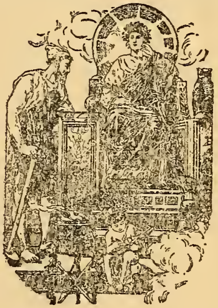

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CONDUCTED BY

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AND
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"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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NUMBER XXV.—JANUARY 1903.

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NUMBER XXIX.—MAY.

NUMBER XXX.—JUNE.

PLATES.

ERRATUM IN VOL. IV. (Sept. 1902).

Page 329:

For $$\frac{E_1}{E_2}=\frac{\lambda_1 W_1}{\lambda_2 W_2}=\frac{5\lambda_1}{\lambda_2}=\frac{5\times 2740}{14}=1000 \text{ approx.},$$

read $$\frac{E_1}{E_2}=\frac{\lambda_1 W_1}{\lambda_2 W_2}=\frac{\cdot 5\lambda_1}{\lambda_2}=\frac{\cdot 5\times 2740}{14}=100 \text{ approx.}$$

Later 1/100 *instead of* 1/1000.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JANUARY 1903.

I. *On Oscillatory Discharges.*

By A. Battelli *and* L. Magri [*].

Part I.

General Description of Method.

1. THOUGH experiments have been made for some time in order to test Thomson's [†] theory of condenser discharges, no systematic and simultaneous study has, so far, been effected of the influences capable of modifying in the case of those discharges the period of oscillation, as the experimental disposition hitherto employed failed to prove adequate for researches extending over any considerable ranges, and did not allow of taking account of—if not all—even the principal elements.

Nor has the importance of the spark ever been carefully considered; notwithstanding Cardani's and Heydweiller's researches, no exact value of its resistance has been obtained, according to the most considerable mutability of the spark from one case to another, and the variability of its resistance, from the moment of its beginning to the moment of its disappearing. Moreover, in the case of oscillating discharges the current is not uniformly distributed over the whole section of the conductor.

This complication—modifying, as was first shown by Maxwell, and afterwards more fully by Lord Rayleigh,

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[*] Communicated by the Authors.

[†] Phil. Mag. [4] v. p. 393 (1853).

Stefan, and Barton, the value of the resistance and the self-induction—has been taken into account only in the case of discharges along rectilinear wires, the true resistance and the true self-induction for rapidly oscillating currents having been calculated in this special case only.

Finally, to treat this argument in a complete manner there would be required the knowledge of the energy spent in the different parts of the circuit, including the spark; and, as a matter of fact, a study of this distribution has formed the object of important researches, such as those of Riess, Paalzow, Villari, and more recently of Heydweiller and of Cardani; but in all the experiments above mentioned, though the relation between the measured quantities and the capacity, self-induction, and resistance of the circuit is allowed for, yet it is not ascertained how the distribution of energy may be influenced by the period of discharge. In the case of oscillating discharges, in fact, measurements have been made either for a single value of the period of oscillation only, or those made for different periods, by different experimenters, are difficult to compare with each other. A general and systematic study of such elements as may have a bearing on the oscillatory discharge phenomenon is therefore wanting. This we intended to undertake.

2. In this paper we give an account of the first part of our researches, the results arrived at being already worthy of notice. For these experiments we connected in the same apparatus:

(1) A device for measuring the period of oscillation;

(2) Condensers free from the defect of delay of polarization, and circuits with exactly known coefficients of self-induction;

(3) Special calorimeters to determine the amount of heat evolved by the discharges, either in the spark or in the metallic circuit traversed by them;

(4) An electrometer enabling the potential of discharge to be exactly measured;

(5) A device for determining the residual discharge;

i. e., such apparatus as might enable us to know the period of oscillation, energy disposable at the beginning of the discharge, quantity of electricity effectively discharged, and the energy dissipated in the form of heat in the different parts of the circuit.

I. MEASUREMENT OF PERIOD OF OSCILLATION.

A. *Anterior Researches.*

3. Since Feddersen's beautiful experiments, calling the attention of physicists to the phenomenon of condenser

discharges, numerous researches have been performed, either to show experimentally the existence of electric oscillations, or to test the well-known theoretical formula

$$T = \frac{2\pi}{\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

established by W. Thomson [Lord Kelvin] for the period of oscillation.

These experiments—which we think useful to record briefly—may be divided into two groups, according as they were made in order to ascertain the value of T by Feddersen's method, or with a view to determine the curve representing the time variations of the intensity of the charge or discharge current of a condenser.

4. *Experiments performed with Spark-Photographs.*—H. Feddersen* was the first to measure the period of the oscillatory discharge of a condenser, by photographing the spark after its reflexion by a rotating mirror; but as he did not make any absolute measurements of the capacity and self-induction, he only obtained qualitative laws, which we do not think worth while recording here.

Feddersen's experiments were then repeated by Lorenz†, who stated that the values calculated for the duration of oscillation of the discharge, though corresponding to those observed as regards order of magnitude, were always somewhat higher, probably on account of the too small value ascribed to the dielectrical constant of the glass forming the insulating medium of the condensers used.

In order to eliminate this cause of uncertainty, Trowbridge and Sabine ‡ tested the discharge of an air-condenser by photographing the spark by means of Feddersen's method. They found the formula

$$T = 2\pi\sqrt{LC},$$

to which (1) is reduced for small values of R—as was the case in their experiments—to be fairly well verified, provided the value of L as calculated by Rayleigh's formula for rapidly alternating currents be adopted. The values of T obtained are of the order of 0·0000031 sec., in most satisfactory agreement with theoretical values.

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* Pogg. *Ann.* ciii. p. 69 (1858); cviii. p. 497 (1859); cxiii. p. 437 (1861); cxvi. p. 132 (1862).

† Wied. *Ann.* vii. p. 161 (1879).

‡ Phil. Mag. xxx. p. 323 (1890).

Without discussing at length Boys's[*] experiments (their main object being a didactical one), where the spark was photographed by means of a rapidly turning objective, we rather wish to point out those undertaken by Miesler[†], with a view to test Thomson's formula. He photographed the spark due to the discharge of some leyden-jars by means of a lens and of a plane mirror set rotating by clockwork, using a circuit formed by several brass spirals: the periods found ranged from 0·000016 to 0·0000052 sec., which agrees well with theoretical values.

But specially remarkable on account of the favourable experimental conditions and the accuracy of the measurements are the researches carried on by Lodge and Glazebrook[‡], who, using an air-condenser and an induction-coil of great self-induction but small resistance, photographed the spark of discharge on a rotating plate, the velocity being capable of being maintained constant and being measured with great accuracy. Though Lodge and Glazebrook's measurements are relative to very slow oscillations only (from $\frac{1}{880}$ to $\frac{1}{1600}$ sec.), yet their results are of special importance, as the single determinations exceed in accuracy those of all previous experimenters.

In order only to show the rapidity of oscillations so far reached in those spark photographs, we will mention that much shorter periods (of the order $\frac{1}{5,000,000}$ sec.) have been investigated by Decombe[§], who photographed the spark of a Hertz resonator by combining a lens and a rotating mirror; and Trowbridge and Duane[||], in a paper where the velocity of transmission of electrical oscillations in metallic wires was tested, photographed, by the usual method of the rotating mirror, sparks of a period of about 2×10^{-7} sec.

5. *Experiments performed by the method of charge and discharge curves.*—The values of the period of oscillation may conveniently be derived from the form of the curves representing the behaviour of the charge or discharge of a condenser, both of them taking place through a circuit containing a resistance and a self-induction.

Among the most accurate researches made with this method there are to be quoted Hiecke's[¶] measurements, whose results agree perfectly with theoretical deductions.

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[*] Phil. Mag. xxx. p. 248 (1890).

[†] *Wien. Ber.* xcix. II *a*, p. 579 (1890).

[‡] Cambr. Phil. Trans. xviii. p. 136 (1899).

[§] *Compt. Rend.* cxxvi. p. 518 (1898).

[||] Phil. Mag. xl. p. 211 (1895).

[¶] *Wien. Ber.* xcvi. II. *a*, p. 134 (1887).

More recent experiments are those of Robb*, who kept the condenser in communication with the source of electricity for intervals gradually increasing from very small values, determined by the duration of the contact established by two steel spheres striking against one another ; but the uncertainty attending this method of evaluating the duration of the time of charge imparts to those experiments a merely qualitative character.

Similarly Wulf †, in an investigation on the dissipation of energy in dielectrics, determined by means of an interrupter moved by a falling weight the curve of residual discharge; and whereas for condensers not subject to the phenomenon of charge-penetration he obtained values agreeing well with those calculated from the formula $T=2\pi\sqrt{LC}$, he found notable departures in the case of two paraffin-paper condensers.

Tallqvist's ‡ experiments afford more adequate arrangements for quantitative verifications. By means of a pendulum interrupter, he obtained a satisfactory verification of the formulæ expressing the charge of a condenser as a function of time, for periods of about five-thousandths of a second ; and so do Seiler's similar researches, equally carried on with a pendulum interrupter allowing of still more exact measurements of the time of charge.

Seiler first found the formula $T=2\pi\sqrt{LC}$ to be verified for periods ranging from 0·0012 to 0·0045 sec., L being maintained constant and C taking variable values ; but he failed to state a satisfactory agreement between the experimental values of the logarithmical decrement of oscillations and those derived from theory.

Similar investigations, based upon Helmholtz and Schiller's§ classical method, have recently been made—for periods between 0·0000246 and 0·0000586 sec.—by Webster ‖, using an air-condenser and two spirals wound in a suitable way, so as to cause their capacity to be negligible. The interruption of contacts was effected, instead of by the pendulum, by means of a weight falling down from different heights (of about 75 cm.); by starting successively two levers, this device enabled—according to Webster's statements—measurements of time intervals as small as 0·0000005857 sec. to be made.

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* Phil. Mag. xxxiv. p. 389 (1892).

† *Wien. Ber.* cv. II. *a*, p. 667 (1896).

‡ *Ibid.* lx. p. 248 (1897).

§ *Ibid.* lxi. p. 30 (1897).

‖ Phys. Rev. vi. p. 297 (1898).

6. In the table given below the values of periods, as so far observed, are recorded :—

Periods of oscillation of discharges.

a. *Determinations by spark photographs.*

Feddersen (1858)	from 4·46	to 1·56	$\times 10^{-5}$	sec.
Trowbridge and Sabine (1890)		3·1	$\times 10^{-6}$	„
Boys (1890)		3	$\times 10^{-4}$	„
Miesler (1890)	from 5	to 13	$\times 10^{-6}$	„
Trowbridge and Duane (1896)		2	$\times 10^{-7}$	„
Lodge and Glazebrook (1899)	from 1·2	to 0·6	$\times 10^{-3}$	„

b. *Determinations by curves of charge and discharge currents.*

Tallqvist (1897)	from 2·18	to 9·65	$\times 10^{-3}$	sec.
Seiler (1897)	from 1·4	to 4·47	$\times 10^{-3}$	„
Webster (1898)	from 2·4	to 5·8	$\times 10^{-5}$	„

It should, however, be borne in mind that only Trowbridge and Sabine's, Miesler's, and Lodge and Glazebrook's investigations are really oscillation measurements by method (*a*). Now the investigations of Trowbridge and Sabine, as well as of Lodge and Glazebrook, though important on account of their being made with great accuracy, are each of them relative to one particular case only, and do not, therefore, afford a complete verification of this theory. As regards Miesler's researches, made in more variable conditions, it will be shown below that the values derived from them cannot be said to be reliable, on account of the uncertainties attending the measurements of time and of spark-photographs. The investigations made by method (*b*) are, on the other hand, fairly satisfactory; but the periods reached there are not very short ones.

It was therefore desirable to undertake new and more extensive researches on so important a question.

Of the two methods used in those researches that of the curves of condenser charges and discharges—no sparks being comprised in the circuit—will most approach the theoretical conditions which served to establish the above formula ; but in addition to the imperfections proper to this method, it does not refer to the cases of greatest practical importance, a spark being always produced in those cases.

As regards such imperfections as attend this method the principal one is that relative to the measurements of the time passing between the breaks of contacts, effected either by a pendulum or a falling weight. In fact, though theoretical considerations may lead us to regard extremely small fractions of a second as capable of being measured, those ten-millionths of a second are hardly to be relied upon, as Webster assumes (see above), except in the case of the weight determining the openings of contacts having a very great velocity (15 mm./sec. at the least), and special devices being employed enabling the action of the opening spark to be rendered either negligible or, at the least, constant.

In addition to what has been said it should be borne in mind that those indirect methods cannot be used in the case of very short periods, they being, at the most, capable of ascertaining with security periods not inferior to some ten-millionths of a second.

The method of spark-photographs, on the other hand, in addition to its allowing very short periods to be measured, is capable of affording also an idea of the importance of such modifications as the spark produces in the movement of electricity.

Among the forms of apparatus used with this method (*e. g.* the classical rotating mirror arrangement, Boys' rotating objective, Lodge and Glazebrook's rotating photographical films), the two latter ones do not afford a means of reaching very high angular velocities, in addition to their being inadequate for periods of some millionths of a second.

The turning-mirror arrangement is, without any doubt, the one enabling even very small periods to be measured, provided all those special precautions enumerated below be taken in effecting them.

B. *Method and Apparatus used in our Experimental Measurement of the Period.*

7. On account of the reasons above quoted we adopted the rotating-mirror method.

In this method the necessary condition for exact measurements is that the distance between the different luminous intervals composing the image of the discharge may be of sufficient magnitude with respect to the width of those intervals. Within certain limits this may be obtained by diminishing the magnitude of the image of the spark, and employing high velocities of this image on the film; this velocity being given by

$$v = 4\pi r a,$$

r being the distance of the film from the mirror, and a the number of turns effected in a second by the latter.

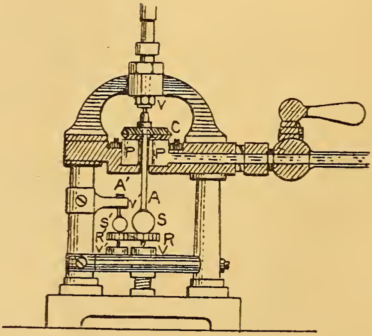
For practical use it proves more convenient, as a rule, to take r as great as possible and to chose moderate values of a (from 60 to 200 turns per second). But in order not to complicate the apparatus by adding rotating arms (similar to those used by Feddersen and by Trowbridge and Sabine to enable the spark to be produced at the very moment of the mirror being in convenient position for reflecting its image on the photographic film), we preferred adopting a form of apparatus capable of imparting to the image an extremely great angular velocity and of making r very small. This arrangement, moreover, allowed of fairly luminous images of the spark being obtained, photographic films of moderate size being employed.

During the first part of our investigations we employed a Froment clockwork, whose last axis could effect about 450 turns per second, but not even this velocity was sufficient in all our researches. Moreover, as is always the case with those instruments where only the friction and resistance of the medium is made use of to regulate the velocity, we found it impossible to maintain the movement constant.

This defect, inevitable in the case of rotating instruments driven by clockwork, may arouse some doubt as to the accuracy of the results obtained by Miesler.

For the same reason we rejected our first sets of observations, adopting, for the definite investigations, to produce the rotation of the mirror, a special turbine whose action we found to be perfectly regular.

Fig. 1.



8. This turbine, constructed by the mechanician of our Institute, Mr. Giuseppe Pierucci, as represented by fig. 1, is in its essential parts similar to that of Foucault.

The steam enters the chamber PP, and leaving it by two openings strikes against the wreath of vanes C, fixed on the spindle A, together with the steel mirror S and the toothed wheel R.

This latter gears into another perfectly similar wheel R′, secured to the spindle A′, where in the ordinary manner the mirror S′ is fixed. The spindles are kept in position by the screws VV, V′V′. These screws are pierced through their whole length, and they carry sapphire pillows, also pierced in order to allow of an abundant oiling, which has to be made all the time the turbine is working.

At the beginning we availed ourselves of a much overheated jet of aqueous vapour to start the apparatus, but later on we found it more convenient and suitable to make use of a jet of air compressed to 6 atm., taken from a large reservoir.

The regularity of speed of the turbine depends very much on the oiling of the spindles, which should be continuous but not excessive. The rotation of the axis becomes in fact very irregular by lack of oil, the friction being then too great, as well as by an excess of it, as in this case some oil will enter between the moving disk and the distribution box.

It is, moreover, absolutely necessary that the air injected into the turbine should not carry any oil-drops on to the pump, nor dust particles of any considerable size, as the turning and the fixed parts are distant from one another only $\frac{2}{10}$ of a millimetre. To ensure this the air was admitted through a large recipient fitted with a long filter formed by several sheets of straight metallic nets.

To ascertain the velocity of rotation a small and light aluminium disk, to whose edge a short hair was attached, was fixed on the axis A of the turbine. Next to this disk a rotating brass cylinder covered with smoked paper was disposed, the hair making a mark on the paper at each turn of the axis of the turbine.

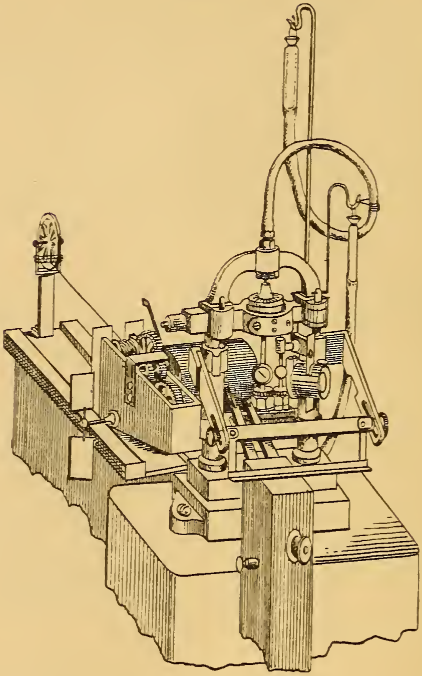
The time interval corresponding to the interval between two marks made by the hair, and hence the number of turns effected per second by the rotating axis, was deduced in the usual manner from a comparison with the oscillation curve of an electromagnetic tuning-fork (whose period of oscillation was accurately known), recorded on the same cylinder.

A conveniently regulated clockwork was fitted with a contrivance enabling the cylinder to effect one turn only, with suitable velocity, so that the cylinder, after a small fraction of a turn (say about $\frac{1}{6}$), reached a fairly constant speed.

Fig. 2 (p. 10) represents a general view of the turbine, the rotating cylinder, and the tuning-fork.

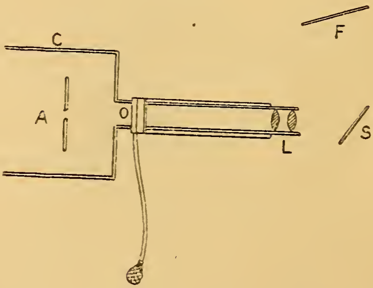
Two solid iron rods, fastened on the turbine columns, carried a small frame with the photographic plate, whose dimensions were 3 × 12 cm.

Fig. 2.



9. The spark to be photographed was produced in A (fig. 3) within a large wooden box, intercepting any irradiation of light by the spark.

Fig. 3.



This box, C, had a hole O capable of being opened and closed by means of an ordinary pneumatic shutter, as used in photography.

A card-paper tube reaching as far as the objective L (an astigmatic Zeiss objective) projected from O. The image formed by L was reflected by the rotating mirror S on to the photographic plate F, if the mirror was in the proper position.

A suitable screen prevented the light emitted by the opening sparks of the electromagnetic tuning-fork falling on the photographic plate (so as to avoid any ghosts prejudicial to the clearness of images).

10. Experiments were carried on in the following way:—The pressure of air in the reservoir having reached 5 to 6 atmospheres, the photographic plate was placed in position; then, after starting the electromagnetic tuning-fork, the compressed air was led into the turbine, the rate of its entering the turbine being regulated by means of a convenient screw-cock, enabling the velocity to be augmented slowly and regularly until the suitable value was reached; comparison of the note produced by the movement of the axis with that given by the electromagnetic tuning-fork, afforded a means of ascertaining approximately whether this velocity had been reached.

As a rule, this was so considerable that the proper sound of the turbine had already exceeded the limit of perceptibility, and the sound of the axis was alone to be heard. The constancy of this latter sound, and hence the uniformity of speed, could be stated with certainty from a comparison with the sound produced by the electromagnetic tuning-fork maintained in vibration during the experiments. Those two sounds, in the case of most of our experiments, were nearly in unison.

After having, in the above manner, ascertained the uniformity of speed of the turbine, the discharge between the spheres of the spark-gap was produced, and immediately on detecting on the photographic plate the reflected image of the mirror, the shutter of the objective was closed, and the rotating cylinder was started, the axis of the turbine and the point of the tuning-fork tracing the respective curves on it. Accordingly we had but to develop and to fix the film by the usual processes.

As a rule 6 or 7 photographs per period of oscillation were taken for each explosive distance.

11. The experiments being finished the velocity of the image was easily deduced from that of the mirror and the distance between this latter and the plate; a measure of the speed of the mirror was next obtained directly from the formula

$$N = \frac{517 \cdot 2 \, . \, n'}{n},$$

n being the number of vibrations included in a certain part of the curve, and n' the number of lines traced on the corresponding part of the curve by the hair connected to the axis of the turbine, 517·2 being the number of complete oscillations made by the tuning-fork in a second at 25°.

In this first part of our experiments (where we always made use only of one axis of the turbine) the velocity of the image on the photographic plate was

$$V = 4\pi d N,$$

d being the distance between the mirror and the plate, this distance being in our case equal to 19·4 cm.

In order to determine the distances between the images of the different partial sparks, special care and a certain amount of practice was found to be necessary. With our preliminary experiments this determination was effected by making use of a Froment comparator divided in half-millimetres, the vernier giving one-hundredth of a millimetre. On the moving part of this comparator, carrying the vernier, an eyepiece of small magnifying-power with a cross hair was fixed. Measurements on the plate were made four times, twice in either direction, the mean value being adopted.

We never found any noticeable differences in the value of the distances comprised between the single sparks corresponding to complete periods.

But as these measurements will often be attended by too great uncertainty towards the end of the discharge owing to the feeble luminosity, we took care to reject those last sparks in our determinations.

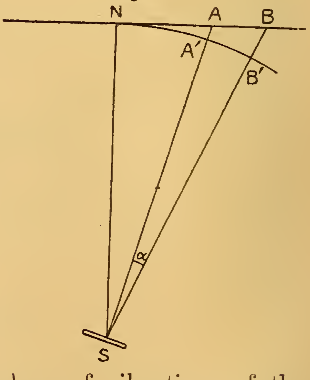
In all cases, however, we made measurements for one and the same discharge as well for such sparks as exhibited a maximum luminosity at the upper electrode, as for those that showed it at the inferior electrode.

The reading of those distances (N A, N B, fig. 4), as determined directly on the plates, was then reduced to the arc of the circle. The arc $\alpha = A'B'$ will afford the value of T by means of the formula

$$T = \frac{n}{4\pi \,.\, 517{\cdot}2 \,.\, n' \,.\, p} \alpha,$$

this formula being very suitable for numerical calculations.

Fig. 4.



12. We give in the annexed tables some examples relating to the measurements of period of oscillation. D and D′ are the distances N B and N A respectively of fig. 4, n and n' the numbers of vibrations of the tuning-fork and of the turns of the turbine counted on corresponding parts of the respective graphs, p is the number of periods comprised on the measured part of the plate.

Experiments with the large spiral wound on marble. Self-induction of the spiral 4546000 cms. Capacity of condenser C=14175 cms.

$T=\frac{2\pi}{v}\sqrt{LC}=0{\cdot}00005317$. Explosive distance 2 mm.

Number of order of Plate.	*n*.	*n′*.	D.	D′.	*p*.	T.
14	148	24	5·0495	0·5205	4	0·00005404
	......	......	4·4705	0·0015	4	0·00005374
15	138	21·8	2·818	4·748	7	0·00005339
	......	......	3·423	5·280	8	0 00005363
16	122	18·9	5·326	2·031	3	0·00005417
	......	......	4·706	1·431	3	0·00005434
17	151	30	2·1675	4·7525	5	0·00005444
	......	......	1·4875	5·3945	5	0·00005386
18	156	35	5·433	0·712	3	0·00005403
	......	......	4·605	0·021	3	0·00005303
19	133	23·9	2·54	4·84	6	0·00005347
	......	......	1·97	4·096	5	0·00005296

Theoretical value 0·00005317. Mean value 0·00005376.

Experiments with the small spiral wound on ebonite. Total self-induction of circuit 57797 cms. Capacity of condenser C=3568 cms.

$T=\frac{2\pi}{v}\sqrt{LC}=0{\cdot}00003008$. Explosive distance 2 mm.

Number of order of Plate.	*n*.	*n′*.	D.	D′.	*p*.	T.	Remarks.
1	122	122	2·656	5·005	6	0·000002986	
			2·827	5·226	6	0 000003037	
2	147	149·2	3·365	1·682	13	0·000003011	
			3·342	0·345	9	0·000003173 (?)	
3	......	......	......	......	......	....	Not distinct.
4	144	144·3	1·2975	5·2485	10	0·000003032	
			1·1545	4·3095	8	0 000003053	
5	126	129·8	4·683	1·077	9	0·000003011	Two sparks following one another in short intervals on the plate were measured.
			4·934	1·300	9	0·000003022	
			0·265	3·721	10	0·000003034	
			0·056	3·462	9	0·000002981	
6	129	131	3·517	5·062	4	0·000002904 (?)	
			3·685	5·316	4	0·000003039	
7	144	147·3	0·611	4·976	14	0·000003036	
			0·791	4·718	14	0·000003001	
			2·281	4·300	5	0·000003042	
			2·10	4·928	7	0·000003021	

Theoretical value 0·000003008. Mean value 0·000003024.

Experiments with circle-shaped circuit of copper wire. Total self-induction of circuit for T=0·00000120, 9242 cm. Capacity of condenser C=3568 cms.

$T=\frac{2\pi}{v}\sqrt{LC}=0{\cdot}000001201.$ Explosive distance 5 mm.

Number of order of Plate.	*n.*	*n′.*	D.	D′.	*p.*	T.
77	134·5	133	4·941	2·585	15	0·000001213
	......	......	4·863	2·526	15	0·000001205
79	158	157	5·202	0·634	29	0·000001224
	......	......	5·296	0·398	31	0 000001229
80	122	120	2·580	2·451	33	0·000001220
	......	.. ...	2·521	0·854	22	0·000001232
81	143	140	2·347	5·378	19	0·000001194
	......	......	2·275	5·212	19	0·000001205
82	74	76	1·818	5·493	23	0·000001189
	......	......	1·742	5·438	23	0·000001197
83	162	162	2·966	3·050	39	0·000001210
	......	......	2·893	2·843	37	0·000001221
85	153	153	3·147	1·153	28	0·000001210
	......	......	3·080	0·959	26	0·000001224

Theoretical value 0·000001201. Mean value 0·000001212.

From the tables above given it may be seen that even when the difficulties of measurements are greatest the possible error in evaluating the period will not reach 2 per cent.; whereas for not very short periods a still greater accuracy may be attained. We believe that in the actual state an accuracy superior to that reached by us cannot be obtained, the reason of which will be given below.

Now in order to compare the experimental value with the value of the period as derived from Thomson's theory, it was necessary to obtain the values of the elements entering into Thomson's formula, *i. e.* capacity, resistance, and self-induction of the discharge-circuit, with an accuracy not inferior to that pointed out above. It is thus necessary to explain briefly the method and the precautions used in measuring those elements of the circuit.

