directly to a knowledge of the paths or trajectories traced out in this space by the representative points as they follow the different possible motions of the system. We must not, in the present investigation, assume any special dynamical laws, but the general law of causation enables us to suppose that through every point in the generalized space there is one and only one trajectory, and that as a point moves along a trajectory, and so follows the motion of a system, its velocity at any point depends only on the co-ordinates of the point and not on the time.

In the usual manner, we imagine every region of the generalized space which represents a physically possible state of the system to be filled with so many representative points that the whole collection of points may be regarded as forming a continuous fluid. The law of causation now states that this fluid moves along fixed stream-lines and that the velocity at any point remains constant.

The initial distribution of density of the imaginary fluid in the generalized space remains entirely at our disposal. Since the motion is along fixed stream-lines with velocities fixed at each point, this initial distribution of density can be so chosen that, as the motion progresses, the density at every point of the space shall remain always equal to the initial density at the point. We elect to arrange the initial distribution of fluid in this way, and the motion of the fluid becomes "steady-motion" in the usual hydrodynamical sense. The state of the fluid is the same at all instants of time, so that we need only discuss it at one single instant.

The mass of fluid, considered at any single instant, may be compressed, distorted and dilated, in such a way as to become of uniform density at every point*. After this distortion a hydrodynamical steady motion taking place along the distorted stream-lines will represent all possible motions of the dynamical system under discussion. Let us take new orthogonal Cartesian co-ordinates in this new (distorted) space, to be denoted by $P_1, P_2, \ldots P_n$.

4. The hydrodynamical condition for steady motion is

$$\Sigma \frac{\partial \dot{P}_s}{\partial P_s} = 0 \text{ , } \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

so that we have seen that corresponding to any system of laws of motion of the dynamical system, at least one set of co-ordinates can always be chosen such that equation (1) is satisfied identically. And if there is one such set of co-ordinates there must necessarily be an infinite number, for a homogeneous fluid can be strained in an infinite number of ways so as to remain homogeneous.

For example, if the motion of the dynamical system is governed by Newtonian laws, one set of co-ordinates which satisfy relation (1) is found in the Lagrangian co-ordinates and momenta, while other sets are obtained by taking $P_1, P_2, \ldots P_n$ to be any series of linear functions of the Lagrangian co-ordinates and momenta such as determine a set of orthogonal lines in the generalized space.

5. The mass of fluid moving in the generalized space provides a basis for the introduction of the calculus of probabilities.

At this stage it may perhaps be permissible to draw attention to a point which is often overlooked in the application of this calculus to problems of statistical mechanics, namely that any discussion of probabilities is meaningless until the basis of calculation of the probability is clearly stated. The question "What is the probability that the entropy of a gas shall be W?" is, unless a definite basis of probability is stated, as meaningless as the question "What is the probability that the temperature of a gas shall be T, or that the gas shall be hydrogen?" Also, for the application

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* This is obviously true for a 1, 2 or 3-dimensional space and a proof by induction is easily constructed to extend to n-dimensions.

of the calculus to be legitimate we are not compelled to choose any one particular basis for the calculation of probabilities. We may select any basis we please, and the use of the calculus of probabilities will be legitimate provided we retain the same basis throughout the whole investigation.

In the present investigation we shall agree to say that the probabilities of a system being in states A or B are in the ratio of W_A to W_B if the regions of the generalized space occupied by points representing systems in states A or B are in the ratio of W_A to W_B. Or, in simpler language, in estimating probabilities, we think of the system as being selected at random from all systems in the generalized space, equal volumes of the space having equal chances of selection. This way of estimating probability leads at once, as we shall see, to Boltzmann's relation between entropy and probability.

Let the points representing systems in different states A, B, C ... occupy regions which are in the ratios $W_A : W_B : W_C \ldots$. Then, if a system is selected at random, the probabilities of its possessing characteristics A, B, C ... are in the ratios $W_A : W_B : W_C \ldots$. From the steadiness of the hydrodynamical motion, it also follows that if the system is selected at random and allowed to follow its natural motion for any time t, the probabilities of its possessing characteristics A, B, C ... at the end of this time will be in the ratios $W_A : W_B : W_C \ldots$. And if the system is not initially selected at random, but starts from a known state, and moves for an indefinite time under its laws of motion, the probability of its possessing characteristics A, B, C ... at the end of this time will in general also be in the ratio $W_A : W_B : W_C \ldots$. But this requires obvious modifications if the system is so started that at the end of infinite time it must inevitably have characteristics X, Y, Z .... The statement is then only true if $W_A : W_B : W_C \ldots$ measures the ratio of those parts of the space in which the characteristics AXYZ, BXYZ, CXYZ, ... obtain.

Let A, B, C ... now be characteristics of different parts of the system, such that the co-ordinates involved in the specification of any one characteristic are not involved in any of the others. Then the whole system may possess two or more of the characteristics simultaneously, and the probability that it possesses them all is of the form

$$W = K W_A W_B W_C \ldots \qquad . \quad . \quad . \quad . \quad (2)$$

where K is a constant. The value of W is obtained by pure multiplication of W_A, W_B, W_C ... because the co-ordinates are orthogonal ; it is in no way necessary to suppose that

A, B, C ... are independent events. We put $S = k \log W$, and S is then Boltzmann's measure of the entropy, probabilities now being measured on the basis provided by the generalized space.

6. Let $E_1, E_2, \ldots$ be the energies of those parts of the system with which the properties A, B, C... are associated, and let E be the total energy given by

$$E = E_1 + E_2 + \ldots \qquad (3)$$

The total entropy S is given by

$$S = k \log W_A + k \log W_B + \ldots + k \log K. \qquad (4)$$

The characteristics A, B, C... may be chosen so as to determine the partition of energy. To be precise, let characteristic A be satisfied if E_1 lies between $E_1' - \frac{1}{2}\epsilon_1$ and $E_1' + \frac{1}{2}\epsilon_1$; let B be satisfied if E_2 lies between $E_2' - \frac{1}{2}\epsilon_2$ and $E_2' + \frac{1}{2}\epsilon_2$, and so on. Let it be assumed, as a property of the system, that if left to itself, it will assume a state in which the energy is divided in a definite manner, namely one in which $E_1, E_2, \ldots$ become equal to $E_1', E_2' \ldots$, at least to within small ranges $\epsilon_1, \epsilon_2, \ldots$ Then W must be equal to unity for these values of $E_1, E_2 \ldots$, and this is not only the maximum value of W, but is greater than the sum of all other values. It follows that S also must be a maximum, when $E_1, E_2, \ldots$ have the values $E_1', E_2', \ldots$ subject to condition (3). The analytical condition for this is, in the usual way, that $E_1', E_2', \ldots$ shall be given by the system of equations

$$\frac{\partial S}{\partial E_1} = \frac{\partial S}{\partial E_2} = \ldots \qquad (5)$$

combined with equation (3).

We can find the value of each fraction by supposing that part of the system is a perfect gas. We may assume this part of the system to obey the Newtonian laws, so that its co-ordinates $P_1, P_2, \ldots P_m$ may be supposed identical with its Lagrangian co-ordinates and momenta, and its energy E_1 will be of the form

$$E_1 = \Sigma \alpha_1 P_1^2, \qquad (6)$$

the sum extending to m terms. The value of W_A is now proportional to the volume of the region of the generalized space in which $\Sigma \alpha_1 P_1^2$ lies between $E_1 - \frac{1}{2}\epsilon_1$ and $E_1 + \frac{1}{2}\epsilon_1$, and is therefore of the form $cE^{\frac{1}{2}m-1}\epsilon_1$, where c is a constant.

Hence

$$\frac{\partial S}{\partial E_1} = k\frac{\partial}{\partial E_1}\log W_A = \frac{k}{E_1}(\tfrac{1}{2}m-1) = \frac{km}{2E_1}, \quad . \quad (7)$$

since m may be supposed very great.

If T is the absolute temperature of the gas, and R the gas constant, the value of E_1 is $\frac{1}{2}m\mathrm{RT}$, so that the value of $\partial S/\partial E_1$ becomes k/RT.

If k is taken to be identical with R, then equation (5) becomes

$$\frac{\partial S}{\partial E_1} = \frac{\partial S}{\partial E_2} = \ldots = \frac{1}{T} \quad . \quad . \quad . \quad . \quad (8)$$

giving the second law of thermodynamics.

7. This method of procedure shows the second law of thermodynamics to be more general than any system of dynamical laws: the same can at once be shown to be true of the theorem of equipartition of energy. For suppose that any other part of the energy, say E_2, can be expressed in the form given by equation (6), the summation now extending to n terms. The value of W_B can be calculated in the same way as W_A, and, just as in equation (7), we have

$$\frac{\partial S}{\partial E_2} = \frac{Rn}{2E_2}$$

since k is now identical with R. Since, by equation (8), $\partial S/\partial E_2$ must be equal to 1/T, it follows that

$$E_2 = \tfrac{1}{2}n\mathrm{RT},$$

expressing the law of equipartition of energy. The same result is clearly true if E_2 is any quadratic function of n of the co-ordinates. Moreover, if E_2 is a linear, cubic, biquadratic or any other homogeneous function of the coordinates, the result is still true in a modified sense, provided that E_2 is necessarily always positive. For if

$$E_2 = f_s(P_1, P_2, \ldots P_n),$$

a homogeneous function of degree s, then W_B is the volume of the generalized space included between the surfaces

$$f_s(P_1, P_2, \ldots P_n) = E_2 \pm \tfrac{1}{2}\epsilon_2.$$

This is of the form $cE_2^{m/s-1}\epsilon_2$, where c is a constant, so that

$$\frac{1}{T} = \frac{\partial S}{\partial E_2} = \left(\frac{m}{s}-1\right)\frac{R}{E_2} = \frac{mR}{sE_2}.$$

Hence we have $E_2 = mRT/s$. Thus in any part of the energy which is expressible as a homogeneous and necessarily positive function of the co-ordinates, the average energy of any m co-ordinates is proportional to m and to T; but this is exactly the theorem of equipartition of energy.

Experimental knowledge of wave-motion seems to place it beyond question that the energies of waves of different frequencies must be represented by different sets of co-ordinates, and that each energy must be necessarily positive. If this is granted, the necessity for equipartition of energy between the different waves follows, and in a state of maximum entropy the total radiant energy must always be proportional to the temperature.

This establishes the main proposition of the present paper. It may in addition be of interest to examine in detail the form assumed by the general argument when it is applied to the special problem under discussion.

Special Investigation of Wave-motion.

8. The system to which we shall now confine our attention will consist of a volume of æther in which a very small amount of matter is embedded, the function of the matter being solely to make possible the transfer of energy in the æther between vibrations of different wave-lengths. Let there be supposed to be n vibrations in the æther, and let the co-ordinates of the sth vibration be Q_s and R_s. Let the number of additional degrees of freedom introduced by the presence of the matter be m, and let a typical one of these co-ordinates be S_r.

We shall suppose that $2m$, the number of co-ordinates associated with the matter, is infinitesimal in comparison with $2n$, the number associated with the æther. It will also be assumed that m is so small that, for all configurations which are of importance, the energy residing in the matter is negligible in comparison with that residing in the æther.

For this system equation (1) assumes the form

$$\sum_1^n \left(\frac{\partial \dot{Q}_s}{\partial Q_s} + \frac{\partial \dot{R}_s}{\partial R_s}\right) = -\sum_1^{2m} \frac{\partial \dot{S}_r}{\partial S_r}. \quad . \quad . \quad . \quad (9)$$

In this equation the number of terms on the right is small compared with that on the left. If all matter were entirely absent the terms on the right would vanish altogether, and since the waves of different periods would then become independent dynamical systems, the terms on the left would vanish separately. It follows that when the matter is sufficiently reduced in amount, the value of each term on the left is infinitesimal *.

We accordingly suppose as an approximation that

$$\frac{\partial \dot{Q}_s}{\partial Q_s}+\frac{\partial \dot{R}_s}{\partial R_s}=0 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

for each value of s and proceed to examine the nature of the co-ordinates Q_s, R_s. Equation (10) is the condition that $\dot{Q}_s dR_s - \dot{R}_s dQ_s$ shall be a perfect differential. Calling this $d\phi_s$, we have

$$\dot{Q}_s=\frac{\partial \phi_s}{\partial R_s}; \quad \dot{R}_s=-\frac{\partial \phi_s}{\partial Q_s}. \quad . \quad . \quad . \quad . \quad (11)$$

The rate of change of ϕ_s is given by

$$\dot{\phi}_s=\frac{\partial \phi_s}{\partial Q_s}\dot{Q}_s+\frac{\partial \phi_s}{\partial R_s}\dot{R}_s=0$$

by equations (11). Thus ϕ_s does not vary with the time.

The energy E_s of the sth vibration is some function, at present unknown, of Q_s and R_s. Its rate of change is

$$\begin{aligned}\frac{\partial E_s}{\partial t}&=\frac{\partial E_s}{\partial Q_s}\dot{Q}_s+\frac{\partial E_s}{\partial R_s}\dot{R}_s\\&=\frac{\partial E_s}{\partial Q_s}\frac{\partial \phi_s}{\partial R_s}-\frac{\partial E_s}{\partial R_s}\frac{\partial \phi_s}{\partial Q_s}\\&=\frac{\partial(E_s, \phi_s)}{\partial(Q_s, R_s)}.\end{aligned}$$

Since the energy must remain unaltered with the time, the Jacobian must vanish, so that ϕ_s must be a function of E_s.

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* An exception would occur if the matter were arranged so as to have free periods of its own, so introducing resonance effects; then the right hand of (9) might be mainly balanced by a few terms only on the left hand. But even if this is the case, there is no difficulty; we can confine our attention to wave-lengths for which the resonance effects are negligible.

If β stands for $\partial\phi_s/\partial E_s$, a constant, the equations (11) become

$$\dot{Q}_s = \beta\frac{\partial E_s}{\partial R_s}; \quad \dot{R}_s = -\beta\frac{\partial E_s}{\partial R_s},$$

in which the analogy with the Hamiltonian form is obvious.

9. On giving different values to ϕ and E as functions of Q and R we obtain different systems of equations of motion. Some of these may of course be incapable of representing wave-motion at all.

The simplest form which can be given to ϕ is that of a linear function of Q and R, and this may without loss of generality be taken to be AR. The equations of motion become

$$\dot{Q} = -A, \quad \dot{R} = 0,$$

of which the integrals are

$$R = \text{cons.}; \quad Q = B - At.$$

These will represent wave-motion if Q, R are taken to be phase and amplitude or phase and energy respectively, but will not satisfy the condition of the co-ordinates being determined uniquely from the state of the system, unless we suppose the space limited to a range 2π in the values of Q.

10. The next simplest form which can be given to ϕ is that of a quadratic function of Q and R, and this may without loss of generality be taken to be $\frac{1}{2}(CR^2 + DQ^2)$. The equations of motion become

$$\dot{Q} = -CR; \quad \dot{R} = DQ, \quad . \quad . \quad . \quad . \quad (13)$$

of which the integrals represent simple harmonic motion.

11. Equations (11) show that the motion of the fluid in the generalized space is the steady motion of a homogeneous fluid along the system of stream-lines $\phi = \text{constant}$. For this to be capable of representing wave-motion the curves $\phi = \text{constant}$ must be a series of closed non-intersecting curves. The mass of fluid and system of co-ordinates may now be distorted so that these (or rather their projections on the plane Q_s, R_s) become a system of concentric circles, and this may be done in such a way that the fluid remains homogeneous. On taking new axes the equations of motion become identical with (13), so that to represent wave-motion the co-ordinates must become identical with the Lagrangian co-ordinates and momenta.

It follows that, however far removed the general equations of matter and æther may be from the standard form, yet when the matter is made to diminish indefinitely in amount, we may suppose, without any loss of generality, that the equations of wave-motion are of the standard form, and that the co-ordinates Q, R are the Lagrangian co-ordinates and momenta. Equipartition of energy follows as a direct consequence.

12. In the general analysis of §7 it was assumed that the whole of the generalized space was filled with fluid. The fluid must, however, be excluded from any parts which represent physically impossible configurations, and if these parts are of sufficient extent, the exclusion of fluid may affect the final result. Let us examine whether any arrangement of fluid can be found which shall so modify the result as to change the law of equipartition into the widely different law of Planck.

Let us consider N vibrations having frequencies differing only infinitesimally from $2\pi\nu$. Their total energy E must, according to Planck's law, be given by

$$E = \frac{Nh\nu}{e^{h\nu/kT}-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where h is Planck's constant. Eliminating the temperature between this and equation (6), which is true no matter what parts of the generalized space are excluded, we obtain

$$\frac{\partial S}{\partial E} = \frac{1}{T} = \frac{k}{h\nu}\log\left(1+\frac{Nh\nu}{E}\right).$$

This gives on integration

$$S = k\left\{\left(N+\frac{E}{h\nu}\right)\log\left(N+\frac{E}{h\nu}\right) - \frac{E}{h\nu}\log\frac{E}{h\nu}\right\} + \text{cons.}$$

$$+ \text{ terms arising from the other vibrations.} \quad . \quad (15)$$

Let W be proportional to the volume of that region of the generalized space (less the excluded parts) in which E lies between $E-\frac{1}{2}\epsilon$ and $E+\frac{1}{2}\epsilon$.