C. *Capacity, Resistance, and Self-Induction of Circuit.*

(a) *Condenser.*

13. In order to know the capacity with due accuracy, as well for measuring the period as for measuring the disposable energy, which we had to determine when studying

the distribution of the discharge over the different parts of the circuit, it was first of all necessary that the condenser should not offer such difficulties as would arise from the penetration of the charge and from a delay of polarization, which always occur with condensers having solid dielectrics.

This could be obtained only by adopting an air-condenser constructed especially for this investigation.

It was made up of 70 plates of mirror-glass, plane, coated with tinfoil on both sides and separated from one another by small glass prisms.

The mirror-glass plates are rectangular; their surface is 70 × 35 cms., with a thickness variable from one plate to another, and ranging from 7 to 10 mm. On each of them, as has been mentioned, there is extended on both faces a thin sheet of tinfoil of one piece, caused to adhere to the glass by special precautions, so as to prevent folds as well as any air-bubbles being formed. The tinfoils, after being extended on the glass, were all cut to the exact dimensions 63 × 28 cms., so as to leave free around them a margin of glass 3·5 cms. in breadth. The two tinfoils of each plate were connected to each other by means of a thin brass strip (about 4 mm. in breadth), which at the same time served to establish convenient communications.

These 70 plates were arranged in two piles of 35 each, the first and last plates of either pile having tinfoil on the internal face only. As the interval between two successive plates should remain unaltered and well known, each couple was separated by six small glass prisms, chosen equal among themselves to a hundredth of a millimetre by means of a spherometer.

The prisms of the pile of condensers No. 1 we found to be of a mean thickness of 0·743 cm., those of the pile No. 2 being of a mean thickness of 0·738 cm. In both of these two condensers the even-numbered and the uneven-numbered plates respectively were put in connexion with each other, the respective brass strips being then gathered in two clusters, which were connected to two terminals carried by glass rods.

Each condenser was placed on a solid wooden bench, the respective plates being carried laterally by six glass angles, so as to secure absolute stability. The apparatus was finally protected by a glass jacket, in the interior of which the air was kept dry by means of sulphuric acid.

(b) *Measurements of Capacity.*

14. As the dimensions of our condenser are known with accuracy, its capacity could be derived from the well-known formula of Maxwell (‘Treatise,’ vol. i. § 196).

But we did not limit ourselves to this theoretical value in calculating the results of our investigations, as it results from experiments (not yet published) made for this purpose in our Institute by Dr. Gragnani, that the above formula does not hold for condensers of the dimensions used by us; and as, moreover, in this condenser each armature is formed by two sheets of tinfoil separated by a plate of glass from 7 to 10 mm. in thickness, the departures from the theoretical conditions this formula holds for are still greater.

In addition, it is impossible to calculate with certainty what influence the neighbourhood either of conductive masses or of the walls and the floor may have on the effective capacity.

Moreover, though the plates as used with our experiments are of mirror-glass and well worked, one cannot warrant their being perfectly plane and accurately parallel among one another.

We therefore measured the capacity of our condenser, either by comparison with a standard condenser or by determining experimentally the absolute value.

Experimental Value.

15. (1) *By comparison with a Standard Condenser.*—The standard, kindly lent by Prof. Roiti, bears the number 1099 of the firm Latimer Clark, Muirhead, & Co. (Westminster), and is made up of plates of tinfoil separated by sheets of mica. The value of the capacity as assigned by the constructing firm is $\frac{1}{3}$ microfar.; that found by Prof. Roiti * by means of special determinations is 0·3359 microfar., very nearly the same as the value 0·3336 found by Glazebrook † for another standard forwarded by the same firm.

It should be borne in mind, however, that in calculating the absolute value of the capacity, Roiti adopted for the B.A. unit of resistance the value 0·9883 legal ohms; whereas in the Chicago Congress of the year 1893 it was established that 1 B.A. should be equal to 0·98703 international ohms; the value as given by Roiti should hence be multiplied by $\frac{0\cdot9883}{0\cdot98703}=1\cdot0013$, in order to reduce it to the absolute units now adopted.

It thus becomes

$$0\cdot3359\times1\cdot0013=0\cdot3363 \text{ microfarad.}$$

The comparison between this standard and our air-condenser

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* *Nuovo Cimento* [3] xxi. p. 137 (1887).

† Phil. Mag. [5] xviii. p. 98 (1884).

was made by discharging them successively through a ballisti galvanometer, after bringing their armatures to potential-differences whose ratio was known, and which were chosen so as to have deflexions of the galvanometer-needle of the same order of magnitude in both cases.

The charging current was given by three Tudor accumulators, whose circuit was kept permanently closed through a thick argentan spiral, of a total resistance 51·14 B.A.

To charge the standard condenser a deviation of the current between one terminal A of the spiral and a point B distant about $\frac{1}{20}$ of the length of the spiral was taken; to charge the air-condenser the deviation was taken at the two terminals of the spiral.

The ballistic galvanometer was of the Du Bois and Rubens type, the duration of a complete oscillation of its needle being 13 seconds. The charge of the condenser was kept on 1 second.

From this comparison we obtained for our condenser the value C=0·016001 microf., this value agreeing very well with the value C=0·015972 microf. obtained by substituting for the resistances AB and AC of the rheostat above mentioned two other far greater resistances, composed of two Edelmann resistance-boxes of 530 and 9690 units respectively.

The average of those two values gives for the capacity in question

$$C=0{\cdot}015987 \text{ microf.},$$

i. e. 14388 electrostatic C.G.S. units.

16. (2) *Absolute Measurements of the Capacity.*—In order to have more reliable values for the capacity of our air-condenser we decided to make, as above stated, determinations in absolute measure also by the bridge method, as suggested by J. J. Thomson*.

The arrangement used by us is exactly the same as the one previously adopted and described by Prof. Roiti †.

Let a, b, d, g, and p denote the resistances of the three branches of the bridge, the galvanometer, and the pile respectively, and n the number of oscillations per second of the tuning-fork; the value of the capacity will be given by

$$C=\frac{a[(a+d+g)(a+b+p)-a^2]}{n[(a+b+p)(a+d)-a(a+b)][(a+d+g)(a+b)-a(a+d)]}$$

As an interrupter we made use of an electromagnetic tuning-fork run by another tuning-fork in unison. These tuning-forks, kindly lent by Prof. Roiti, are constructed in

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* Phil. Trans. of the R. Soc. part iii. p. 707 (1883).

† *Nuovo Cimento,* [3] xxi. p. 137 (1887).

a manner perfectly similar to that described in the above quoted article. The number n of complete oscillations was about 126 per second. The very regular speed of the tuning-forks—the duration of whose oscillations was obtained by comparison with a Graham pendulum regulated by means of a chronometer of the Royal Navy—facilitated the execution of these measurements, from which we derived the following values:—

Condensers I. and II. in parallel......	0·015750 microf.
Condenser No. I.	0·0079763 „
„ No. II.	0·0078849 „

17. Resuming, we may write in the following table the values of the capacities as obtained by the various methods:—

A. *The two condensers in parallel.*	Electro-static Units. [C.G.S.]	Microf.
Capacity derived from comparison with Latimer-Clark standard ...	14388	0·015987
Capacity derived from bridge measurements	14175	0·01575
B. *Condenser No. 1 only.*		
Capacity derived from bridge measurements	7178	0·007976
C. *Condenser No. 2 only.*		
Capacity derived from bridge measurements	7096	0·007885

The sum of the capacities of condensers No. 1 and No. 2 thus agrees fairly well with that of these two condensers when connected in parallel, the more so as measurements of the capacity of each condenser apart will present less certainty on account of their small value, and as the neighbourhood of the other condenser will have a slight influence on the capacity of either of them.

The smallness of the difference between the absolute value as found by us by the bridge method and the one derived from a comparison with the Latimer-Clark standard may be considered as an evidence of the accuracy of our measurements. This difference is probably due to the fact that the standard may have undergone a slight variation in the fifteen years passed since Prof. Roiti made his experiments, and that with the comparative experiments the charge lasted 1 sec., whereas with those performed with the bridge it lasted only about $\frac{1}{500}$ of a sec.

With the latter ones a greater approximation to the conditions of action of the condenser during the measurements of the period of oscillation is thus secured.

We will therefore presume that the value most suitable for our calculations is the one derived from our absolute determinations, *i. e.*

	Capacity. [C.G.S.]	Microf.
For condenser No. 1......	7178	0·007976
„ No. 2......	7096	0·007885
For both condensers in parallel	14175	0·01575
For both condensers in series	3568	0·003965

18. To these values for the capacity of the condenser there are to be added those of the capacity of the remaining portions of the circuit; but within the limits of accuracy of our determinations in most cases this additional amount may simply be neglected.

The case, in fact, where in our experiments this supplementary capacity had its maximum value, was the one of the discharge-circuit being made up of a wire 1594 cm. in length, 0·08 cm. in diameter, and arranged in the form of a square at 85 cm. from the walls of the room where experiments were made.

The capacity of this wire, as calculated in electrostatic measure by the formula

$$C = \frac{l}{2 \log \frac{2d}{r}}$$

(r being the radius of the wire, l its length, and d its distance from the walls) was found to be equal to 97 cm. In this case we took this correction into account, whereas in all other cases it was found to be quite negligible as compared with the capacity of the condenser, which for no experimental arrangement was below 3568 cm.

D. *Resistance of Metallic Circuit and of Spark.*

α. *Principle of Method.*

19. With these first researches the value of the resistance of the circuits used by us was negligible in calculating the period of oscillation by Thomson's formula. But on the other hand, the knowledge of the true value of the resistance

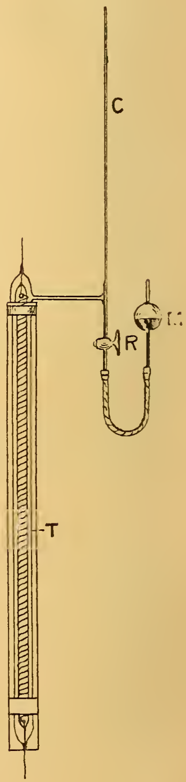
offered by the metallic parts to the oscillatory discharge was indispensable to us as an element of comparison, in order to derive from it the effective resistance of the spark.

This comparison was made by measuring the amount of heat evolved by the same discharge either in the single metallic portions of the circuit or in the spark, and for this purpose we made use of special calorimeters.

β. *Calorimeters.*

20. *Calorimeters for metallic circuit.*—Those adopted by us for measuring the energy evolved in the metallic portions of the circuit had the form shown in fig. 5.

Fig. 5.



The rectilinear wire or the spiral through which the condenser was discharged terminated in two short platinum wires fused to both ends of a glass tube. To this tube there was connected in a vertical position the uniform capillary tube C, conveniently divided and soldered by its lower part to a wider tube, to which the cock R was connected, the latter being, by means of a rubber tube, put into connexion with the small mercury reservoir M. The whole of the tube T, the interior of the tube on which the spiral was wound, and part of the capillary tube C were filled up with toluol.

The mercury reached at least one centimetre above the cock R, allowing thus of the height of toluol in the capillary tube C being regulated, and preventing its leaving by the cock R. Round the calorimeter thus formed a glass jacket was placed, in order to regularize the interchange of heat with the atmosphere.

21. *Calorimeter for spark.*—This was made up of two ovoidal recipients RR′ (fig. 6), one of which was interior to the other, the interval being filled up with toluol occupying also the capillary tube T.

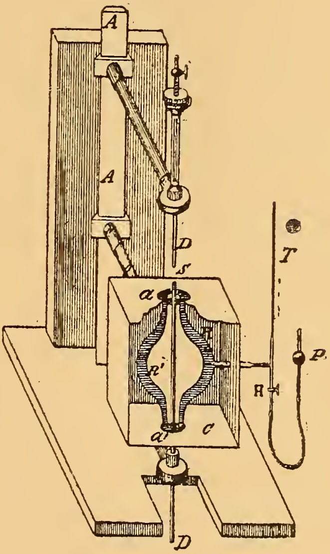
The latter was, on the other hand, connected to a reservoir P containing mercury by a tube furnished with a cock and a rubber tube. By raising or lowering P, the height of mercury in the tube, and thus that of the toluol in the tube T could be varied.

Round the exterior recipient R there was wound a sufficient layer of wool cloth, the whole being placed within a wooden box C, and being capable of moving by means of the arm NO, to which it was attached, along the brass rod A, and being thus raised to different heights.

We had to make use of the arrangement above described in order to cause the spark to pass freely when taking the photographs.

When photographs had to be taken, the box was fixed at the level shown in fig. 6. In order next to insert the spark into the calorimeter it sufficed to raise the arm NO.

Fig. 6.



A good closing of the two openings *aa′* of the calorimetric recipient R was obtained by passing the brass rods D, D′ of the spark-gap through rubber tubes at the part near the interruption where the spark occurred. This method of closing allowed of placing the calorimeter in position with all desirable facility and speed when the heat evolved in the spark was to be determined.

This form of calorimeter seemed more adequate than those previously used by other experimenters, as we avoided the trouble due to the explosive and electrostatic effects of the spark. Moreover, we avoided the difficulties met with in the case of air-calorimeters being used, in the accurate determination of the part played by the expansion of the gas in the displacement of the liquid column in a capillary tube. If the tube be not of perfectly constant calibre, this displacement is influenced to a notable degree by the capillary action.

γ. *Standardizing of Calorimeters.*

22. In order to obtain in absolute measure from the displacement of the meniscus in the capillary tube of the calorimeters the energy evolved within them we effected their standardizing in the following manner :—

(*a*) In the case of the metallic spiral calorimeters there was kept on during a given time a continuous current of known intensity, from whose value, together with the value of the resistance offered by the spiral to continuous currents (this resistance being measured by an Elliott bridge), the energy spent in the spiral was calculated, and hence the relation between this energy and the displacement of the toluol column in the calorimeter was obtained.

(*b*) In the case of the spark calorimeter we proceeded in the same manner, after, however, connecting the two terminals of the spark-gap with a small constantan spiral of known resistance.

The readings of the calorimeters—made at a distance with a telescope—were effected in both cases by determining from minute to minute the displacements presented by the top of the toluol column five minutes before beginning experiments, during experiments, and five minutes afterwards.

The passage of the continuous current during the standardizing experiments, as well as the passage of discharges during those of definitive measurements, did not last beyond 40 seconds. Readings were always taken by night, in order to have as small variations as possible of temperature in the room, and heat changes with the exterior were taken account of by calculations analogous to those made in pyrheliometric researches.

In the table below the data relative to the five calorimeters we made use of during our researches are recorded.

Spiral Calorimeter.

	Diam. of wire, cm.	Extern. Diameter of spiral, cm.	No. of turns.	Length of spiral.
Calor. No. 1 ...	0·078	1·521	220·25	36·8
,, ,, 2 ...	0·078	1·78	423	69
,, ,, 3 ...	0·078	1·64	102	15·6

Rectilinear Wire Calorimeter.

	Diameter of wire, cm.	Length, cm.
Calor. No. 4 ...	0·078	100
„ „ 5 ...	0·078	147

The constant of the spark calorimeter was found equal to $C_5=0{\cdot}0429$ cal./gr. For the remaining calorimeters we found

$$\begin{aligned} C_1&=0{\cdot}0668 \text{ cal./gr.} \\ C_2&=0{\cdot}0876 \quad ,, \\ C_3&=0{\cdot}0871 \quad ,, \\ C_4&=0{\cdot}0399 \quad ,, \end{aligned}$$

δ. *Resistance of Metallic portions of Circuit and its Dependence on Nature of Discharge.*

23. We have already pointed out the importance that an exact knowledge of the metallic portions of the discharge-circuit had for our researches.

In the case of common copper wires stretched out into a straight line, the resistance R′ opposed by a conductor of length l to an oscillating current is given, according to Lord Rayleigh*, by

$$R'=R\left(1+\frac{1}{12}\frac{p^2l^2\mu^2}{R^2}-\frac{1}{180}\frac{p^4l^4\mu^4}{R^4}+\ldots\right), \quad . \quad (1)$$

R being the resistance of the same wire for continuous currents, μ its magnetic permeability, and $p=2\pi n$, n being the frequency of current.

For the highest values of frequency, Lord Rayleigh's theory shows that this resistance R′ has a limiting value as follows :—

$$R'=\sqrt{\frac{pl\mu R}{2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$R'=\pi a R\sqrt{\frac{n\mu}{\sigma}},$$

a being the diameter and σ the specific resistance of the conductor.

This formula is equal to the one deduced for very high values of n from the theory of electric oscillations in rectilinear conductors developed by Stefan†.

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* Phil. Mag. [5] xxi. p. 781 (1886).

† Wied. *Ann.* xli. p. 400 (1890).

In the case, however, of circuits wound into a spiral we cannot say, *a priori*, that the same formulæ will hold which give the true resistance for rectilinear wires, and as a theoretical investigation of this problem is wanting, we had to undertake experimental researches in order to compare the resistance presented by a spiral with the resistance opposed to the same discharge by a wire drawn out into a straight line.

We determined the heat evolved in two successive parts of the same circuit made up of two wires of the same diameter and of the same substance—the one drawn out into a straight line, the other wound into a spiral—first in the case of both being traversed by a continuous current, next both being traversed by an oscillatory discharge.

For this purpose we used the calorimeters Nos. 1, 2, 3, 4, 5, previously described.

Let n and n' denote the displacements of the meniscus in the capillary tubes of the spiral calorimeter and in the rectilinear-wire calorimeter respectively, in the case of the same continuous current traversing both of them; let n_τ and n_τ' denote the displacements produced in the same calorimeters by the passage of a certain number of discharges.

Accordingly, let Q, Q′, Q_τ, Q_τ' denote the amounts of heat evolved in the four cases above mentioned respectively.

From the relations

$$\frac{Q}{Q_\tau} = \frac{n}{n_\tau}; \quad \frac{Q'}{Q_\tau'} = \frac{n'}{n_\tau'}$$

we have in the first place

$$\frac{n_\tau}{n_\tau'} : \frac{n}{n'} = \frac{Q'}{Q_\tau} \quad \frac{Q}{Q'}.$$

On the other hand, denoting by l, l' the lengths of the spiral wire and the rectilinear wire respectively, by R and R′ their resistances, we have for the current with the period τ

$$\frac{Q}{Q'} = \frac{l}{l'}; \quad \frac{Q_\tau}{Q_\tau'} = \frac{R}{R'};$$

hence we may write:

$$\frac{n_\tau}{n_\tau'} : \frac{n}{n'} = \frac{R}{l} : \frac{R'}{l'}.$$

Now, as $\frac{R}{l}$ and $\frac{R'}{l'}$ represent the resistance per unit of length of two wires, one of them wound into a spiral, the other drawn out into a straight line, we may write, denoting them for brevity's sake by ρ and ρ' respectively.

$$\frac{\rho}{\rho'} = \frac{n_\tau}{n_\tau'} : \frac{n}{n'}.$$

We may say also that the quotient

$$\frac{\rho}{\rho'}$$

represents the ratio between the resistance of a wire wound into a spiral and the resistance of the same wire drawn into a straight line for discharges of period τ.

24. Before undertaking the experiments for determining this ratio, we made up our minds to test whether the calorimetric method, as used by us, was adequate for affording reliable indications.

There may, in fact, arise the suspicion that within the toluol dielectric viscosity phenomena may take place, these phenomena, owing to the heat they evolve in the insulator, being capable of disguising to a considerable degree the evolution of heat in the spiral due to the Joule effect.

But two series of measurements made with special calorimeters perfectly warranted our rejecting this suspicion.

The first series, performed with two calorimeters in which the spiral and the wire were immersed in air, gave results identical with those obtained with toluol calorimeters.

The second series was made with a calorimeter of the usual form, where in the place of the spiral there was immersed in toluol a condenser made up of two cylindrical armatures. Having placed this calorimeter in parallel with one of the spirals traversed by the discharge, we were not able to ascertain in it any sensible evolution of heat.

On the other hand, the objection could be raised that, as a rule, the displacement of the toluol meniscus, in addition to its depending upon the amount of heat evolved in the wire, will depend upon the rate of this amount being given off to the surrounding medium; since in the case of a calorimeter containing a rectilinear wire the radiating surface is greater than in the case of a calorimeter containing the same wire wound into a spiral, one would expect that on this account the discharges were capable of producing greater effects in the former calorimeter than in the latter.

We performed some new experiments, however, using continuous currents, sent through the calorimeters at long intervals.

The arrangement adopted for this purpose consisted in closing the accumulator circuit by means of a pendulum which carried a point entering a mercury beaker placed below, in the position corresponding to the position of rest. This pendulum was 2·50 m. in length and accomplished an oscillation of 1·80 m. in 1·6 sec.

The length of the mercury beaker was 1 cm., so that the duration of the passage of the current was about $\frac{1}{285}$ of the interval separating two successive passages.

With these currents so markedly intermittent we obtained also between the amounts of heat evolved in the two portions of circuit, the same ratio as obtained in the case of a continuous passage of current.

We may therefore conclude that the indications of our calorimeters are really due to the heat evolved in the metallic wire.

As we do not think it necessary to give here the tables containing the results of the measurements made to ascertain the value of the ratio $\frac{\rho}{\rho'}$, we record the final values derived from them, *i.e.*, the means of three series agreeing well with one another (p. 27).

From an inspection of the table opposite it results that the effective resistance of a spiral (ratio between the calorific energy absorbed by the latter and the mean square of the intensity of current) is greater than the effective resistance offered by the same wire when drawn out into a straight line.

25. In order to test the possible influence of the neighbourhood of the spiral on this increase of resistance, we made some experiments with four other spirals, *a*, *b*, *c*, *d*, and, by the method above mentioned, determined the ratio $\frac{\rho}{\rho'}$. The copper wires the spirals *a*, *b*, *c* were constructed with had equal length and thickness, whereas the spiral *d* contained a greater length of wire.

Simultaneously we investigated the possible influence of the frequency of current, owing to the more or less considerable capacities it inserts into the discharge circuit.

Mean of Deviations Observed.

With Continuous Current in the Calorimeter No.		With Oscillatory Discharge in the Calorimeter No.	
2 (spiral).	5 (rectil. wire).	2 (spiral).	5 (rectil. wire).
32·1	10·23	24·28	4·32
Ratio $= \rho' = 3·14$		Ratio $= \rho = 5·62$	
		$\frac{\rho}{\rho'} = 1·79$ for $\tau = 6·7 \times 10^{-6}$.	
1 (spiral).	5 (rectil. wire).	1 (spiral).	5 (rectil. wire).
16·88	8·99	17·89	4·87
$\rho' = 1·878$.		$\rho = 3·67$.	
		$\frac{\rho}{\rho'} = 1·96$ for $\tau = 4·3 \times 10^{-6}$.	
,,	,,	20·60	5·11
$\rho' = 1·878$.		$\rho = 4·03$.	
		$\frac{\rho}{\rho'} = 2·15$ for $\tau = 3 \times 10^{-6}$.	
,,	,,	20·60	5·05
$\rho' = 1·878$.		$\rho = 4·08$.	
		$\frac{\rho}{\rho'} = 2·17$ for $\tau = 2·2 \times 10^{-6}$.	
3 (spiral).	4 (rectil. wire).	3 (spiral).	4 (rectil. wire).
4·66	3·01	9·39	3·30
$\rho' = 1·55$.		$\rho = 2·85$.	
		$\frac{\rho}{\rho'} = 1·84$ for $\tau = 1·7 \times 10^{-6}$.	

N.B. Calorimeters are placed in series.

The results are recorded in the following table, where they are arranged for increasing values of frequency and of the number of turns of wire in unit of length of the spiral.

Spiral.	No. of turns per cm.	Values of $\frac{\rho}{\rho'}$.				
		Continuous current.	30 large glass leyden-jars and air-condensers in parallel.	Air-condensers in parallel.	2 air-condensers in series.	One small condenser.
Spiral *a*	2·42	1	1·02	1·14	1·18	1·30
„ *b*	3·82	1	1·17	1·31	1·34	1·70
„ *c*	6·22	1	1·48	1·66	1·68	1·89
„ *d*	7·52	1	1·56	1·72	2·03	2·37

From these results it may be seen that for every spiral the resistance will always increase with increase of frequency and also with diminution of distance of the spires.

This phenomenon leads us to suppose that, while in a rectilinear conductor the current will pass through a thin superficial layer only, it becomes localized in a still more reduced space when the same conductor is wound into a spiral; and this may be expected, considering the mutual induction effects between the various portions of the circuit.

This localization is likely to affect the value of the self-induction coefficient of the circuit, but it may be easily understood—a fact borne out by the experiments we undertook for this purpose—that this influence is quite insignificant in comparison with the effect upon the resistance.

26. From all the facts above mentioned it thus results that the true value of the resistance of our spirals for a given period will be obtained by multiplying the value for the resistance R_τ, exhibited by the same wire when drawn out to a straight line, for the same period, by the ratio $\frac{\rho}{\rho'}$, as found experimentally in the above manner.

We thus have for our experiments the following values for R_τ':—

For the calorimeter No. 2 :

$$R'_{\tau=6\cdot7\,.\,10^{-6}}=0\cdot983\times1\cdot79=1\cdot76.$$

For the calorimeter No. 1 :

$$R_{\tau'=4\cdot3\times10^{-6}}=0\cdot539\times1\cdot96=1\cdot06;$$

$$R_{\tau'=3\ \times10^{-6}}=0\cdot643\times2\cdot15=1\cdot38;$$

$$R_{\tau'=2\cdot2\times10^{-6}}=0\cdot761\times2\cdot17=1\cdot65.$$

For the calorimeter No. 3 :

$$R_{\tau'=1\cdot7\times10^{-6}}=0\cdot440\times1\cdot84=0\cdot827.$$

F. *Self-Induction.*

27. In the case of the self-induction also the theoretical treatment with regard to alternating currents has been worked out only for some special forms of plain circuits, and calculations relating to circuits wound into a spiral are completely wanting, as in this case neither Maxwell's method of the mean geometrical distance [*] nor Lord Rayleigh's [†] method, nor those derived from the theory of oscillatory discharges may be made use of, as pointed out by Stefan [‡].

As, however, we wanted to ascertain this element also with sufficient accuracy, we used the following circuits in our experiments relative to the period measurements, the theoretical value of the self-induction being known in those cases.

(*a*) Square of copper wire: radius of section of wire 0·04 cm.; length of side $l=398\cdot6$ cms.

(*b*) Circle of copper wire:—

Circle No. 1 : radius of section of wire 0·226 cm. ; diameter of circle 201 cms.

Circle No. 2 : radius of section of wire 0·226 cm.; diameter of circle 57·2 cms.

The wires these circuits are made up of are stretched out on suitable wooden frames, and the necessary insulation is obtained by small ebonite cylinders.

In order to keep the sides of the square as far as possible from conductive masses during the experiments, the wooden frame was inclined at 50 degrees to the horizon, and had one side at the level of the spark-gap. The mean distance between the sides of the square, the walls of the room, and the ceiling was 0·85 m.

Now, according to Lord Rayleigh [§], the effective self-induction L′ of a plane conductor, l in length and of an ohmic

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[*] *Cfr.* Wien, Wied. *Ann.* liii. p. 928 (1894).

[†] Phil. Mag. xxi. p. 381 (1886).

[‡] Wied. *Ann.* xli. pp. 400 & 421 (1890).

[§] Phil. Mag. [5] xxi. p. 381 (1886).

resistance equal to R, for currents of high frequency will be given by

$$L' = l\left(A + \sqrt{\frac{R}{2pl}}\right),$$

p being $= 2\pi n$ and A being a constant. This constant, as results immediately from formula (20) of the quoted paper, by putting $p = 0$, is connected to the self-induction for continuous currents by the relation

$$L_0 = l(A + \tfrac{1}{2}).$$

Hence the preceding formula may be given the form

$$L' = L_0 - \frac{1}{2}\left(1 - \sqrt{\frac{R}{\pi n l}}\right). \quad . \quad . \quad . \quad . \qquad (1)$$

For the various circuits above mentioned the value for L_0 is given for a square* of the perimeter l by

$$L_0 = 2l\left(\log_e \frac{l}{r} - 1{\cdot}9103\right),$$

for a circle of the radius a by

$$L_0 = 4\pi a\left(\log_e \frac{8a}{r} - 1{\cdot}75\right),$$

r being the radius of the wire †.

Wien ‡ controlled the values for L_0, calculated by these formulæ and agreeing with each other to 0·1 per cent., by those obtained from accurate measurements ; they thus deserve full credit. By substituting them in the formula (1) we may calculate the self-induction the above circuits exhibit for each period of the discharges we have photographed the spark of.

The following values were thus obtained :—

For the square of copper wire :

T=0·00000425, 0·00000303,

L=27390 cms., 27329 cms.

For the circle No. 1 :

T=0·00000235, 0·00000167, 0·00000120,

L=7829 cms., 7824 cms., 7810 cms.

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* This formula may be deduced by simple algebraical operations from the one given in Mascart, *Electr. et Magn.* vol. i. p. 630, of the second edition.

† Mascart, *l. c.* p. 633.

‡ Wied. *Ann.* liii. p. 928 (1894).

For the circle No. 2 :

$$T = 0{\cdot}0000007,$$
$$L = 1768.$$

In addition to these plane circuits we also made use of the two following spirals in our period measurements.

Spiral A.—This spiral is wound on an ebonite tube accurately worked and traversed throughout its length by a glass rod preventing any deformations of the former. The wire is placed in a helix cut on the tube by means of the lathe. The diameter of the copper wire it is made up of is 0·08 cm., the mean radius of the cross-section of the spires being 0·713 cm. The number of spires per centimetre is 6·3025. The whole of the spiral contains 485 spires. Its self-induction, as measured by Nernst's method with currents of high frequency (see p. 32), is 57,230 cms.

Spiral B.—The support of this spiral is a large marble cylinder, worked on the lathe with extreme care in the mechanical workshop of our Institute. Its surface may be considered as that of a practically perfect cylinder. The variations of diameter of its cross-section, in fact (this being 23·821 cms. at 23° C.), never reached 0·1 mm.

The length of this cylinder is 98 cms. The spiral occupies 85 cms., the number of spires being 283. The mean thickness of the wire it is made up of is 1·435 mm. The spiral itself has been directly wound upon the marble by means of the lathe. In order to prevent any displacement of the spires the whole has been coated with a thick varnish layer of gum-lac. The self-induction of this spiral is 4·546000 cms.

28. To these values there have to be added the values relative to the portions of the circuit establishing the communications between the condenser and the spark-gap. In order to diminish the resistance and to have for those portions an easily calculated self-induction, we established the connexions by means of big brass tubes, their external radius being $\rho_1 = 1$ cm., the internal radius $\rho_2 = 0{\cdot}88$ cm., and of copper strips 5 cms. in width and $\frac{2}{10}$ mm. in thickness. For these tubes the self-induction is given by *

$$L = 2l\left\{\log_e \frac{2l}{\rho_1} + \frac{\rho_2^4}{(\rho_1^2-\rho_2^2)^2}\log_e \frac{\rho_1}{\rho_2} - \frac{1}{4}\,\frac{3\rho_2^2-\rho_1^2}{\rho_1^2-\rho_2^2} - 1\right\},$$

and for the strips by

$$L = 2l\left\{\log_e \frac{2l}{b} - \frac{\pi}{3}\,\frac{a}{b} + \frac{1}{2}\right\},$$

l being the length, a the thickness, and b the width.

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* Wien, Wied. *Ann.* liii. p. 928 (1894).

Hence for the three tubes used by us, being 90 cms., 80 cms., and 71 cms. in length respectively, we have the values

$$L_1 = 762 \text{ cms.}$$
$$L_2 = 658 \quad ,,$$
$$L_3 = 567 \quad ,,$$

and for the strip, 20 cms. in length,

$$L_4 = 103 \text{ cms.}$$

29. With those experiments which served us to determine the resistance of the spark and whose results we availed ourselves of in order to compare the energy disposable in the discharge with the energy exhibited by the various portions of the circuit, we made use of circuits wound in spirals, as has already been stated; and with those experiments also we photographed the spark.

In order to compare the values for the period of oscillation as obtained experimentally for those sparks with the corresponding theoretical values, it would be necessary to know the self-induction of the spirals, whose dimensions are recorded on page 22.

As theoretical formulæ to calculate accurately these self-inductions are wanting, we had to compare them with that of circuits capable of being theoretically calculated.

For these comparisons we availed ourselves of the Nernst* differential exciter slightly modified, as to obtain the equilibrium we maintained constant the two comparison capacities and varied one of the two self-inductions. The variable self-induction was made up of a copper wire spiral, of which any number of spires could be employed in our experiments (mean radius of spiral 0·713 cm., thickness of wire 0·8 mm., number of spires to the unit of length 6·3025).

The arrangement adopted is shown diagrammatically by

Fig. 7.

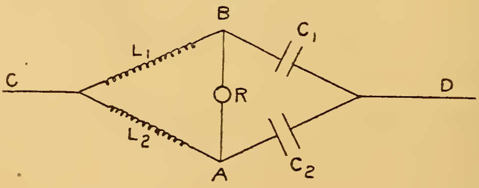

fig. 7, where L_1 denotes the spiral, L_2 is the comparison circuit, C_1 and C_2 are the two comparison condensers, and R is the detector.

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* Wied. *Ann.* lx. p. 600 (1897).

After connecting the points C and D with the electrodes of a spark-gap and with the poles of a Ruhmkorff coil, there could be sent through the differential exciter currents with a frequency of the same order of magnitude as those of the sparks we have photographed.

Then it was tested whether the contact points A and B between each self-induction and the corresponding condenser were at the same potential. For this purpose we found most convenient the detector suggested by Nernst, made up of a vacuum-tube without electrodes, on whose terminals two strips of tinfoil connected with A and B respectively had been wound.

As is known, the luminosity of the tube will be minimum when the condition

$$L_1C_1 = L_2C_2$$

is satisfied.

The accuracy of this method depends upon the precision with which this minimum is determined, as any one of the four quantities L_1, L_2, C_1, C_2 undergoes a small variation. This precision is greatest when the degree of exhaustion in the tube is the one corresponding to the first appearance of cathode rays.

Various numbers of spires of the spiral were successively used until the detector showed a minimum of luminosity. The self-induction L_2 of the spiral could be considered as proportional to the number n_0 of spires used: denoting by k the coefficient of proportionality, the above-mentioned condition of minimum was represented by

$$L_1C_1 = kn_0C_2.$$

The wire with known self-induction was next replaced by the spiral whose self-induction x had to be determined, and the number of spires was again varied, until for some number n the minimum with the detector was arrived at.

The minimum condition became

$$xC_1 = knC_2.$$

Those two determinations gave the self-induction to be found

$$x = \frac{n}{n_0} L_1$$

for high-frequency currents. Our experimental conditions allowed of such a precision in determining the minimum that the numbers n and n_0, ranging as a rule between 70 and 350, were ascertained to less than a unit.

We succeeded in reaching this degree of accuracy by using the following precautions :—

1. Using two comparison condensers whose capacities C_1 and C_2 differ as little as possible from each other.

2. Covering all the portions of apparatus employed to produce high-frequency currents (Ruhmkorff-coil, spark-gap, &c.) with a metallic cage, in order to avoid electrostatic actions between those latter and the various branches of the Nernst bridge.

3. Covering with a metallic cage also the two comparison condensers.

4. Avoiding the use of any conductors in the neighbourhood of the wires, and especially of the spirals.

By this method the following values for the self-induction of our circuits have been obtained :—

Circuit.	Self-induction.
Spiral No. 1	29470
,, No. 2	74140
,, No. 3	17460
Wire No. 4	3669

In these values the self-induction of tubes and copper strips establishing the connexions are also included.

II. *On the Magnetic Effect of Electrical Convection.*—II.

By HAROLD PENDER, *Ph.D.*[*]

SINCE the publication of the results of his first experiments on the magnetic effect of a moving charged body[†], the author has continued his investigations, with results in every way confirmatory of those of the previous experiments. A brief account of these later experiments may not be without interest, as they were performed under entirely new and more favourable conditions, and gave results which are far more consistent than those previously obtained.

M. Crémieu[‡], in criticizing the previous paper of the author, suggested that the agreement between the observed and calculated values of the magnetic effect of the moving charged disks was due to the fact that the speeds and potential of the disks were of such critical values that a slight leak in the insulation would produce the observed effect. The first step then was to test this criticism by varying the speeds and

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[*] Communicated by Prof. J. S. Ames.

[†] Phil. Mag. ii. p. 169 (1901); Phys. Rev. xiii. p. 203 (1901).

[‡] *Journ. de Phys.*, Dec. 1901.

potential within as great limits as possible. To do this, the same method as that previously used by the author, and first introduced by M. Crémieu, was adopted, namely, to measure the current induced in a coil when the charge on a rapidly rotating disk close to it is suddenly reversed.

The great difficulty encountered in the experiments of last year was the impossibility of shielding the needle of the sensitive galvanometer employed to detect this current from the disturbing magnetic effects of the electric circuits in the vicinity of the laboratory, although the experiments were conducted at night after the electric cars had ceased running. Through the kindness of Prof. Ames, Director of the Physical Laboratory of the Johns Hopkins University, I was enabled to move the entire apparatus to the country. The apparatus was therefore set up at McDonogh School, twelve miles from the city of Baltimore and two miles from the nearest electric car-line. Experiment showed that this car-line was too distant to affect the galvanometer. Electric power for running the various motors was furnished by the school.

The room first put at my disposal was a large garret. The apparatus was set up here, and considerable time was spent in vain attempts to mount the galvanometer so as to be free from mechanical jarring. This was finally given up as impossible, as it was found that the wind caused the whole building to rock considerably. The apparatus was then taken down and set up once more in a large basement room of another building. This room was 14·5 × 19·5 m. in size and had a cement floor, which was so solid that when the galvanometer was mounted on a stout table the needle was entirely free from mechanical jarring.

The various parts of the apparatus and their general arrangement were essentially the same as employed last year. There were, however, a few changes made which will be briefly noticed.

The disk apparatus was changed only in a minor point, which, however, obviated a source of great inconvenience. This change was the mounting of the brushes making contact with the surfaces of the disks in such a way that the insulation of the cores could be cleaned without taking the apparatus apart. Special care was taken to clean this insulation thoroughly before each set of readings.

A new needle for the galvanometer was made having a greater sensibility than the old one, and the ground-glass scale was placed two metres from the galvanometer. With the new needle and scale thus arranged it was possible to get four times the sensibility previously secured. But it was found more advantageous to sacrifice sensibility to steadiness of the needle, so that the galvanometer was usually adjusted to have only about one and a half times the sensibility of last year, a current of $\cdot 7 \times 10^{-10}$ amperes giving a deflexion of 1 mm. on a scale 2 metres distant. At this sensibility the spot of light was ideally steady, the zero position seldom varying more than 2 mm. during the time required for the determination of a deflexion (the period of the needle was about 35 seconds), although there was sometimes a slow drift of the light to the left. Any error due to this effect was easily eliminated by taking a reading first on one side of the zero position and then on the other.

On the shaft of the combined reverser and commutator which served to reverse the sign of the charge on the disks and to commutate the galvanometer terminals, a second reverser was mounted and connected in series with a Daniell's cell, resistance-boxes, and the test-coil T on the disk apparatus. My idea was to adjust the value of the current through this coil until its effect on the large coil I between the disks was just equal and opposite to the effect of the moving charged disks, thus employing a zero method. It was found more convenient, however, to note first the deflexion produced by passing a known current through the test-coil with the disks discharged, then to break the circuit of the conduction current, connect in the Voss machine so as to charge the disks, and note the deflexion produced by the convection current, then again note the effect of the conduction current, and so on. This was accomplished by means of a set of switches operated by the observer at the galvanometer. The conduction current was adjusted so as to give about the same deflexion as the convection current. Its value was determined from the known resistance of the circuit and the E.M.F. of the Daniell cell. The zero method was abandoned on account of the great length of period of the galvanometer needle, nearly a minute being required to detect any slight variation from the zero position.

The above method of procedure obviated the necessity of determining the sensibility of the galvanometer and the speed of the reverser for each set of readings, and also the constant "A" of the former paper. Much trouble was experienced in getting brushes for the conduction current reverser which would make a steady contact, but finally this difficulty was overcome by making the brushes of very soft copper foil, each brush consisting of ten layers of foil. It was necessary, in the course of the experiments, to replace these brushes several times.

As before, a Voss machine and battery of leyden-jars were used to charge the disks. Instead, however, of connecting each pole of the Voss machine to the inside coats of three jars, one pole of the Voss was earthed and the other connected to the inside coating of all six jars, the outer coats of which were earthed. The employment of this method rendered possible the developing of a higher potential, but the convection current produced by the moving charged disks was no longer reversed, but simply made and broken by the reverser. The reverser was run at such a speed that this make and break occurred about ten times a second.

The potential to which the disks were charged was measured by a Thomson electrostatic voltmeter having a range of 0 – 1200 volts. This instrument was carefully calibrated by comparison with the standard guard-ring electrometer at the Physical Laboratory of the Johns Hopkins University.

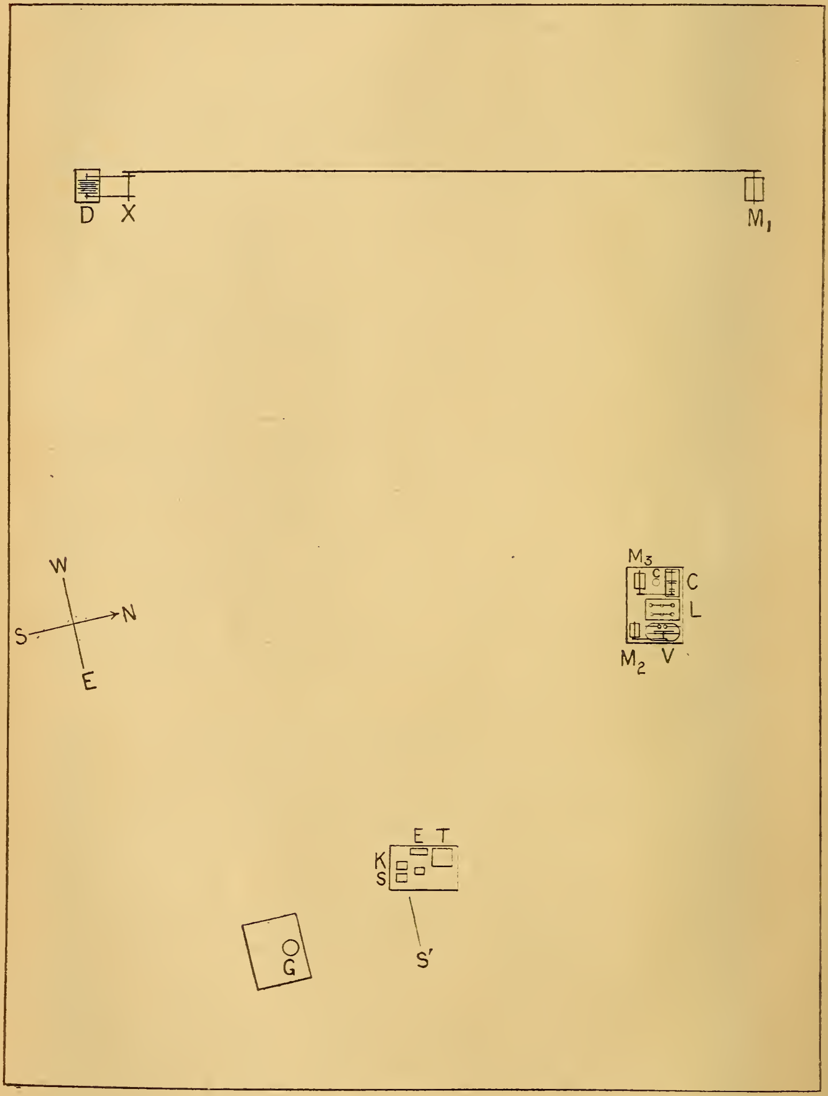
The following diagram (fig. 1, p. 38) will make clear the general arrangement of the apparatus.

The letters indicate the following:—D, the disks and induced coil. M_1, motor driving the disks. X, countershaft. C, commutator and reverser. M_3, motor driving the same. L, leyden-jars. V, Voss machine. M_2, motor driving the same. E, electrometer. T, resistance-boxes and switch in test circuit. S, high potential switch. K, key in galvanometer circuit. G, galvanometer. S′, scale for same.

Connexions are omitted for the sake of clearness. They were essentially the same as previously used except that a separate circuit had to be employed to carry the test-current through the new reverser.

A number of sets of readings were now taken to determine the relation between the deflexion d of the galvanometer produced by rapidly reversing a known current in the test-coil, and commutating the galvanometer terminals connected with the induced coil; and the deflexion D, produced by charging and discharging the disks at the same rate, the galvanometer terminals being commutated as before. The deflexions actually measured were $2d$ and 2D (see preceding paper). In each set of readings five determinations of both $2d$ and 2D were made with the disks running in each direction. $2d$ and 2D were determined alternately. In the first five sets of readings the potential was kept practically constant, and the speed of the disks varied from 9·9 to 92·4 revolutions a second, and in the next six sets the speed was kept practically constant, and the potential of the disks varied from 905 to 5900 volts. To show how closely the various quantities could be determined the following table, giving all the data for one complete set of observations, is appended. A comparison of this table with Table III. of the previous paper

Fig. 1.



will show how greatly the conditions of the experiment have been improved. In the latter the greatest deviation from the mean of 2D is 42 per cent., while in the table below it is only 4·4 per cent.

The symbols have the following meanings:—E is the electrometer reading, from which is deduced V, the potential of the disks in volts, by means of the calibration curve of the electrometer, T_1 the number of seconds required by the east disk to make 1990 revolutions, T_2 the same for the disk on the west side, N the mean number of revolutions of the two disks per second deduced therefrom, *i* the test-current measured in amperes, *d* and D as described above. The ratio of the two systems of units is calculated from these data in the manner described below.

TABLE I.

March 25, 1902.

Direction of rotation: east disk +, west disk −.

2*d*.	2D.	E.	T_1.	T_2.	*i*.
73	78	59·7	37·8	42·4	·389 × 10−4
75	81	61·0	38·8	42·2	
72	80	59·5	38·6	42·4	
73	82	60·5	38·8	42·0	
72	85	61·0	38·2	41·8	
73·0	81·2	60·3	38·4	42·2	·389 × 10−4

V = 6310 volts. N = 49·3. Hence $v = 3·00 \times 10^{10}$.

Direction of rotation: east disk −, west disk +.

2*d*.	2D.	E.	T_1.	T_2.	*i*.
72	83	60·5	38·6	42·2	·389 × 10−4
72	79	61·0	39·0	42·6	
73	85	59·8	38·6	42·8	
72	80	58·0	38·0	42·4	
75	81	59·5	38·4	42·2	
72·8	81·6	59·8	38·5	42·5	·389 × 10−4

V = 6260 volts. N = 49·1. Hence $v = 2·95 \times 10^{10}$.

Mean value of v: $2·98 \times 10^{10}$.

To compare the observed values of 2D with those which should be expected on the assumption that the magnetic effect of a moving charged body is similar to that produced by a conduction current, the ratio v of the two systems of electric units was calculated in the same manner as described in the previous paper. No attempt was made at an accurate comparison until all the observations had been completed.

Referring to my previous paper we have

$$v = \frac{4VN\Delta}{(B-\beta)D}\left[\mu + \nu\frac{B}{\pi}\log_e\left(2\cos\frac{\pi\beta}{2B}\right)\right]$$

where the symbols have the meanings there given. (I take this opportunity to call attention to two slips made in the printer's copy of my former paper, namely, the symbol π for V in the formula on pp. 199 and 200, and 4 for 8 in the formula at the bottom of p. 197.) In deducing this formula the assumption was made that the charge on the disks was reversed from a positive to an equal negative value and *vice versâ* by the reverser. In all the experiments here described the disks were alternately charged and discharged, sometimes negatively and sometimes positively. Hence to apply to these experiments the above formula must be written

$$v=\frac{2\mathrm{VN}\Delta}{(\mathrm{B}-\beta)\mathrm{D}}\left[\mu+\frac{\nu\mathrm{B}}{\pi}\log_e\left(2\cos\frac{\pi\beta}{2\mathrm{B}}\right)\right].$$

Δ is the deflexion produced by reversing unit current in the test-coil at the same rate as the disks are charged and discharged. Hence if d is the deflexion produced by the current i under the same conditions,

$$\Delta=\frac{d}{i}.$$

If the potential is measured in volts and the current in amperes the above formula then becomes

$$v=\frac{2\mathrm{VN}d}{30(\mathrm{B}-\beta)\mathrm{D}i}\left[\mu+\nu\frac{\mathrm{B}}{\pi}\log_e\left(2\cos\frac{\pi\beta}{2\mathrm{B}}\right)\right].$$

μ and ν were determined in the manner described in the former paper. The distance between the condensing plates was kept constant. While the disks were running at a high speed one day in the early spring the east disk flew off the axle and was so badly damaged that it could not be used again. Instead of waiting to have it repaired, which would have taken considerable time, I went ahead with the remaining disk, making a virtue of necessity by thus varying the conditions of the experiment.

The constants in the above formula are as follows:—

Mean value for the two disks.	Value for the west disk.
$\mathrm{B}=2{\cdot}432$	$\mathrm{B}=2{\cdot}469$
$\beta={\cdot}356$	$\beta={\cdot}356$
$\mu=115{\cdot}0$	$\mu=115{\cdot}0$
$\nu=28{\cdot}8$	$\nu=28{\cdot}8$

It so happened that the two disks were arranged almost perfectly symmetrically with respect to the coil, so that μ and ν for the two sides were identical within the limits of accuracy of measurement. Hence for the two disks

$$v=4{\cdot}18\,\frac{\mathrm{VN}d}{i\mathrm{D}},$$

and for the single disk

$$v=2{\cdot}06\,\frac{\mathrm{VN}d}{i\mathrm{D}}.$$

Below are given the mean values, determined from a series of observations similar to that recorded in Table I., of the variable quantities in the above formulæ for the various speeds and potentials employed. Those sets in which the single disk was used are marked with a *.

TABLE II.

i.	2*d.*	2D.	N.	V.	*v.*
$\cdot 103\times 10^{-4}$	20·5	15·5	9·94	5690	$3{\cdot}03\times 10^{10}$
·229	38·8	36·8	25·6	6250	3·08
·389	72·9	81·5	49·2	6275	2·98
·577	92·6	83·9	63·0	5960	3·00
·792	113·4	115·8	92·4	6230	2·98
From former	paper	67·2	102·2	3110	3·00
·0813	20·5	18·8	59·4	905	3·01
·134	26·0	32·7	59·6	2030	3·00
* ·1005	18·7	22·0	59·2	2950	3·04
* ·249	83·5	56·1	57·6	4090	2·92
* ·249	47·1	38·1	57·9	5010	2·97
* ·273	54·0	47·1	58·4	5900	2·98
				Mean...	3·00

Surely no more conclusive refutation of M. Crémieu's criticism could be desired than that contained in the above results. Such close agreement between the observed and calculated effect under such varying conditions cannot be ascribed to the effect of a conduction current caused by any leak in the insulation, for such a current would certainly, from its very nature, be independent of the speed. It is to be noted, however, that the exact coincidence of the value of *v* as determined from the above experiments with its known value must be considered as an accident only, for an error of at least one per cent. might readily have occurred in the determination of the constants of the apparatus.

In one of his experiments on the magnetic effect of a rotating charged disk on a magnetic needle suspended near it*, M. Crémieu observed a deflexion of the needle when between it and the charged disk there was only a single condensing plate connected to earth, but when between the needle and this plate a second metallic plate connected to earth was introduced no effect could be obtained. It therefore seemed worth while to try a similar experiment with the apparatus above described. In this experiment only one disk was used. Between the condensing plate next the coil and the coil itself was introduced a brass plate 1·5 mm. thick connected to earth. On setting the disk in rotation, but without charging it, a great unsteadiness of the needle was noticed. It was discovered that this was due to traces of iron in the brass plate. By gently tapping the plate when the disk was at rest the same effect could be produced. To keep the plate sufficiently steady to make any observations on its shielding effect it was therefore necessary to run the disk at a very low speed. With the disk running at such a low speed, the Voss machine was connected in, and the deflexion of the galvanometer needle observed. Then, without making any other change, the brass plate, connected to earth, was introduced, and the deflexion again noted. This was done several times. The means of a number of readings with the plate out and in were respectively 12·8 and 13·0 mm. deflexion. From this we can conclude that the introduction of the plate was without any such effect as noted by M. Crémieu. It may be of interest to note in this connexion that an attempt to use a solid aluminium disk in place of the gilded disk in my first experiments was foiled by the magnetic disturbances caused by the traces of iron in the aluminium, although the purest metal obtainable was employed.

The next experiment tried was the application of Crémieu's method to the investigation of the magnetic effect of a dielectric moving in a uniform electrostatic field, or, in other words, the magnetic action of a moving apparent charge. This question was first investigated by Röntgen† in 1888. Röntgen showed that a moving polarized disk was capable of deflecting a magnetic needle suspended near it. The maximum deflexion observed by Röntgen was 3 mms. One objection offered to Röntgen's experiment was that the effect observed might have been caused by the disk assuming a real charge by leakage across from the condensing plates on each side of it. Crémieu's method precludes any such action as this, inasmuch as the condensing plates are rapidly charged and

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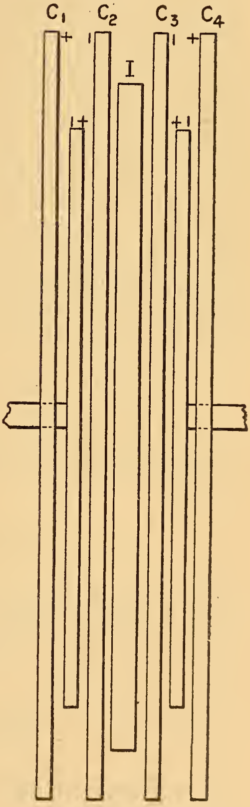
* *C. R.* cxxxi. p. 797 (1900).

† Wied. *Ann.* xl. p. 93.

discharged, and even though there should be a slight leakage of a real charge across to the surface of the disk, this charge could produce no deflexion of the galvanometer, as the charge would tend to assume a constant value, whereas the deflexion of the galvanometer is due to a *change* in the electrical condition of the disk.

For this experiment two ebonite disks were made, diameter 30·5 cms., thickness ·8 cm. The gilded micanite disks used in the first experiment were replaced by these (see fig. 2). The two condensing plates C_2 and C_3 next to the induced coil I were earthed. The other two condensing plates C_1 and C_4 were connected through the interrupter to the pole of the Voss machine, so that they might be rapidly charged and discharged. Everything else remained exactly the same as in the first experiments. When the two outer plates C_1 and C_4 are charged positively, for example, the two ebonite disks become polarized, so that the surfaces next to the outer condensing plates assume an apparent negative charge, and the surfaces nearer the inner condensing plates C_2 and C_3 assume an apparent positive charge. Since the positively charged surfaces are nearer the induced coil than the surfaces negatively charged, when the outer plates are suddenly discharged while the disks are rotating, there will be a slight current induced in the coil I. Since the two surfaces oppose each other in their magnetic action the resultant effect is very small, being greater the thicker the disks, for the same surface-density of the apparent charge. A slight deflexion of the galvanometer was observed with the disks arranged as just described, but it was found that a greater effect could be obtained by mounting the two disks flat up against each other on the same axle, thus using only one side of the apparatus. This arrangement amounted to the use of a single disk 1·60 cm. thick, *i. e.* twice the thickness of one of the disks. Also it was possible to charge to a higher potential

Fig. 2.