On comparison of equations (4) and (15) we have

$$\log W = \left(N+\frac{E}{h\nu}\right)\log\left(N+\frac{E}{h\nu}\right) - \frac{E}{h\nu}\log\frac{E}{h\nu} + \text{cons.}$$

If we write P for $E/h\nu$, and use Stirling's approximation, this becomes

$$W = C\frac{(N+P)!}{P!}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where C is a constant. This is of course Planck's formula obtained by working backwards from Planck's law. What is important is that (16) follows inevitably from (14); in other words, formula (14) can only be true in a generalized space in which the regions excluded are such that the remaining volume is given by (16). Furthermore, the necessity for an indivisible unit of energy follows inevitably from (16), for Planck's assumption of this indivisible unit is known to lead to formula (16), and there can be only one way of distributing the fluid in the generalized space so that W is a given function of E for all values of E.

The analysis has, however, shown that the truth of Planck's law requires something more than appeared in Planck's original papers. It is now apparent that it is not enough to postulate systems of vibrators capable only of holding definite multiples of a fixed unit of energy ; we see that the energy in the æther itself must also be atomic. Moreover, it is not sufficient that the energy should always in nature occur in complete atoms ; what is required is that it should be physically impossible to divide these atoms. For instance, the requirements of this condition are not met by imagining a system of radiators which always give off energy in complete units ; we must also have an æther structure such that no vibrations can possibly exist in it except in atomic amounts. If it is agreed that these conditions do not hold in nature, then we are driven to supposing that the state of the æther represented by Planck's law is not a final steady state, or in other words that there is not thermodynamical equilibrium between the matter and the different vibrations.

13. In conclusion, it may be worth noting an alternative method of arriving at Planck's law.

Other things being equal, if a vibration can have energies $0, \epsilon, 2\epsilon, \ldots$, then the ratio of the probabilities of these events as in the usual gas-theory calculations, is

$$1 : e^{-2h\epsilon} : e^{-4h\epsilon} : \ldots .$$

where $h = 1/2RT$, or, replacing h by its value,

$$1 : e^{-\epsilon/RT} : e^{-2\epsilon/RT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If out of N vibrations under consideration, M have zero energy, then the number which have energy ϵ is $Me^{-\epsilon/RT}$, the number having energy 2ϵ is $Me^{-2\epsilon/RT}$, and so on. Thus

$$N = M(1+e^{-\epsilon/RT}+e^{-2\epsilon/RT}+\ldots) = M/(1-e^{-\epsilon/RT}),$$

and if E is the total energy of the N vibrations,

$$\begin{aligned} E &= M\epsilon(e^{-\epsilon/RT}+2e^{-2\epsilon/RT}+\ldots) \\ &= M\epsilon e^{-\epsilon/RT}/(1-e^{-\epsilon/RT})^2 \\ &= \frac{N\epsilon}{e^{\epsilon/RT}-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18) \end{aligned}$$

which gives Planck's law on taking $\epsilon = h\nu$.

It will, I think, be found that this calculation of Planck's formula is based on exactly the same physical ideas as those of the original theory of Planck. One essential and necessary feature of the theory is that it supposes the unit of energy for vibrations of moderate wave-length to be so great that the chance of a vibration having even one unit of energy is very slight. We notice that only a fraction $(N-M)/N$, or $e^{-\epsilon/RT}$, of the total number of vibrations possess any energy at all. At wave-length $\lambda_{\max.}$, $\epsilon/RT = 4{\cdot}965$, so that only one wave-length in 140 possesses any energy. At wave-length one-half of this the proportion is about one in 20,000.

14. An interesting question is whether, if this theory is to be accepted at all, it ought not also to be expected to account for the failure of certain other degrees of freedom to receive the share of energy allotted to them by the theorem of equipartition. Many types of motion, such as the internal vibrations of the atom, and the rotations of atoms or molecules, must have direct interchange of energy with the æther vibrations, so that if the latter are in temperature equilibrium, the former might be expected to be so. A rough estimate of the energy possessed by such degrees of freedom is furnished by the values of the specific heats. For a degree of freedom which has one thousandth of its equipartition energy, ϵ/RT must be about 9·1, and only one degree of freedom in 9100 will have any energy at all. This result, when applied, for instance, to the rotation of the atoms of mercury vapour, is somewhat startling.

Cambridge, Aug. 17.

CVII. *The Volatilization of Radium Emanation at Low Temperatures.* *By* R. W. BOYLE, *Ph.D.*, 1851 *Exhibition Science Scholar, McGill University* *.

Introduction.

FROM the researches of Rutherford † and of Gray and Ramsay ‡ we now have definite knowledge concerning the condensation and volatilization of radium emanation at temperatures higher than − 127° C. These researches, which have been carried out with quantities of emanation as large as are available, have given definite values of the vapour pressures corresponding to certain fixed temperatures.

At the suggestion of Prof. Rutherford the writer has recently been investigating the volatilization of this emanation at temperatures from −180° C. upwards. It has been necessary to adopt different experimental methods to suit the widely different quantities of emanation employed.

When extremely small quantities of emanation, say of the order of the equilibrium amount from 0·001 mgm. of radium, are condensed upon a surface, one can no longer speak of the emanation being in a "liquid" or in a "solid" state. For, in these circumstances, the condensed "layer" must be of less than molecular thickness §, and it would hardly be expected that volatilization would proceed in full accordance with the vapour-pressure laws as ordinarily understood.

For experimenting under these conditions the method devised by Rutherford and Soddy ‖ in 1903 is best applicable. It will be recalled that the method was to condense from a current of gas, acting as carrier, a very small quantity of emanation upon the interior surface of a spiral tube, which was immersed in a bath at very low temperature. Afterwards, while allowing the temperature of the bath to rise slowly, a very slow gas current was sent through the spiral. The emanation on volatilizing was swept out of the spiral and through an ionization vessel, where it marked its presence by causing an increase of ionization.

The temperature of maximum volatilization was readily

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* Communicated by Prof. E. Rutherford, F.R.S.

† Phil. Mag. [6] xvii. p. 723 (1909).

‡ Proc. Chem. Soc. xxvi. p. 82 (1909); and later, Journ. Chem. Soc. xcv. p. 1073 (1909).

§ Based on the determination by Rutherford, later substantiated by Gray and Ramsay and by Debierne, that the equilibrium amount of emanation from 1 gm. of radium has a volume of 0·6 cub. mm. at N.T.P.

‖ Phil. Mag. [6] v. p. 561 (1903).

obtained by noting the temperature of the spiral when the ionization attained its maximum value.

Using this method with condensing spirals of copper tube, Rutherford and Soddy[*] found that the volatilization of these small quantities of emanation was rather sharply defined, within a range of a few degrees about the temperature of −150° C. More recently Mons. Laborde[†] applied the same method, using condensing spirals of different materials, and as a result claimed to have found marked differences in the temperatures at which the emanation will volatilize from the surfaces of different materials. Thus, from surfaces of iron, tin, silver (a silver tube), and of copper, the volatilization is claimed to take place at $-155 \pm 2°$ C.; from the surface of a silver deposit on glass, $-175 \pm 2°$ C.; and from the surface of glass itself, $-177 \pm 2°$ C. It is remarkable that there should be a difference of 20° C. between the temperatures of maximum volatilization from the surface of a *silver* tube and from the surface of a thick *silver* deposit on glass; and it is noticeable that these temperature differences were only found where glass spirals were concerned in the experiments.

These results had an important bearing upon the problem of the writer's investigations, and in consequence some experiments were performed to examine the effect of glass and metal surfaces upon the temperatures in question.

Method of Experiment.

The arrangement of apparatus is represented in fig. 1. The condensing spiral DSD′ was of tubing 0·35 cm. diameter, and was immersed in sufficient pentane to cover the spiral in a test-tube of 3 cm. diameter. Usually there were ten or twelve turns in the spiral.

The test-tube was immersed, almost the whole of its length, in a Dewar cylinder of 4 cm. diameter filled nearly to the top with liquid air. The spiral and the electroscope KK′ were "short-circuited" by the tubes Z and F respectively, so that a current of air could be used to sweep the conducting tubes free from uncondensed emanation without disturbing the condensed emanation in the spiral, and without unnecessarily contaminating the electroscope.

The operation of an experiment was as follows:—Emanation, which had been mixed with air and stored in the

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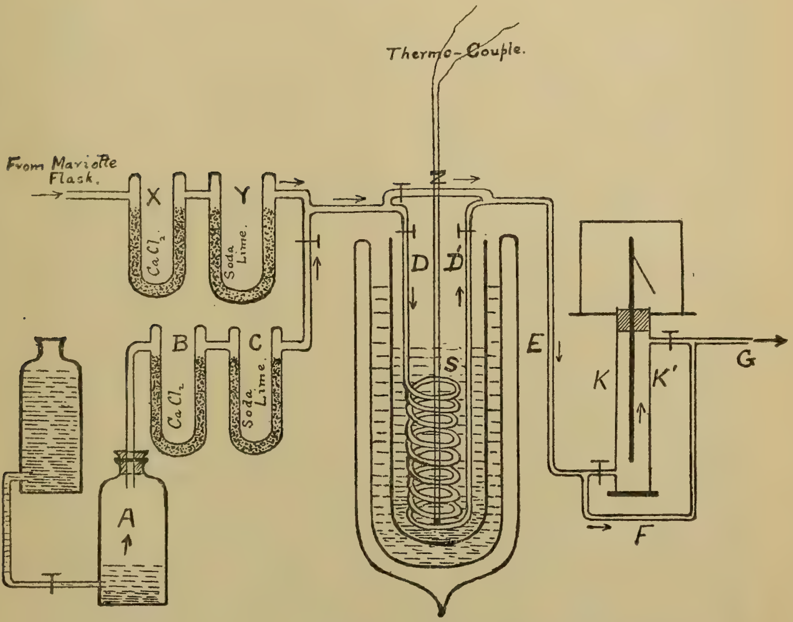
[*] *Loc. cit.*

[†] *Le Radium*, vi. p. 289 (1909).

receiver A, was forced slowly—usually about 0·4 c.c. per sec.—over the path ABCDEFG (see diagram).

Carbon dioxide and water vapour were removed in the tubes B and C containing calcium chloride and soda-lime respectively. Condensation of the emanation from the purified current of air took place in the spiral S cooled nearly to liquid air temperature. The uncondensed emanation passed to the open air outside the laboratory building through the tubes F and G. After condensation of the emanation a current of air (7·5 c.c. per sec.) was blown for several minutes from a Mariotte flask, through the calcium-chloride tube X and the soda-lime tube Y, over the path XYZEFG. This air current carried outside the building the emanation remaining about the tubes leading to the electroscope.

Fig. 1.



Next, a very *slow and constant* current of air from the Mariotte flask was sent through the condensing spiral over the path XYDEFG. This current was made *very slow* in order for it to attain quickly the temperature at any point of the spiral.

Throughout the above operations the Dewar cylinder was kept nearly full of liquid air, but immediately they were finished the cylinder was rapidly drawn away from the pentane bath, quickly emptied of its liquid air contents, and then set back in place over the bath. The stop-cocks of the electroscope were then opened. Under these conditions the temperature of the bath rose very slowly—about 0°4 C. per minute at the bottom.

As soon as the electroscope stop-cocks were opened there was a slight rise in ionization. This was due to slight amounts of uncondensed emanation not completely expelled from the spiral and the conducting tubes. This initial rise was in no way connected with the relatively large increase in ionization which marked the volatilization at the temperatures presently shown.

As already mentioned, pentane was used as a temperature bath. The pentane employed became very viscous at about −150° C., and consequently could not be stirred below this temperature. On this account the temperature of the bath was not uniform throughout but increased gradually from the bottom to the top.

Under these conditions the temperature required must be that of the coldest part of the condensing spirals, namely, the bottom coil. This must certainly be the case, for the writer has found from a few special experiments in which emanation was condensed in U-tubes, that condensation takes place in the limb of the tube through which the air current carrying the emanation enters. (The fact was ascertained by noting that the phosphorescence caused by the emanation and active deposit was confined to this limb of the U-tube.) Similarly with spirals: condensation takes place in that half of the spiral through which the air current enters. If, when the process of warming has started, any emanation volatilizes in the upper and warmer coils of the spiral, the air current bears it to the lower and colder coils, where it immediately recondenses provided that the temperature rises slowly. It is therefore necessary that the air current should be very slow, and that the spiral should rise very slowly in temperature.

For the above reason, the temperature of the bottom coil of the spirals was measured in all experiments; but opportunity was taken whenever possible to probe the other parts of the bath with a thermo-couple in order to acquire some information regarding the temperature distribution.

The temperatures were measured by means of thermocouples; the sensitiveness of the two element copper-constantan set, used in most of the experiments, was, on an average, 5 millimetre scale-divisions per degree centigrade. A calibration curve was constructed by means of the fixed temperatures of melting ice (0° C.), a mixture of solid CO_2 and ether (−79° C.), boiling ethylene (−103° C.), boiling methane (−164° C.), and liquid air of which the percentage of oxygen was determined by analysis (−186° C.). Some of the calibration curves were checked by further determinations from the melting-points of pure ether and of ethylene, but these points were difficult to fix with accuracy.

At the beginning of the work an iron-nickel couple with a Gambrell moving-coil galvanometer was employed, but occasion arose to change these for couples of copper-constantan with an Ayrton and Mather moving-coil galvanometer. The wires of the thermo-couples were No. 30 double-cotton covered, and the junctions were bare, without any protective covering, in order to avoid an appreciable temperature lag. Most of the present results were obtained with the warmer junction of the couple at the temperature of melting ice. A few others were taken with this junction at ordinary room temperatures, for which the necessary corrections were obtained.

Instead of an electrometer as detector of ionization, an electroscope of low cubical capacity was employed. The degree of sharpness of the volatilization temperatures can be the better detected the smaller the ionization chamber. In consequence, the ionization chamber was merely a small air-tight brass tube, 11·0 cms. long, through which ran an insulated brass rod carrying at the end outside the ionization chamber a gold-leaf system. The volume of the free space in this chamber was about 6 c.c.

In some of the experiments where metal spirals were used, the tube forming the spiral did not rise above the surface of the pentane bath. In these cases the conducting tubes D and D′ (see diagram, fig. 1) were made of glass and were joined to the tube of the spiral by rubber connexions, which experience proved to be quite satisfactory. This arrangement prevented the conduction of heat to the pentane bath along metal conductors, and consequently ensured a slower rate of rise of temperature.

Discussion and Results.

On a close examination of this flow method of experiment, it should be remembered that the *temperature corresponding to maximum ionization in the testing vessel is the temperature at which the rate of volatilization of emanation from the condensing surface begins to decrease very rapidly to zero.*

It is known that when emanation is condensed on the inner wall of a vessel at any temperature, even down to the liquid air temperature, the emanation can be practically all removed by continuously pumping. The fact shows that there is an appreciable vapour phase of the emanation at all temperatures down to the temperature of liquid air. Consequently, in an experiment by the flow method, if the emanation be at first condensed, and the temperature be kept constant while the gas current is allowed to flow indefinitely, the molecules of emanation in the vapour phase will become entrained in the gas current and be removed. More molecules will then volatilize into the vapour phase from the condensed layer, and these in turn will also be carried away. This process will continue until all the emanation has been removed. It follows, therefore, that with a temperature not fixed but gradually rising, and with a constant gas flow, the temperature at which all the emanation has just been removed from the surface of the condenser will depend on (1) the quantity of emanation condensed, (2) the rate of rise of temperature. Experiments by the flow method to compare the influences of different surfaces on the process of volatilization should be carried out with the conditions regarding (1) and (2) at least approximately alike *.

The quantities of emanation employed in the experiments varied between the equilibrium amounts from 2×10^{-4} to 2×10^{-3} mgm. of radium. Experience showed that the rate of volatilization at the final temperature is increasing so rapidly that variations in the quantity of emanation, much larger than the above, give very similar results. The range of accuracy in the experiments is considered to be $\pm 2°$ C.

Curves I. and II. of fig. 2, which represent the connexion between ionization and temperature for spirals of lead and of glass, are typical of the behaviour for all the substances examined. The dotted curves represent the rise of temperature at the bottom of the bath with time.

The maximum ordinates GH and IK of the ionization curves give the temperatures at which the volatilization of emanation from the condensing surface very rapidly diminishes or ceases altogether. We may say that at these temperatures the emanation is all removed from the surface.

But the ordinates, such as AB, CD, EF, and also MN, QR, show that at still lower temperatures there is appreciable volatilization. This could no doubt be noticed down to liquid air temperature if the electroscope could be kept from

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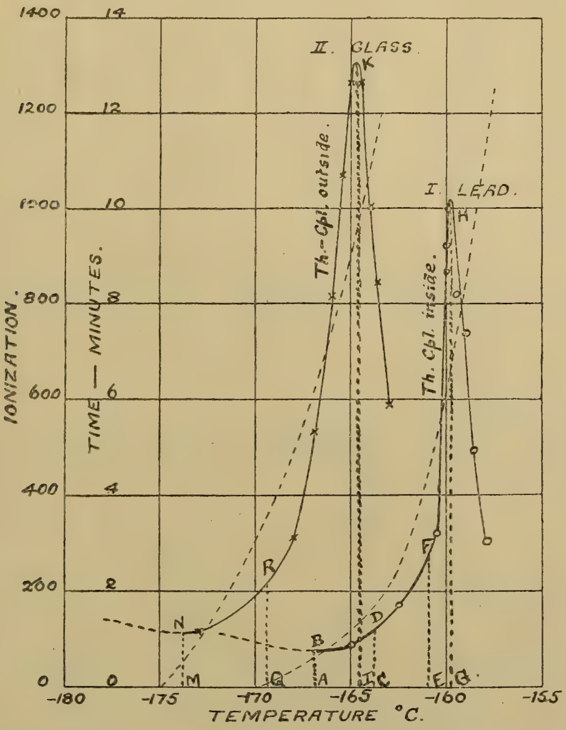
* It is not meant here that the quantity of emanation cannot be varied from one amount over a range of ten or twenty times that quantity, but it should not be varied over thousands or tens of thousands of times.

contamination by the first sweeping through of uncondensed emanation. With still smaller quantities of emanation this gradual volatilization as the temperature rises is more easily

Fig. 2.



noticed, for then there is not so much uncondensed emanation to contaminate the electroscope. With larger quantities of emanation the rise of ionization to a maximum appears all the more sudden, because the amounts of emanation volatilizing at the lower temperatures are relatively much smaller than the amounts at the temperatures corresponding to maximum ionization.