¼ Actual Size

the single condenser thus formed than the two condensers above described, for a given speed of the Voss machine and the interrupter. (It may be here noted that the Voss machine was always run at the highest possible speed. A machine of greater capacity would have made possible the procuring of a greater deflexion.)

To calculate the deflexion which should be expected on the assumption that a moving apparent charge has a magnetic action, a method similar to that employed in the previous calculation was adopted. Let σ be the surface-density of the apparent charge on the surface of the disk next to the coil, assumed uniform as a first approximation, N the number of revolutions of the disk per second, v the ratio of the two systems of magnetic units, r the radius of an imaginary ring on the surface of the disk with its centre at the centre of the disk and of width dr, δ the deflexion of the galvanometer-needle produced by a unit current in such a ring on the surface of the disk next to the induced coil, rapidly made and broken the same number of times a second as the disk is polarized and depolarized, δ' the same for a unit current in such a ring on the opposite surface of the disk. Then the deflexion of the galvanometer-needle due to the rapid polarizing and depolarizing of the rotating disk will be

$$D=\frac{2\pi N\sigma}{v}\int_0^R r(\delta-\delta')\,dr:$$

σ is determined from the formula (Webster, Elec. and Mag. p. 364)

$$\sigma=\frac{(\mu-1)V}{4\pi[\mu(d_1+d_2)+d]},$$

where μ is the dielectric constant of the disk (for ebonite 2·5), d_1 the distance between the outer condensing plate C_1 and the surface of the disk, d_2 the distance between the inner condensing plate C_2 and the surface of the disk, d the thickness of the disk, and V the potential of the outer plate, the inner plate being earthed.

The integral $\int_0^R r(\delta-\delta')dr$ was determined by a "calibration of the apparatus" in a manner similar to that employed in the first experiments. A set of coils of known radii was clamped up against the surface of the disk next to the induced coil. A known current i was sent through the reverser and one of these coils. While the current was being thus reversed in this coil, the frame carrying the disk was drawn back from the induced coil a distance equal to the thickness of the disk, and the resultant change A in the galvanometer-deflexion noted. The frame was then pushed up into its former position, and the change in deflexion again noted. A second known current i_1 was then sent through the reverser and the test-coil on the frame carrying the disk, and the change in galvanometer-deflexion B resulting from a known change (i_1-i_2) in this current noted. i, i_1, and i_2 were so chosen that the deflexion produced by the current i_1 in the test-coil was equal to the deflexion produced by the current i in the coil on the surface of the disk, and the change in deflexion A was approximately equal to the change in deflexion B. In this way the quantities A and B were measured at the same part of the galvanometer-scale, thus avoiding any error due to a lack of proportion between the current and the deflexion, which was considerable in the galvanometer employed. Let ρ_1 be the ratio of the deflexion produced by unit current flowing through the reverser and any coil on the surface of the disk next to the induced coil to the deflexion produced by unit current flowing through the test-coil, ρ_2 the corresponding quantity when the coil is on the opposite surface of the disk. Then

$$\rho_1-\rho_2=\frac{\mathrm{A}}{i}\times\frac{(i_1-i_2)}{\mathrm{B}}.$$

From the observations taken as above described $\rho_1-\rho_2$ was calculated and plotted for twelve different coils.

Let Δ be the deflexion produced by a unit current flowing through the reverser and test-coil. Then

$$\delta-\delta'=\tfrac{1}{2}\Delta(\rho_1-\rho_2);$$

($\delta-\delta'$ is the deflexion due to the making and breaking of a current, whereas A and B are the deflexions resulting from a reversal of current, hence the factor $\tfrac{1}{2}$). The formula for D therefore becomes

$$\mathrm{D}=\frac{\pi\mathrm{N}\Delta\sigma}{v}\int_0^{\mathrm{R}} r(\rho_1-\rho_2)dr.$$

The integral $\int_0^{\mathrm{R}} r(\rho_1-\rho_2)dr$ was calculated graphically from the plat of $\rho_1-\rho_2$.

A number of observations of the deflexion D were made, which always agreed in direction and fairly well in amount with the deflexion as calculated. A close agreement could not be expected, inasmuch as the assumption that σ is uniform at the edge of the disk is only a rough approximation to the truth, and even under the best conditions the deflexion is necessarily small. The following data, which are the mean values from one set of readings, will suffice to illustrate the capabilities of the method.

$d=1{\cdot}60, \qquad d_1={\cdot}30, \qquad d_2={\cdot}75.$

$V=24{\cdot}9$ C.G.S. electrostatic units ($=7470$ volts).

$\sigma={\cdot}70$ electrostatic units.

$\Delta=2{\cdot}51\times10^7$ mms. per electromagnetic unit.

$N=57{\cdot}8.$

$$\int_0^R r(\rho_1-\rho_2)\,dr=22{\cdot}8.$$

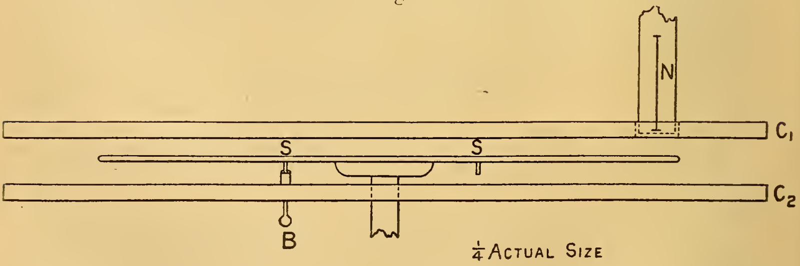
2D calculated 4·85.

2D observed 4·5.

2D was the actual deflexion measured, not D.

Considering the importance of the question as to the magnetic action of a moving static charge, the following experiment, in which was observed the direct magnetic action of a moving charged disk on a magnetic needle suspended near it, may be of interest, though similar results have been obtained by other experimenters. The uninjured one of the two micanite disks used in the first experiments was provided with a row of sixteen brass studs set at equal intervals apart in a circle of 5 centimetres' radius around the centre of the disk. The gilded surface of the disk was then divided into sixteen sectors on each side, each pair of sectors carrying a stud. The sectors were separated from one another by a strip of micanite surface 1 cm. in width. The tinfoil on both the condensing-plates, with the exception of a sector on each twice the width of a sector on the disk, was removed. The tinfoil sectors were earthed, and the sectors on the disk could be connected one at a time, through a brush B (fig. 3) set so as to make contact with the studs S, with one pole of the Voss machine, the other pole of which was earthed. The frame carrying the disk was so arranged that the disk could be set

Fig. 3.



in rotation about a vertical axis. A hole about 2 cms. in diameter was cut through the upper ebonite plate C_1 diametrically opposite the tinfoil segment, and so that its centre came 1 cm. over the edge of the disk. This hole was covered on the side next to the disk with a thin sheet of mica. Fitting loosely into the hole so as not to touch the sides or the mica plate at the bottom was a brass tube in which was suspended a delicate astatic needle N. The two magnets forming the needle were 5 cm. apart. The needle and attached mirror weighed about 3 mgs., and was suspended by a fine quartz fibre. With the control-magnet properly placed the needle could be given a period of 25 seconds. The case in which the needle was suspended was fixed to a frame built over the disk apparatus, having an independent support, so that when the disk was set in rotation there was no jarring of the needle. The position of the needle was read by the reflected image of an electric-light filament on a ground-glass scale 2 metres distant.

When the disk was set in rotation and the brush making contact with the studs was connected to the Voss machine, a deflexion of the needle was obtained which was in the proper direction and of the proper amount to be accounted for on the assumption of the magnetic action of a moving charge. The arrangement here adopted precludes any conduction of charge in the condensing-plates or in the disk itself, two possibilities which have been suggested to account for the deflexion observed with solid condensing-plates and a disk of uniform metallic surface. The results of one set of observations will suffice to give an idea of the magnitude of the quantities involved.

Mean distance between the two surfaces of the disk and needle 1·61 cm.

Distance between the two condensing segments (one on each ebonite plate C_1 and C_2) 2·18 cms.

Thickness of disk ·356 cm.

Potential of the disk 5000 volts.

Speed of disk 69·7 revolutions per second.

Observed deflexion 47·9.

Calculated deflexion 56·0.

The calculation was made in a manner similar to that employed in the previous experiments, the principle of it being a calibration of the disk apparatus such as above described. Only a rough calculation was attempted, as it would be a matter of some difficulty to calculate the exact distribution of the charge on the sectors. As a first approximation this distribution was assumed uniform. The agreement between the observed and calculated values of the deflexion is therefore as good as could be expected.

My chief object in setting up the apparatus with the magnetic needle was to test experimentally certain criticisms made in my former paper on M. Crémieu's experiments, especially his experiments on open electric circuits*. However, in consequence of unavoidable delays, it was not until the 1st of June that I was ready to proceed with the work. But now the damp and sultry weather of the summer had set in and put an end to all experiments with static electricity for the time being.

I wish here to express my thanks to Prof. Ames of the Johns Hopkins University, to whose kindness I am indebted for the opportunity of carrying out these experiments, and whose criticisms and suggestions have proved of great value.

Baltimore, Md., July 1, 1902.

III. *On the Thermodynamical Correction of the Gas-Thermometer. By* H. L. CALLENDAR, *M.A., F.R.S., Professor of Physics, Royal College of Science* †.

1. *Introduction.*

THE correction of the gas-thermometer to the absolute scale is a subject possessing considerable theoretical interest; it has also acquired some practical importance at the present time in view of the increasing accuracy attainable in thermometric measurements. A number of papers on the subject have recently appeared in the Philosophical Magazine and other periodicals. These show some divergence in the methods proposed and in the results deduced, and little has yet been done in the direction of calculating tables of corrections for different gases, or in the practical application of the results to thermometric measurements.

I propose in the present paper to give some account of the theoretical and experimental work bearing on the subject; to explain a method of expression in terms of the "Co-aggregation Volume" which I have found very convenient in treating similar problems relating to imperfect gases; and to show how to calculate tables of corrections in a simple and practical manner.

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* *Comptes Rendus,* cxxxii. p. 1108.

† Communicated by the Physical Society. Read March 26th, 1901. Publication was delayed to await the results of experiments in progress at University College. But in consequence of my removal to the Royal College of Science, it has been found impossible to include this experimental work in the present paper.

The earliest work of any value was that of Regnault (*Mémoires de l'Institut*, Paris, 1847) (1) on the deviations of gases from Boyle's law; (2) on the pressure- and expansion-coefficients at various pressures; (3) on the comparison of the thermometric scales of different gases over the range 0° to 300° C. These experiments established the suitability of the gas-thermometer as a standard, but the order of accuracy attained in the comparisons did not suffice to detect any difference between the scales of the more permanent gases.

The Absolute or Thermodynamic scale of temperature was invented shortly afterwards by Lord Kelvin, who devised a very delicate method of detecting the deviations of actual gases from the ideal state (Trans. Roy. Soc. Edinb. vol. xx. p. 289, April 1851; Phil. Mag. [4] 1852, p. 481), and explained how to reduce the indications of the gas-thermometer to the absolute scale. The experimental measurements were carried out shortly afterwards in conjunction with Joule (Phil. Trans. 1854, p. 321), and still remain among the most important data for the determination of the thermodynamical correction. The history of this investigation is contained in Sir Wm. Thomson's Mathematical and Physical Papers, vol. i. pp. 333–455, and need not be considered in detail; but it will be necessary to give a brief account of the method for the elucidation of the notation adopted and the method of calculation proposed in the present paper.

2. *Theory of the Porous-Plug Experiment* *.

The notation adopted is as follows:—

E = intrinsic energy of fluid per unit mass.
p = pressure; v = volume of unit mass.
$F = E + pv$ = total heat of fluid per unit mass.
H = heat supplied per unit mass from external sources.
$Q = (d\theta/dp)_F$ = "Cooling Effect," or fall of temperature per unit fall of pressure in adiathermal expansion at constant F.
$S = (dH/d\theta)_p$ = specific heat of fluid at constant pressure.
$T = (pv/R)$ = temperature by gas-thermometer.
θ = temperature on the thermodynamic scale.

We have the following relations between the different quantities:—

By the first law of thermodynamics,

$$dE = dH - pdv. \quad \ldots\ldots \quad (1)$$

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* For practical details see Preston, 'Theory of Heat,' p. 702 (1894); Edser, 'Heat for Advanced Students,' p. 384.

By the second law of thermodynamics,

$$(d\mathrm{H}/dp)_\theta = -\theta(dv/d\theta)_p. \quad . \quad . \quad . \quad . \quad (2)$$

Whence,

$$\begin{aligned} d\mathrm{F} &= d\mathrm{E} + d(pv) = d\mathrm{H} + vdp \\ &= (d\mathrm{H}/d\theta)_p d\theta + (d\mathrm{H}/dp)_\theta dp + vdp \\ &= \mathrm{S}d\theta - (\theta(dv/d\theta)_p - v)dp. \quad . \quad . \quad . \quad (3) \end{aligned}$$

When a fluid is flowing steadily along a tube through a porous plug or throttling aperture without external loss or gain of heat, as in the experiment of Joule and Thomson, the function, $\mathrm{F} = \mathrm{E} + pv$, will remain constant provided that the kinetic energy of flow is the same on either side of the plug. It is convenient to have a name for this function, which I have called the Total Heat, employing the expression used by Regnault for the same quantity in the case of a saturated vapour. Expansion through a porous plug is frequently spoken of as "free" or "unresisted" expansion, but this term appears to be inappropriate, since the external work done is $d(pv)$ and not zero, as in Joule's original experiment. It is often said to be "adiabatic" in the sense that no heat is supplied to the fluid from external sources. But this may lead to some confusion, as the process is not isentropic. I have found the term "Adiathermal" more convenient, as implying that there is no heat-transmission, and that the total heat remains constant ($d\mathrm{F} = 0$).

Applying the condition $d\mathrm{F} = 0$, we have by (3) above the well known relation,

$$\mathrm{SQ} = \mathrm{S}(d\theta/dp)_\mathrm{F} = \theta(dv/d\theta)_p - v. \quad . \quad . \quad . \quad (4)$$

This equation gives the "cooling effect" in adiathermal expansion under the condition of constant total heat, which is the quantity measured in the porous-plug experiment. It is convenient to employ the single letter Q for the cooling effect $(d\theta/dp)_\mathrm{F}$, and to measure it in degrees of temperature centigrade per atmosphere ($p = 10^6$ C.G.S. $= 75$ cms. Hg. at 0° C. and lat. 45°), in which case S should also be measured in terms of a unit 10^6 ergs. The sign of Q is positive when a fall of temperature accompanies a fall of pressure, as in the case of air and CO_2. It is negative, a heating effect, in the case of hydrogen at ordinary temperatures.

It is important to observe that the vanishing of the cooling effect is not in itself a sufficient criterion of the ideal gaseous state, $pv = \mathrm{R}\theta$. The condition $\theta(dv/d\theta)_p = v$ would evidently be satisfied by any fluid possessing the characteristic equation

$v/\theta=f(p)$, where $f(p)$ is any arbitrary function of p. But if the fluid satisfies Boyle's law at all temperatures, we must have $pv=f(\theta)$, and the two conditions together are satisfied only by the ideal gas. Similarly Joule's experiment on the expansion of a gas into a vacuum ($d\mathrm{E}=0$) leads to the condition $\theta(dp/d\theta)_v=p$, if there is no change of temperature, which is satisfied by any fluid possessing the characteristic equation $p/\theta=f(v)$, where $f(v)$ is any arbitrary function of v. This condition, in conjunction with Boyle's law, again suffices to define the ideal state; but no one of the three conditions is sufficient by itself.

3. *Application to the Gas-Thermometer.*

In the practical application of the gas-thermometer, we assume an equation of the form $pv=\mathrm{RT}$, in which T is the temperature by gas-thermometer, and differs from θ in proportion as the gas in question deviates from the ideal state. In order to apply the results of the porous-plug experiment to the correction of the scale of the gas-thermometer, Thomson originally proposed to estimate the difference $\theta-\mathrm{T}$ approximately by the following method:—

Suppose the experiment to be performed in a calorimeter *at constant temperature*, so that the gas after passing the plug is restored to its initial temperature. The heat absorbed in the calorimeter is evidently equal to the amount $\mathrm{S}d\theta$ which would have been required to heat the gas up to the original temperature at constant pressure if the experiment had been performed adiathermally with a fall of temperature $d\theta$. But the heat absorbed at constant temperature in the calorimeter is also by the first law equal to the increase of intrinsic energy $(d\mathrm{E}/dv)_\theta dv$ of the gas, together with the external work $d(pv)_\theta$ done by the gas. Writing for $(d\mathrm{E}/dv)_\theta$ its value $\theta(dp/d\theta)_v-p$, we have

$$-\mathrm{S}d\theta=(\theta(dp/d\theta)_v-p)dv+d(pv), \quad . \quad . \quad (5)$$

which is evidently equivalent to the equation (4) previously given, but with v instead of p as independent variable, since $(dp/d\theta)_v(dv/dp)_\theta=-(dv/d\theta)_p$. Integrating this expression over the range of an experiment from $p'v'$ to $p''v''$ at constant temperature, and putting on the left the observed value of the fall of temperature $(\theta'-\theta'')$, we obtain Thomson's original equation,

$$\mathrm{S}(\theta'-\theta'')=\theta(d\mathrm{W}/d\theta)_v-\mathrm{W}+p''v''-p'v', \quad . \quad (6)$$

in which W is the work represented by the integral of pdv

at constant temperature. The integral W and its variation with temperature cannot be determined for the gas without an exact knowledge of the form of the isothermals, and of the coefficient $(dp/d\theta)_v$ in terms of the absolute scale. Thomson therefore proposed to make an approximate estimate by assuming (1) that the gas obeyed Boyle's law $p'v' = \mathrm{RT} = p''v''$, (2) that the degrees on the absolute scale were nearly the same size as on the constant-volume gas-thermometer at the temperature of experiment, or that we may write $(dp/d\theta)_v = (dp/d\mathrm{T})_v = p/\mathrm{T} = \mathrm{R}/v$. Making this approximation, we obtain immediately,

$$\theta - \mathrm{T} = \mathrm{S}(\theta' - \theta'')/\mathrm{R} \log_e (v''/v'). \quad . \quad . \quad . \quad (7)$$

This approximation is unsatisfactory, because if we knew the absolute value of the pressure-coefficient and the deviations from Boyle's law, the gas-thermometer might be corrected to the absolute scale without performing the porous-plug experiment. The quantities neglected are evidently of the same order as the quantity sought. Thomson and Joule clearly realized this, and devised other methods of correction, but unfortunately the first approximate solution is still retained in many text-books *, in a slightly different form, as the final and correct solution of the problem. The method of exposition generally adopted is as follows :—

Assuming that the degrees on the scale of the constant-pressure gas-thermometer are of the same size as those of the absolute scale at the temperature of the experiment, we may write $dv/d\theta = dv/d\mathrm{T} = \mathrm{R}/p$ in equation (4). Rearranging the terms and substituting T for pv/R, we then obtain

$$\theta - \mathrm{T} = \mathrm{S} p d\theta / \mathrm{R} dp. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Assuming further that the small difference $(\theta - \mathrm{T})$ is independent of p, the right-hand side is integrated from p' to p'', substituting for $d\theta$ the actual difference of temperature $(\theta' - \theta'')$ observed when the gas expands adiathermally from a pressure p' to a pressure p''. This gives again the expression

$$\theta - \mathrm{T} = \mathrm{S}(\theta' - \theta'')/\mathrm{R} \log p'/p'' = \mathrm{S}(\theta' - \theta'')/\mathrm{R} \log v''/v'. \quad (9)$$

When the experiment was tried, it was found that the fall of temperature $(\theta - \theta')$ was *not* proportional to log (p/p'), but simply to $(p - p')$, so that the second assumption involved in solution (9) is evidently erroneous. As a matter of fact,

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* *E. g.* Maxwell's 'Heat,' p. 214 (1897); Tait's 'Heat,' p. 340 (1895).

Joule and Thomson did not make any direct use of the approximate solution in this form. But owing to its frequent repetition, it has proved a stumbling-block to many who have attempted to apply the results of these experiments to the calculation of the difference between the scales.

In order to calculate the correction for the *air*-thermometer over the whole range, Joule and Thomson proceeded in 1854 by a different method. Combining Regnault's formula for the pressure-coefficient at various constant densities, namely,

$$\text{Pressure-coefficient of Air} = \cdot00365343 + \cdot000011575\, V_0/v, \quad . \quad (10)$$

with his experiments on the deviations from Boyle's law at 4° C., and with their own experiments on the cooling-effect, they calculated the following formula (the units being feet and pounds) to satisfy all the available experimental data:—

$$pv = R(\theta - (\cdot0012811 - 1\cdot3918/\theta + 353\cdot2/\theta^2)V_0/v). \quad (11)$$

This is a very simple and direct method provided that the data employed are accurate and consistent. Calculating from this formula they obtained the value of the freezing-point of water on the absolute scale 0° C. = 273·72 Abs., which is still frequently quoted, and was universally accepted for many years. They also calculated a table of corrections for the air-thermometer which has been quoted in many recent books (*e. g.* Guillaume's *Thermométrie*, Paris, 1889) as the final result of their work. It is evident, however, that the value 0° C. = 273·72 Abs. is simply the reciprocal of Regnault's limiting coefficient at zero initial pressure, namely, ·00365343, and does not depend at all on the value of the cooling-effect; and since Regnault's formula (7) is well known at the present time to be erroneous, it is not to be wondered at that the values of the thermodynamical correction given in Joule and Thomson's original table should be very greatly in excess of the true difference between the scales.

Other attempts have been made on similar lines to calculate tables of reduction for the gas-thermometer, notably by Jochmann (1860), and by Weinstein (1881), whose results are quoted in Guillaume's *Thermométrie*, p. 261 [*]. Weinstein quotes Jochmann's equation, and endeavours to adapt the method for calculation of the corrections of the constant-volume thermometer. By a somewhat complicated method, taking

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[*] Jochmann, Schlomilchs' *Zeit. Math. Phys.* v. pp. 24 & 96; Weinstein, *Metron. Beitr.* n. 3, p. 65.

account of Regnault's data in addition to those of Joule and Thomson, he arrives at an empirical equation of the form

$$\theta/\theta_0=(1+{\cdot}003654\,t)^{1{\cdot}00029}, \quad . \quad . \quad . \quad (12)$$

in which t is the temperature on the centigrade scale. The values of the corrections calculated by this method are much smaller than those in the original table of Joule and Thomson, and are of the right order of magnitude between 0° and 100°, but it does not appear that an equation of this type correctly represents the phenomena.

4. *Rankine's Equation for* CO_2.

In the same paper (Phil. Trans. 1854, p. 337) Joule and Thomson quoted another empirical formula for CO_2 contained in a letter from Rankine, namely,

$$pv=R\theta-aR\theta_0v_0/\theta v, \quad . \quad . \quad . \quad . \quad (13)$$

in which the value of the constant a (in degrees of temperature) was given as 1·9, and was deduced solely from Regnault's observations of the pressure-coefficient of CO_2 at various constant densities. In a previous paper (Trans. Roy. Soc. Edinb. xx. p. 561) Rankine had given an estimate of θ_0, the absolute zero, obtained by plotting Regnault's values of the pressure-coefficients of air and CO_2, which led to the value $\theta_0=274°{\cdot}6$, but in the formula quoted he employed $\theta_0=274°{\cdot}0$. This formula agreed very well with Regnault's coefficients of expansion for CO_2, and also with his observations on the compressibility. Joule and Thomson further showed that it satisfied their own observations on the cooling-effect at that time available, employing the expression $Q=3Ra\theta_0^2/S\theta^2$, deduced from Rankine's formula. Taking Rankine's value for a, and putting $R=1{\cdot}89\times10^6$, $S=8{\cdot}4\times10^6$ C.G.S. we find Q at 0° C.$=1°{\cdot}28$ per atmo., which is in fair agreement with the value actually observed.

At a later date (Phil. Trans. 1862) Joule and Thomson succeeded in obtaining more accurate measurements of the cooling-effect over a range of temperature extending from 4° to 96° C., and found that the cooling-effect for air and CO_2 varied nearly as $1/\theta^2$, and could therefore be represented by Rankine's formula. By adopting the expression $Q=A/\theta^2$ for the cooling-effect, and integrating equation (4), neglecting the variations of S, and assuming that the equation must approximate indefinitely to $v=R\theta/p$ at high temperatures, they obtained the following type of characteristic equation,

$$v=R\theta/p-AS/3\theta^2, \quad . \quad . \quad . \quad . \quad (14)$$

which may also be obtained by substituting $pv = R\theta$ in the small term of Rankine's. They found, however, that the heating-effect in the case of hydrogen increased slightly with rise of temperature, and could not be represented by the formula. Assuming Rankine's formula, it would evidently be easy to calculate the value of the absolute zero, and to deduce tables of corrections for the gas-thermometer. But as the formula did not represent the case of hydrogen, which was the most important for thermometric purposes, they did not publish any further tables of corrections, and the absolute zero was still taken at $-273^\circ{\cdot}7$ C., as calculated in their previous paper from Regnault's limiting value for the pressure-coefficient in the case of air.

5. *Estimation of the Absolute Zero.*

The problem of the thermodynamical correction of the gas-thermometer is naturally divided into two parts : (1) the determination of the value of the freezing-point of water on the absolute scale in terms of the fundamental interval, which may be called the value of the Absolute Zero ; (2) the determination of the correction to be applied at other points of the scale to reduce an interval of temperature measured on the scale of the gas-thermometer to the corresponding value measured on the absolute scale, which may be called the Scale-Correction. The latter depends essentially on the type of empirical formula assumed to represent the mode of variation of Q with temperature, whereas the former may be approximately estimated without any such assumptions. Moreover, the scale-correction is necessarily small for gases at ordinary temperatures, whereas the absolute zero correction may be considerable, and is required for determining the variations of the pressure- and expansion-coefficients.

A simple and accurate method of determining the value of the absolute zero from observations of the cooling-effect alone, was given by Sir Wm. Thomson in his article "Heat" in the *Encyclopædia Britannica* (vol. xi. p. 554, 1880). The differential equation (4) may be written in the form

$$d\theta/\theta = dv/(v + SQ), \quad . \quad . \quad . \quad . \quad (15)$$

in which, if we require only to make an approximate estimate of the absolute zero correction, we may put SQ *constant* and equal to its average value between 0° and 100° C. Integrating this at constant pressure p_0 between limits 0° and 100°, and writing T_0 for the expression $100v_0/(v_{100} - v_0)$ (the reciprocal of the fundamental coefficient of expansion, which may be called the "fundamental zero"), we obtain for the absolute zero correction the simple result,

$$\theta_0 - T_0 = Sp_0Q/R. \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

This expression was applied to calculate the coefficients of expansion at various constant pressures, and to determine the value of the absolute zero from Regnault's coefficients of expansion of air, hydrogen, and CO_2 at $p_0 = 76$ cms.

The following table contains the results given in the article in question :—

Table I.—Absolute Zero from Regnault's Expansion-Coefficients.