Experiments by another method will be described in a later paper showing that a gradual and continuous volatilization can be detected from -180° C. upwards. The fact that the maximum ordinates of curves I. and II. do not fall at the same temperature is explained later.

The results of a number of experiments, using spirals of the materials named and of diameter of tube 0·35 cm., are given in the following tables. In these experiments, attempts

Table I.

Material of Spiral.	Rate of Air-Flow.	Rate of Rise of Temperature.	Maximum Ionization.	Temperature at Max. Ionization.	Remarks.
Copper.	0·12 cc. per. sec.	0·36° C. per min.	400	−162° C.	Using iron-nickel couple.
	0·13 ,, ,,	0·40 ,, ,,	640	−159	Using copper-constantan, double, couple.
	0·14 ,, ,,	0·45 ,, ,,	500	−159	
			Mean ……	−160°	
Lead.	0·12 cc. per sec.	0·41° C. per min.	220	−160° C.	Iron-nickel couple.
	0·13 ,, ,,	0·40 ,, ,,	360	−161	Copper-constantan, double, couple.
	0·12 ,, ,,	0·30 ,, ,,	230	−162	
	0·10 ,, ,,	0·35 ,, ,,	640	−159	
			Mean ……	160·5°	
Silvered Glass.	0·12 cc. per sec.	0·38° C. per min.	440	−163° C.	Iron-nickel couple.
	0·11 ,, ,,	0·40 ,, ,,	400	−160	Copper-constantan, double, couple.
			Mean ……	−161·5° C.	
Glass.	0·10 cc. per sec.	0·49° C. per min.	1300	−164·5° C.	Copper-constantan, double, couple.
	0·11 ,, ,,	0·35 ,, ,,	1800	−166	
	0·10 ,, ,,	0·40 ,, ,,	880	−164	
	0·10 ,, ,,	………	520	−163	
			Mean ……	−164·4°	

were always made to keep the conditions regarding (1) the rate of flow of air-current, (2) the rate of rise of temperature, and (3) the quantity of emanation condensed the same for all materials. Experience showed that there could be considerable latitude in all three factors without obtaining final temperature results outside the error of experiment. This is especially so with regard to the quantity of emanation.

The numbers tabulated under "Maximum Ionization," representing divisions per minute in the electroscope, give a rough approximation of the relative amounts of emanation used in the different experiments; those under "Rate of Rise of Temperature" refer to the bottom temperatures of the bath at the time of maximum ionization. The "Rates of Air-Flow" refer to a temperature of −160° C.

The temperature correction for the time taken by the volatilized emanation to pass from the condensing spiral to the electroscope was negligible in comparison with the error of experiment.

It will be noticed from the diagram and table (Table I.) that in the case of glass the temperature was consistently a few degrees lower than in the case of metals. The difference in the case of silvered glass was not so large, and in consequence, the smaller heat conductivity in glass, compared with metals, was not quite satisfactory as a reason for the differences shown. To obtain more information on the point further experiments were performed. In these, condensation of the emanation took place in small glass and lead spirals of only two or three coils, the planes of the coils when placed in the bath being vertical instead of horizontal, and the spirals being just covered with pentane. Under these circumstances there could only be very little temperature variation over the spirals. The thermo-couple (a single copper-constantan element) was threaded through the spiral tube so that the temperature on the inside of the tube was the one determined. The wires of the thermo-couple were brought to the open, outside the bath, through the walls of the glass conducting tubes, and the holes through which the wires emerged were closed by sealing-wax. Taking these precautions, the final temperatures with both lead and glass spirals come, within the experimental error, to the same value, as can be seen from the table which follows.

This result, taken in conjunction with what has gone before, has one of two explanations. Either the condensed emanation volatilizes from the surfaces of glass, thermo-couple wires, and of lead at the same temperature; or, some emanation remains condensed upon the surface of the thermo-couple

TABLE II.

Material of Spiral.	Rate of Air-Flow.	Rate of Rise of Temperature.	Maximum Ionization.	Temperature at Max. Ionization.	Remarks.
Lead.	0·11 cc. per sec.	0·45° C. per min.	1000	−160° C.	Bath 3·5 cm. high.
	0·12 ,, ,,	0·35 ,, ,,	630	−162	
	0·10 ,, ,,	0·35 ,, ,,	....	−163	Bath 4·5 cm. high. Middle of bath at −158° C.
			Mean	−161·7° C.	
Glass.	0·13 cc. per sec.	0·45 C. per min.	300	−159° C.	Bath 5·0 cm. high.
	0·11 ,, ,,	0·30 ,, ,,	1500	−163	Bath 3·5 cm. high.
	0·13 ,, ,,	....	520	−162	
	0·10 ,, ,,	0·50 ,, ,,	....	−159	Middle temp. −154° C.
			Mean	−160·8°	

wires at a temperature a few degrees higher than that at which the emanation volatilizes from glass.

In any case it can be said that the temperature differences in the present experiments were small. The emanation could not have volatilized from the glass surfaces at temperatures as low as −177° C., for then the volatilized emanation would have shown its presence in the ionization chamber immediately after opening the stopcocks, and without any appreciable wait for the temperature to rise. Moreover, in some experiments condensation only took place at −177° or −178° C.

Mention has been made before of attempts to get an idea of the temperature distribution in the bath by means of a second thermocouple. It was found that no matter how the temperatures throughout the rest of the bath varied, the bottom temperature at maximum volatilization of the emanation was about the same in all cases. The temperatures at the top and middle parts of the bath would of course depend on the depth of pentane in the bath, an average value of the temperature gradient being about 2° C. per centimetre depth.

It was not considered necessary to experiment with iron, tin, and other metals, since M. Laborde obtained the same result with these as with copper and silver.

No doubt the above volatilization temperatures could have been fixed with greater precision if a bath which remained liquid over the required range of temperature could have been used. But it was not feasible to procure the large quantities of a liquefied gas (such as ethylene) and of liquid air, which would be necessary for such a large number of experiments. The experiments of M. Laborde must have suffered from this same disadvantage, for it is not likely that a metallic bath of granulated copper would be of uniform temperature throughout. Some trials by the writer, duplicating as nearly as possible the conditions, have shown that after the process of warming from the liquid-air temperature sets in, there is, as one would expect, a continuous and large temperature gradient from the bottom of the bath to the top. A metallic bath also is of a discontinuous structure, and allows the penetration of air down to the bottom as soon as the liquid air has evaporated. For these reasons the use of metallic copper as a temperature bath was abandoned in favour of pentane.

Conclusion.

In the series of experiments just described only small, and almost inappreciable differences (4° C.) can be found in the temperatures at which small quantities af radium emanation, when once condensed, will volatilize from the surfaces of glass and of metals. With this flow method of experiment, using quantities of emanation varying between the equilibrium amounts from 2×10^{-4} and 2×10^{-3} mgm. of radium, and with a rate of rise of temperature of about 0°·4 C. per minute, it was found that there is a slight and gradually increasing volatilization until the temperature approaches −160° C. Approaching this temperature, the volatilization becomes relatively very rapid, and above it volatilization practically ceases.

The temperature, −160° C., mentioned above, is merely the final temperature of separation of the emanation from the condensing surfaces in the experiments; its measurement serves as a method of comparing the effect of the various surfaces mentioned on the volatilization. This temperature is some degrees lower than the majority of results in the original experiments of Rutherford and Soddy, where the temperatures measured were the average temperatures over the whole of the condensing spiral, and where there was a higher rate of rise of temperature.

It is not to be understood that it is impossible for emanation to remain condensed on a metallic or glass surface at temperatures higher than −160° C.; for further experiments by another method have shown that the temperature of final separation from the surface depends, as would be expected, on the quantity of emanation condensed. These experiments will be described in a later paper.

The writer is glad to acknowledge great kindness and assistance on the part of Prof. Rutherford.

University of Manchester,
August 1910.

CVIII. *A Means of Measuring the Apparent Diameter of the Pupil of the Eye, in very feeble Light. By* T. H. Blakesley [*].

THE advantage obtained by the magnifying power of a telescope or a microscope may be very seriously diminished if the orifice of the eyepiece through which the light issues to the eye is so small as not to fill the pupil with light. The magnification is inversely proportional to the focal length of the eyepiece, and therefore to the orifice with which it is furnished, which therefore has a smaller

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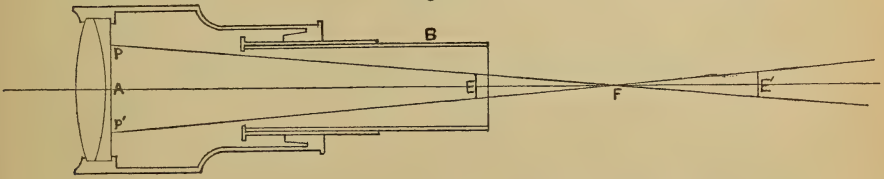
[*] Communicated by the Author.

diameter the greater the magnifying power, as depending upon the eyepiece.

If the object in view is a very faint star or nebula in the case of a telescope, or an ultra-microscopic subject in the case of a microscope, the field is necessarily very dark. All side light must be carefully avoided, and the pupil of the eye is, without doubt, in a highly expanded condition, so that the eyepiece employed may have an orifice smaller than the pupil. The object of this communication is to show how the diameter of the pupil may, with fair accuracy, be measured in such all but complete obscurity.

The accompanying sketch will illustrate the means employed to effect this.

Fig. 1.



The apparatus consists of what is virtually one tube of a common opera-glass, with the eyepiece removed. Into the sliding tube is inserted another tube B of suitable length, and this is pushed home until it is stopped by the offset at the far end of the sliding tube. With the apparatus at its longest the distance from the open end to the near side of the object-glass may be measured, and also the exposed portion of the sliding tube. In any other position the defect in the latter is equal to that in the former, the value of which is thus at any time readily determined.

In the cell of the object-glass and in contact with it on its near side, is inserted a screen made of the black opaque paper used by photographers. Two small pinholes PP′ are made upon one diameter, at equal distances from the axis AF of the lens. F is the principal focus of the lens. The focal distance AF requires to be known, and it is a quantity which can be determined with considerable accuracy.

The instrument is directed upon a distant and solitary light when the night is dark. A pair of fine beams will then pass through the pinholes PP′, and converge to the focus F.

These will both be visible to an eye placed coaxially with the lens, if the apparent diameter of the pupil of the eye is not less than the distance apart of the beams in the position along the axis which the apparent pupil happens to occupy.

Let E be a position in which this is just possible, E being nearer to the object-glass than is F the principal focus. Then if D denotes the distance between the pinholes, d the diameter of the apparent pupil, and v the focal distance AF, the following equation is true, viz.:

$$d=\frac{D}{v}.FE.$$

In making this observation the eyelids must be held against the open end of the tube B, not merely with a view to exclude any external light but also to ensure a fixed relative position of the eye and the tube.

The tube B is now withdrawn, and a second tube of the same calibre takes its place, of a length suitable for dealing with the second position E′ where the pupil will have a diameter equal to the distance between the beams of light. A second adjustment is made resulting in the equation

$$d=\frac{D}{v}.FE'.$$

Adding the two equations,

$$d=\frac{D}{v}.\frac{EE'}{2}.$$

Now, as the two tubes employed have the same diameter, the position of the eye relatively to the ends of the tubes will be the same, or EE′ will be equal to the difference between the distances from the lens of the open ends of the two tubes when in adjustment.

Denoting therefore these distances by L and l respectively, the diameter of the apparent pupil is given by the equation

$$d=\frac{D}{v}.\frac{L-l}{2}.$$

The following observations may be made. It is necessary on approaching adjustment that the eye should be fixed upon A, half way between P and P′.

Let the diameter PP′ be supposed horizontal, and suppose the eye to be slightly nearer the object-glass than the position E. Neither beam is seen if the eye is directed to A, but if the eyeball is turned to the right, the pupil is shifted in the same direction, and P at once is seen.

If the eye is just on the side of E remote from the object-glass, both beams are seen when the eye is directed to A, but a turn of the eyeball to the right puts P′ out of view.

If the eye is slightly nearer the object-glass than the position E′, and directed to A, both beams are seen, but if the eyeball is turned to the right, instead of P (which appears to the right always) becoming more plainly seen, it disappears.

And finally, if the eye is just on the side of E′ remote from the object-glass, and directed to A, nothing is seen. But if the eye is turned to the right, P′, towards the left, becomes visible.

These facts, obvious enough, are pointed out as assisting very considerably the process of adjustment. If difficulty is experienced in keeping the eye fixed upon A, a small pinhole may be made in the screen at that point. The beam of light through it will, during the processes described, be always visible.

The values of the diameter of the apparent pupil, under the circumstances indicated, in the writer's own case, have been found to vary from 6·74 to 7·20 millimetres, the higher values being less frequent. He cannot but look upon the value ⅓ of an inch (8·47 millimetres), quoted occasionally in text-books, as extremely abnormal.

CIX. *The Study of Variable Currents by means of the "Phaseograph."* *By* Manne Siegbahn[*].

[Plate XIX.]

Introduction.

In order to characterize the electric state of a conductor through which an electric current passes, the two variables, strength of current (i) and voltage (e), may conveniently be made use of. As long as we have to deal with metallic conductors and constant currents, there is between these two variables the simple relation:

$$\frac{e}{i} = \text{const.} = m, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the constant m signifies the ohmic resistance in the conductor concerned.

In the general case, variable currents and conductors of different kinds, the connexion between the variables is more complicated. In order to obtain a survey of matters in these

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[*] Communicated by the Author.

cases one variable may be expressed as the function of the other,

$$e=f(i). \qquad (2)$$

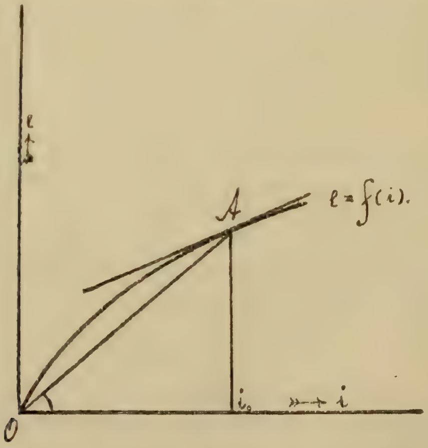
For a long time we have used the graphic representation for the magnetic magnitudes, and thus learnt to master them. Also in a closely connected branch of electricity, *i.e.* the electric machines, the graphic method has been used to advantage. This has particularly been the case, since Hopkinson's epoch-making works made it possible for us to calculate "magnetic loops." For alternate currents this excellent method has only recently begun to be made use of. It was not until Kauffmann [*] had proved its applicability to electricity passing through gases, and developed the conditions of stability, that it could come into proper use where alternate currents are concerned.

I. *Characteristics.*

If the function (2) is graphically represented, the so-called *characteristic curve* is obtained. We will now consider the most important qualities of these curves.

Fig. 1 reproduces a characteristic curve or, more shortly, a characteristic. It gives for any i-value the corresponding value of e, supposing *i.e.* one has in every point to deal with a *stationary* state. To exemplify our case we may take

Fig. 1.



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[*] W. Kauffmann, *Ann. d. Physik* (4) ii. p. 158 (1900).

the given curve to represent the characteristic of a carbon filament lamp. How is the resistance now obtained for a certain strength of current (i_0)? The resistance is defined by the equation (1). Consequently the resistance graphically expressed is the tangent of the angle (iOA). If on the other hand the resistance is defined as

$$\frac{de}{di},$$

another value would be obtained. Hence it follows that the function (1) used for stationary currents in metallic conductors, is of little value in more complicated cases. Its place is taken by the characteristic, where variable currents or inhomogeneous conductors are concerned. If the characteristics of *two* conductors are known, the characteristic of a conductor composed of the two can be constructed from them. Here the following laws for coupling in series and parallel coupling of the two characteristics hold good.

A. *Coupling in Series.*—For a certain strength of current (i) the two e-values are added.
B. *Parallel Coupling.*—For a certain voltage (e) the two i-values are added.

Fig. 2.

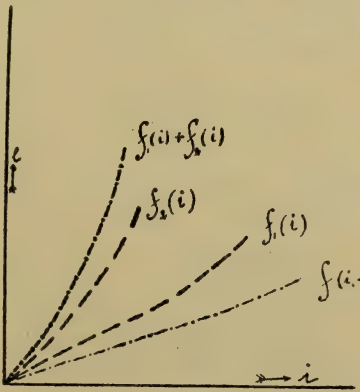


Fig. 2 shows the graphical construction of the characteristics in question.

If the voltage (E) and the two characteristics are given, we are in possession of the means necessary for the determination of the e- and i-values. According to the additional theorem

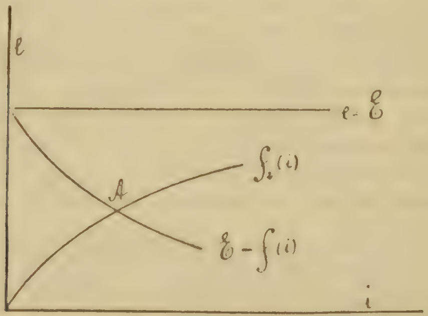
$$E = f_1(i) + f_2(i), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

$$E - f_1(i) = f_2(i). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This alteration of our formula gives us a simple method of graphically finding the e- and i-value.

Fig. 3.



From the line $e = E$, $f_1(i)$ is set off: its intersection with $f_2(i)$ is the required point of equilibrium A.

From this Kauffmann's conditions of stability are easily found. From (3) is obtained by differentiation with respect to the strength of current (i),

$$f_1 + f_2 + \frac{\partial f}{\partial i} + \frac{\partial f_2}{\partial i}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

for a stable equilibrium, it is required that this expression shall be greater than the given voltage E; or

stable: $$\frac{\partial f_1}{\partial i} + \frac{\partial f_2}{\partial i} > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

indifferent: $$\frac{\partial f_1}{\partial i} + \frac{\partial f_2}{\partial i} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

unstable: $$\frac{\partial f_1}{\partial i} + \frac{\partial f_2}{\partial i} < 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Graphically $\frac{\partial f_1}{\partial i}$ signifies the angular coefficient of the tangent at the point in question.

II. *Methods of Registering Characteristics.*

We can distinguish between two different kinds of characteristics.

A. Statical characteristics.
B. Dynamic characteristics.

A refers to stationary or quasi-stationary currents; these can be registered by ordinary voltmeters or ammeters. B, the dynamic characteristics, occur with variable especially alternate currents; these must be registered by instruments which at every moment indicate strength of current and voltage. For this purpose various oscillographs with two movable systems are used: one registering strength of current, the other voltage. By the construction of the connected values in a co-ordinate system the required characteristic is obtained. Consequently, this is practically an indirect method, which besides implies much waste of time. Another difficulty also arises which makes the results uncertain, *i.e.* the defective adjustment. The adjustment is effected by directing the reflexions from the mirrors of the two movable systems towards the same point. If these reflexions were, let us say, geometrical circles with the same intensity of light, the adjustment would, no doubt, be possible, but as they present irregular figures, it can be done only with a limited degree of accuracy. To this may be added also the circumstance that the adjustment sometimes is altered while the instrument is registering. On another occasion I will deal more closely with this question. To avoid the difficulties just mentioned, particularly the tedious redrawing of the curves, the two movable systems must in some way be made to co-operate. The apparatus I am going to describe is based on this idea.

III. *The Phaseograph.*

In a communication to the *Physikalische Zeitschrift* * I have demonstrated the chief features of the construction. As shown by fig. 5 (Pl. XIX.), the apparatus consists of two parts: the electromagnet and a box of brass with an ebonite or slate lid. In the first construction the electromagnet was made of two soft iron bows, each bar being provided with a solenoid. This arrangement, however, proved useless. Of the four magnetic fields required, only two were sufficiently strong, *i.e.* those formed between the two bars of the same bow. In the final construction the electromagnet was made

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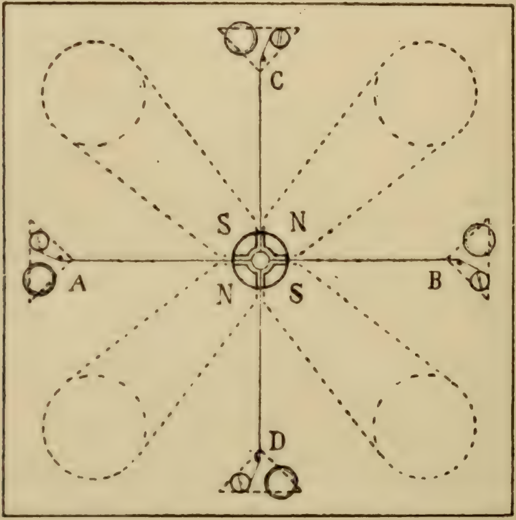
* M. Siegbahn, *Phys. Zeits.* x. 1909, p. 1017.

of a soft iron ring with four upright iron rods. Each of these is covered with a solenoid of copper wire. The solenoids have been arranged so as to close to 80 volts if coupled in series. In the brass box are fixed four pole-pieces of the shape indicated by fig. 4. Each of these is provided with a cylindric plate which fits one of the four electromagnets. In the magnetic fields NS, N′S′ are extended two thin silver wires (diameter 0·02 mm.), AB and CD. The tension in these wires can be regulated by means of special screws. The larger screws will be used for turning on the electric current. At the crossing-point the two wires are insulated with a plate of mica, and also provided with a small mirror.

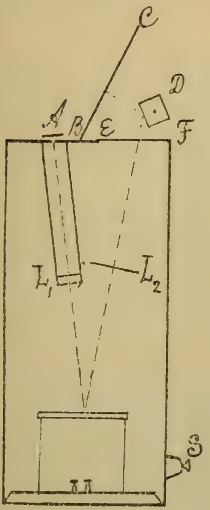
Fig. 4.



If a constant current is made to pass through one wire, *f. i.* A B, one-half will be lifted, owing to the magnetic field, the other will be pressed down; hence the mirror will be turned at a certain small angle. With sufficiently small angles the turning is proportional to the strength of current. Owing to the great tension in the wire, the new equilibrium is not restored until after a considerable time of oscillation. If the box is filled with a suitable damping fluid, this movement can be made *aperiodical.* With the ordinary two-stringed oscillographs, vaseline-oil is used for this purpose. With this apparatus the vaseline-oil did not act as a sufficiently strong damper. Caster-oil, however, proved effective.

There remains to be described the mounting and the special arrangements, as shown by fig. 6.

Fig. 6.



The Nernst-style A throws a sharp light on a small diaphragm, which at exposure can be shut with a shutter. By the aid of the two lenses, L_1 and L_2, an image is formed on the ground glass-plate EF. For photographic purposes the latter can be replaced by a chassis with plate. The lens and the diaphragm are sheltered from outside light by a cardboard tube.

If we want to study a current curve, *i. e.* use the phaseograph as an ordinary single oscillograph a revolving mirror with driver is put on, and the ground glass-plate is removed. The image then appears on the screen BC; the desired current curve is obtained by putting the mirror in rotation.

By means of binding-screws and interrupters ($S_{1\,2\,3}$) on the outside of the box the electric current is conducted to the electromagnet (S_1) and the two measuring-wires (S_2S_3)

IV. *Other double Oscillographs.*

In this place it may be convenient to mention some other oscillographs with two co-operating systems, which were constructed about the same time as the one I have just described.

According to a communication in *Verhandl. der deutsch. Phys. Gesellsch.* xi. (1909), A. Wehnelt has made use of two oscillograph-slides, one of which was introduced into a magnetic field, which was to be examined for the demonstration of magnetization curves. At the request of Siemens and Halske, Berlin, Hansrath tried to use this principle for registering hysteresis curves. The method in this form, however, proved useless, and the instrument brought into the market was composed of an "abstimmbar" vibration galvanometer on an ordinary oscillograph-slide.

The "Hysteresigraph" constructed by H. Abraham served the same purpose.

F. Piola's double oscillograph may also be mentioned. It consists of two turning-coils at right angles. Its use is confined to slowly variable fields.

V. *Theory of the Phaseograph.*

In theory the phaseograph can be treated in the same way as the oscillograph. For the movable system the following equation is obtained :—

$$K\frac{d^2\vartheta}{dt^2}+A\frac{d\vartheta}{dt}+C\vartheta=F. \quad . \quad . \quad . \quad . \quad (9)$$

The letters signify :

K, moment of inertia ;
A, damping factor ;
C, directive force ;
F, applied force.

If a Fourier's series is put for F,

$$F=\sum_{k=1}^{\infty}\mathfrak{F}_k\sin(k\omega t-\phi_k), \quad . \quad . \quad . \quad . \quad (10)$$

the integral to (9) will be

$$\vartheta=\frac{1}{C}\sum\frac{\mathfrak{F}_k}{\sqrt{(1-k^2\lambda^2)^2+4\alpha^2k^2\lambda^2}}\sin(k\omega t-\phi_k-\gamma_k); \quad (11)$$

$$\alpha=\frac{A}{2\sqrt{CK}}; \qquad \lambda=\frac{2\pi}{\tau}\sqrt{\frac{K}{C}}; \quad . \quad (12, 13)$$

$$\tan\gamma_k=\frac{2\alpha k\lambda}{1-k^2\lambda^2}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If the mirror-oscillations are to represent the proposed Fourier's series F, the integral ϑ for $\alpha=1$:

$$\vartheta_1=\frac{1}{C}\sum\frac{\mathfrak{F}_k}{1+k^2\lambda^2}\sin(k\omega t-\phi_k-\gamma_k) \quad . \quad . \quad (15)$$

must give the same curve as F. Any experimental test of this formula is almost out of the question.

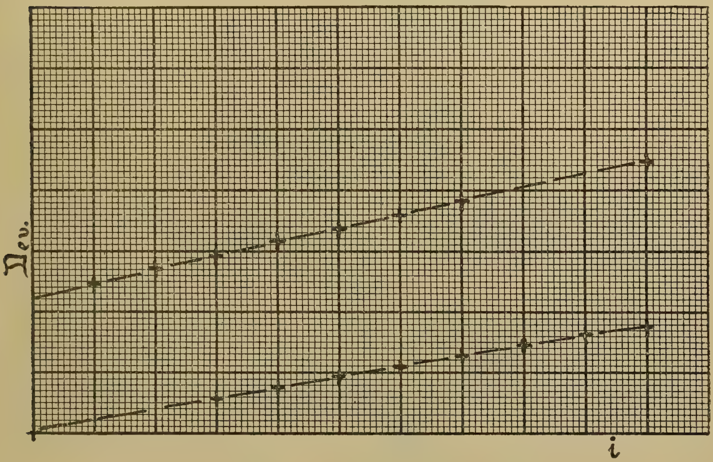
VI. *Working of the Apparatus.*

When using the apparatus it is necessary to ascertain if the deviation is proportional to the strength of current. For this purpose the ground-glass plate was replaced by a glass scale, and simultaneous readings were made on this scale (from any 0-point) and an ammeter. The following values were obtained :—

Strength of current.	Deviation.	
	1.	*2.*
$100 . 10^{-3}$ amp.	1·77	
90	1·61	2·49
80	1·45	2·71
70	1·28	2·93
60	1·10	3·15
50	0·94	3·37
40	0·76	3·60
30	0·58	3·83
0	0·00	4·48

1 is noted when one measuring-wire only was used, *2* when the same current passed through both the wires. In the subjoined graphical diagram the direction of *2* is reversed.

Fig. 7.



The diagram shows that there is proportionality between deviation and strength of current.

If the instrument is used for registering characteristics, the method is obvious: we have merely to shunt part of the current off to one measuring wire, while through the other a current is passed that is proportional to the examined voltage Later on I will give complete coupling-diagrams for this use of the apparatus.

Another way is to compare two alternate currents with each other, *f. i.* strength of current and voltage in transformers, phase-differences between current and tension by self-induction and capacity. Through one wire passes then a current

$$i=i_0 \sin \omega t, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and through the other

$$e=e_0 \sin(\omega t+\phi). \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

By the combined action of these oscillations the luminous point describes a figure the equation of which is obtained from (16) and (17) by the elimination of t:

$$\frac{i^2}{i_0^2}+\frac{e^2}{e_0^2}-\frac{2ei}{e_0 i_0}\cos\phi=\sin^2\phi. \quad . \quad . \quad . \quad (18)$$

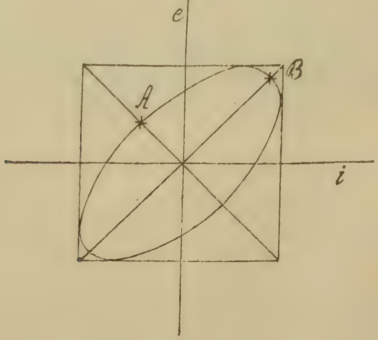
In the general case the luminous point, consequently, describes an ellipse. What is of interest in this case is the phase-difference between the two currents. It is especially interesting as by the phase difference can be calculated *e. g.* the self-induction of a bobbin. For the phase-difference between current and voltage we have

$$\tan\phi=\frac{2\pi L}{\omega\tau}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

τ, period;
L, self-induction coefficient;
ω, ohmic resistance.

I will now show a very simple way of calculating the phase-difference from the registered ellipse.

Fig. 8.



By letting the two currents (e and i) register one at a time the resistance is altered, till the same amplitudes are obtained,

$$i_0=e_0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The equation (18) is then simplified to

$$i^2+e^2-2ei\cos\phi=i_0^{\,2}\sin^2\phi. \quad . \quad . \quad . \quad . \quad (21)$$

This equation represents ellipses inscribed in a quadrangle. Its axes are consequently the lines

$$e=\pm i.. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad , \quad (22)$$

If e is eliminated between the equations (21) and (22) we obtain

$$2i^2\mp 2i^2\cos\phi=i_0^{\,2}\sin^2\phi. \quad . \quad . \quad . \quad . \quad (23)$$

The two i-values obtained from this formula are the coordinates of A and B. They can be exchanged for the semiaxes a, b,

$$a=i_1\sqrt{2}\,; \qquad b=i_2\sqrt{2}\,;$$

$$a^2=2i_1^{\,2}\,; \qquad b^2=2i_2^{\,2};$$

$$a^2(1-\cos\phi)=i_0^{\,2}\sin^2\phi\,;$$

$$b^2(1+\cos\phi=i_0^{\,2}\sin^2\phi.$$

By division is obtained

$$a^2-a^2\cos\phi=b^2+b^2\cos\phi\,;$$

$$\cos\phi=\frac{a^2-b^2}{a^2+b^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

We have consequently only to measure the axes of the ellipse to find phase-difference and from this self-induction and capacity.

There remains to be mentioned a third way in which the apparatus can be worked, *i. e.* by the use of an auxiliary current in one measuring wire. In the first place we can then think of the use of a constantly decreasing or increasing current which gives to the luminous point a lateral deviation with constant rapidity, at the same time as the other measuring-wire registers the desired current-curve. Here belong also the methods of registering the characteristics of electric machines. In another place we will deal more fully with this subject. There remains to be considered some applications of the above-mentioned methods.

VII. *Alternate Currents.*

Under this heading I will bring together some registerings of the relations between current and voltage with self-inductions, capacities, transformers, &c.

Figs. 9 and 10 (Pl. XIX.) show some current-voltage diagrams with a self-induction bobbin; in the latter case a soft-iron cylinder has been introduced into the bobbin.

Figs. 11 and 12 (Pl. XIX.) show the current-diagram of the primary and secondary coils of a transformer according to the following coupling-diagram (fig. 13).

Fig. 13.

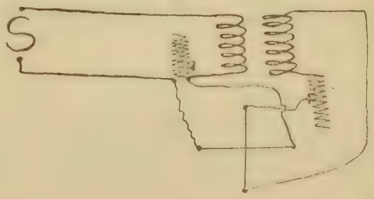


Fig. 11 without iron core, fig. 12 with. In the phaseograms the higher oscillations of the alternate-current machine are clearly visible.

We further subjoin, with no other comment, a phaseogram registered with a Wehnelt interrupter (fig. 14, Pl. XIX.). It shows that the apparatus can be used also for these rapid oscillations.

To instance the method of calculating the self-induction from the phaseogram, we subjoin the following diagram (fig. 15, Pl. XIX.). For phase-difference we obtained above the following formula:—

$$\cos\phi = \frac{\left(\frac{a}{b}\right)^2 - 1}{\left(\frac{a}{b}\right)^2 + 1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where $\frac{a}{b}$ expresses the relation between the chief axes. In the diagram

$$\frac{a}{b} = 2{\cdot}94\,;$$

from which is obtained

$$\phi = 37^\circ\ 34'.$$

The self-induction is L.

$$L = \frac{\omega}{2\pi N} \tan\phi. \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

ω = ohmic resistance = 1 ohm;

N = the frequency = $\frac{1720}{60}$;

L = 0·0043 henry.

VIII. *Aluminium Cell.*

To show phaseograms by more irregular currents, I have made some experiments with an aluminium cell consisting of an aluminium wire against sheets of lead in dilute sulphuric acid (accumulator acid).

The three phaseograms show the cell in various stages: fig. 16 soon after the closing of the current; fig. 17 when the current has passed for a while; lastly fig. 18 shows an inactive cell (Pl. XIX.).

CX. *The Positive Thermions emitted by the Alkali Sulphates.*

By O. W. Richardson, *M.A., D.Sc., Professor of Physics, Princeton University*[*].

[Plate XX.]

EXPERIMENTS by the author [†] and Mr. Hulbirt [‡] have shown that the bulk of the positive thermions emitted by the commoner conductors, which can be heated to a sufficiently high temperature, possess very nearly the same value of e/m: a value which corresponds to a molecular weight m for the ions of about 25, on the assumption that they carry the same charge as the atom of hydrogen in electrolysis. There are a number of different ways in which it might happen that the various substances investigated might give rise to ions having the same specific charge, and these are discussed at length in the papers referred to. One of these views, and the one which seemed to have the most evidence in its favour, was that the ions consisted of atoms of sodium which were present as a common impurity in all the substances investigated. This view is supported among other things by the well-known fact that sodium compounds are very widely distributed, and by the fact that the value of m for the ions is very close to the atomic weight of sodium (23·05).