Gas employed	Air.	H_2.	CO_2.
Coefficient of Expansion, α	·0036706	·0036613	·0037100
Fundamental Zero of Gas, $T_0 = 1/\alpha$ ...	272°·44	273°·13	269°·50
Correction to Absolute Zero, $\theta_0 - T_0$ ...	+·70	−·13	+4·4
Absolute Zero deduced, θ_0	273·14	273·00	273·90

Thomson remarks as the result of these figures that the correct value is probably within a tenth of a degree of 273°·0, and that it is satisfactory to find that a gas so imperfect as CO_2, with so large a value of the correction, should differ so little when corrected from air and hydrogen. As a matter of fact, the discrepancy, small as it is, appears to be due to an error in Regnault's coefficient of expansion, for if we adopt instead Chappuis' value of the expansion-coefficient for CO_2 at 100 cms. pressure, namely ·003742, which gives $T_0 = 267°·24$, we find (increasing the correction in the ratio 100/76) the value of the absolute zero $\theta_0 = 267·24 + 5°·8 = 273°·04$, which agrees with hydrogen.

A similar method has been applied by other writers to estimate the zero correction for the constant-volume thermometer. If we neglect the term $d(pv)$ in equation (5) (which is *not* justifiable), and write $-(d\theta/dv)_F = Qp/v$ (which is a good approximation considering that this term is small), we obtain

$$1 + SQ/v = (dp/d\theta)_v \theta/p. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Integrating this at constant volume, *assuming* SQ *constant*, we have the solution

$$\log_e(\theta/\theta_0) = \log_e(p/p_0)/(1 + SQ/v), \quad . \quad . \quad . \quad (18)$$

from which, since SQ is small, we have the approximate value of the correction,

$$\theta_0 - T_0 = 1{\cdot}163 S p_0 Q/R. \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

This is equivalent in effect to the method adopted by Lehfeldt (Phil. Mag. April 1898, p. 363), who takes for Q the value of the "proper mean cooling-effect" given by Thomson. Applying the correction to the value of the pressure-coefficient for CO_2 found by Chappuis at $p_0 = 100$ cms., namely, ·0037251, $T_0 = 268°{\cdot}45$, he finds $\theta_0 = 274°{\cdot}83$, which is evidently much too large. The error is chiefly due to the neglect of the term $d(pv)$. He also applies formula (18) to evaluate the scale-correction between 0° and 100° for comparison with Chappuis' observations. His results for the scale-difference between the nitrogen and hydrogen thermometers are given in Table VI. (p. 67), and indicated by the dotted curve in fig. 1 (p. 69). They appear to be somewhat in excess of the true values, partly in consequence of the assumption SQ = constant, which cannot be made in deducing the scale-correction.

There is a much simpler method of deducing the absolute zero correction directly from the differential equation, without integrating on the assumption SQ = constant, which, so far as I am aware, has not been previously noticed.

For the constant-pressure thermometer, we take the equation in the form (4), and substitute $dv/d\theta = R/p$, and $T = pv/R$, which gives the simple result,

$$\theta - T = SpQ/R, \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

which is accurately true at a point in the neighbourhood of 50° C., where the degrees on the scale of the gas-thermometer are of the same size as those on the absolute scale. To find the value of the zero correction $\theta_0 - T_0$, we have merely to subtract the value of the scale-correction at this point. But the latter must be very small compared with the zero correction, since the whole number of degrees between 0° and 100° C. is the same by definition for both thermometers. If, therefore, we substitute the proper mean value of SQ, which corresponds to the point where the degrees are of equal size, we shall obtain a very good approximation to the absolute zero correction, which is in fact seen to be the same as that given by Thomson for the constant-pressure thermometer.

To make a similar estimate for the constant-volume thermometer, we take the differential equation in the form (5), which may be written

$$-\mathrm{SQ}(dp/dv)_{\mathrm{F}}=\theta(dp/d\theta)_v-p+(d(pv)/dp)(dp/dv)_\theta. \quad (21)$$

In the small terms it is justifiable to make the approximations $(dp/dv)_{\mathrm{F}}=(dp/dv)_\theta=-p/v$. If we also put $(dp/d\theta)_v=\mathrm{R}/v$, which is only true at the point where $d\mathrm{T}/d\theta=1$, we obtain

$$\theta-\mathrm{T}=\mathrm{S}p\mathrm{Q}/\mathrm{R}+(d(pv)/dp)_\theta p/\mathrm{R}. \quad . \quad . \quad (22)$$

In order to evaluate this for CO_2 we may take $\mathrm{SQ}=7{\cdot}9$ c.c. as the proper mean value. We require in addition the value of $d(pv)/dp$ at or near 50° C., which may be taken as 2·4 c.c. from Amagat's observations on CO_2. The value of p is the pressure in the gas-thermometer at the point considered. Adopting Chappuis' value of the pressure-coefficient for CO_2 at 100 cms. initial pressure, namely, ·0037251, $\mathrm{T}_0=268^\circ{\cdot}45$, we have $p=119$ cms. $=1{\cdot}58\times10^6$ C.G.S. at 50°. Taking $\mathrm{R}=1{\cdot}89\times10^6$, we find the value of the correction $4^\circ{\cdot}55$, which gives $\theta_0=273^\circ{\cdot}0$. This neglects the scale-correction at 50°, which, however, is less than ·05°. It is clear that the correction depending on $d(pv)$ cannot be neglected. If we could replace Q by the cooling-effect in "free" expansion ($d\mathrm{E}=0$), as in Joule's original experiment, this term would not be required.

6. *The Equations of van der Waals and Clausius.*

The above method of deducing the value of the absolute zero from the cooling-effect may appear at first sight to be wanting in precision; but it assumes only that the effect is small, and diminishes continuously with increase of temperature, and the results to which it leads are really quite as accurate as the available experimental data. By way of contrast we may take a method which appears at first sight to be unimpeachable, but which leads to results which are obviously wrong.

Van der Waals, in his celebrated essay "On the Continuity of State" (Phys. Soc. Translation, Cap. XI. p. 440), was the first to interpret the cooling-effect in terms of the capillary pressure represented by the term a/v^2 in his well known equation

$$(p+a/v^2)(v-b)=\mathrm{R}\theta. \quad . \quad . \quad . \quad . \quad (23)$$

Taking this equation, he showed that, if the capillary pressure varied inversely as the square of the volume, and the covolume b was constant, the fall of temperature in the Joule-

Thomson experiment must be to a first approximation proportional to the fall of pressure, or the ratio Q independent of p. The expression which he gave for the cooling effect is equivalent to the following :

$$SQ=2a/R\theta-b. \qquad . \quad . \quad . \quad . \quad (24)$$

As applied to the constant-volume thermometer, the equation gives very simple results, since p is accurately a linear function of θ, so that the scale-correction is identically zero. The absolute zero correction is given by the formula

$$\theta_0-T_0=a/Rv=ap_0/R^2\theta_0. \qquad . \quad . \quad . \quad (25)$$

Van der Waals himself observed that the values of a and b which he adopted for CO_2 to represent the experiments of Regnault and Andrews did not satisfy the results of Joule and Thomson on the cooling-effect. Rose-Innes, however, has shown (Phil. Mag. March 1898, p. 227) that a formula of the type $Q=A/T-B$ (which is the same as that given by van der Waals) represents the cooling-effect much better than that of Rankine, including the case of hydrogen, and has calculated the appropriate values of the constants. Adopting his values of the coefficients A and B, and taking $S=8{\cdot}4\times10^6$, we find for CO_2

$$a/R\theta_0=11{\cdot}9 \text{ c.c.}, \quad b=12{\cdot}3 \text{ c.c.} \qquad . \quad . \quad (26)$$

Rose-Innes applied this formula to calculate the absolute zero from Regnault's expansion-coefficients, and obtained results practically identical with Lord Kelvin's ; but he did not apply it to calculate the absolute zero from the pressure-coefficient. If we take, as before, Chappuis' pressure-coefficient for CO_2 at $p_0=100$ cms., namely, ·003725, $T_0=268^\circ{\cdot}45$, the correction is $8^\circ{\cdot}4$, which gives $\theta_0=276^\circ{\cdot}9$, a result which is obviously much too large.

This discrepancy is partly due to the fact that the type of formula assumed to represent the variation of Q with temperature is wrong, although it represents the observations perfectly over the experimental range. It shows very clearly that the method previously given, which does not assume any particular type of formula, but deduces the zero correction directly from the observations, is much to be preferred, although it may appear less rigorous at first sight. Moreover, it is evident that the values of a and b deduced from the cooling-effect in this manner would not satisfy the observations of Regnault or Amagat on the isothermal compressibility, since they would make $d(pv)/dp$ at 0° C.

(which is approximately given by the expression $-(a/R\theta_0-b)$) positive and equal to about $+0{\cdot}4$ c.c., *i. e.* the gas would appear "pluperfect," like hydrogen, whereas it is very much the reverse. If on the other hand we take the values of the constants given by van der Waals, which would be equivalent to the following,

$$a/R\theta_0=4{\cdot}42 \text{ c.c.}, \quad b=1{\cdot}16 \text{ c.c.}, \quad . \quad . \quad (27)$$

the compressibility at 0° C. is well represented, but the value of the cooling-effect is much too small. At higher temperatures the formula gives values of the cooling-effect which are more nearly correct, but the value of $d(pv)/dp$ at 200° C. is found to be $-1{\cdot}40$ c.c., which is nearly twice as large as the value given by Amagat's observations. The formula would also make the scale-correction of the constant-volume thermometer vanish at all temperatures, whereas the observations of Chappuis (see below) prove that it is quite large in the case of CO_2.

On these and similar grounds we are justified in concluding that the formula of van der Waals does not represent the behaviour of CO_2 at moderate pressures with sufficient accuracy to be of practical value. Clausius, however, has shown (Phil. Mag. June 1880) that the agreement is greatly improved if we suppose the coefficient a in the capillary pressure to vary inversely as θ, which leads to a formula of the same type as that proposed by Rankine, but with the addition of the covolume b. For the purposes of gas-thermometry, or for calculations at moderate pressures, we may neglect quantities of the second order, and may write the equation of Clausius in the form

$$v=R\theta/p-a/R\theta^2+b. \quad . \quad . \quad . \quad . \quad (28)$$

Love (Phil. Mag. July 1899) has shown that a formula of this type represents all the observations on the cooling-effect very well, but he has not applied it to the calculation of the absolute zero, or the scale-correction of the gas-thermometer.

7. *Expression in Terms of the Co-aggregation-Volume* c.

In the application of this or similar equations to represent the behaviour of imperfect gases at moderate pressures, I have found it very convenient to employ the single letter c to represent the term $a/R\theta^2$. The quantity c represents a volume, expressible in cubic centimetres, which is to a first approximation a function of the temperature only, and which may be called the "co-aggregation-volume," as it denotes the diminution of volume caused by the formation of molecular aggregates. All the thermodynamical properties of the gas may be simply expressed (as I have shown, Proc. Roy. Soc. 1900, vol. lxvii. p. 266) in terms of the co-aggregation-volume. This method of expression is more convenient for practical purposes than expression in terms of the capillary pressure, since the latter is a function of both volume and temperature. It is convenient to assume that c varies inversely as the nth power of θ, so that we may write

$$c = c_0(\theta_0/\theta)^n, \quad . \quad . \quad . \quad . \quad . \quad (29)$$

where c_0 is the value of c at θ_0. The value of the index n is apparently 2 for CO_2, but it may have different values for other types of molecules. The general expression for the cooling-effect deduced from (4) on this assumption is

$$SQ = (n+1)c - b, \quad . \quad . \quad . \quad . \quad . \quad (30)$$

and the expression for the slope of the isothermals obtained by plotting the product pv against p is

$$d(pv)/dp = -(c-b). \quad . \quad . \quad . \quad . \quad (31)$$

For an imperfect gas like CO_2 or nitrogen, c is greater than b. The gas becomes "pluperfect," like hydrogen, at the point where $c = b$. The isothermals on the pv, p diagram are straight lines, the inclinations of which to the axis of p diminish as the temperature rises. This is a much better approximation than might be supposed at first sight, because experiment shows the isothermals to be nearly straight for a considerable range of pressure and temperature.

If we calculate the values of the constants c_0 and b for each gas from the experiments of Joule and Thomson on the cooling-effect, employing the equation (28) above with the value $n = 2$, so that $SQ = 3c - b$, we obtain the results given in the following table :—

Table II.—Values of Constants from Observations of Joule and Thomson.

Gas employed.	R.	S.	Q_0.	Q_{100}.	c_0.	b.	C.
	$\times 10^6$.	$\times 10^6$.	Per atmo. (10^6 C.G.S.)		c.c.	c.c.	$c_0 p_0/373R$.
Air	2·871	10·05	0°·271	0°·147	0·90	− ·002	·00085
CO_2	1·887	8·40	1·368	0·610	4·56	2·18	·00656
H_2	41·5	145·3	− ·029	− ·048	2·01	10·23	·000132

The constant C is employed in calculating the scale-corrections in Table VI. below. The values are given for $p_0=76$ cms. $=1{\cdot}0133\times10^6$ C.G.S.

8. *Method of Calculating the Correction.*

An incomplete table of corrections, for the air-thermometer only, was calculated by Rowland (Proc. Amer. Acad. vol. vii. 1880, p. 114) with the object of correcting the air-thermometer which he employed in the reduction of his observations on the mechanical equivalent of heat. The method of calculation was not given, but he employed only Joule and Thomson's later results (1862) as represented by Rankine's equation. His work was probably the first application of the thermodynamical correction to the actual results of experiment.

A similarly incomplete table of corrections for the air-thermometer was given in my own paper "On the Practical Measurement of Temperature" (Phil. Trans. A. 1887, p. 162) for reducing the indications of the platinum-thermometer to the absolute scale. The method of calculation adopted was as follows.

For purposes of gas-thermometry the characteristic equation of the gas employed may be written in the following form:

$$\theta=pv/\mathrm{R}+q, \quad . \quad . \quad . \quad . \quad . \quad (32)$$

in which q is a small quantity of the dimensions of temperature, which represents the deviations of the gas from the ideal state. In using a gas-thermometer we assume an equation of the type $\mathrm{T}=pv/\mathrm{R}'$, in which T is the temperature on the scale of the gas-thermometer, and R′ is a constant, differing slightly from R, and depending to some extent on the method of thermometry employed. The values of R and R′ are determined in each case from the observations at the fixed points 0° and 100° C., which give the following relations:

$$\mathrm{R}'=(p_1v_1-p_0v_0)/100, \quad \mathrm{R}=\mathrm{R}'(1+(q_1-q_0)/100), \quad (33)$$

in which p_0, v_0, q_0 are the values of p, v, q at 0° C., and p_1, v_1, q_1 are the values at 100° C. In deducing these relations small quantities of the second order involving squares and products of q are neglected.

To find the value of the absolute zero we have the equation

$$\theta_0=p_0v_0/\mathrm{R}+q_0=\mathrm{T}_0+q_0-(q_1-q_0)\,\theta_0/100. \quad . \quad (34)$$

To find the value of the correction dt to be added to the centigrade temperature t on the scale of the gas-thermometer to reduce to temperature centigrade on the thermodynamical scale, since the temperature centigrade on the scale of the gas-thermometer is given by the formula

$$t=\mathrm{T}-\mathrm{T}_0=(pv-p_0v_0)100/(p_1v_1-p_0v_0), \quad . \quad (35)$$

we have evidently the simple expression

$$dt=(\theta-\theta_0)-(\mathrm{T}-\mathrm{T}_0)=(q-q_0)-(q_1-q_0)t/100. \quad (36)$$

It may be noticed with regard to the separate terms in this expression that q_0 is the zero-correction, and the second part $(q_1-q_0)t/100$ is the correction for the fundamental interval. The correction at any point of the scale is not simply $q-q_0$, as might appear at first sight, because the values of the constants R and R′ are different, and the correction must vanish at 100° C. as well as at 0° C.

In order to apply formula (36) to the calculation of a table of corrections, we may select any empirical formula which represents satisfactorily the properties of the gas under consideration. The equation is then thrown into the form (32), and the expression for q is simplified as far as possible by rejecting all quantities of the second order, and is expressed in terms of p_0 and T or θ. As a simple example we may take the equation devised by Clausius to represent the deviations of CO_2 from the formula of van der Waals,

$$(p+a/\theta(v+\beta)^2)(v-b)=\mathrm{R}\theta. \quad . \quad . \quad (37)$$

Neglecting small quantities of the second order, this may be put in the form

$$\theta=pv/\mathrm{R}+(a/\mathrm{R}\theta^2-b)p/\mathrm{R}, \quad . \quad . \quad . \quad (38)$$

whence

$$q=(a/\mathrm{R}\theta^2-b)p/\mathrm{R}=(c-b)p/\mathrm{R}. \quad . \quad . \quad (39)$$

Writing p_0 for p we have the value of q for the constant-pressure thermometer. For the constant-volume thermometer we must substitute $p_0\theta/\theta_0$ for p. The values of the constants may be immediately calculated (as above, Table II.) from the observations of Joule and Thomson on the cooling-effect, without reference to any other experimental data. A table of corrections calculated in this manner may not be the most accurate possible at the present time, when so many more observations are available, but it is of special interest to compare the results of an investigation made so long ago with those of the latest thermometric researches. For this reason I have calculated the following table of corrections on the basis of equation (38), assuming only the data already given for the cooling-effect according to Joule and Thomson.

In the simple case here considered it is unnecessary to calculate the values of q for each temperature separately, and then apply formula (36) to find the correction dt. The expression for dt may with advantage be greatly simplified, before beginning the calculation, by putting in the numerical values of θ_0 and θ_1, namely, 273 and 373, and substituting t for $\theta - \theta_0$. We thus obtain the following simple formulæ.

For the Constant-Volume Thermometer:—

$$\text{Absolute Zero-Correction,} \quad \theta_0 - T_0 = 646C, \quad . \quad (40)$$

$$\text{Scale-Correction,} \quad dt = Ct(t-100)/\theta, \quad . \quad (41)$$

in which C is used as an abbreviation for the constant factor $c_0 p_0/373R$, which has the values given in Table II. above for an initial pressure $p_0 = 760$ mm.

For the Constant-Pressure Thermometer:—

$$\text{Absolute Zero-Correction,} \quad \theta_0 - T_0 = 846C - bp_0/R, \quad . \quad (42)$$

$$\text{Scale-Correction,} \quad dt = Ct(t-100)(1{\cdot}732 + 273/\theta)/\theta. \quad (43)$$

The covolume b occurs only in the zero-correction of the constant-pressure thermometer. The values of the constant C are the same as for the constant-volume thermometer. The corrections for the constant-pressure thermometer are deduced from those for the constant-volume thermometer by multiplying by the factor $(1{\cdot}732 + 273/\theta)$, which has values between 2 and 3 at ordinary temperatures. When the corrections for any one gas have been calculated, those for any other follow by simple proportion. The corrections given in the table are all calculated for an initial pressure $p_0 = 760$ mm. The corrections for any other initial pressure are simply proportional to the pressure.

If we apply the above formulæ to calculate the value of the absolute zero from Regnault's pressure-coefficients, we find considerable discrepancies in the results, as illustrated by the following table.

Table III.—Absolute Zero from Regnault's Pressure-Coefficients.

Gas employed	Air.	Hydrogen.	CO_2.
Pressure-Coefficient ($p = 76$ cms.), a ...	·0036650	·0036678	·0036880
Fundamental Zero of Gas, $T_0 = 1/a$ ...	272°·85	272°·64	271°·2
Correction to Absolute Zero, $\theta_0 - T_0$ ...	+ ·56°	+ ·09°	+4°·2
Absolute Zero deduced, θ_0	273°·41	272°·73	275°·4

It appears that these discrepancies are due in the main to errors of Regnault's pressure-coefficients, which subsequent observations have shown to be much less accurate than his expansion-coefficients, though Regnault himself considered them more accurate. If we employ Chappuis' values of the pressure-coefficients, which are certainly nearer the truth than Regnault's, we obtain the following results.

TABLE IV.—Absolute Zero from Chappuis' Pressure-Coefficients.

Gas employed	Nitrogen.	Hydrogen.	CO_2.
Pressure-Coefficient ($p_0=100$ cms.), a .	·0036747	·0036625	·0037251
Fundamental Zero of Gas, $T_0=1/a$ ...	272°·11	273°·03	268°·45
Correction to Absolute Zero, θ_0-T_0 ...	+0°·98	+0°·11	+5°·55
Absolute Zero deduced, θ_0	273°·09	273°·14	274°·00

These evidently agree very closely with the results deduced for the same gases from Regnault's expansion-coefficients. The cooling-effect for nitrogen was found by Joule and Thomson to be larger than for air in the proportion of 103 to 88. I have allowed for this in Table IV. and also in Table VI. as it gives a better agreement with experiment on the assumption $n=2$. But Joule and Thomson did not regard their experiments on nitrogen with much confidence, and the true value of n is probably more nearly 1·5 for diatomic gases (see below, section 20). The value found for CO_2, namely 274·0, differs from that calculated by the direct method of formula (22), which is certainly correct. The explanation of this apparent discrepancy is given below in section 15.

The values of the scale-correction for the same gases, calculated by formulæ (41) and (43) with the values of the constants given in Table II., deduced from the observations on the cooling-effect alone on the assumption $n=2$, are given in the following table. The table covers a wide range of temperature, and is intended to illustrate the general effect of the correction, but it must be remembered that the observations on which it rests were confined to the range 0° to 100° C.

TABLE V.—Scale-Correction for Air, H_2, and CO_2.

Temp. Cent.	Constant-Volume, p_0=76 cms.			Constant-Pressure, 76 cms.		
	Air.	Hydrogen.	CO_2.	Air.	Hydrogen.	CO_2.
− 200°	...	+·109	...	...	+·586	
− 150	+ ·258	+·040	...	+1·02	+·158	
− 100	+ ·099	+ 015	...	+ ·328	+·050	
− 50	+ ·029	+·005	+ ·22	+ ·086	+·015	+ ·65
− 20	+ ·0080	+·0012	+ ·062	+ ·022	+·0035	+ ·172
− 10	+ ·0036	+·0006	+ ·027	+ ·010	+·0017	+ ·076
+ 10	− ·0027	−·0004	− ·0207	− ·0073	−·0011	− ·056
+ 20	− ·0046	−·0007	− ·0356	− ·0122	−·0019	− ·095
+ 30	− ·0059	−·0009	− ·0452	− ·0155	−·0024	− ·119
+ 40	− ·0065	−·0010	− ·0500	− ·0169	−·0026	− ·130
+ 50	− ·0066	−·0010	− ·0504	− ·0170	−·0026	− ·130
+ 60	− ·0061	−·0009	− ·0470	− ·0155	−·0025	− ·120
+ 70	− ·0052	−·0008	− ·0398	− ·0132	−·0020	− ·101
+ 80	− ·0039	−·0006	− ·0295	− ·0098	−·0015	− ·074
+ 90	− ·0021	−·0003	− ·0162	− ·0052	−·0008	− ·040
+ 150	+ ·015	+·002	+ ·115	+ ·036	+·006	+ ·274
+ 200	+ ·036	+·006	+ ·275	+ ·083	+·013	+ ·635
+ 300	+ ·089	+·014	+ ·683	+ ·196	+·031	+ 1·51
+ 450	+ ·186	+·029	+ 1·42	+ ·392	+·061	+ 3·00
+1000	+ ·600	+·093	+ 4·60	+1·16	+·181	+ 8·93
+2000	+1·42	+·221	+10·9	+2·62	+·407	+20·2

9. *Comparison with Chappuis' Experiments.*

It is interesting to compare the results calculated in this table with the experiments of Chappuis (Bureau Internat. Reports, 1888) on the differences between the scales of the nitrogen, hydrogen, and carbonic acid gas-thermometers. The most accurate and important of his experiments were made with the constant-volume thermometer at an initial pressure of 100 cms. The gas-thermometers were not directly compared, but the same instrument was employed successively with the different gases, and the readings at intervals of 5° up to 50° C., and also at 61° and 78°, were compared with those of four standard mercury thermometers.

The results of the comparisons of the mercury thermometer (t_m) with the nitrogen and hydrogen thermometers (t_n and t_h) were represented by the following empirical formulæ:—

$$t_n - t_m = t(100-t)(-55{\cdot}541 + 0{\cdot}48240t - 0{\cdot}0024807t^2) \times 10^{-6},$$

$$t_h - t_m = t(100-t)(-61{\cdot}859 + 0{\cdot}47351t - 0{\cdot}0011577t^2) \times 10^{-6}.$$

In order to make a comparison with Joule and Thomson' it is necessary to take the difference between the nitrogen and hydrogen scales by subtracting the second formula from the first, which gives the expression

$$t_n - t_h = t(100-t)(+6{\cdot}318+0{\cdot}00889t-0{\cdot}0013230t^2)\times 10^{-6}. \quad . \quad (44)$$

This is the formula which is generally quoted for the difference between the nitrogen and hydrogen scales; but it must be remembered that it refers to an initial pressure of 100 cms. at constant volume, and that it is obtained as the difference between two comparisons with the mercury thermometer, which may have introduced small constant errors, especially at the higher points of the scale. The differences calculated by formula (44) are compared with those taken from Table V., corrected from air to nitrogen by the factor 103/88, and increased in the proportion 100/76 to reduce to 100 cms. initial pressure, under the heading $n=2$, in the following table, together with later reductions.

Table VI.—Difference between Scales of Constant-Volume Nitrogen and Hydrogen Thermometers $t_n - t_h$ at 100 cms. initial pressure.

Temp. Cent.	Joule-Thomson.		Chappuis *.		Lehfeldt, Phil. Mag. 1898.	Rose-Innes. Phil. Mag. 1901.
	$n=1{\cdot}5$.	$n=2$.	Formula (44).	Corrected 1888.		
−20°	−·0065	−·0107	−·0135	−·0173		
−10	−·0030	−·0048	−·0067	−·0074		
+10	+·0022	+·0036	+·0057	+·0053	+·006	+·0010
+20	+·0040	+·0060	+·0095	+·0087	+·011	+·0018
+30	+·0049	+·0077	+·0113	+·0105	+·014	+·0023
+40	+·0055	+·0087	+·0110	+·0110	+·017	+·0025
+50	+·0055	+·0087	+·0086	+·0103	+·019	+·0025
+60	+·0050	+·0078	+·0049	+·0090	+·019	+·0024
+70	+·0045	+·0064	+·0010	+·0069	+·018	+·0020
+80	+·0034	+·0048	−·0024	+·0045	+·015	+·0015
+90	+·0018	+·0028	−·0032	+·0022	+·010	+·0008

It will be observed that formula (44) gives negative values of the difference $t_n - t_h$ at 80° and 90° C.; but these are of the same order as the probable error of observation, which was ·003° or ·01 mm. Hg. The only observation actually taken at this part of the scale, namely, at 78° C. in the vapour

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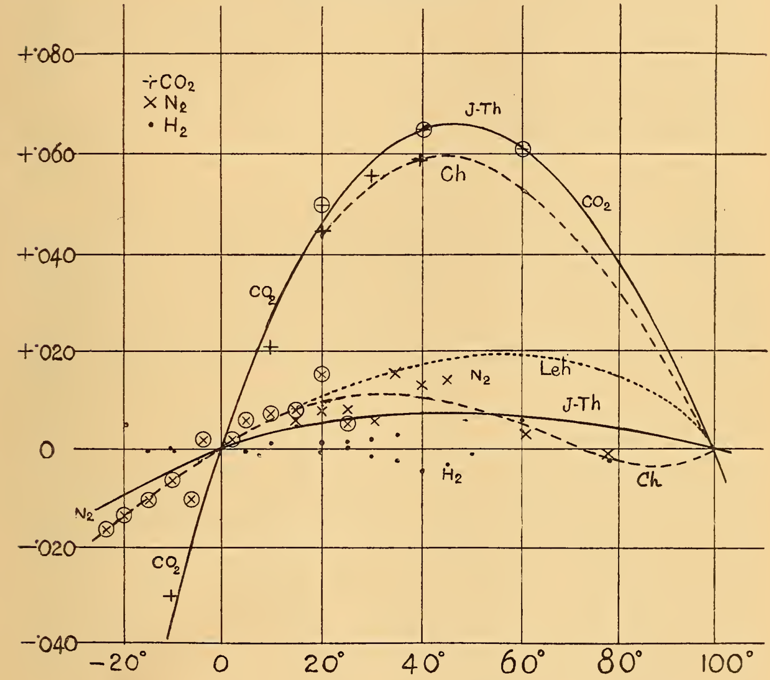
* Chappuis' latest observations ('Bureau Internat. Reports,' 1902) make the difference $t_n - t_h = +{\cdot}005$ at 20°, and $+{\cdot}008$ at 40° C., which agree better with Joule and Thomson.

of alcohol, shows a small positive difference of ·001°. The negative differences are undoubtedly due in part to the type of empirical formula chosen. Chappuis himself considered them to be impossible, because they imply that the mean coefficient of expansion of nitrogen, after diminishing from 0° to 70° C., begins to increase again at this point, which is highly improbable. For this reason, in the same paper in which formula (44) is given, he calculated another formula, with two terms instead of three, for deducing the mean coefficient of expansion of nitrogen by reference to hydrogen. He does not give the values of the scale-difference corresponding to this formula, but I have calculated the values given in the column headed "Corrected 1888" from the values which he tabulates of the mean coefficient of expansion of nitrogen. It is at once evident that the formula of two terms gives a more probable type of divergence between the scales than the three-term formula (44) which is always quoted. It agrees closely with that of Joule and Thomson at the higher points, but gives rather larger differences at the lower points, increasing to nearly double at $-20°$ C.

10. *Graphic Method of Comparison.*

Since the thousandths of a degree in this table are uncertain to the extent of at least ·003°, it is hardly necessary to say that the most that can be expected is a general agreement in the order of magnitude of the correction. The value of the experimental evidence is most readily appreciated by the graphic method. The actual observations are plotted in fig. 1, in which the zero line represents the hydrogen scale, and the ordinates of the curves the scale-differences. The continuous curves represent the differences calculated from the observations of Joule and Thomson, the broken curves the differences calculated from the formulæ of Chappuis. The black dots about the zero line represent the deviations of the observations with the hydrogen thermometer from the smooth formula chosen to represent them, and indicate the order of accuracy of the comparison of the hydrogen and mercury thermometers. The crosses (×) similarly indicate the divergences of the observations with the nitrogen thermometer from the smooth curve. The crosses inclosed in circles represent the observations in the second series of comparisons of the nitrogen thermometer, extending from $-24°$ to $+25°$ C. In reducing these observations it was found that the curve representing them did not pass through the zero point, as of course it should. Chappuis assumed that this discrepancy was due to an error in the zero pressure, which had to be determined separately under conditions different from those

Fig. 1.—Comparison of Chappuis' Observations with Results calculated from Cooling-Effect.



of the thermometric comparisons. A reduction of ·025 mm. in the zero pressure* was required to make the curve pass through the origin. This correction had the effect of raising all the observations by nearly ·007°, which is a quantity of the same order as the difference between the nitrogen and hydrogen scales. If the circled observations in the figure were depressed by ·007°, it is evident that they would be brought into rather better agreement with the Joule-Thomson curve between 0° and 25° C., but that the discrepancy below 0° C. would be increased. The nitrogen observations are seen to be rather more discordant than the hydrogen, but they were taken first in point of time, and the error of the temporary rise of zero

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* The minuteness of this correction (1 in 40,000 on the zero pressure) indicates the extreme difficulty of the work, which could not have been carried out successfully without the highest experimental skill and the most refined apparatus.

produced in a mercury thermometer by exposure to a low temperature (corresponding to the temporary depression produced by exposure to a high temperature), was discovered for the first time in the course of this series of observations. Taking these facts into consideration, we may conclude that the difference of the scales between 0° and 50° is probably less than that given by Chappuis' formula, and that the Joule-Thomson curve is more nearly correct, though, as we shall see, there is other evidence tending to show that even the latter is too high.

11. *Extrapolation to Higher and Lower Temperatures.*

Since the observations of Joule and Thomson were confined to the range 0° to 100° C., the estimates of the corrections given in Table V. (p. 66) are liable to much greater uncertainty beyond this range, since they depend on the validity of the type of equation (39) assumed. According to the table, the difference between the scales of the constant-volume and the constant-pressure hydrogen thermometers would be about half a degree at the temperature of liquid air. This has been recently confirmed by Travers (B. A. Rep. 1901), and may be taken as an indication that the divergence indicated in the table is at least of the right order of magnitude, even in the case of hydrogen. Similarly the corrected value of the boiling-point of sulphur given by Chappuis (Phil. Mag. 1902), namely 444°·7, obtained with a constant-volume nitrogen thermometer at 56 cms. initial pressure, when compared with the value 444°·5 obtained with a constant-pressure air thermometer (Phil. Trans. 1891) agrees in sign and order of magnitude with the difference of the scales (0°·2) at this point indicated in the table. Chappuis has recently proposed an empirical method of estimating the correction, which leads to a much smaller result. His original formula (44) is evidently of a type unsuitable for extrapolation; but if we employ it to calculate the true coefficient of expansion of nitrogen at *t*, assuming hydrogen to be an ideal gas, we find that the coefficient diminishes from ·00367698 at 0° C. to ·00367378 at 80° C., and then increases to ·00367393 at 100° C. Chappuis supposes that this increase is illusory, and that the coefficient really diminishes to a minimum value, namely ·00367378, and then remains constant at all higher temperatures. This assumption would make the scale-difference linear above 100° C., increasing by ·017° for each 100°, and amounting to ·076° at the boiling-point of sulphur for a constant-volume thermometer at 100 cms. initial pressure, or ·043° for $p_0=56$ cms. He finds, as the result of some experiments between 0° and 100°, that the scale-difference of the constant-pressure thermometer is about twice that of the constant-volume instrument. This agrees very fairly with the result deduced from the Joule-Thomson equation and exhibited in Table V. Assuming the ratio 2, the correction for the constant-pressure thermometer at 445° would be about +·115° at 76 cms. initial pressure, which would give a difference of ·072° between our instruments at the boiling-point of sulphur. Chree has since detected a small error in Chappuis' calculation which would increase this estimate in the proportion of ·023 to ·017. A direct comparison between the constant-volume and constant-pressure scales at this temperature would certainly be desirable and feasible; but in the meantime the estimate derived from the Joule-Thomson equation appears to be more probable than that of Chappuis, and more in accordance with the known behaviour of gases deduced by other methods of investigation.

12. *Thermodynamical Correction of* CO_2 *Thermometer.*

The case of CO_2 is of particular interest because the properties of this gas have been so widely studied, and because the deviations from the thermodynamical scale and the values of the Joule-Thomson effect are so much larger and more easily measured. A study of the properties of this gas might be expected to throw light on the effects to be expected with other gases more perfect and better suited to thermometry; but it must not be forgotten that the type of the molecule is different, and that for this reason it might be expected to behave in a different manner to the diatomic or monatomic gases. The gas actually employed by Joule and Thomson was not quite pure, but they corrected their results empirically to the case of pure gas, and their value of the cooling-effect at 17° C. has been independently confirmed by Natanson (Wied. *Ann.* xxxi. p. 502, 1887) employing gas from cylinders of liquid CO_2. The values given by Table V. for the difference from the hydrogen scale in the case of the constant-volume thermometer at $p_0=100$ cms. are compared with the observations of Chappuis at −10°, +10°, 20°, 30°, 40°, and 60° C., which are represented by the crosses (+) in fig. 1. The full curve, as before, indicates the differences calculated by the Joule-Thomson equation, the broken curve indicates the formula of Chappuis. Three of Chappuis' observations at 30°, 40°, and 60° were taken with a thermometer filled with gas at a slightly lower initial pressure, $p_0=87$ cms. The observed values for the difference in these cases have been increased in the ratio 100/87, as required by theory, and the crosses are distinguished by inclosing them in circles. It will be observed that the corrected observations agree in the most remarkable manner with the Joule-Thomson curve, although their agreement with Chappuis' formula is slightly impaired. This would appear to be a striking confirmation of the validity of the proposed formula in the case of CO_2. But when we compare the actual values of c and b calculated as above from the observations on the cooling-effect alone, with those calculated directly from the slope of the isothermals, we find certain discrepancies which, although they are often within the limits of experimental error, require examination as possible indications of some defect in the theory. For instance, in the case of CO_2, which agrees so well with Chappuis' thermometric comparisons, the value of c according to Table II. would become equal to that of b at about 120° C., and the gas above this temperature should behave like hydrogen, with an upward slope of the isothermal. The observations of Amagat show, on the other hand, that CO_2 is still notably imperfect at a temperature of 261° C. This might conceivably be due in part to some effect of surface-condensation, which would be relatively important in the fine tubes employed by Amagat; but it is mainly attributable to the large value of b deduced from the observations on the cooling-effect. It is evident that the value of b cannot be deduced so accurately as that of c from these observations, since the expression for SQ is $3c-b$. Moreover, no account has been taken of the variation of S with temperature, which according to Regnault is considerable in the case of CO_2. Both these considerations would be of relatively small importance as affecting the thermometric comparisons between 0° and 100°, since b does not enter into the expression for dt, and we employ the mean value of S at 50°; but they would materially affect the extrapolation of the value of $c-b$. It would be quite possible to readjust the values of c and b in such a manner as to agree better with Amagat at higher temperatures, while not seriously impairing the agreement with Chappuis at 50°. The values of c and b for hydrogen appear to be more nearly of the right order of magnitude, giving $c-b=8{\cdot}2$ c. c. as against Amagat's value 8·8 c.c. On the other hand, the value of b for air is practically zero according to the observations of Joule and Thomson, *i. e.* air would always remain imperfect. Observation shows, however, that it becomes "pluperfect" at a temperature somewhere below 100° C. Here again the value of b is undoubtedly in error. It may also be observed that the error of the value of the absolute zero deduced in Table IV. from Chappuis' pressure-coefficient for CO_2, namely 274·0, is too large to be attributed to errors of observation in the coefficient or in the measurement of the cooling-effect. These discrepancies suggest either that the type of formula is wrong (*i. e.*, that c does not vary inversely as the square of the absolute temperature), or else that the variations of the specific heat are too large to be neglected.

13. *Other Types of Formulæ**.

Instead of attempting to readjust the values of the constants in the original formula so as to obtain the best average agreement with experimental data, we might proceed, as suggested by Joule and Thomson in 1854 (Phil. Trans. p. 360), by the more usual method of introducing sufficient arbitrary constants into the formula to enable it to reconcile all the apparently discordant data. This method has recently been applied by Rose-Innes (Phil. Mag. July 1901), who adopts a formula with *three* constants, of the same type as that employed by Joule and Thomson, No. (11) above, in the calculation of their original table of corrections. But in place of Regnault's observations Rose-Innes adopts the later observations of Joule and Thomson on the cooling-effect, in conjunction with Amagat's values of $d(pv)/dp$. The values of $t_n - t_h$ calculated by Rose-Innes are given in Table VI. (p. 67). He does not apply his formula to the case of CO_2. The difference between the values of the absolute zero deduced by Rose-Innes from Chappuis' pressure-coefficients for H_2 and N_2 is rather larger than that given in Table IV., and would make the value lie somewhere between 273·15 and 273·36, which appears hardly probable.

To facilitate the comparison of the formulæ and the calculation of the corrections, we may employ the notation already explained in Section 8 above. The formula of Rose-Innes is equivalent to the assumption

$$\theta = pv/\mathrm{R} + (c' + c'' - b)p/\mathrm{R}, \quad . \quad . \quad . \quad . \quad (45)$$

in which c' and c'' vary inversely as the first and second powers of the temperature respectively. The corresponding formulæ for the corrections are:—

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* This section was added subsequently to the reading of the paper.

Constant-volume, zero correction,

$$\theta_0 - T_0 = 646\,C'' + c_0'p_0/R, \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Scale correction,

$$dt = C''t(t-100)/\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

Constant-pressure, zero correction,

$$\theta_0 - T_0 = 846\,C'' + 646\,C' - bp_0/R, \quad . \quad . \quad . \quad (48)$$

Scale correction,

$$dt = (C''(1{\cdot}732 + 273/\theta) + C')t(t-100)/\theta. \quad . \quad (49)$$

The formulæ are the same as before as regards c'', but additional terms are introduced to represent the effect of c'. The numerical values of the constants are given in the following table as deduced from those calculated by Rose-Innes.

Table VII.—Values of Constants deduced from Formulæ of Rose-Innes.

Gas employed.	b. c.c.	c_0'. c.c.	c_0''. c.c.	C'. $c_0'p_0/373R$.	C''. $c_0''p_0/373R$.
Air	1·62	1·89	0·182	·00179	·00017
Nitrogen ...	2·03	2·09	0·378	·00182	·00035
Hydrogen ...	10·73	1·19	1·45	·000078	·000095

The values of the scale-correction calculated by these formulæ for the constant-volume air-thermometer are about five times smaller than those given in Table V., but the values for the constant-pressure thermometer are nearly of the same magnitude as those in Table V. In general we may observe that the corrections for the constant-pressure thermometer are nearly independent of the type of formula assumed within reasonable limits, and are therefore less uncertain than those of the constant-volume thermometer. The values of C and C'' given above correspond, as before, to an initial pressure $v_0 = 76$ cms.

14. *Variation of Specific Heats.*

The method followed by Joule and Thomson, and by the majority of subsequent writers, has been to assume a formula for the variation of the cooling-effect Q, which is then integrated to find the constants in the characteristic equation, neglecting the variations of the specific heat S. This is perfectly justifiable in the case of the more permanent gases, for which experiment and theory both indicate that the variations of the specific heat should be small. But in the case of vapours like steam or CO_2 these variations cannot be neglected; and it is better to employ the reverse method as in Section 7 above, assuming a convenient type of characteristic equation and deducing the corresponding expression for the cooling-effect for comparison with the results of observation. In this case it is easy to take account of the variations of the specific heat by simply inserting the appropriate value of the specific heat in equation (30).

We observe by reference to the differential equations (4) or (5) that the appropriate value of S is that corresponding to the final pressure p'' in each experiment, and to the mean temperature $(\theta' + \theta'')/2$. The variation of the specific heat with temperature can be determined only by experiment. The variation with pressure must be consistent with the characteristic equation chosen, and can be calculated in the following manner.

Referring to equation (3) for the variation of the total heat, $\mathrm{F} = \mathrm{E} + pv$, we have the following values of the partial differential coefficients:—

$$(d\mathrm{F}/d\theta)_p = \mathrm{S}, \quad (d\mathrm{F}/dp)_\theta = v - \theta(dv/d\theta)_p = b - (n+1)c, \quad . \quad (50)$$

which give for the variation of S with p at constant θ,

$$(d\mathrm{S}/dp)_\theta = d_2\mathrm{F}/d\theta dp = -\theta(d_2v/d\theta^2)_p = n(n+1)c/\theta. \quad . \quad (51)$$

Integrating this at constant temperature from 0 to p, we obtain

$$\mathrm{S} = \mathrm{S}_0 + n(n+1)cp/\theta, \quad . \quad . \quad . \quad . \quad (52)$$

where S_0 is the limiting value of S at zero pressure and temperature θ.

This equation enables us to find the complete variation of S, if we observe the values of S experimentally at any standard pressure such as 1 atmo, over the required range of temperature.

Proceeding similarly for the specific heat s at constant volume, we obtain by considering the variation of the intrinsic energy E,

$$(d\mathrm{E}/d\theta)_v = s, \quad (d\mathrm{E}/dv)_\theta = \theta(dp/d\theta)_v - p, \quad (ds/dv)_\theta = \theta(d_2p/d\theta^2)_v. \quad (53)$$

whence

$$s = s_0 + n(n - 1 - nc/\mathrm{V})cp/\theta. \quad . \quad . \quad . \quad . \quad (54)$$

where s_0 is the limiting value of s at zero pressure, and $\mathrm{V} = \mathrm{R}\theta/p$. This formula is of comparatively little use.

because the direct measurement of s by experiment is generally impracticable; but it serves to trace the probable variations of the ratio of the specific heats $S/s=g$.

In the special case in which $n=s_0/R$ the formulæ may be somewhat simplified, since $R=S_0-s_0$, and may be written as follows:—

$$S=S_0(1+nc/V), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

$$s\ =s_0(1+nc/V)(1-c/V), \quad . \quad . \quad . \quad . \quad (56)$$

whence

$$g\ =S/s=g_0/(1-c/V). \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

This appears to be the case for steam (Proc. R. S. vol. lxvii. p. 266, 1900), but is not true generally.

In the case of a diatomic gas, if we assume the limiting ratio of the specific heats to be $g_0=1{\cdot}400$, as indicated by theory, we have $S_0=3{\cdot}5R$, $s_0=2{\cdot}5R$, if the limiting values of the specific heats are constant. The ratio of the specific heats, if $n=2{\cdot}5$, would be $g=1{\cdot}400(1+c/V)$. If $n=2$, as in Rankine's equation, we should have $g=1{\cdot}400(1+{\cdot}92c/V)$ approximately. Inserting $c_0=0{\cdot}90$ c. c., $V=784$ c. c. for air at 0° C. and 75 cms. pressure, we should find $g=1{\cdot}4015$, which illustrates the smallness of the variation with pressure for the permanent gases. Taking the density of air as 1·2930 gm. per litre at 0° C. and 760 mm. in lat. 45°, and assuming the value of $c-b$ at 0° to be 0·50 c. c. from Amagat's observations, we should find $R=2{\cdot}8725\times10^6$ C.G.S., which would give $S=3{\cdot}5R=1{\cdot}0055$ joules per gramme-degree; or 0·2405 calories at 20° C., if the calorie at 20° C. is taken as 4·180 joules. This is about 1 per cent. larger than the value found by Regnault, namely $S={\cdot}2375$. The observations of Joly at constant volume give $s={\cdot}1721$ cals. at 60° C. and $v=49$ c. c., when reduced to the same unit. The theoretical value at this pressure, assuming $c=0{\cdot}61$ c. c. at 60° C., would be 0·1736 calories, which is also nearly 1 per cent. larger than that observed. It should be remarked, however, that even apart from the difficulty of the experiments, there is considerable uncertainty in the units of heat employed. Joly used Regnault's value for the latent heat of steam at 100°, namely 536·7; but his own experiments with the steam calorimeter give 540·2 in terms of the calorie at 20°. The difference is nearly sufficient to account for the discrepancy in the observed and calculated values. Considering the difficulty of experiments on the specific heats of gases, we are probably justified in the assumption that the limiting values of the specific heats are constant for the more permanent diatomic gases, and that the variations with pressure may be estimated by the formulæ already given.

15. *Constants for* CO_2 *corrected for Variation of* S.

In order to correct the values of c_0 and b for CO_2 calculated in Table II. from the observed values of Q on the assumption that S was constant and equal to $8{\cdot}4 \times 10^6$ C.G.S., we may take Regnault's values of S at 0° and 100° at a pressure of 1 atmo, since the final pressure in Joule and Thomson's experiments was always approximately atmospheric. The values of S required may be taken as

$$S_0 = 7{\cdot}85 \times 10^6 \text{ C.G.S.}, \quad \text{and} \quad S_{100} = 8{\cdot}95 \times 10^6 \text{ C.G.S.};$$

but the absolute values, as well as the rate of variation, are necessarily a little uncertain on account of the defects of Regnault's thermometry, and of the error of his formula for the variation of the specific heat of water.

Adopting the values of Q_0 and Q_{100} given in Table II., and assuming $SQ = 3c - b$, we obtain the following values of the constants,

$$c_0 = 3{\cdot}76 \text{ c. c.}, \qquad b = 0{\cdot}58 \text{ c. c.}$$

This would reduce all the values of the corrections for CO_2 given in Table V. nearly in the proportion of 5 to 6, since they depend only on c_0. The agreement with Chappuis' observations * plotted in fig. 1 would be slightly impaired, but the Joule-Thomson curve would coincide more nearly with Chappuis' empirical formula. The value of the absolute zero correction for the constant-pressure thermometer is scarcely altered; so that the value deduced from Chappuis' expansion coefficient is still correct. But on the other hand the zero correction for the constant-volume thermometer (Table IV.) by formula (40) is reduced in the proportion 376/456 from 5°·55 to 4°·60, which gives $\theta_0 = 273°{\cdot}05$, thus agreeing with the direct method of calculation given in Section 5, formula (22).

If we compare the values of the compressibility deduced from the corrected values of the constants, with the values observed by Amagat, we find again the agreement much improved, which confirms the importance of the correction for the variation of the specific heat. It should be remarked, however, that the values of $c - b$ deduced from Amagat's observations are a little uncertain, as the observations do

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* More recent observations by Chappuis ('Int. Bureau Reports,' 1902) make the scale-correction for CO_2 at $p_0 = 100$ cms., $+{\cdot}039°$ both at 20° and 40° C. instead of ·043° and ·059°.

not extend below a pressure of 50 atmos at 100° C. The following table exhibits the comparison.

Table VIII.—Comparison with Amagat.

Temperature centigrade	0°.	100°.	200°.
Values of $c-b$ calculated	3·18	1·44	0·67
„ „ observed............	3·30	1·5	0·72

There is a small systematic difference which might possibly be explained by surface condensation, but is hardly beyond the limits of uncertainty of the data.

It is possible by means of formula (54) to make a rough estimate of the variation of the specific heat of CO_2 at constant volume for comparison with the experiments of Joly. Neglecting the small term nc/V, and putting $n=2$, the formula may be written approximately $s=s_0+2Rc/V$, where $V=v+c-b$. Joly's observations give for $v=87$ c.c., $s=\cdot1684$; and for $v=27$ c.c., $s=\cdot1734$. These values are in calories, and correspond to a mean temperature of 55° C. The mean value of c may be taken as 2·61 c.c., so that $2Rc=9\cdot8\times10^6$ c.g.s. The values of V are 89 and 29 c.c. respectively, so that the calculated difference between the values of s comes out $0\cdot228\times10^6$ c.g.s., or 0·0054 calorie. The observed difference is seen to be 0·0050 calorie, which agrees quite as well as could be expected with the calculated value. It should be observed, however, that if we extrapolate to zero pressure, we find the limiting value of the specific heat s from Joly's observations about 0·1655 calorie per gramme-degree. The corresponding value for S from Regnault's observations at 55° C. is 0·2014. The difference of these is only 0·0359 cal., or $1\cdot51\times10^6$ c.g.s., whereas the value of R is $1\cdot887\times10^6$ c.g.s. The discrepancy is nearly 5 per cent. of the value of S instead of only 1 per cent. as in the case of air.

16. *Application of the Method to Steam.*

The large range of variation of the specific heat of CO_2 with temperature shows that the molecule must undergo some fundamental change of structure within the limits of temperature considered. It is possible that this may be associated with the variation of the specific heat of carbon itself. There is no evidence of a similar variation in the case of the diatomic gases. In the case of steam, which is also triatomic, large variations of the specific heat, from $S=\cdot387$ at 100° C. to $S=\cdot665$ at 160° C., have been found experimentally by Grindley, employing the Joule-Thomson method

(Phil. Trans. A, 1900), and assuming Regnault's formula for the total heat of saturated steam. The following values have also been deduced by other writers on theoretical grounds: Zeuner, S = ·568; Gray, 0·385; Tumlirz, 0·536 to 0·475; Perry, 0·306 to 0·463. I find, however, by direct experiment, employing the continuous electrical method with a vacuum-jacket calorimeter, the value S = 0·497 at 1 atmo and 108° C., which agrees fairly with Regnault's value 0·475 at 175° C., allowing for the variation due to the coaggregation by formula (52). I have endeavoured to show (Proc. R. S. lxvii. p. 266, 1900) that all the properties of steam may be consistently calculated on the assumption that the limiting value of the specific heat is constant, employing the same type of equation as for CO_2, but leaving the value of n to be determined from observations of the cooling-effect at various temperatures. If we adopt this type of formula, it appears from the observations of Grindley (Phil. Trans. 1900) that the value of n for steam should be about 3·8 instead of 2. My own observations on the cooling-effect and the specific heat of steam would give the values $n = 3·3$, and $c = 26·3$ c.c. at 100° C. In calculating the properties of steam by this formula in the paper above referred to, I adopted the mean value 3·5 for the index, partly to facilitate calculation and partly in consequence of an hypothesis (doubtfully attributed to Maxwell) that the number of degrees of freedom of a molecule containing m atoms is $2m+1$. This hypothesis would make the ratio of the specific heats S/s at constant pressure and volume, 5/3 for a monatomic gas, 7/5 for a diatomic gas, 9/7 for a triatomic gas, and so on; values which agree very fairly with the ratios of the specific heats actually observed in many cases. Later and more accurate experiments on the specific heat of steam have shown that the ratio s/R should be more nearly 3·3, and have so far confirmed the value of the index given by my experiments on the cooling-effect.

Adopting the experimental value S = 0·497 at 1 atmo and 108° C. we find by applying formula (52) the limiting value $S_0 = 0·478$ at zero pressure. If we employ this value in place of the value 4·5R adopted on Maxwell's hypothesis in the paper above referred to, we find that the agreement with experiment in the values of the total heat and the saturation pressure is somewhat improved, but the general nature of the conclusions remains unaltered. Since the value of the index n cannot be determined very accurately from the cooling-effect, it is better in this case to take it equal to s/R for the sake of simplifying the equation of the isentropics, which then takes the form $c/V=$constant, or $p/\theta^{n+1}=$constant, or $p^n(v-b)^{n+1}=$constant.

In the case of steam the constancy of the specific heat, and the accuracy of the value found by experiment, may be further verified by calculating the values of the total heat and saturation pressure as follows:—

Adopting the assumption $S_0=$constant, it is possible to express the thermodynamical properties of any imperfect gas or vapour in terms of c by means of very simple formulæ: thus we find

$$\text{Entropy, } \phi=S_0\log_e\theta-R\log_e p-ncp/\theta+A, \quad . \quad (58)$$

$$\text{Energy, } E=s_0\theta-ncp+B, \quad . \; . \; . \; . \; . \; . \; . \; . \quad (59)$$

in which A and B are indeterminate constants of integration. The values of the other thermodynamic functions follow immediately from those of E and ϕ. Thus we find for the total heat

$$F=E+pv=S_0\theta-(n+1)cp+bp+B; \quad . \; . \; . \quad (60)$$

and for the thermodynamic potentials at constant pressure and volume,

$$G=F-\theta\phi=S_0\theta(1-\log_e\theta)-R\theta\log_e p-(c-b)p-A\theta+B, \quad (61)$$

$$J=E-\theta\phi=s_0\theta-S_0\theta\log_e\theta-R\theta\log_e p-A\theta+B. \quad . \; . \; . \quad (62)$$

Observing that the difference of the total heats of the liquid and vapour at any temperature is equal to the latent heat L, and the difference of the entropies equal to L/θ (or equating values of G for the liquid and vapour), we obtain the equation for the saturation-pressure,

$$R\log_e p=A'-B'/\theta-(s'-S_0)\log_e\theta+(c-b)p/\theta, \quad . \quad (63)$$

in which the specific heat s' of the liquid is assumed to be constant. A' is a constant to be determined by the observation of the boiling-point; B' is the difference of the constants B in the expressions for the total heats of the vapour and liquid, which may be determined by the observation of the latent heat at the same point.

It should be observed that the equations for the thermodynamic potentials and for the vapour-pressure are independent of the assumption that c varies inversely as the nth power of the temperature, and are generally true provided that $c-b$ is a function of the temperature only; but the assumption $c=c_0(\theta_0/\theta)^n$ satisfies Regnault's observations of the saturation-pressure very accurately.