It was this view that suggested the present investigation. For it was felt, since the alkali metals and their compounds are so similar to one another in both chemical and physical properties, that if sodium compounds gave rise to positive ions having a certain specific charge, it ought to be possible to obtain ions having other values of e/m by substituting salts of the other alkali metals for those of sodium. The author therefore decided to measure the value of e/m for the positive ions emitted by the sulphates of the different alkali metals when heated.

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[*] Communicated by the Author.

[†] Phil. Mag. [6] vol xvi. p. 740 (1908).

[‡] Phil. Mag. [6] vol. xx. p. 545 (1910).

The method adopted consists in measuring the deflexion of the path of the ions, between two parallel plates at different potentials, produced by a known transverse magnetic field. It was, in fact, the same as that used in the investigation of the specific charge of the ions emitted by hot bodies. So that, for the description of the apparatus and the method of using it, it will be sufficient to refer to the first of the two papers mentioned, which contains a very full account of the matter.

The experiments were carried out in the following manner: a strip of platinum 0·5 cm. long, ·002 cm. thick, and about ·05 cm. wide, was mounted in the apparatus. The distribution of the ionization over a parallel plate about ·5 cm. away was then determined in the usual manner, with oppositely directed magnetic fields of about 4700 lines per cm. From the displacement of the maximum the value of e/m for the positive ions from platinum could be calculated.

After the measurement had been made, the platinum was strongly heated for several hours until it gave only a negligible leak at the temperature at which the test was made. The apparatus was then taken down, and a layer of the pure alkali salt to be tested was melted over the front surface of the strip. The apparatus was again set up and exhausted. It was now found that a large positive ionization could be obtained at a temperature below that at which the test on the platinum had been made, showing that the ionization was due to the alkali salt and not to the platinum. The distribution of the ionization on the opposite plate was now determined with the magnetic field in opposite directions, and the displacement of the maximum measured.

From this displacement together with the distance and difference of potential between the plates and the strength of the field the values of e/m and of m could be calculated from the formula: $e/m = \frac{9}{2} \cdot \frac{\mathrm{V}x^2}{\mathrm{H}^2 z^4}$. In calculating the value of m the ions were assumed to carry the same charge as an atom of hydrogen in electrolysis, and the value of e/m for the hydrogen ions in electrolysis was taken to be $9 \cdot 66 \times 10^3$ E.M. units. In the present case we have a valuable check on the results thus obtained, on account of the simultaneous measurements which were made of the displacement in the case of the ions from platinum. Previous work has shown that the value of e/m for the positive ions emitted by this metal* does not vary much for different

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* Richardson & Hulbirt, *loc. cit.*

specimens of the metal. By assuming the ions from platinum to have the average value (25·5) previously found, it was possible to calculate the values of e/m and m for the salts investigated without making use of the linear dimensions of the apparatus. If we could rely on the constancy of e/m for the positive ions from platinum, we could in this way get rid of the uncertainty arising from the difficulty of knowing the distance between the hot strip and the plates accurately. It is probable, however, that the value of e/m for the positive ions from platinum is only approximately constant, so that this method can only be regarded as a check on the other. The disagreement between the two methods was not much greater than the errors of experiment.

It has already been pointed out that the method is liable to an error on account of the uncertainty as to the position of the strip when heated. On account of the expansion and consequent curvature of the strip, this is not the same as when it is cold. This uncertainty was avoided in the former experiments by using the apparatus to measure the known value of e/m for the negative electrons. Assuming that the measurements would be liable to the same error whatever the sign or mass of ions, this enables us to determine a correction to be applied to the positive ions,

In the present investigation this procedure has not been followed. The distances z which have been measured are those between the back of the strip and the front of the plates in the neighbourhood of the strip. The distances between the plane from which the ions are emitted and the slit-planes will, therefore, be less than this by the thickness of the platinum plus the thickness of the layer of salt. The former was ·002 cm. and the latter about as much. The platinum strip was arranged so that it curved away from the plates when heated. It is believed that the increase of the distance due to the curvature more than counterbalances the effect of the neglected thickness. The effect of these errors in the distance is probably to make the values of m deduced from the observations too low. On the other hand, there is an intrinsic error, due to the apparatus not satisfying the theoretical conditions, which tends to make m too high. It is believed that these effects just about balance one another when the value of z as determined above is substituted in the formula. At any rate, it is clear that however considerations of this kind may affect the absolute values of e/m and m, they can have very little influence on the relative values of these quantities.

Preliminary Experiments.

On account of the very close similarity in the properties of the alkali metals and their compounds, we should expect that the sulphates of the different alkali metals would give rise to positive ions whose values of e/m and m would be determined by the atomic weight of the metal under investigation. This conclusion is to be expected whether the ions contain more than one chemical atom or not; for it is to be expected, from the similarity of the properties of the alkali metals already alluded to, that the ions from the different metals will be similarly constituted whatever their constitution may be. For example, if the ions from lithium sulphate were molecules of Li_2SO_4 which had lost a negative electron, we should expect the ions from potassium sulphate to be molecules of K_2SO_4 less a negative electron: if the ions from lithium sulphate were atoms of lithium less a negative electron, we should expect the ions from potassium sulphate to be atoms of potassium less a negative electron, and so on. We should thus expect the values of e/m to exhibit a regular diminution, and those of m a regular increase in proceeding from lithium sulphate to cæsium sulphate. The difference of the values in these sequences will, of course, be greatest if the ions are the atoms of the elements whose compounds are used: if the ions are themselves of a compound nature, the differences will be not be so great, but will be in the same direction. Thus both the absolute values of e/m and m and their relative values, also, should afford us valuable information as to the structure of these ions.

The first experiments made were of a rather qualitative character. The method was adopted of comparing the deflexion of the ions of the salt used with that of the platinum ions from the same strip and in the same magnetic field. It was found that the ions from sodium sulphate were deflected rather more, and those from potassium sulphate rather less, than those from platinum. This was in accordance with previous expectation. A surprise was in store, however, when lithium sulphate was tried. It was found that on the first trial the ions from this substance were deflected to almost exactly the same extent as those from platinum but rather less if anything, whereas on the view expressed above the deflexion for the ions from lithium sulphate should have been very much bigger than for those from the two metals of higher atomic weights. Instead of this, the values for lithium sulphate were between those for the sulphates of sodium and potassium.

It occurred to the author that the explanation of this result might be as follows: It is well known that at low temperatures, when the salts of the alkali metals are ionized by heat, the amount of ionization produced is much greater the higher the atomic weight of the metal used. This tendency is well shown, for example, in experiments by Smithells, Dawson, and Wilson * on the conductivity imparted to flames by alkali salt vapours. Now lithium sulphate is certain to contain the sulphates of potassium and sodium as impurities, and these will give rise to an amount of ionization more than proportionate to the amount of them which is present. In fact, it is quite conceivable that the bulk of the ionization from the lithium sulphate at first may be caused by the comparatively small quantities of the sulphates of the metals of higher atomic weight mixed with it. On this view, we should expect that the value of e/m would increase and that of m diminish with continued heating of the lithium sulphate, and for two reasons. In the first place, the decomposition and consequent removal by ionization is greater the greater the atomic weight, and, in addition, the volatility of the salts of the alkali metals increases as the atomic weight of the metal increases. Careful observations were therefore made from time to time on the deflexion, in a magnetic field, of the positive ions from a specimen of lithium sulphate, which was heated continuously for about 70 hours. It was found that the deviation of the ions produced by the magnetic field gradually increased with the lapse of time, and in fact the results were in complete accordance with the view that the initial values were due to the presence of salts of the metals of higher atomic weight.

The results of the observations on the different salts will now be considered in detail in the order of the atomic weights of the constituent metals, commencing with lithium sulphate.

LITHIUM SULPHATE.

The lithium sulphate used was supplied as pure by Messrs. Eimer & Amend, New York. As was the case with all the sulphates investigated, experiments were first made with the initial ionization from the platinum itself. The residue of this was then driven off by heating all night at a somewhat higher temperature. After the emission of positive ions from the platinum itself had fallen to a small value, the platinum was taken down and a small quantity of lithium sulphate laid

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* Phil. Trans. A. vol. 193. p. 108 (1899).

on the strip. The latter was then heated until the salt melted. In this way, a uniform layer of the salt was obtained over the whole of the front surface of the strip. The apparatus was again set up and exhausted. The distribution of the positive ionization on the opposite planes was now determined after the salt had been heated for different lengths of time. Throughout this investigation a difference of potential of 200 volts was maintained between the plane containing the strip and that containing the slit, the strip being positive. In all the experiments with lithium sulphate the transverse magnetic field was of strength 4700 lines per cm., and measurements were made with it first in one direction and then in the other. In some cases experiments were also made in the absence of a magnetic field. The distance z between the plates near the slit and the back of the strip was measured, by focussing with a microscope furnished with a micrometer arrangement for vertical displacements, from time to time during the course of the experiments. The apparatus was continuously exhausted by means of a Gaede pump, and the pressure recorded on the McLeod gauge was kept below ·001 mm. In some of the experiments it was as low as 10^{-5} mm. Provided the pressure is less than ·01 mm., its actual value does not seem to influence the results.

The results of the experiments can best be exhibited by means of curves showing the fraction of the total number of ions received by the plates which pass through the slit for different positions of the latter. The rationale of this is fully explained in the first of the papers already referred to *. The units used are arbitrary since a capacity of ·001 microfarad was always placed in parallel with the plates, whereas there was no capacity except that of the electrometer and its connexions attached to the slit electrode; and the capacity of the electrometer and its connexions was not determined. It was, however, the same in all the experiments.

The results of the experiments on the ionization from platinum alone are shown in fig. 1 (Pl. XX.). These represent two successive series of measurements with the magnetic field in each direction. The points for the first series are shown thus: ⊕, and for the second series thus: ×. Although the curves are not quite coincident, the displacement of the maximum which gives the values of e/m and m is practically identical for both sets. At the beginning of this experiment, two measurements of the value of z gave ·480 and ·478 cm.

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* Phil. Mag. [6] vol. xvi. p. 740 (1908).

respectively, and at the end ·489 and ·485. The mean of these values of z is ·483 cm.

The observations taken immediately after the lithium sulphate was placed on the strip are exhibited in fig. 2. Here again we have the result of two determinations taken immediately after one another, for each direction of the magnetic field, the first being shown thus: ⊕, the second thus: ×. As before, the corresponding curves are not quite identical but the displacement of the maximum is the same for each pair. It is slightly less than that for platinum, indicating that the ions emitted by fresh lithium sulphate are slightly heavier than those emitted by that metal. The curves are also rather broader than those for platinum. Immediately before this series of measurements was made the value of z was measured and found to be ·485 cm. These curves have only one maximum, showing either that the ions are all of one kind, or at any rate that the value of e/m for the different kinds, if more than one, does not vary enough for them to be separated by the magnetic field used.

The next curve (fig. 3) shows the effect of heating the lithium sulphate continuously for twelve hours. The right and left hand curves, points thus: ⊕, are those obtained when the magnetic field is applied; the central curve, points thus: ×, is what is obtained in the absence of the magnetic field. We see that the curves obtained in the presence of the magnetic field are now more complex than before. Instead of having a single maximum we now have two maxima separated by a minimum. The obvious explanation of this is that there are now two kinds of ions present which are differently deflected by the magnetic field. That this is the correct explanation is shown by the curve obtained in the absence of the magnetic field. This possesses only one maximum, and is in all respects similar to those obtained earlier, in the magnetic field. The shape of this curve entirely precludes the possibility that the humps are due to some irregularity which has developed in the distribution of the salt along the strip.

The distance between the two inner humps, corresponding to the heavier particles, is about the same as that given by a new platinum wire or a fresh specimen of lithium sulphate; whereas the distance between the two outer humps is very much greater and corresponds to ions of much smaller mass. The value of z in this experiment was ·477 cm.

As the heating is continued it is found that the outer hump grows whilst the inner hump diminishes. After 30 hours heating the outer humps were much bigger than the inner ones. The whole pattern was also rather irregular, and part of this irregularity persisted in the absence of the magnetic field. This distortion is probably due to the salt not being so uniformly distributed after all this heating as it was at first. The appearance presented after 44 hours heating is shown in the next curve (fig. 4). Here the main part of the curve consists of the two well-marked outer humps. The value of z was not measured at this stage, but it may be taken as ·480 cm., which is half way between the value ·477 cm. after 12 hours heating and the value ·4835 cm. attained after 70 hours heating.

When the heating was continued further, it was found that the ionization got smaller and smaller, so that increasing temperatures had to be employed in making the measurements. In addition, a small hump gradually developed on the inside of the outer one. This got larger whilst the old one became smaller and smaller. After about 70 hours heating there was again practically only one hump, and the displacement of this on reversing the magnetic field was very little bigger than that given by the ions emitted from fresh platinum. The curves obtained after heating for 70 hours are shown in the next diagram (fig. 5). The breadth and irregularity of the curves is probably due to there still being a small amount of the lithium salt present. Two measurements of z at the end of this experiment gave ·484 and ·483 cm. respectively, the mean of which is ·4835 cm. On attempting to carry the experiment still further it was found necessary, in order to get a measurable amount of ionization, to raise the strip to a temperature so high that it melted.

The foregoing results can be readily explained if we assume that the positive ionization emitted by fresh lithium sulphate is due to the salts of the alkali metals of higher atomic weight (sodium and potassium) which it contains as impurities; that the ionization which these substances produce at a low temperature is so great in comparison that it completely masks that due to the much larger quantity of lithium sulphate present, and that the continued heating drives off the sulphates of higher atomic weight, so that we then get the much bigger displacements due to the lighter ions given off by the lithium salt itself. Finally if the heating is continued long enough the lithium salt is driven off. We then get, at a much higher temperature, a small quantity of the ionization characteristic of the platinum itself.

The evidence in favour of this view has so far been of a rather qualitative nature. It receives additional support when the values of e/m and m deduced from the above experiments are considered. The numerical results are exhibited together in the following table :—

Lithium Sulphate—Positive Ions.

Substance.	Time heated (hours).	z (cms.)	V (volts).	H (lines per cm.^{2})	x (1 = ·063 cm.).	e/m (E.M. units).	m (H = 1).
Pt	0	·483	200	4700	·99	297	32·5
Li_2SO_4 ...	0	·485	200	4700	·95	269	35·9
,, ...	12	·477	200	4700	·85	231	41·8 *
,, ...	12	·477	200	4700	2·35	1760	5·5 †
,, ..	44	·479	200	4700	2·35	1735	5·57
,, ...	52	·481	200	4700	2·05	1300	7·43
,, ...	70	·4835	200	4700	1·25	470	20·6

* The value calculated from the two inside humps.
† The value calculated from the two outside humps.

The first column gives the material experimented with, the second shows the time the lithium sulphate had been heated, the third gives the distance in cms. between the back of the strip and the plate, the sixth gives half the displacement of the maximum produced by reversing the magnetic field given in the fifth column, whilst the meaning of the numbers in the remaining columns are obvious. The values of m represent the ratio of the mass of the ions to that of an atom of hydrogen on the assumption that the ions carry the same charge as that carried by an atom of hydrogen in electrolysis. The value of e/m for hydrogen was taken to be $9{\cdot}66 \times 10^3$ E.M. units.

The value of m for the platinum ions (32·5) is not very different from the mean (25·7) of the values given by Richardson and Hulbirt*, and is within the limits of the range of values found by them. On the view that the positive ions emitted by hot metals are due to the presence of alkaline impurities, this value would correspond to that from a mixture of potassium (atomic weight 39·15) and sodium (atomic weight 23·05). This is on the assumption that the ions are positively charged atoms of the metals in question. We shall see that this is substantiated in so far that the positive ions emitted by the sulphates of the alkali metals are atoms of the metals they contain.

The value of m for the ions from fresh lithium sulphate (35·9) is very near the atomic weight of potassium, and is in

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* *Loc. cit.*

agreement with the view that the initial ionization is due principally to the admixture of salts of this element, perhaps with some sodium in addition. The value 41·8, for the inner of the humps which developed after the twelve hours heating, again is of approximately the same magnitude, pointing to the presence in smaller relative amount of the same impurity. The value (5·5), calculated from the two outer humps, agrees satisfactorily with the atomic weight of lithium (7·05). A still better agreement is obtained after the inner humps have disappeared, and we obtain the value of m which presumably corresponds to the pure lithium salt. The value after 44 hours heating was found to be 5·57, and after 52 hours heating 7·43. The mean of these values is 6·5 instead of 7·05. The value (20·6) obtained after 70 hours heating is what we should expect if it were due to the platinum ions, for which m was found to be 32·5, mixed with a certain amount of the more deviable ions from the lithium salt. Thus the view we have taken of these effects gives a satisfactory account of the phenomena exhibited by lithium sulphate. The position is still further strengthened when the salts of the other alkali metals are examined.

SODIUM SULPHATE.

The specimens of sodium and potassium sulphates used were presented to the author several years ago by Professor H. A. Wilson. They had been specially prepared for use in obtaining standard temperatures from their melting-point, and are believed to be very pure. At any rate, the sodium sulphate is not likely to contain anything with more capacity for emitting ions than itself, with the possible exception of traces of potassium sulphate. We should therefore expect that sodium sulphate would behave quite differently from lithium sulphate. The deflexion of the maximum by the magnetic field ought to be quite constant, except in so far as any trace of potassium sulphate present might make the deflexion a little smaller at first than later. There ought to be no development of widely divergent humps as in the case of the lithium sulphate. As a matter of fact this is exactly what was observed.

As before, two sets of curves for the initial ionization from the platinum strip (a fresh one) were taken. The distance between the maxima for one set of curves was 1·96 turns of the screw and for the other 2·04 turns, the mean being 2·00 turns. The value of z was ·492 cm. The strength H of the magnetic field in this set of experiments was 4650 lines per cm. The above numbers give $m=33·7$, which is practically identical with the value found from the specimen of platinum used in the experiments on lithium sulphate.

In this set of experiments it was not possible to make measurements on the ionization from sodium sulphate until the heating had gone on for about two hours. Three sets of observations were taken, after heating for two hours, eight hours, and twenty-four hours respectively. The results are shown in fig. 6. In this experiment the field strengths &c. had the following values:—$V=200$ volts, $H=4650$ lines per cm.^{2}, $z=\cdot 497$ cm.

It will be seen that the maxima are deflected to nearly the same extent in every case. However the first curves, points thus: ×, obtained after two hours heating, give a slightly smaller deviation (2·3 turns) than the others and lead to the value $m=26\cdot 6$. The next, points thus: ×, after eight hours heating, give a deviation of 2·45, corresponding to $m=23\cdot 4$. After heating twenty-four hours, points thus: ⊕ and ⊠, the deviation is practically unaltered at 2·5 turns, corresponding to $m=22\cdot 5$. The effect of continued heating on the sodium sulphate is clearly very different from that of lithium sulphate.

The very small size of the humps obtained after heating the sodium sulphate for twenty-four hours seemed suspicious, and was investigated further. It was found that these two humps represented only an isolated portion of the curve, which really extended over a much greater length in the direction of x than that shown in the figure. Detailed observations taken after thirty hours heating showed that a measurable fraction of the ionization passed through the slit all the way from $x=10$ turns to $x=11$ turns. There were several humps in the curve, which resembled a panoramic view of a range of mountains. There was, however, no evidence of any splitting up of the ions into groups characterized by different values of e/m. The patterns were displaced as a whole by the magnetic field, corresponding points being displaced about equal distances, and the form of the curve was the same in the absence of the magnetic field as with it. It was quite different from the behaviour of lithium sulphate shown in fig. 3. The peculiarities observed could be explained if the sodium sulphate after continued heating tended to collect in lumps at the edges of the strip where the electric field is irregular. When the apparatus was taken down, the salt which was left was too small in amount to be visible. It was observed, however, that the strip had become contorted somewhat, which would also explain the peculiar effect encountered.

Another set of observations made on sodium sulphate confirms the preceding results and brings out one or two new points as well. This set is represented in fig. 7. The curves at the top (fig. 7, A), points thus: ×, exhibit the effect of heating the platinum by itself. In these experiments $V=200$ volts, $H=4700$ lines per cm.^{2}, and $z=\cdot556$ cm. The displacement 2·85 turns for the platinum ions leads to the values $e/m=349$ and $m=27\cdot7$, in agreement with those found previously.

Three curves are given, fig. 7, B, representing observations on sodium sulphate. Those with points thus: ⊕, were obtained when the salt was first heated. It will be noticed that they are broader than and not so high as the later ones. The displacement of the maximum, 2·95 turns, corresponds to $m=25\cdot9$. It is greater than that for the platinum ions, and less than that, 3·3 turns, obtained after the sodium sulphate had been heated longer. The two remaining curves were taken in succession after the salt had been heated for about fourteen hours. The curves with points thus: ×, were taken first, those with points ⊕ and $\boxed{\times}$ later. The displacement of the maximum is the same in both cases, and the character of the curves is very much the same. The value of m calculated from the displacements is 22·0.

The greater value of m and the greater breadth of the curves obtained on first heating is readily explained if we suppose that the sodium sulphate contains a small quantity of potassium sulphate which would be much more effectively ionized, at the lower temperature at which the observations commenced.

The results of the measurements with the sodium sulphate are gathered together for reference in the following table. The units &c. are the same as in the table for lithium sulphate.

Sodium Sulphate—Positive Ions.

Substance.	Time heated.	z (ions).	V (volts).	H (lines per cm.^{2}).	x (1·0635 cm.).	e/m (E.M. units).	m (H=1).
Platinum .	0	·492	200	4650	1·00	287	33·7
Na_2SO_4 ...	2	·497	200	4650	1·15	363	26·6
Na_2SO_4 ...	8	·497	200	4650	1·225	413	23·4
Na_2SO_4 ...	24	·497	200	4650	1·25	430	22·5
Platinum .	0	·556	200	4700	1·425	349	27·7
Na_2SO_4 ...	0	·556	200	4700	1·475	373	25·9
Na_2SO_4 ...	13	·556	200	4700	1·60	439	22·0
Na_2SO_4 ...	15	·556	200	4700	1·60	439	22·0

POTASSIUM SULPHATE.

Several sets of observations were made on the ionization from the fresh platinum strip which was used in this experiment. In these experiments the values of the field &c. were $V=200$ volts, $H=4650$ lines per cm.^{2}, and $z=\cdot 501$ cm. Immediately after the heating of the strip was commenced the displacement $2x$ of the maximum was found to be 2·42 turns, giving $e/m=390$ and $m=24\cdot 8$. After heating for about one hour $2x$ had become 2·28 turns, giving $e/m=346$ and $m=27\cdot 9$. After six hours heating it was found that $2x=2\cdot 00$ turns, $e/m=266$, and $m=36\cdot 3$.

The gradual increase of m as the heating is continued is in agreement with the author's previous experiments on platinum *. It would seem to indicate that the source of the positive ionization of lower atomic weight from platinum is more easily driven off by heating than that of higher atomic weight. The results are in agreement with the view that the ions of lower atomic weight are sodium atoms, but as the substance of higher atomic weight is less easily driven off by heat, it would appear that some impurity other than potassium or its salts has to be looked for. So far the writer has not been able to observe the development of humps in the curves for the ionization from platinum similar to those from lithium sulphate. This would seem to indicate, if the observed change in the nature of the ions is real, that it takes place very gradually, as there is no evidence of the simultaneous emission of two groups of ions with widely separated values of e/m. The experiments on the platinum ionization were not continued further, as the ionization at the temperature at which the experiments were being carried out became very small at the end of the last experiment.

The curves given by potassium sulphate itself were very simple in character. They consisted of just a single hump, and remained almost unchanged during sixty hours heating. At the same time the displacement of the maximum was constant within the limits of experimental error. After about eighteen hours heating of the salt, however, the curves broadened very considerably, but this may have been due to some temporary contortion of the strip as it disappeared later, and all the time afterwards the curves were simple as at first and gave the original value of e/m.

The results of the first few heatings of the salt are exhibited in fig. 8. The left-hand curve with points thus :— ×, was taken as soon as the heating commenced. The magnetic

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* *Cf.* Phil. Mag. [6] vol. xvi. p. 750 (1908).

field was then reversed, and the curve with points thus :—×, taken. The field was again changed back to its original value and the position of the first maximum redetermined. The points are shown thus :—$\overline{\times}|$. The position of the first maximum was found to be unchanged within the limits of experimental error.

The curves with broken lines, points ⊕, represent similar observations taken after six hours heating. Although the positions are displaced a little, the displacement of the maximum due to the field is the same as in the preceding case. In the experiments represented in this diagram the values of the numerical quantities were :—$V=200$ volts, $H=4600$ lines per cm., $z=\cdot 501$ cm., and $2x=1\cdot 98$ turns. These values, which are the same for both sets of observations, give $e/m=261$ and $m=37\cdot 0$.

Similar sets of observations were taken after 18, 24, 36, 42, and 60 hours heating. As, except for the temporary broadening mentioned above, which was observed after eighteen hours heating, all the curves were similar in character, it will be sufficient to give the last one of them. This is shown in fig 9, and represents the results obtained after sixty hours heating. The data pertaining to this curve, as well as the other observations mentioned, are given in the following table :—

Potassium Sulphate—Positive Ions.

Substance.	Time heated (hours).	z (ions).	V (volts).	H (lines per cm.²).	x (1·0635 cm.).	e/m (E.M. units).	m (H=1).
Platinum .	0	·501	200	4650	1·21	390	24·8
„	1	·501	200	4650	1·14	346	27·9
„	6	·501	200	4650	1·00	266	36·3
K_2SO_4 ...	0	·501	200	4650	·99	261	37
„ ...	6	·501	200	4650	·99	261	37
„ ...	24	·486	200	4650	·93	261	37
„ ...	36	·486	200	4650	·95	272	35·5
„ ...	42	·486	200	4650	·94	266	36·3
„ ...	60	·486	200	4650	·94	266	36·3

Mean value of m for K_2SO_4 = 36·5

It will be seen that the different values of e/m and m for the positive ions from potassium sulphate given by this set of observations are all very near one another and quite close to the value for the atom of potassium. The atomic weight of this metal is 39·15.

Another set of observations on potassium sulphate gave for the initial ionization from platinum $2x=1·88$ turns. The corresponding quantity immediately after heating potassium sulphate was found to be 1·80 turns. The value of z for this experiment was not measured, so that the values of e/m and m could not be calculated. The relative values for platinum and potassium sulphate, however, confirm those obtained in the more complete series of experiments just described.

RUBIDIUM SULPHATE.

The ionization obtained from the platinum strip used in this experiment gave a high value of m, probably owing to the strip having been heated for some time before the measurements were made. The data for this part of the experiment are:—$V=200$ volts, $H=4700$ lines per cm.^{2}, $z=·512$ cm., and $2x=2·00$ turns. These values give $e/m=240$ E.M. units and $m=40·3$.

The results of the observations on rubidium sulphate are exhibited in fig. 10 (Pl. XX.). These were taken shortly after commencing to heat the salt, but the exact interval of time was not recorded. The left-hand curve with points thus:—×, was taken first. The magnetic field was then reversed, and the right-hand curve with points thus:—×, obtained. The original direction of the magnetic field was now restored, and the left-hand points ⊕ were obtained. The field was again reversed, giving the right-hand points, ⊕. The displacement between the first two maxima is 1·24 turns, that between the two second 1·30 turns. The mean is 1·27 turns. The other data for this experiment are $V=3200$ volts, $H=4700$ lines per cm.^{2}, and $z=·506$ cm. These give $e/m=101$ and $m=96$. The atomic weight of rubidium $=85·5$.

The experiments with rubidium sulphate were not continued further, as it was thought at the time that this was a satisfactory agreement. It may be, however, that the rubidium sulphate contains some cæsium as an impurity, and that further heating would have increased the value of e/m. It is worthy of note in this connexion that rubidium is the only element so far for which the value of m is distinctly above the atomic weight, the other cases tending to fall below it. However, the difference is not greater than the error of observation might well account for.

The specimen of rubidium sulphate used was purchased from Messrs. Eimer and Amend. It was not stated to be especially pure.

CÆSIUM SULPHATE.

Two sets of observations were made with the ionization from the fresh platinum strip used in this experiment, one immediately after the heating was started and the other a few hours later. The first led to the values $2x=2{\cdot}05$ turns, $e/m=344$, $m=28{\cdot}2$, and the second, $2x=1{\cdot}95$ turns, $e/m=295$, $m=32{\cdot}7$.

This increase with lapse of time in the value of m for the ions from platinum is in agreement with that already discussed under the heading of potassium sulphate.

The following data were the same for all the experiments in this series, whether with platinum alone or with cæsium sulphate :—$V=200$ volts, $H=4700$ lines per cm.^{2}, and $z=474$ cm.

The results of the observations on cæsium sulphate are all shown in fig. 11. The first two curves, points :— $\times$, were taken immediately after the heating had started. It will be noticed that these are distinctly broader than the later curves, and the displacement of the maximum was greater. The displacement in this case was $2x=1{\cdot}125$ turns, giving $e/m=101{\cdot}8$, $m=95$.

The curves with points $\oplus$ were obtained after eighteen hours heating. The displacement now is $2x={\cdot}85$ turns, giving $e/m=59{\cdot}1$ and $m=163$. The remaining curves, points $\oplus$ and $\boxed{\times}$, represent the results after twenty-three hours heating. The displacement is again $2x={\cdot}85$ turns, giving the same values of e/m and m as the last.

It may be that the greater breadth of the curves and the greater displacement of the maxima obtained initially represents a real difference in the ionization. It is, however, difficult to be certain about the matter, as the displacements with these heavy ions are small, and the probable experimental error is correspondingly great. The mean of the three measurements gives $m=140$. The atomic weight of cæsium is given as $133{\cdot}9$

The specimen of cæsium sulphate used was prepared by the action of pure sulphuric acid on the chloride. The latter was bought from Messrs. Eimer and Amend, with no specification as to its purity.

General Considerations.

The values of e/m and m which, according to the view of these phenomena developed in the present paper, are characteristic of the positive ions emitted by the pure sulphate of the alkali metals, are collected together in the following table. The values which are believed to be due to the presence of impurities in the material are omitted from the table.

Substance.	Time heated (hours).	e/m (E.M. units).	m (H=1).	Average value of m.	Atomic weight of metal.
Li_2SO_4	12	1760	5·5	...	7·05
Li_2SO_4	44	1735	5·57	...	7·05
Li_2SO_4	52	1300	7·43	6·2	7·05
Na_2SO_4	8	413	23·4	...	23·05
Na_2SO_4	24	430	22·5	...	23·05
Na_2SO_4	13	439	22·0	...	23·05
Na_2SO_4	15	439	22·0	22·5	23·05
K_2SO_4	0	261	37·0	...	39·15
K_2SO_4	6	261	37·0	...	39·15
K_2SO_4	24	261	37·0	...	39·15
K_2SO_4	36	272	35·5	...	39·15
K_2SO_4	42	266	36·3	...	39·15
K_2SO_4	60	266	36·3	36·5	39·15
Rb_2SO_4	...	101	96	96	85·5
Cs_2SO_4	0	101·8	95	...	132·9
Cs_2SO_4	18	59·1	163	...	132·9
Cs_2SO_4	23	59·1	163	140	132·9

The numbers in the last three columns of the table show conclusively that *the positive ions emitted by the sulphates of the alkali metals are atoms of the constituent metal.* The range of e/m, m, and of the atomic weight for the different metals is so great that, although the accuracy of the measurements is not, perhaps, all that might be desired, particularly in the case of the elements of higher atomic weight, nevertheless the general agreement of m over so wide a range is such as to leave no room for escape from the above conclusion.

It also follows that *the positive ions emitted by the sulphates* *of the alkali metals carry the same charge as that carried by an atom of hydrogen in electrolysis*, since this assumption has been made in calculating the values of m and leads to consistent results. We therefore conclude that the positive ions emitted by these substances when heated have the same structure as that which is generally attributed to the nuclei of the positive ions to which the same substances give rise in solution. In other words, *they consist of one atom of the basic metal which has lost a negative electron.*

The similarity between the thermions and the electrolytic ions appears to end with the positive ions. So far the only negative thermions which have been detected have a very large value of e/m and are negative electrons. There is no evidence of the existence of negative thermions similar in structure to those which occur in solution.

The present investigation does not throw any definite light on the chemistry of the processes involved. Since the positive ions are atoms of the metal, it is clear that they must get free from the rest of the molecule somehow. It is possible that the first decomposition consists of a splitting up of the sulphate into positively charged atoms of the metal and a negatively charged SO_4 group, as is the case in solution. This would then presumably be followed by the breaking up of the negatively charged group into its chemical constituents together with a negative electron. The results of the experiments neither affirm nor deny this view. It seems possible that valuable evidence in this connexion might be obtained by looking for a relation between the amount of positive and of negative ionization produced by heated salts. Experiments with this end in view are being instituted. In any event, the present investigation shows that the expulsion of a positively charged atom of the metal is a salient feature of the ionization of heated salts.

The balance of evidence at present is not in favour of the view that the positive ions produced by salt vapours in flames at a high temperature are identical with those here investigated. Their velocities have been measured by different experimenters, and there is a general agreement that the positive ions produced by the salts of all the alkali metals have the same velocity under unit field. This result would not be expected if the ions were atoms of the metals. The absolute values of this common velocity given by different observers are rather divergent. For instance, H. A. Wilson finds 62 cm. per sec., Marx finds 200 cm. per sec., and Moreau 80 cm. per sec. Nevertheless, all these values are higher than what would be expected if the ions were atoms of the metal, particularly in the case of the elements of higher atomic weight. They are, however, in very good agreement with the value calculated from the formula $u = \frac{1}{2} \frac{e}{m} \frac{\lambda}{v}$, where u is the velocity under unit field, e the charge, m the mass, λ the mean free path, and v the mean velocity of agitation of the ions, on the hypothesis that they have the same structure as those discovered by Sir J. J. Thomson * in the canal rays. Moreover, the ratio of the velocity of the negative to that of the positive ions in flames at high temperatures is in good agreement with this view.

Outside of solutions the number of cases of positive ions of which the structure has been definitely determined is not very large. The only ones which occur to the author are the α particle, which Rutherford showed to be an atom of helium carrying twice the electronic charge, and the canal rays in different gases, for which the mass of the carriers has been investigated by Wien, Stark, and Thomson. With the exception, possibly, of the particles having a high value of e/m, isolated by Thomson from the canal rays, all these researches agree with the results of the present investigation in making the primitive positive ion an atom of some known chemical element which has lost one or more negative electrons.

In concluding I wish to thank Mr. Irving B. Crandall, A.B., graduate student in physics, and my assistant, Mr. Cornelis Bol, for their help in taking the observations.

Palmer Physical Laboratory,
Princeton, N. J.