17. *Interpretation of the Index* n.

Some idea of the meaning of the index n may be obtained by considering the expression above given for the Energy E. The energy of an imperfect gas is less than that of the gas in the ideal state at the same temperature by the term ncp, which represents the loss of energy due to coaggregation of the molecules, corresponding to the diminution of volume c per unit mass. Considering first the case of a monatomic gas, in which the whole of the kinetic energy of the molecules consists of energy of flight (corresponding to three degrees of freedom), we have the well-known relation $pv=R\theta=2s\theta/3$. In a diatomic gas, regarded as consisting of pairs of atoms rigidly joined together like dumbbells, it appears probable, as suggested by Boltzmann, that the energy of a molecule may be equally distributed between each of *three* degrees of freedom of translation and *two* degrees of freedom of rotation, supposing that the rotation of a molecule about its axis could not be altered by intermolecular collisions. Such a molecule would have five equal degrees of freedom, and the specific heat at constant volume should be $5R/2$, which is amply confirmed by experiment. Supposing that two monatomic molecules each with three degrees of freedom coaggregate to form a diatomic molecule possessing five degrees of freedom, there would be a loss of energy equivalent to one degree of freedom, or one third of the energy of flight, since the energy of flight of the resulting diatomic molecule would be the same as that of a single monatomic molecule at the same temperature. If the diminution of volume per unit mass due to coaggregation be represented by c, the loss of energy on this hypothesis would be represented by $cp/2$, since the product cp represents two-thirds of the energy of flight in a volume c. We ought therefore to have the index $n=1/2$, in the case of a monatomic gas, on the simple hypothesis of coaggregation in pairs, provided that the coaggregation is a purely physical effect, and that there is nothing in the nature of chemical combination involving evolution of heat.

In the case of a diatomic gas, a similar line of reasoning fails to give a definite result, because we have no sure experimental guide or mechanical analogy to enable us to estimate the number of degrees of freedom of the resulting tetratomic aggregate. If we supposed with Maxwell that the number of degrees of freedom could not exceed six, as for a rigid body, the loss of energy for a pair of diatomic molecules each possessing five degrees of freedom would be equivalent to four degrees of freedom on coaggregation, which would make the value of the index $n=2$, as in the Joule-Thomson equation. There can be no doubt, however, from experimental evidence, that the energy of flight may be less than half the total kinetic energy of a polyatomic molecule, otherwise the ratio S/s of the specific heats could not be less than 4/3. It is probable that the distribution of energy in the molecule depends on the type or form of the molecule, and not merely on the number of atoms it contains, and that the various degrees of freedom are not all of equal value. The ratio of the energy of rotation E'' to the energy of flight E' in the case of CO_2 is about 4/3, corresponding to the ratio of specific heats $S/s=9/7$. Whence, if $n=2$, the ratio E''/E' should be 7/3 for a coaggregated pair of molecules. For steam, which is also a triatomic molecule, the loss of energy on coaggregation is greater. We have $n=3{\cdot}3=s/R$, so that the whole energy of a coaggregated pair is no greater than that of a single molecule. It is further possible that the relative importance of the different kinds of degrees of freedom in a complicated molecule would vary with the temperature. We could not then assume that the limiting value S_0 of the specific heat at zero pressure was constant. The assumption $S_0=$constant is almost certainly true for monatomic or diatomic molecules at ordinary temperatures; but it could not be true for unstable molecules, and there is some evidence that it does not hold for polyatomic molecules of higher orders.

18. *Application to Monatomic Gases.*

The only observations so far available to test the hypothesis $n=1/2$ in the case of monatomic gases, are those of Ramsay and Travers (Phil. Trans. A, 1901) on the compressibility of the inert gases by the capillary-tube method at 11°·2 C. from 20 to 80 metres pressure, and at 237°·3 C. from 30 to 80 metres. These observations are not very suitable for the purpose, as they do not extend to low pressures. They also exhibit, as the authors point out, several anomalies, which may be due to some hitherto unexplained peculiarities in the behaviour of monatomic gases, or perhaps merely to experimental errors. The curves representing the variations of pv with p at the lower temperature are of a perfectly normal type, the gases helium, neon, argon, krypton, and xenon, following naturally in the order of their densities. It should be remarked, however, that if we produce the curves for argon (39·9 gm.) and krypton (81·5 gm.) to zero pressure, they appear to indicate a limiting value of pv equal to 18,500 metre cubic centimetres approximately, whereas molecular weights of the other gases appear to conform to the limit 17,710 m.c.c., which is given as the ideal value for a perfect gas. At the higher temperature, the order of the gases is inverted. Helium and neon appear to be more imperfect than at the lower temperature, and their curves lie below krypton and argon. It seems to be impossible to offer any theoretical explanation of these anomalies ; but if we admit that the limiting values for krypton at zero pressure should be 18,510 m.c.c. at 11°·2 C., and 33,240 m.c.c. (the corresponding value for the same mass of gas) at 237°·3 C., the limiting values of the slope $(c-b)$ may be estimated as 0·84 c.c. and 0·43 c.c. respectively per gramme of gas. In the case of the other gases the slope is too small, or its initial value too uncertain, to afford a comparison. If we assume as above that the coaggregation c should vary inversely as the square root of the temperature $(n=1/2)$, we find $c=1·61$ c.c. at 284°·2 Abs. and $c=1·20$ c. c. at 510°·3 Abs., whence $b=0·77$ c. c. If on the other hand we assumed $n=1$, we should find $c=0·52$ c. c. at 510°·3 Abs., and $b=0·09$ c. c. A higher value such as $n=2$ would make b large and negative, which would be impossible, or at least incapable of rational interpretation. The volume of liquid krypton at its boiling-point was found to be 0·46 c. c. per gramme, so that the value of b deduced on the assumption $n=1/2$ is perhaps the most probable. The fact that helium appears to be less perfect than hydrogen, and neon nearly as imperfect as nitrogen at 11°·2 C., also supports the hypothesis of a very low value of n for monatomic gases.

Adopting provisionally the basis $n=1/2$, I have calculated the following tables of corrections for argon and helium in addition to krypton, since, as I have previously explained (Phil. Mag. Dec. 1899, p. 541), the inert monatomic gases are peculiarly suitable for thermometric purposes. I have assumed the values of b for helium and argon to be equal to the volumes of the liquids (which are estimated at 3·3 c. c., and 0·83 c. c. respectively) multiplied by the ratio 0·77/0·46 found above in the case of krypton. The values of c are deduced from the observed compressibilities at 11°·2 C. For helium I have assumed $c_0=b$, since the pv line for helium is practically horizontal up to a pressure of 50 metres. It must be admitted that these data are somewhat uncertain, but they afford at least a reasonable basis for comparison with experiment.

TABLE IX.

Values of Constants assumed for Monatomic Gases.

Gas employed.	c_0. c. c.	b. c. c.	c_0-b. c. c.	R $\times 10^{-6}$.	S $\times 10^{-6}$.	Factor c_0p_0/R. 76 cms.	Factor c_0p_0/R. 100 cms.
Krypton...	1·64	0·77	0·87	1·064	2·66	1·567	2·063
Argon......	2·18	1·39	0·79	2·175	5·43	1·016	1·337
Helium ...	5·5	5·5	0·00	20·8	52·0	0·268	0·352

Assuming the value $n=0{\cdot}5$, $c=c_0(\theta_0/\theta)^{0{\cdot}5}$, $c_0-c_1=0{\cdot}1445\,c_0$, we have the following formulæ for the zero correction :—

Zero Correction, Constant-Pressure,

$$\theta_0-\text{T}_0=(c_0-b+2{\cdot}73\times{\cdot}1445\times c_0)p_0/\text{R},$$

" " Constant-Volume,

$$\theta_0-\text{T}_0=3{\cdot}73\times{\cdot}1445\times c_0p_0/\text{R},$$

from which we deduce the values of the expansion- and pressure-coefficients given in the following table, assuming the value $\theta_0=273^\circ{\cdot}10$:—

TABLE X.

Expansion- and Pressure-Coefficients for Monatomic Gases.

Gas employed.	Constant-Pressure, 76 cms. $\theta_0-\text{T}_0$.	Constant-Pressure, 76 cms. T_0.	Constant-Pressure, 76 cms. $1/\text{T}_0$.	Constant-Volume, $p_0=100$ cms. $\theta_0-\text{T}_0$.	Constant-Volume, $p_0=100$ cms. T_0.	Constant-Volume, $p_0=100$ cms. $1/\text{T}_0$.
Krypton ...	1°·52	271°·65	·0036812	1°·11	272°·00	·0036761
Argon	0·77	272·33	·0036717	0·72	272·38	·0036710
Helium	0·10	273·00	·0036628	0·19	272·91	·0036640

The value of the pressure-coefficient observed by Travers (Proc. R. S. lxx. p. 485) for helium at a mean initial pressure of 60 cms. is from ·0036624 to ·0036631, mean ·0036627. The calculated value at this pressure would be ·0036632, which is within the limits of possible error, but may indicate that the value of c assumed is too large.

The values of the scale-correction for the monatomic gases given in Table XI. are calculated by the following formulæ:—

$$\text{Constant-Pressure, } dt=(0{\cdot}1445\, t/100-1+(\theta_0/\theta)^{0{\cdot}5})c_0p_0/\mathrm{R},$$

$$\text{Constant-Volume, } dt=(-0{\cdot}1689\, t/100-1+(\theta/\theta_0)^{0{\cdot}5})c_0p_0/\mathrm{R}.$$

Table XI.

Scale-Correction for Monatomic Gases.

Temp. cent.	Constant-Pressure, 76 cms.			Constant-Volume. $p_0=100$ cms.		
	Krypton.	Argon.	Helium.	Krypton.	Argon.	Helium.
−250°	...	...	+0·557	...	...	−·101°
−200	...	...	+ ·173	...	−·194	−·051
−150	...	+·278	+ ·073	− ·156	−·101	−·0265
−100	+ ·175	+·114	+ ·0298	− ·072	−·047	−·0123
− 50	+ ·053	+·034	+ ·0091	− ·0242	−·0157	−·0041
− 20	+ ·0155	+·0101	+ ·00265	− ·0070	−·0045	−·00120
− 10	+ ·0069	+·0045	+ ·00118	− ·0031	−·0020	−·00053
+ 10	− ·0052	−·0034	− ·00089	+ ·0027	+·0017	+·00045
+ 20	− ·0093	−·0060	− ·00159	+ ·0045	+·0029	+·00077
+ 30	− ·0116	−·0075	− ·00198	+ ·0058	+·0038	+·00098
+ 40	− ·0130	−·0084	− ·00222	+ ·0064	+·0041	+·00109
+ 50	− ·0130	−·0084	− ·00222	+ ·0065	+·0042	+·00113
+ 60	− ·0124	−·0080	− ·00212	+ ·0062	+·0040	+·00106
+ 70	− ·0105	−·0068	− ·00180	+ ·0056	+·0036	+·00095
+ 80	− ·0078	−·0051	− ·00133	+ ·0041	+·0027	+·00070
+ 90	− ·0042	−·0027	− ·00072	+ ·0021	+·0014	+·00035
+150	+ ·0315	+·0204	+ ·0054	− ·0180	−·0116	−·00306
+200	+ ·075	+·049	+ ·0128	− ·045	−·029	−·0076
+300	+ ·194	+·126	+ ·0332	− ·119	−·077	−·0203
+450	+ ·415	+·269	+ ·071	− ·275	−·178	−·0468
+1000	+1·42	+·92	+ ·243	−1·09	−·71	−·187

It will be observed that the correction is negative for the constant-volume thermometer at temperatures below 0° C. According to Travers (*loc. cit.*) the helium thermometer reads 0°·1 above the hydrogen thermometer at the boiling-point of oxygen, and 0°·2 above at the boiling-point of hydrogen. The hydrogen correction is opposite in sign, and nearly equal in magnitude. The true values of the boiling-points, obtained by interpolating between the hydrogen and helium values, would be

Oxygen B.-P. 90°·13 Abs. Hydrogen B.-P. 20°·31 Abs.

19. *Variation of the Covolume* b.

Van der Waals, in his essay on the Continuity of State (Phys. Soc. Translation, 1890, p. 372), gives a theoretical discussion of the effect of the size of the molecules on the length of the free path, from which on certain simple assumptions he deduces that for moderate pressures the effect may be represented by attributing to the covolume b a value equal to four times the actual volume of the molecules regarded as spheres. The theory indicates, however, that the value of b should diminish with increase of pressure somewhat rapidly when the volume approaches the value $2b$. He verifies this by applying his equation to represent the behaviour of CO_2 as observed experimentally by Andrews. Adopting for the constant a in his equation the value ·00874 (the unit of pressure being 760 mm. and the unit of volume the volume of the gas at 0° C. and 760 mm.) he finds values of b ranging from ·0023 to ·0025 for the vapour, but falling to ·0016 and ·0018 for the liquid. It appears both on theoretical and experimental grounds that b cannot be regarded as constant for a large range of pressure, and that no weight can be attached to calculations of the critical temperature based on the assumption that b is the same, as in van der Waals' equation, for both vapour and liquid. It nevertheless appears probable that the range of variation of b is not large, and that its value for moderate pressures is nearly constant with respect to both temperature and pressure. The value of b cannot be determined theoretically, because the actual volume of the molecules is unknown, and because the theoretical assumptions on which the estimate of the ratio 4 is based are extremely uncertain. Meyer, adopting a slightly different assumption, finds that b should be $4\sqrt{2}$ times the volume of the molecules. If we assumed, as many writers have supposed, that the molecules of the liquid at low temperatures are practically in contact, and that the volume of the liquid in this case may be taken as the volume of the molecules, we should find, if we multiply by the factor 4 or $4\sqrt{2}$, values of b which are much too large to be reconciled with the observed behaviour of gases at moderate pressures. We may, however, assume with some degree of confidence that the volume of the liquid, or the limiting volume of the gas at very high pressures, is a limit below which the value of b at moderate pressures cannot greatly fall; and we may with propriety reject formulæ or experiments which lead to much lower values. The limiting volumes of hydrogen and CO_2 at high pressures are given by Amagat as 8·7 c. c. and

0·86 c. c. respectively, which are evidently quantities of the same order of magnitude as the volumes of the liquids. The difficulty in the determination of b from experiments at moderate pressures lies in the fact that it is of the order of a tenth of one per cent. of the volume of the gas at atmospheric pressure, that it cannot be determined independently of c, and that the values of both b and c depend on small differences between larger quantities in which the errors of observation are often of the same order as b itself. Boltzmann (*Gas-Theorie*) and van der Waals (*Arch. Néer.* iv. p. 299, and vi. p. 47, 1901) have recently given formulæ for the variation of b with pressure, which might theoretically be applied to correct the values of b obtained from observations at higher pressures so as to deduce the values at atmospheric pressure required for the correction of the gas thermometer or for the behaviour of gases at moderate pressures. But the development of these formulæ rests on assumptions even more uncertain than the discordant estimates of Meyer and van der Waals, and the range of variation indicated (Boltzmann says it is probably not greater than 1 to 10), would make the extrapolation of such formulæ very doubtful. It seems better to adopt a formula of the type already quoted, and to determine c and b from observations of the compressibility or the cooling-effect on the assumption that b is constant. The application of this method appears to lead to the conclusion that the value of b at moderate pressures does not differ greatly, if at all, from the volume of the liquid at or below its boiling-point. In applying the equation to calculate the properties of steam, in which case b is so small compared with c that it cannot be determined with any accuracy, I have for this reason simply assumed b equal to the volume of the liquid, and then calculated the values of n and c from the observations on the cooling-effect. The error involved is necessarily small since the value of $(n+1)c$ at the boiling-point in this case is more than a hundred times the assumed value of b.

With regard to the variation of b with temperature, we can learn nothing from theory, and the indications of experiment cannot be interpreted with certainty. From an empirical point of view the assumption $b=$constant is the simplest, and since it appears to satisfy the observations better than any other simple assumption, it should be retained unless it is decisively disproved.

20. *Application to Diatomic Gases.*

The application of the theory to diatomic gases is of particular interest and importance on account of the general employment of hydrogen, nitrogen, and air in gas-thermometers. It also presents peculiar difficulties, as compared with the case of a less perfect gas like CO_2, because the deviations to be measured and compared are so much smaller, while the probable error of observation remains the same. For instance, in the case of the three gases above mentioned, the deviations from Boyle's law are of the order of one part in a thousand only per atmosphere, and the order of accuracy of measurements of the compressibility by the capillary-tube method does not reach 1/1000 except under the best conditions. The advantage of the porous-plug method is that the cooling-effect represents the whole deviation sought, but the order of accuracy of the individual observations of Joule and Thomson did not exceed 5 or 10 per cent. at the higher temperatures. One of the final series of observations on air at 40° C. differs from the smoothed curve by more than 5 per cent., and one of the observations on nitrogen at 92° C. differs from the other by about 20 per cent. The nitrogen was prepared by burning phosphorus in air, and the values of the cooling-effect exceeded those for air by about 20 per cent., whereas the compressibility of nitrogen is decidedly less than that of air. The formula of Rose-Innes, with three constants, was designed to reconcile this apparent discrepancy, but if we extrapolate it to lower temperatures we find that it makes the compressibility of nitrogen much greater than that of air at $-100°$ C., which is certainly contrary to fact. In Tables IV. & V., I have made a rough allowance for the fact that the observed cooling-effect for nitrogen was greater than for air, but little or no weight can be attached to this estimate. Nor can we overlook the fact that Joule and Thomson considered their observations on nitrogen much less satisfactory than those on air.

Air.—In order to obtain a satisfactory measurement of the constants c and b and of their rate of variation with temperature, it is obviously necessary to make experiments over a much wider range of temperature, and especially at lower temperatures, where the deviations are much larger and more easily measured. The observations of Witkowski (Phil. Mag. xli. p. 288, 1896) on Air appear to be the only ones available for the purpose. His method consisted in filling two similar bulbs with air at the same pressure but at different temperatures. The quantities of air in the two bulbs were then compared by discharging them into eudiometers at atmospheric pressure and temperature. From these data he deduced the mean coefficient of expansion at the given pressure, and all the data required for constructing a diagram of the variations of pv with p at constant temperature. The method, though troublesome, is evidently capable of great accuracy. It avoids or minimizes the effects of surface-condensation, which are so great an objection to the more convenient capillary-tube method. Witkowski observes in fact that his method always gave lower measurements of compressibility than the capillary-tube method, amounting to about 0·5 per cent. at 15° and 90 atmos, which may probably be explained as due to surface condensation in the capillary-tube method. For our purpose it will suffice to take one of Witkowski's isothermals for air, namely that at $-78^\circ\cdot 3$ C., which appears to have been determined with especial care, and which is so nearly straight up to high pressures that it is easy to make an estimate of the initial value of dpv/dp, which gives:—

Air at $-78^\circ\cdot 3$ C., $c-b=1\cdot 47$ c. c.; at 0° C., $c-b=0\cdot 50$ c. c.

The values of c and b for air calculated from the cooling-effect alone, assuming $n=2$, namely, $c_0=0\cdot 90$, $b=-\cdot 002$, give $c-b$ at 0° C. $=0\cdot 92$ c. c., whereas the value should be 0·50 c. c. to agree with Amagat's observations. The value at $-78^\circ\cdot 3$ C. would be 1·79 c. c., which is also greater than that found by Witkowski. Moreover the negative value of b cannot be interpreted, and would make the error of the calculated compressibility much greater at higher temperatures. It is clear that the value of b requires emendation. If we retain the same type of formula with $n=2$, and calculate the values of c_0 and b to satisfy the observed values of $c-b$ above given, we find:—

$n=2$, $c_0=1\cdot 01$ c. c., $b=0\cdot 52$ c. c., $Q_0=0^\circ\cdot 250$, $Q_{100}=0^\circ\cdot 110$.

The value of b thus found is still too small; the values of the cooling-effect deduced are also smaller than the observed values, namely, $0^\circ\cdot 271$ and $0^\circ\cdot 147$, and the air would not become "pluperfect" till 105° C.

A much better agreement between the cooling-effect and the compressibility is obtained by taking $n=1\cdot 5$ in the formula. This is not improbable theoretically, as the number of degrees of freedom lost by two diatomic molecules (each possessing five degrees of freedom) in coaggregating should be less than for triatomic molecules like CO_2. It is most unlikely that the tetratomic aggregate would possess only six degrees of freedom. The value $n=1\cdot 5$ implies the loss of three degrees of freedom, which is more likely, if we suppose for simplicity that the number lost must be an integer. We then obtain

$n=1\cdot 5$, $c_0=1\cdot 48$, $b=0\cdot 98$, $Q_0=0^\circ\cdot 271$, $Q_{100}=0^\circ\cdot 135$.

With these values air would become pluperfect at about 90°C., and the value of b is not much smaller than the volume of the liquid at low temperatures. The agreement with the observations on the compressibility is very good over a wide range of temperature. The agreement with the observations of the cooling-effect is exact at 0° C., and the difference at 100° C. does not exceed the possible error of the experiments. If we abandon the hypothesis of *integral* degrees of freedom for triatomic or tetratomic molecules, we might of course calculate the value of the index n so as to obtain a better average agreement with observation, but even from a purely empirical point of view it is a matter of great convenience to have a simple value for the index n, provided that it satisfies the observations within the limits of probable error. Moreover the hypothesis of Maxwell, which is supported by the experiments on monatomic and diatomic gases, is so simple and helpful that it is desirable to retain it as far as possible.

In applying the formula with the value $n=1{\cdot}5$ to determine the zero-correction and the scale-correction, the simplest method of proceeding is to find q for each temperature, and apply formulæ (34) and (36). The results for the constant-pressure thermometer do not differ materially from those previously calculated. The zero-correction for the constant-volume thermometer may be put in the form

$$\theta_0 - \mathrm{T}_0 = 3{\cdot}73\ (c_0 - c_1)p_0/\mathrm{R}.$$

Taking $c_0=1{\cdot}48$ c. c., this gives $0^\circ{\cdot}72$ for the correction at 76 cms., or $0^\circ{\cdot}95$ at 100 cms. If we assume the correction for nitrogen to be the same as that for air, and employ Chappuis' pressure-coefficient, we find $\theta_0=273^\circ{\cdot}06$. The values of the scale-correction for the air-thermometer are as follows at 50° C. and 450° C. :—

Constant-Pressure, 76 cms.
at 50° C., $dt=-{\cdot}0185^\circ$; at 450° C., $dt=+{\cdot}470^\circ$.

Constant-Volume, $p_0=76$ cms.
at 50° C., $dt=-{\cdot}0044^\circ$; at 450° C., $dt=+{\cdot}136^\circ$,

Constant-Volume, $p_0=100$ cms.
at 50° C., $dt=-{\cdot}0057^\circ$; at 450° C., $dt=+{\cdot}179^\circ$.

The constant-pressure correction is nearly one-tenth larger, the constant-volume correction is nearly one-third smaller than in Table V., according to the previous method of calculation with $n=2$. The constant-volume correction is still nearly twice as large as that given by the Rose-Innes formula for nitrogen, and more than three times as large as that given by his formula for air. For nitrogen, if we simply adopt the values of the constants given for air, we find that they satisfy the observations of the compressibility at low temperatures, and of the pressure-coefficient (0°·—100° C.) rather better than those given by Rose-Innes, which depend on the very doubtful observations of the cooling-effect.

Nitrogen.—Although we should probably be well within the limits of experimental error in taking the corrections for nitrogen to be the same as those for air, I have thought it worth while to calculate the values of the constants for nitrogen from Chappuis' pressure-coefficient at 100 cms., assuming $\theta_0 = 273^\circ{\cdot}10$. This gives $c_0 = 1{\cdot}58$ c. c. Whence if $c-b$ at 0° C. $= 0{\cdot}44$ c. c., we have $b = 1{\cdot}14$ c. c. Chappuis' observations of the compressibility at 0° C. give $c_0 - b = 0{\cdot}35$ c. c., which would make $b = 1{\cdot}23$ c. c. The volume of the liquid at its boiling-point is 1·26 c. c., but this is probably too large, so I have taken $b = 1{\cdot}14$. The corrections calculated with these values are seen to be practically the same as for air.

Hydrogen.—In calculating the values of the constants for hydrogen on the assumption $n = 1{\cdot}5$, I have taken Chappuis' value of the slope of the isothermals at 0° C., namely, $c_0 - b = -6{\cdot}5$ c. c., which is in close agreement with Regnault's values, 5·5 to 6·6 c. c. at 4° C. Adopting also Joule and Thomson's value of the heating-effect at 0° C., namely $Q_0 = {\cdot}0293^\circ$ per atmo, we have $c_0 = 1{\cdot}50$ c. c., $b = 8{\cdot}0$ c. c. The value of b is slightly smaller than Amagat's limiting volume 8·7 c. c. at high pressures, and much smaller than the volume of the liquid 14 c. c., but it appears that hydrogen is much more compressible than other gases or liquids under these conditions.

Table XII.

Values of Constants assumed for Diatomic Gases.

Gas employed.	c_0. c. c.	b. c. c.	$c_0 - b$. c. c.	R $\times 10^{-6}$.	S. $\times 10^{-6}$.	Factor $c_0 p_0/\mathrm{R}$. 76 cms.	Factor $c_0 p_0/\mathrm{R}$. 100 cms.
Air …………	1·48	0·98	0·50	2·872	10·05	0·516	0·678
Nitrogen …	1·58	1·14	0·44	2·966	10·38	0·540	0·710
Hydrogen …	1·50	8·00	−6·50	41·5	145·3	0·0367	0·0482

The value of the Absolute Zero $\theta_0 = 273^\circ{\cdot}101$ is deduced from the pressure-coefficient of hydrogen, and the pressure-and expansion-coefficients of the other gases are deduced on the assumption $\theta_0=273^\circ{\cdot}10$.

Table XIII.

Expansion- and Pressure-Coefficients of Diatomic Gases.

Gas employed.	Constant-Pressure. 76 cms.			Constant-Volume, $p_0=100$ cms.		
	θ_0-T_0.	T_0.	$1/T_0$.	θ_0-T_0.	T_0.	$1/T_0$.
Air	0°·71	272°·39	·0036709	0°·96	272°·14	·00367425
Nitrogen ...	0·70	272·40	·0036708	0·99	272·11	·00367466
Hydrogen ...	− ·135	273·235	·00365985	+ ·067	273·034	·00366254

Regnault's values of the expansion-coefficient for hydrogen at 76 cms. range from ·0036642 to ·0036586. Chappuis at 100 cms. finds ·0036600 for hydrogen at constant pressure, and ·0036726 to ·0036735 for nitrogen, the calculated values being ·0036593 and ·0036737 respectively.

The values of the thermodynamical corrections for the diatomic gases are calculated by the following formulæ :—

Assuming $n=1{\cdot}5$, $c=c_0(\theta_0/\theta)^{1{\cdot}5}$, $c_0-c_1=0{\cdot}3738c_0$.

Zero-Correction C. P.,

$$\theta_0-T_0=(c_0-b+2{\cdot}73\times{\cdot}374\times c_0)\,p_0/R.$$

Zero-Correction C. V.,

$$\theta_0-T_0=3{\cdot}73\times{\cdot}374\times c_0p_0/R.$$

Scale-Correction C. P.,

$$dt=(0{\cdot}3738\,t/100-1+(\theta_0/\theta)^{1{\cdot}5})c_0p_0/R.$$

Scale-Correction C. V.,

$$dt=(0{\cdot}1445\,t/100-1+(\theta_0/\theta)^{0{\cdot}5})c_0p_0/R.$$

The densities of oxygen and nitrogen at the boiling-point of oxygen at a pressure of 760 mm. have been directly determined by Dewar (Proc. Roy. Soc. lxix. p. 360) by the method of weighing. The resulting values of the specific volumes were:—Oxygen, $v=225{\cdot}8$ c.c. per gramme, Nitrogen, $v=256{\cdot}8$ c. c. at 90°·5 Abs. with a possible error of 0·5 per cent. The ideal volumes at this temperature and pressure are:—Oxygen, 231·8 c. c., Nitrogen, 264·9 c. c. The values of $c-b$ at 90°·5 Abs. are: Oxygen, $c-b=6{\cdot}0$ c. c.; Nitrogen,

TABLE XIV.