CXI. *The Positive Thermions emitted by the Salts of the Alkali Metals.* By O. W. RICHARDSON, *M.A.*, *D.Sc.*, *Professor of Physics, Princeton University* †.

IN the preceding paper the author has shown that the positive ions emitted by the sulphates of the different alkali metals are atoms of the constituent metal carrying a single electronic charge. The sulphates were used in the investigation because they are readily obtainable in a state of reasonable purity and are comparatively non-volatile. There is no reason to expect that the sulphates are exceptional in regard to the positive ions they emit. We should, therefore,

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* Phil. Mag. [6] vol. xvi. p. 657 (1908).

† Communicated by the Author.

expect that all the salts of a given alkali metal would emit positive ions having a value of e/m which is the same for all of them and is equal to the value of that quantity for the salts of the corresponding metal in electrolysis.

Experiments to test this point were made with sodium fluoride and sodium iodide as well as sodium sulphate. Sodium salts were chosen as it is desirable to use an element of low atomic weight; since the influence of the non-metallic part of the compound will then be relatively greater. Lithium was rejected on the ground that its salts are liable to contain those of the elements of higher atomic weight as impurities, and the ionization from these is apt to mask that from the lithium salt. The fluoride and iodide were chosen as they differ widely in their molecular weight from each other and in chemical constitution from the sulphate.

Measurements of the e/m for the positive ions from sodium fluoride were made after two hours, four and a half hours, sixteen hours, and thirty-six hours heating. Similar measurements with sodium iodide were made after two hours, six hours, and eighteen hours. In neither case did any of the values obtained differ from the electrolytic value for sodium salts by more than five per cent., which is about the order of accuracy claimed for the observations.

We therefore conclude that the positive ions emitted by the salts of the alkali metals depend only on the nature of the constituent metal and are, in fact, atoms of the metal which have lost a negative electron.

Since the alkali metals are monovalent we should expect, on chemical grounds, that their ions would contain only one unit of electronic charge. In the case of the metals of higher valency we stand a better chance of getting ions which carry more than one unit of charge. Although, in any case, multiply charged ions will have to contend with a much stronger tendency to recombination, and will, on that account, be less likely to be liberated than singly charged ions. For these reasons the nature of the positive ions liberated by the salts of the other metals when they are heated is of great interest, and experiments on them are now being made by the same method.

Palmer Physical Laboratory,
Princeton, N.J.

CXII. *The Problem of the Whispering Gallery.*
By Lord RAYLEIGH, *O.M., F.R.S.*[*]

THE phenomena of the whispering gallery, of which there is a good and accessible example in St. Paul's cathedral, indicate that sonorous vibrations have a tendency to cling to a concave surface. They may be reproduced upon a moderate scale by the use of sounds of very high pitch (wave-length = 2 cm.), such as are excited by a bird-call, the percipient being a high pressure sensitive flame[†]. Especially remarkable is the narrowness of the obstacle, held close to the concave surface, which is competent to intercept most of the effect.

The explanation is not difficult to understand in a general way, and in 'Theory of Sound,' § 287, I have given a calculation based upon the methods employed in geometrical optics. I have often wished to illustrate the matter further on distinctively wave principles, but only recently have recognized that most of what I sought lay as it were under my nose. The mathematical solution in question is well known and very simple in form, although the reduction to numbers, in the special circumstances, presents certain difficulties.

Consider the expression in plane polar coordinates (r, θ)

$$\psi_n = \mathrm{J}_n(kr)\cos(kat - n\theta), \quad . \quad . \quad . \quad (1)$$

applicable to sound in two dimensions, ψ denoting velocity-potential; or again to the transverse vibrations of a stretched membrane, in which case ψ represents the displacement at any point[‡]. Here a denotes the velocity of propagation, $k = 2\pi/\lambda$, where λ is the wave-length of straight waves of the given frequency, n is any integer, and J_n is the Bessel's function usually so denoted. The waves travel circumferentially, everything being reproduced when θ and t receive suitable proportional increments. For the present purpose we suppose that there are a large number of waves round the circumference, so that n is great.

As a function of r, ψ is proportional to $\mathrm{J}_n(kr)$. When z is great enough, $\mathrm{J}_n(z)$, as we know, becomes oscillatory and admits of an infinite number of roots. In the case of the membrane held at the boundary any one of these roots might be taken as the value of $k\mathrm{R}$, where R is the radius of the boundary. But for our purpose we suppose that $k\mathrm{R}$ is

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[*] Communicated by the Author.

[†] Proc. Roy. Inst. Jan. 15, 1904.

[‡] 'Theory of Sound,' §§ 201, 339.

the *first* or lowest root (after zero) which we may call z_1. In this case $J_n(z)$ remains throughout of one sign. For the aerial vibrations, in which we are especially interested, the boundary condition, representing that $r=R$ behaves as a fixed wall, is that $J_n'(kR)=0$. We will suppose that k and R are so related that kR is equal to the *first* root (z_1') of this equation. The character of the vibrations as a function of r thus depends upon that of $J_n(z)$, where n is very large and z less than z_1 or z_1'. And we know that in general, n being integral,

$$J_n(z)=\frac{1}{\pi}\int_0^\pi \cos(z\sin\omega-n\omega)\,d\omega. \quad . \quad . \quad . \quad (2)$$

Moreover, the well known series in ascending powers of z shows that in the neighbourhood of the origin $J_n(z)$ is very small, the lowest power occurring being z^n.

The tendency, when n is moderately high, may be recognized in Meissel's tables*, from which the following is extracted:—

z.	$J_{18}(z)$.	$J_{21}(z)$.	z.	$J_{18}(z)$.	$J_{21}(z)$.
24	−0·0931	+0·2264	16	+0·0668	+0·0079
23	+0·0340	0·2381	15	0·0346	0·0031
22	0·1549	0·2105	14	0·0158	0·0010
21	0·2316	0·1621	13	0·0063	0·0003
20	0·2511	0·1106	12	0·0022	0·0001
19	0·2235	0·0675	11	0·0006	0·0000
18	0·1706	0·0369	10	0·0002	
17	0·1138	0·0180	9	0·0000	

From the second column we see that the first root of $J_{18}(z)=0$ occurs when $z=23·3$. The function is a maximum in the neighbourhood of $z=20$, and sinks to insignificance when z is less than 14, being thus in a physical sense limited to a somewhat narrow range within $z=23·3$.

The above applies to the membrane problem. In the case of aerial waves the third column shows that $J_{21}(z)$ is a maximum when $z=23·3$, so that $J_{21}'(23·3)=0$. This then is the value of kR, or z_1'. It appears that the important part of the range is from 23·5 to about 16.

The course of the function $J_n(z)$ when n and z are both large and nearly equal has recently been discussed by Dr. Nicholson†. Under these circumstances the important part

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* Gray and Matthews' Bessel's Functions.

† Phil. Mag. xvi. p. 271 (1908); xviii. p. 6 (1909).

of (2) evidently corresponds to small values of ω. If $z=n$ absolutely we may write ultimately

$$J_n(n)=\frac{1}{\pi}\int_0^\pi \cos n(\omega-\sin\omega)d\omega=\frac{1}{\pi}\int_0^\infty \cos n(\omega-\sin\omega)d\omega$$

$$=\frac{1}{\pi}\int_0^\infty \cos\frac{n\omega^3}{6}\,d\omega=\frac{1}{\pi}\left(\frac{6}{n}\right)^{\frac{1}{3}}\int_0^\infty \cos\alpha^3\,d\alpha$$

$$=\Gamma\left(\tfrac{1}{3}\right).\,2^{-\frac{2}{3}}\,3^{-\frac{1}{6}}\,\pi^{-1}\,n^{-\frac{1}{3}}, \qquad \ldots\ldots\ldots \quad (3)$$

one of Nicholson's results.

In like manner when $n-z$, though not zero, is relatively small, (1) may be made to depend upon Airy's integral. Thus

$$J_n(z)=\frac{1}{\pi}\int_0^\infty \cos\left\{(n-z)\,\omega+\tfrac{1}{6}z\omega^3\right\}d\omega. \quad \ldots \quad (4)$$

In the second of the papers above cited Nicholson tabulates $z^{\frac{1}{3}}J_n(z)$ against $2{\cdot}1123\,(n-z)/z^{\frac{1}{3}}$. It thence appears that

$$z_1=n+\frac{2{\cdot}4955}{2{\cdot}1123}n^{\frac{1}{3}}=n+1{\cdot}1814\,n^{\frac{1}{3}}. \quad \ldots \quad (5)$$

The maximum (about 0·67) occurs when

$$z=n+{\cdot}51\,n^{\frac{1}{3}}, \quad \ldots\ldots\ldots \quad (6)$$

and the function sinks to insignificance (0·01) when

$$z=n-1{\cdot}5\,n^{\frac{1}{3}}. \quad \ldots\ldots\ldots \quad (7)$$

Thus in the membrane problem the practical range is only about $2{\cdot}7\,n^{\frac{1}{3}}$.

In like manner

$$z_1'=n+\frac{1{\cdot}0845}{2{\cdot}1123}n^{\frac{1}{3}}=n+{\cdot}51342n^{\frac{1}{3}}; \quad \ldots \quad (8)$$

so that in the aerial problem the practical range given by (7) and (8) is about $2{\cdot}1\,n^{\frac{1}{3}}$.

To take an example in the latter case, let $n=1000$, representing approximately the radius of the reflecting circle. The vibrations expressed by (1) are practically limited to an annulus of width 20, or one fiftieth part only of the radius. With greater values of n the concentration in the immediate neighbourhood of the circumference is still further increased.

It will be admitted that this example fully illustrates the observed phenomena, and that the clinging of vibrations to the immediate neighbourhood of a concave reflecting wall may become exceedingly pronounced.

Another example might be taken from the vibrations of air within a *spherical* cavity. In the usual notation for polar coordinates (r, θ, ϕ) we have as a possible velocity-potential $\psi=(kr)^{-\frac{1}{2}}\,\mathrm{J}_{n+\frac{1}{2}}(kr)\sin^n\theta\cos(kat-n\phi)$, and the discussion proceeds as before.

So far as I have seen, the ultimate form of $\mathrm{J}_n(z)$ when n is very great and z a moderate multiple of n has not been considered. Though unrelated to the main subject of this note, I may perhaps briefly indicate it.

The form of (2) suggests the application of the method employed by Kelvin in dealing with the problem of water waves due to a limited initial disturbance. Reference may also be made to a recent paper of my own*.

When n and z are great the only important part of the range of integration in (2) is the neighbourhood of the place or places, where $z\sin\omega-n\omega$ is *stationary* with respect to ω These are to be found where

$$\cos\omega_1 = n/z, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{9}$$

from which we may infer that when z is decidedly less than n, the total value of the integral is small, as we have already seen to be the case. When $z>n$, ω_1 is real, and according to (9) would admit of an infinite series of values. Only one, however, of these comes into consideration, since the actual range of integration is from 0 to π. We suppose that z is so much greater than n that ω_1 has a sensible value.

The application of Kelvin's method gives at once

$$\mathrm{J}_n(z)=\sqrt{\left(\frac{2}{\pi z}\right)}\frac{\cos\{z\sin\omega_1-n\omega_1-\frac{1}{4}\pi\}}{\sqrt{\{\sin\omega_1\}}}. \quad . \quad . \tag{10}$$

We may test this by applying it to the familiar case where z is so much greater than n as to make $\omega_1=\frac{1}{2}\pi$. We find

$$\mathrm{J}_n(z)=\sqrt{\left(\frac{2}{\pi z}\right)}.\cos\{z-\tfrac{1}{2}n\pi-\tfrac{1}{4}\pi\}, \quad . \quad . \tag{11}$$

the well known form.

As an example of (10),

$$\mathrm{J}_n(2n)=\sqrt{\left(\frac{2}{n\pi\sqrt{3}}\right)}.\cos\{(\sqrt{3}-\tfrac{1}{3}\pi)\,n-\tfrac{1}{4}\pi\}. \tag{12}$$

Although in (2) n is limited to be integral, it is not difficult to recognize that results such as (3), (5), (12), applicable to large values of n, are free from this restriction.

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* Phil. Mag. xviii. p. 1, immediately preceding Nicholson's paper just quoted.

CXIII. *On Magnetic Hysteresis.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

THE interesting article in your September issue in which Professor S. P. Thompson applies the Fourier analysis to Hysteresis Curves in the magnetization of iron closes with some observations regarding the nature and effects of hysteresis to which I think exception must be taken. He remarks (p. 436): "Hysteresis is commonly regarded as an irreversible process and as such involving a degradation of energy into heat. But in view of the present analysis of the hysteresis loop it is necessary to revise this opinion." I cannot see why. Hysteresis in the magnetization of iron means a lagging of the magnetism behind the magnetizing force when the magnetizing force is made to suffer any change. This lagging causes each stage of the process to be irreversible and involves a degradation of energy into heat. The area enclosed by the curve of magnetism and magnetizing force measures the energy so dissipated in a cyclic process. These fundamental facts are in no way affected by the analysis, and it is not apparent that any revision of ideas is required. Neither can one accept the statement that "the energy waste does not involve or produce any phenomenon of lag." It is, on the contrary, the lag of magnetism behind magnetizing force that involves waste of energy.

Professor Thompson seems to have in mind, when he speaks of lag, the lag of current behind impressed electromotive force in a circuit such as that of a choking coil, and he is at pains to point out that "hysteresis does not cause any lag in the current." But to suggest that it might would be to put the cart before the horse. It is the current that represents the magnetizing force, and the lag which hysteresis involves is the lag of something else (namely the magnetism) behind the current, not any lag of the current behind something else.

Yours faithfully,
J. A. EWING.

Froghole, Edenbridge, Kent,
5 Nov., 1910.

CXIV. *Notices respecting New Books.*

Introduction to Physical Chemistry. By Professor HARRY C. JONES. New York: The MacMillan Company, 1910. $1.60 net.

THE vitality of Physical Chemistry is exhibited as much in the number of text-books written upon it as in the rapid progress which is being made in this branch of science itself. The appearance of still another will doubtless be justified, and its merits are such that it will probably prove a strong rival to those already in the field.

Let it be said, in the first place, that the style in which the book is written is an excellent one. The statements are easy to follow; and considering that only a rudimentary account of the subject-matter is intended, they are as complete as could be desired. A doubt will arise in the minds of some readers whether it is well to attempt to give something about everything rather than to concentrate attention in a more thorough manner upon a few things. The writer follows the former course; the result is a very complete elementary resumé of the principal facts, while the explanations of these facts are given in a more imperfect way when given at all. Professor Jones is obviously writing for the man who has no mathematical knowledge, and difficulties frequently occur under these circumstances in giving a satisfactory explanation. We think that he succeeds on the whole; but there are many places where considerable improvement could be effected. A notable case occurs on p. 29, where he attempts to (but scarcely succeeds in) giving an explanation of the additional terms in Van der Waals' equation for a gas while he has not previously explained the occurrence of the terms in the equation of a perfect gas itself.

Leaving such points of mere exposition, we turn to the discussion of the problem (on p. 98) of the abnormal lowering of freezing-point of strong solutions of calcium chloride and aluminium chloride. The writer is correct, we think, in considering this to be a consequence of hydration of the dissolved salt. But we do not think the reasons for his decision to be very illuminative. It is not so much a question of there being less free water owing to the hydration; for, since the *total volume* is not thereby much changed, we would not expect as a consequence much influence (on the gas-theory) upon the osmotic pressure. The important fact to emphasize is that the size of the molecule is thereby increased, and just as in the case of a gas a large value of b in the gas equation means a large pressure (other things being equal), so in this case an abnormally great osmotic pressure is indicated; and this carries with it (owing to a property of *all* isotonic solutions) an abnormal lowering of freezing-point.

Some elementary calculus is employed in the section on chemical dynamics. It is of a very simple kind and does nothing except improve the exposition. The student is in consequence called upon less to accept results on trust without the argument being presented to him.

Besides all the phenomena which we would expect to be dealt with here, an account is given of the phenomena of radioactivity. Curiously enough, these are given, and are the only phenomena described, under the head of photo-chemistry, while their photographic properties are barely mentioned. A short account of photo-chemistry would be a valuable addition and might replace the account of radioactivity which is not called for.

Annuaire pour l'an 1911. Published by the Bureau des Longitudes. Paris: Gauthier-Villars. 1 fr. 50 c.

Besides the usual astronomical and geographic data, this issue contains several important articles. One of these, by M. A. de Gramont, on Stellar Spectra, replaces that of M. Cornu in previous issues. In it will be found a very useful summary of the present state of knowledge on this interesting subject. It includes a comparative table of the several modes of classification adopted by different investigators. M. H. Poincaré summarizes the contributions to the XVIth Conference of the International Geodesic Association at London and Cambridge (1909); and M. G. Bigourdan gives particulars in regard to the total (annular) eclipses of the sun of 1912, the line of totality of which passes close to St. Germain in France.

A Treatise on Electrical Theory and the Problem of the Universe. By G. W. de Tunzelmann, B.Sc. Charles Griffin & Co., Ltd. London, 1910.

The appearance of this book is very timely. It brings together in a form fairly intelligible to a non-mathematical reader the most important recent developments of modern electrical theory. But modern electrical theory now governs the whole domain of physical science; and the time may not be far distant when Maxwell's joke about "the unit of life and of thought" may find its scientific verification in the negatively charged corpuscle. Some thirty or forty years ago it was a kind of accepted axiom that the simplicity of a theory was one of its strongest claims to acceptance: mais nous avons changé tout cela. The "jelly" theory of the æther has had to go, and æther twists have entered into possession. All physical laws as they appeal to our finite intelligences are simply statistical averages of whirling and drifting movements. Each so-called atom of matter is a complex system of discrete particles or corpuscles all in more or less rapid motion, acting and reacting on one another and on the mysterious æther in which they move. The rapidly moving negative corpuscle drags along with it through the æther its trails of magnetic and electric lines of force, and at every change of velocity starts waves of radiant energy through the æther. All this and a vast deal more are expounded in the pages of Mr. Tunzelmann's book. Although much wider in scope and more deep seated in its foundations, this exposition of Electrical Theory may be compared to Lloyd's treatise on the Wave Theory of Light, which in its day did more to spread a general knowledge of the labours of Young and Fresnel than any other book. So here. Mr. Tunzelmann has taken a wide grasp of all the essential features of this modern theory, which by the addition of the electron to the electromagnetic theory as it left the hands of Maxwell has broadened in a remarkable way our whole physical horizon. The difficulties of explaining a theory which is fundamentally mathematical are not small; and although here and there some obscurities (if not inaccuracies) will be found, the general discussion is wonderfully clear and must have cost the author great thought and labour. The book proper consists of twenty-four chapters covering 505 pages, but a series of Appendices mainly mathematical occupies 120 pages more; and these will be found very useful to the student of mathematical physics. The twenty-fourth chapter is on the Place of Mind in the Universe, in which the author argues for the existence of a universal mind, correlating the otherwise separate units forming the minds of all living organisms, and this universal mind is regarded as the origin of evolution.

We have received the volumes of magnetic observations during 1905 and 1906 at Baldwin and Vieques (Porto Rico), two observatories of the U.S. Coast and Geodetic Survey. The volumes resemble generally those for the immediately preceding years, containing hourly measurements of the magnetic curves, and diurnal inequalities based on the ten quietest days of each month. There are lists of the chief magnetic disturbances, and some of the disturbed traces are shown on a reduced scale. The Vieques volume also contains a list of the earthquakes recorded by Bosch-Omori seismographs from their erection in 1903 up to the end of 1906.

CXV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 792.]

March 23rd, 1910.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S., President, in the Chair.

THE following communication was read :—

'On *Palaeoxyris* and other Allied Fossils from the Derbyshire and Nottinghamshire Coalfield.' By Lewis Moysey, B.A., M.B., F.G.S.

April 13th, 1910.— Prof. W. W. Watts, Sc.D., M.Sc., F.R.S., President, in the Chair.

The following communications were read :—

1. 'The Volcano of Matavanu in Savaii.' By Tempest Anderson, M.D., D.Sc., F.G.S.

Savaii is one of the German Samoan Islands in the Central Pacific Ocean. It is entirely volcanic, is formed of different varieties of basic lavas, and is for the most part fringed with coral reefs.

The volcano of Matavanu was formed in 1905. The eruption was at first explosive, but since the first few weeks has been mainly effusive and accompanied by the discharge of an enormous volume of very fluid basic lava, which has run by a devious course of about

Fig. 5.

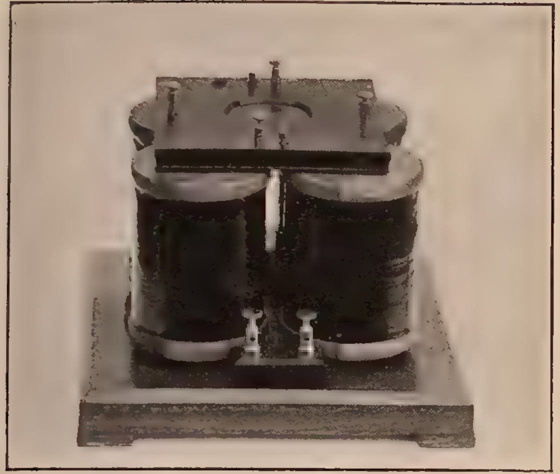


Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12.

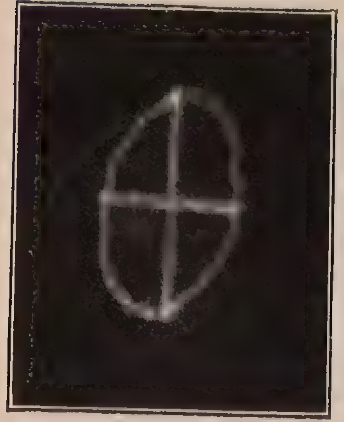


Fig. 14.

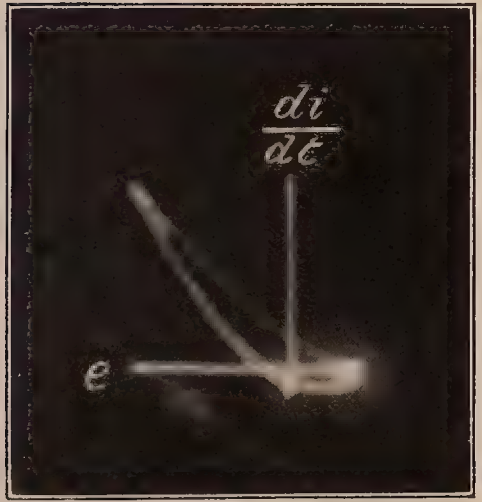


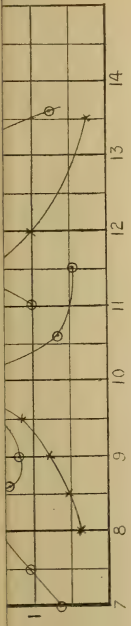
Fig. 15.

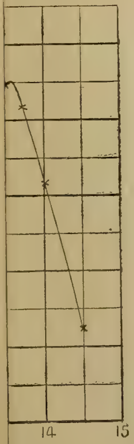
Fig. 16.

Fig. 17.

Fig. 18.

. 3.





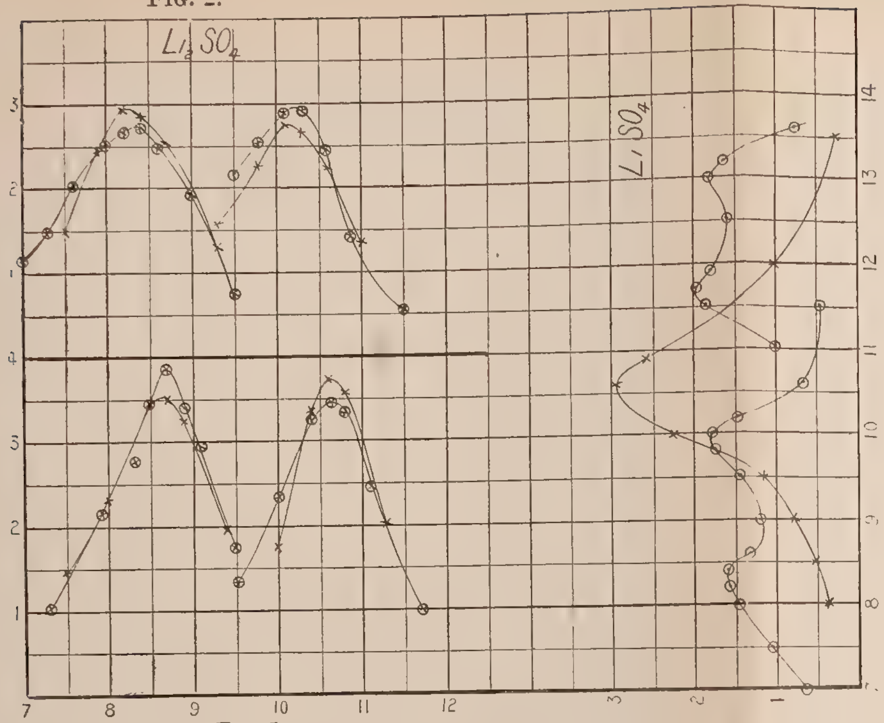


FIG. 2.

FIG. 3.

FIG. 1.

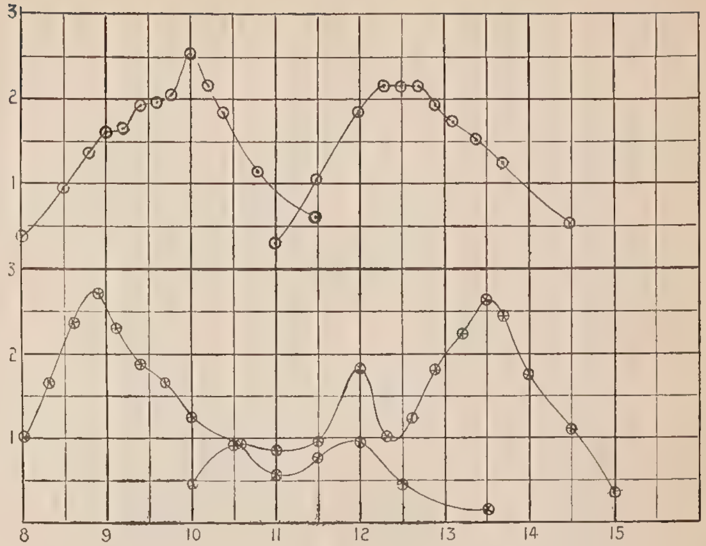


FIG. 5.

FIG. 4.

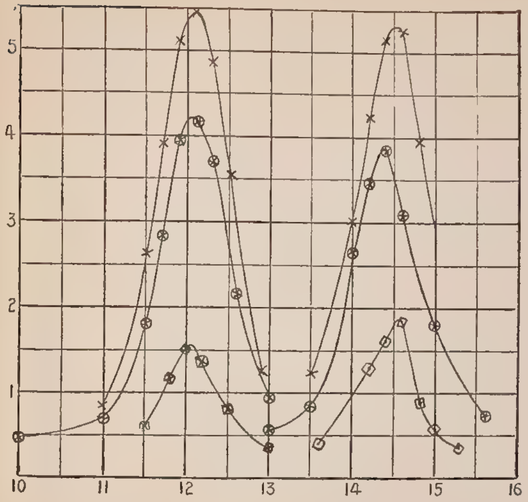


FIG. 6.

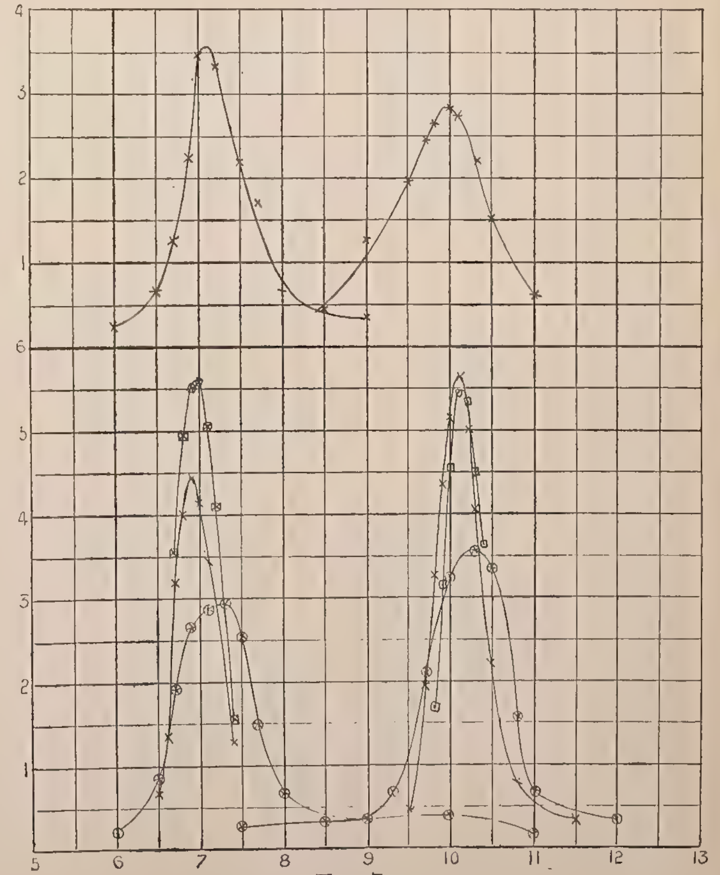


FIG. 7 A.

FIG. 7 B.

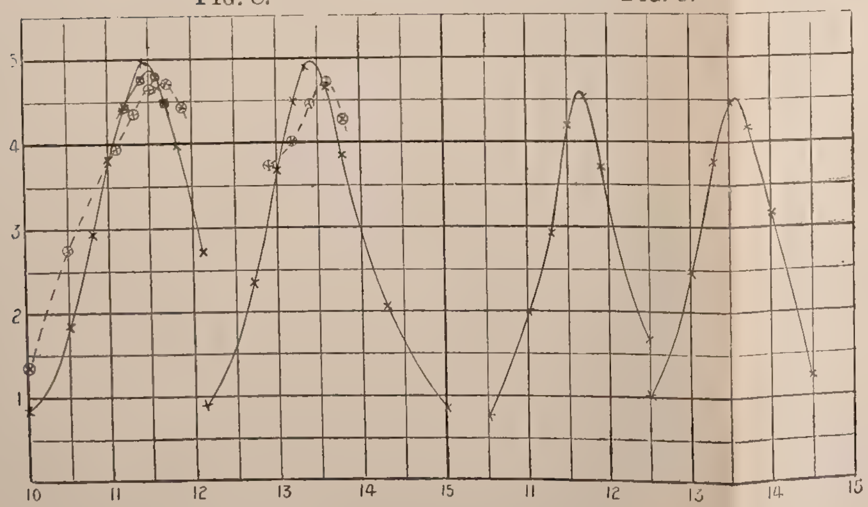


FIG. 8.

FIG. 9.

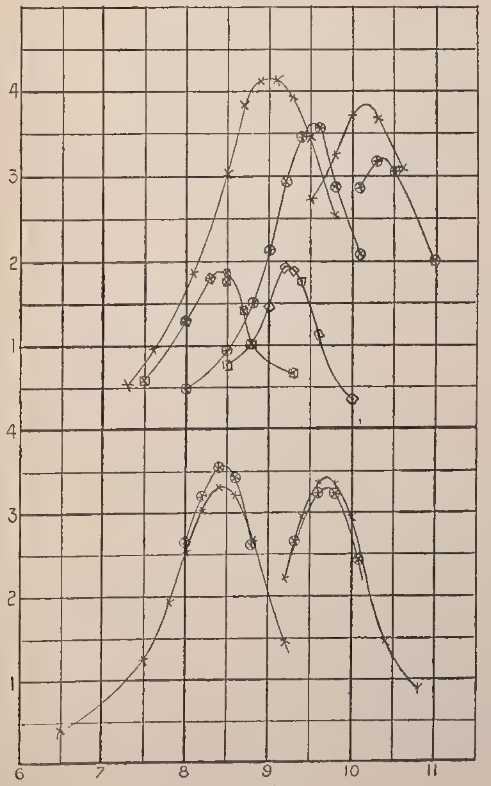


FIG. 11.

FIG. 10.

10 miles to the sea, formed extensive fields of both slaggy and cindery lava (pahoehoe and aa), filled up a valley to a depth in some places of probably 400 feet, and devastated some of the most fertile land in the island. The crater contains a lake, or rather river, of incandescent lava, so fluid that it beats in waves on the walls, rises in fountains of liquid basalt, and flows with the velocity of a cataract into a gulf or tunnel at one end of the crater. It then runs underground along a channel or channels in the new lava-field until it reaches the sea, into which it flows, and causes explosions attended with the discharge of showers of sand and fragments of hot lava, and the emission of vast clouds of steam.

The many resemblances to, and few differences from, the volcano of Kilauea are discussed.

2. 'Notes on the Geology of the District around Llansawel (Carmarthenshire).' By Miss Helen Drew, M.A., and Miss Ida L. Slater, B.A.

In this paper the authors deal with the stratigraphy and geological structure of a small area some 9 miles to the west of Llandovery, and to the north of Llandeilo. In a brief introduction the reasons for the selection of this region are mentioned, and the work of previous observers is touched upon.

The rocks consist of a varied series of sediments, including a coarse conglomerate, grits, shales, and tough blue mudstones; cleavage is almost everywhere intense.

The beds fall naturally into three divisions, as follows:—

C. Llansawel Group.	C 3. Pengelli Shales (Gala fauna).
	C 2. Zone of *Monograptus communis*.
	C 1. Clyn March or *cyphus* Grits and Shales.
B. Caio Group	B 2. Llathige Shales and Mudstones. Zone of *Mesograptus modestus*.
	B 1. Penn-y-ddinas Grits and Shon Nicholas Conglomerates.
A. Beili Tew Group ...	Beili Tew Grits and Shales.

The stratigraphical relationships are seen most clearly in the highest group (C), which is therefore dealt with first. The beds here follow each other in perfectly regular succession, with a uniform strike of E. 30° N. The basal beds, with a fauna belonging to the zone of *Monograptus cyphus*, form a well-marked ridge across country, and Upper Birkhill and Gala Beds follow to the north-west.

The second group (B) occupies a wide tract to the east of the Llansawel Group. The coarse basal deposits, and the characteristic shales and mudstones, are described from many localities.

The lowest group (A) has its greatest development on the south of Llansawel.

The structure in the eastern part of the district shows many points of interest, and is very much more complicated than in the west. The repeated outcrops of the conglomerate in the hilly region around Shon Nicholas are described in detail, and these give the clue to the structure.

The paper concludes with a general summary and a brief comparison of this district with those of Rhayader and Pont Erwyd.

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END OF THE TWENTIETH VOLUME.

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