Scale-Correction for Diatomic Gases.

Temp. cent.	Constant-Pressure, 76 cms.			Constant-Volume, $p_0 = 100$ cms.		
	Air.	Nitrogen.	Hydrogen.	Air.	Nitrogen.	Hydrogen.
− 250°	...	...	+1°·43	...	...	+·1005°
− 200	...	...	+ ·201	+·438	+·460	+·0311
− 150	+ ·901	+ ·945	+ ·064	+·186	+·195	+·0132
− 100	+ ·314	+ ·328	+ ·0223	+·076	+·080	+·0054
− 50	+ ·086	+ ·090	+ ·0062	+·0232	+·0243	+·00164
− 20	+ ·0238	+ ·0250	+ ·00170	+·0067	+·0070	+·00048
− 10	+ ·0105	+ ·0110	+ ·00075	+·0030	+·0032	+·00021
+ 10	− ·0078	− ·0082	− ·00055	−·0023	−·0024	−·00016
+ 20	− ·0134	− ·0141	− ·00095	−·0041	−·0043	−·00028
+ 30	− ·0169	− ·0177	− ·00120	−·0051	−·0053	−·00036
+ 40	− ·0186	− ·0195	− ·00132	−·0056	−·0059	−·00040
+ 50	− ·0186	− ·0195	− ·00132	−·0056	−·0059	−·00040
+ 60	− ·0172	− ·0180	− ·00123	−·0053	−·0054	−·00038
+ 70	− ·0146	− ·0153	− ·00104	−·0046	−·0048	−·00032
+ 80	− ·0108	− ·0113	− ·00077	−·0034	−·0036	−·00024
+ 90	− ·0058	− ·0061	− ·00041	−·0019	−·0020	−·00013
+ 150	+ ·0409	+ ·0428	+ ·0029	+·0136	+·0143	+·00097
+ 200	+ ·096	+ ·101	+ ·0068	+·0332	+·0347	+·00236
+ 300	+ ·232	+ ·243	+ ·0165	+·084	+·088	+·0059
+ 450	+ ·472	+ ·495	+ ·0336	+·180	+·189	+·0127
+1000	+1·464	+1·535	+ ·1040	+·616	+·646	+·0438

$c-b=8{\cdot}1$ c.c. Whence the value for air would probably be, $c-b=7{\cdot}7$ c.c. The calculated values at this temperature, on the hypothesis $n=1{\cdot}5$, would be 6·8 and 7·2 c. c. for air and nitrogen respectively, which are probably within the limits of experimental error. If we assumed Dewar's values of $c-b$ at 90°·5 Abs., and calculated the values of c_0 at 0° C. on the assumption $n=2$, we should find for nitrogen $c_0=0{\cdot}95$ c. c., $b=0{\cdot}51$ c. c., which do not agree so well with the values of the cooling-effect or with Chappuis' values of the coefficients.

The temperature of inversion of the heating-effect in the case of hydrogen has been observed by Olzewski to be about −80° C., when the gas is supplied at a pressure of 117 atmos and escapes at atmospheric pressure. The values of the constants above given on either assumption $n=1{\cdot}5$ or $n=2$, would give a small heating-effect $SQ=-1{\cdot}7$ c. c. at this point. But as the effect amounts to little more than a hundredth of a degree per atmo it would be easily masked by any slight impurity in the hydrogen, so that little stress can be laid on this observation. Assuming that the heating-effect Q is constant up to a pressure of 117 atmos, the observations of Olzewski would require $c_0=2{\cdot}0$ c.c., $b=8{\cdot}5$ c.c. if we take $n=1{\cdot}5$, and $c_0-b=-6{\cdot}5$ c. c. These values would make the heating-effect at 0° C. $Q=-{\cdot}024°$ per atmo, which is rather smaller than that observed by Joule and Thomson, but the difference is hardly beyond the possible limits of error. The absolute zero-correction for the constant-volume thermometer would be larger in the proportion of 2 to 1·5, but that of the constant-pressure thermometer would be smaller, agreeing slightly better with experiment. The value of c_0 for hydrogen probably lies between 1 and 2 c. c., but we can hardly expect to be able to determine it more closely with certainty, since it is of the order of one part in 10,000 only of the specific volume at 0° C. and 760 mm. pressure.

21. *Summary of Conclusions.*

(1) The deviations of a gas or vapour from the ideal state *at moderate pressures* can be represented by an equation of the type $v-b=R\theta/p-c$, in which the "covolume" b is constant, and the "co-aggregation-volume" c is a function of the temperature only. This conclusion follows from the observed form of the isothermals combined with the observation that the "cooling-effect" is independent of the pressure; but it could not be deduced from either observation separately.

(2) The value of the Absolute Zero may be approximately deduced from a knowledge of the cooling-effect Q and the specific heat S at or near 50° C. without any knowledge of the mode of variation of S and Q with temperature. But the determination of the scale-correction of the gas-thermometer essentially requires a knowledge of the mode of variation with temperature.

(3) The simplest assumption with regard to the mode of variation of c with temperature is that it varies inversely as the nth power of θ, or that $c=c_0(\theta_0/\theta)^n$. The value of n is different for different types of co-aggregation or for different kinds of molecules. The law of Corresponding States must be restricted to molecules of the same type which coaggregate in a similar manner.

(4) The index n may be interpreted as half the number of degrees of freedom lost by a molecule in coaggregation, the energy of flight of a molecule representing three degrees of freedom.

(5) The value of n is probably 0·5 for monatomic gases, and 1·5 for diatomic gases, on the simple hypothesis of integral degrees of freedom. These values give very fair agreement with experiment, but there is no *à priori* reason why the number of degrees of freedom should be an integer for a polyatomic molecule.

(6) The properties of CO_2 at moderate pressures are well represented by the assumption $n=2$, provided that account is taken of the variation of the specific heat as observed by Regnault. This reconciles the hitherto discordant results for the cooling-effect and the compressibility.

(7) The properties of Steam, including the variation of the latent heat and the saturation-pressure, are well represented by the value $n=3·3$, if the limiting value of the specific heat at zero pressure is assumed to be independent of the temperature, provided that the variation with pressure is not neglected.

(8) The value of the Absolute Zero, as deduced from the pressure-coefficient of hydrogen, is probably within one or two hundredths of a degree of 273°·10.

IV. *Excited Radioactivity and the Method of its Transmission.* *By* E. Rutherford, *M.A., D.Sc., Macdonald Professor of Physics, McGill University, Montreal*[*].

§ 1.—*Introduction.*

ONE of the most interesting properties of the radioactive substances thorium and radium, is their power of communicating or exciting[†] temporary radioactivity to all bodies in their neighbourhood. If a wire charged to a high negative

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[*] Communicated by the Author. Preliminary accounts of these results were communicated to the American Physical Society, New York, December 27, 1901, and to *Phys. Zeit.* No. 10, 1902.

[†] (*Note*)—The term "*excited,*" has been used throughout these investigations rather than "*induced,*" which has found favour with many

potential is placed in a closed metal vessel containing a thorium or radium compound the excited radioactivity is confined almost entirely to the negative electrode. If the wire is charged positively, it remains inactive, but the excited radioactivity is produced on the walls of the vessel.

When no electric field is acting, excited radioactivity is produced on the surfaces of all bodies in the closed vessel, independently of their being good conductors or insulators.

In previous papers the author has shown that there is a direct connexion between the presence of the radioactive emanation from thorium and radium and the production of excited radioactivity. It will be shown in this paper that the production of excited radioactivity is one of the properties of the emanation from thorium and radium. This excited radiation is caused by the deposit on the surface of bodies of radioactive matter, which is transmitted by positively charged carriers travelling through air in an electric field with about the same velocity as the positive ion, produced in air by Röntgen rays.

§ 2.—*Connexion between Excited Radioactivity and Emanation.*

In a previous paper (Phil. Mag. Jan. 1900) I have shown that thorium compounds continually give off a radioactive emanation. This emanation loses its radiating power rapidly, falling to half value in the course of one minute. Dorn showed later that radium also gave off an emanation, especially when heated. This emanation decayed much more slowly than that from thorium. In some experiments where the radium emanation, mixed with air, was kept in a closed metal vessel, I have found that the activity of the emanation fell to half value after standing several days, but was quite appreciable after a month's interval.

These emanations from thorium and radium behave in all respects like radioactive gases or vapours. They diffuse rapidly through gases and through porous substances like paper, but unlike the gaseous ions which they produce in their path, pass through plugs of cotton wool, and bubble through solutions with no appreciable absorption. In a more detailed investigation (Rutherford and Soddy, Phil. Mag. Sept. 1902) it has been shown that the thorium emanation behaves like an inactive gas, and that its activity is not

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Physicists. I have avoided using the latter term, as to my mind, it conveys the idea that the effect is in some way due to an action across the medium; while the experiments in this paper show conclusively that excited radioactivity is transmitted by means of a convection of positively charged carriers.

appreciably influenced by temperature or by the most drastic chemical treatment.

From the rate of diffusion of these emanations, it appears that they must possess a considerable molecular weight. An investigation of the rate of diffusion of the radium emanation into air, a preliminary account of which appeared in 'Nature,' 1901, p. 157, and Proc. Roy. Soc. Canada 1901, showed that its molecular weight probably lay between 40 and 100. On account of the rapid loss of activity of the thorium emanation it has not so far been found possible to determine with certainty its rate of diffusion into air or other gases.

The emanations from thorium and radium possess very similar properties. They both readily diffuse through gases and porous substances; they both possess the power of ionizing the gas in their neighbourhood and producing excited radioactivity on bodies.

The differences between them can be readily accounted for by supposing them to be radioactive gases or vapours of different molecular weights. According to the results which have been given in previous papers, radioactivity is an accompaniment of chemical change. Taking this view, the difference in the rates of decay of the radioactivity of the emanations from thorium and radium merely indicates a difference in their rate of chemical change, and does not imply any fundamental difference in nature.

Unlike the radiations from the emanations, the excited radiation due to thorium decays much more slowly than that due to radium (see Rutherford and Miss Brooks, Phil. Mag. July 1902, p. 18). In this case, the chemical change proceeds more rapidly in the material responsible for the excited radioactivity from radium than in that from thorium.

Excited radioactivity is always produced on bodies when the radioactive emanations from thorium and radium are present. In order to show the very close connexion existing between the presence of these emanations and excited radioactivity, the following experimental facts may be mentioned:

(1) Only the radioactive substances which emit emanations, viz. thorium and radium, have the power of exciting radioactivity. Uranium and polonium, not giving off any emanation, do not possess the power of exciting radioactivity.

(2) The amount of excited radiation obtained from thorium and radium compounds is directly proportional to the amount of emanation present. For example, thoria gives out far more emanation and produces far more excited activity than thorium nitrate in the solid state. Thoria and radium chloride, partly deemanated by strong heating, lose their power of exciting activity in like ratio.

(3) Excited radioactivity can be produced on bodies if the emanation and not the radioactive substance itself is present. It can be produced at long distances from the radioactive compound by blowing the emanation mixed with air along tubes. In the case of radium, the emanation, which has been introduced into a vessel by blowing a current of air over the active substance, produces excited activity after a month's interval, although the radioactive substance itself has not been placed in the neighbourhood. On the other hand, the power that a thorium or radium compound has of producing excited activity on a body near it is almost completely lost by blowing over the compound a current of air which removes the emanation as rapidly as it is formed.

The amount of emanation or excited activity has no direct connexion with the radioactivity of the compound in its neighbourhood, and cannot be ascribed to any action of the "straight line" radiation in the gas through which it passes. For example, deemanated thoria produces only a small fraction of the amount of excited activity of an equal weight of ordinary thoria although the amount of the straight line radiation is not much affected by the process of deemanation.

§ 3. *Method of Transmission of Excited Activity.*

The characteristic property of excited radioactivity is that it can be confined to the cathode in a strong electric field. It is probable, therefore, that the radioactivity is due to the transport, in the electric field, of positively charged carriers of some kind. Experiments were undertaken to test this and to find the rate at which these carriers moved in an electric field, in order to obtain a rough estimate of their dimensions compared with a gaseous ion.

The method employed to determine this velocity is a modification of one already used in a determination of the velocity of the negative ion, produced at the surface of a metal by ultra-violet light*. It depended on the use of an alternating electric field. By means of a revolving commutator, a direct P. D. was commuted into an alternating P. D. of known frequency. If such an alternating field is applied to two parallel plates, between which a radioactive emanation is kept uniformly distributed, equal amounts of excited activity are produced on each electrode.

If in series with an alternating P. D. $\pm E_0$ a battery is placed of E.M.F. E_1 less than E_0, the positive carrier moves

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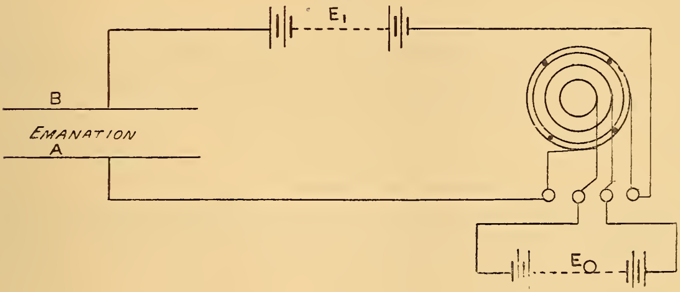
* Rutherford, Proc. Camb. Phil. Soc. 1897.

in a stronger electric field in one half alternation than in the other. A carrier consequently moves over unequal distances during the two half alternations, since the velocity of the carrier is proportional to the strength of the electric field in which it moves. It follows from this that the excited radioactivity will be unequally distributed over the two electrodes. If the frequency of alternation is sufficiently great, only the positive carriers within a certain small distance of one plate can be conveyed to it, and the rest, in the course of several succeeding alternations, are carried to the other plate.

Suppose A and B (fig. 1) are two parallel plates to be made radioactive. The emanation is supposed to be uniformly distributed between them. When B is negatively charged suppose the P. D. between the plates is $E_0 - E_1$, when B is positive the P. D. is $E_0 + E_1$.

Fig. 1.



Let d = distance between the plates,
T = time of a half alternation,
ρ = ratio of the excited radioactivity on the plate B to the sum of radioactivity on the plates A and B.
K = velocity of the positive carriers for unit-potential-gradient

On the assumption that the electric field between the plates is uniform, and that the velocity of the carrier is proportional to the electric field, the velocity of the positive carrier towards B is

$$\frac{E_0 - E_1}{d} \cdot K,$$

and in the course of the next half alternation

$$\frac{E_0 + E_1}{d} \cdot K$$

towards the plate A.

The greatest distances* x_1, x_2 passed over by the positive carrier during two succeeding half alternations is thus given by

$$x_1 = \frac{E_0 - E_1}{d} K . T, \text{ and } x_2 = \frac{E_0 + E_1}{d} K . T.$$

Suppose the positive carriers are produced at a uniform rate of q per second for unit distance between the plates. The number of positive carriers which reach B during a half alternation may be divided into two parts:

(1) One half of those carriers which are produced within the distance x of the plate B. This number is equal to

$$\tfrac{1}{2} x_1 q T.$$

(2) All the carriers which are left within the distance x_1 from B at the end of the previous half alternation. The number of these can be readily shown to be

$$\tfrac{1}{2} x_1 . \frac{x_1}{x_2} q T.$$

Now all the rest of the carriers produced between A and B during a complete alternation will reach the other plate A in the course of succeeding alternations, provided no appreciable recombination takes place. This must obviously be the case, since the positive carriers travel further in a half alternation towards A than they return towards B during the next half alternation. The carriers thus move backwards and forwards in the changing electric field, but on the whole move towards the plate A.

The total number of positive carriers produced between the plates during a complete alternation is $2dqT$. The ratio ρ of the number which reach B to the total number produced is thus given by

$$\rho = \frac{\tfrac{1}{2} x_1 q T + \tfrac{1}{2} x_1 \frac{x_1}{x_2} q T}{2 d q T} = \frac{1}{4} \frac{x_1}{d} . \frac{x_1 + x_2}{x_2} .$$

Substituting the value of x_1 and x_2 we obtain

$$K = \frac{2(E_0 + E_1)}{E_0(E_0 - E_1)} . \frac{d^2}{T} . \rho.$$

In the experiments the values of E_0, E_1, d, and T were varied, and the results obtained were in general agreement with the above equation.

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* In the equations that follow it is assumed that x_1 is less than the distance between the plates. If $x_1 > d$ the equations have to be modified.

§ 4. *Velocity of Carriers of Thorium Excited Activity.*

For experiments on thorium emanation, a thick layer of thoria was placed in a shallow copper vessel inside an ebonite box 11 cms. square and 3 cms. deep, which was tightly waxed down to a metal base. The thoria was completely covered with two layers of filter-paper, which cut off most of the direct radiation, but readily allowed the emanation to pass through. The apparatus was rendered air-tight by a metal lid, dipping into a mercury trough round the top of the ebonite box. At the beginning of an experiment a square sheet of aluminium foil was placed over the paper covering the thoria, a zinc plate on top of the ebonite box, and the lid placed in position. This was done as quickly as possible, and the alternating electric field was then applied.

The emanation rapidly diffused through the paper and thin aluminium foil, and distributed itself between the plates in the electric field. After an interval, varying in the experiments from 20 to 90 minutes, the aluminium and zinc plates were removed and their radioactivity tested in the usual way with the Dolezalek electrometer. The ratio of the excited radioactivity on the two exposed plates was thus determined. This ratio was found to be independent of the time the plates were left before testing, as the radioactivity on each plate decays at the same rate.

The amount of thoria used in these experiments varied from 25 to 100 grammes. The amount of excited activity in a given time varied with the amount of thoria, but the ratio of the activity in the two plates was unaltered. For a given voltage and time of alternation the value of ρ was slightly greater when the lower plate was negative. This is due to the unequal distribution of the emanation between the plates; for on account of the time taken in diffusion, the emanation is more concentrated near the surface of the thoria. The mean of the values of ρ with top plate negative and lower plate negative was taken as the true value.

In the early experiments a two-part commutator driven by a motor was used. In the later experiments for a more rapid rate of alternation a four-part commutator was employed.

With this arrangement of apparatus a large number of experiments were made in order to test the truth of the general theory. Comparisons of the velocity of the carrier have been made over a wide range of period of alternation and of voltage, and for different distances between the plates. The results obtained were in general agreement with the theory put forward. When the voltage was kept constant, the value of ρ was found to decrease with increase in the number of alternations per second. With a constant speed of alternation the value of ρ increased with the voltage.

When the value of ρ is small, the velocities of the carriers, deduced from the equation, were found to be all too high, and also inconsistent among themselves. There are several disturbing factors which have a great influence on the value of ρ when ρ is small. These factors are:—

(1) Recombination and diffusion of the carriers. Unless the electric field is strong, the carriers recombine and diffuse to the electrodes. With a weak electric field the excited radioactivity is distributed on both the positive and negative electrodes.

(2) Inequality of the electric field. In this simple theory we have assumed that the potential-gradient between the plates is uniform. This is far from being the case. The experiments of Child and Zeleny have shown that there is always a sudden drop of potential near the electrodes. The electric field near the electrodes is consequently stronger than the average. For this reason, when the carriers which reach the plate B are only abstracted from within a short distance of the plate, the value of ρ leads to too high a value of the velocity.

(3) Initial velocity of the carrier. From some considerations which will be developed later (see § 9), it seems probable that the positive charge on the carrier is due to the expulsion of a negatively-charged particle of some kind from the neutral molecule. The positive carrier may thus have enough initial velocity imparted to it to carry it some distance against the electric field. This will result in a distribution of some excited activity on the anode, even with a strong field. It is difficult to obtain direct experimental evidence on this point, but there seems little doubt that such an effect is present.

In order to obtain consistent results, it was found necessary to have a considerable difference between the strength of the electric fields during the succeeding half alternations. If the difference is small, the carriers take so long to reach the plate A that recombination and diffusion of the ions become important factors in determining the distribution of excited activity. For the reasons we have explained above, it was necessary to use fairly high voltages and correspondingly rapid speed of alternation in the experiments.

The following tables are examples of some of the results obtained for different voltages and distances between the plates. Temperature 18° C. Air fairly dry.

Plates 1·30 cm. apart.

E_0+E_1.	E_0-E_1.	Alternations per sec.	ρ.	K.
75	50	57	·17	1·7
152	101	57	·27	1·25
225	150	57	·38	1·17
300	200	57	·44	1·24

The value of K is given in cms. per sec. for a potential-gradient of 1 volt per cm.

For the last example, since the carrier travelled over a distance greater than 1·30 cm. during each half alternation, a modified form of the equation was necessary to calculate the velocity.

The value 1·6 cm. per second for 50 volts is too high for the reasons explained above.

Plates 2 cms. apart.

E_0+E_1.	E_0-E_1.	Alternations per sec.	ρ.	K.
273	207	44	·37	1·47
300	200	53	·286	1·45

An average value of the velocity from a large number of alternations for different distances, voltages, and speed of alternations was about *1·3 cm. per sec.* for atmospheric pressure and temperature.

This velocity is not very different from the velocity of the positive ion produced by Röntgen or Becquerel rays. The most accurate determination of this velocity by Zeleny* gave a value of 1·37 cm. per sec. for dry air.

§ 5. *Increase of Excited Radiations with Time.*

In the course of these experiments a remarkable effect was observed. It was found that a plate which has been exposed a short time in the presence of thoria emanation, after being removed, gradually increased in radioactive power for several hours. The amount of increase varied with the time of exposure to the emanation, but in short exposures it increased to three or four times its initial value. For exposures of several hours the effect is not so marked, and is difficult to detect after a day's exposure.

The following tables illustrate the results obtained.

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* Phil. Trans. Roy. Soc. (1900).

(1) Platinum wire, charged −110 volts, exposed 15 minutes in a cylinder containing thoria. First observation five minutes after removal of wire from emanation cylinder.

Time in Minutes.	Movement of Electrometer in scale-divs. per sec.
0	1·9
7·5	2·8
24	4·0
43	4·6
58	5·2
78	5·9
99	6·5

In this case the activity had increased over three times in 99 minutes and had not reached its maximum value.

(2) Aluminium foil as cathode in parallel plate apparatus of fig. 1. Time of exposure 41 minutes. First observation 6 minutes after removal.

Time.	Radioactivity.
0	1
21 minutes.	1·6
31 "	1·8
57 "	2·0
70 "	2·2
91 "	2·5
120 "	2·9
160 "	2·9
180 "	2·9
22 hours.	1·0
49 "	0·21

In this case, for the purpose of comparison, the initial value of electrometer current is taken as unity. The activity increases to nearly three times its initial value after an interval of two hours, and then slowly decreases at the normal rate, *i. e.*, it falls to half value in about 11 hours.

Similar results were obtained if the plate was made active without the action of the electric field. The increase of activity with time is independent of the nature of the electrode, or of the concentration of the radioactive matter upon it. It was not found possible to influence the rate of increase of activity with time or the final maximum by heating the wire to about a red heat.

With increase of time of exposure of the electrode in the thorium emanation, the ratio of increase of activity after removal decreases. For a long interval of exposure the activity begins to decrease at once after removal. This result is to be expected, for the activity of each portion of the radioactive matter deposited increases with time for two or three hours, and then diminishes. Consequently, after the electrode has been exposed for about ten hours or more, the increase of activity of the matter deposited in the last few hours does not compensate for the decrease of activity of the radioactive matter as a whole. This increase of activity with time explains an irregularity in the curve of increase of excited activity from thorium with time of exposure. It was pointed out in a previous paper (Phil. Mag. February 1900, p. 178) that, on the hypothesis of a uniform rate of deposit of radioactive matter, the activity of which decreased in a G. P. with the time, the curve of rise of excited activity with time of exposure is the same as the curve of rise of an electric current in a circuit of constant self-inductance. It was experimentally observed, however, that the rate of increase for the first few hours was much smaller than would be expected on this hypothesis. In the light of the present results, the explanation of this effect is simple. The matter deposited during the first few hours does not reach its maximum activity for several hours, and the initial effect is consequently much smaller than would be expected on the simple theory.

§ 6. *Radium Excited Radioactivity.*

Experiments were made to determine the velocity of the carriers responsible for the excited radioactivity of radium in the same way as for thorium. The radium in my possession gave out too little emanation at ordinary temperatures in the solid state to enable me to use it in the apparatus in place of thoria. The amount of emanation from radium can, however, be increased several thousand times by heating the radium compound below a red heat. A more convenient method of obtaining a large amount of emanation is to dissolve a small quantity of radium chloride in water. Radium in solution gives off several hundred times more emanation than in the solid state. If the solution is kept in a closed vessel the emanation continually collects in the upper part of the vessel It can be transferred at any time to another vessel by bubbling a slow current of air through the solution. The procedure adopted in introducing the emanation into the apparatus was as follows:—

A large amount of emanation was introduced into a metal cylinder of about 3 litres capacity. The plates to be tested were then placed in position in the apparatus of fig. 1.

and the alternating E.M.F. applied. By means of side tubes, the apparatus was put into connexion with the emanation vessel and a small fraction of the emanation introduced into it by sending a slow current of air into the cylinder. The tubes leading into the apparatus were then closed, and the alternating E.M.F. continued for an interval of 15 to 30 minutes. Before stopping the commutator, the emanation was blown out of the apparatus by a slow current of air. The plates were then removed, and the amount of activity on them was compared by means of the electrometer. On account of the initial rapid decay of the radiations, a difficulty arose in comparing the amount of radiation on the two plates. As shown in a previous paper*, the excited radiation from radium, for short exposures, decreases rapidly for the first 5 minutes after removal, but about 15 minutes after removal reaches a value which is maintained fairly constant for an interval of about 10 minutes. It then decays to zero, falling to half value in about 30 minutes. The comparison of the activity on the two plates was made during this constant interval.

When experiments were made under the same conditions as those for thorium, somewhat higher values of the velocity of the carriers were obtained, and the numbers, for different frequencies and voltages, differed considerably among themselves. These discrepancies were found to be due to the fact that even in a strong electric field from 5 to 10 per cent. of the total excited activity was distributed on the anode. In this respect the activity excited by radium differs from that of thorium. Consequently, the value of ρ would be greater for the radium than for the thorium experiment, under the same conditions, even if the carrier of excited radioactivity travelled at the same rate in both cases.

§ 7. *Distribution of Excited Activity on the Anode.*

In order to throw more light on the cause of this distribution of excited activity on the anode, some experiments were made with the apparatus shown in fig. 2 *a*.

The emanation vessel A consisted of a brass cylinder 25·5 cms. long and 8·30 cms. diameter. A long central brass rod B C D E, diameter ·518 cm., passed through an ebonite cork at one end of the tube. The outside cylinder was connected to one pole of a large battery, the other pole of which was earthed. The central rod was connected to earth. The emanation was introduced into the vessel by sending a slow current of air through a radium chloride solution contained

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* E. Rutherford and Miss Brooks, Phil. Mag. July 1902.

in the Drechsel bottle F. The air passed through a tube containing cotton-wool, and through a drying-tube T of calcium chloride. The central rod was made of three removable parts BC, CD, DE, screwed together. After exposure for a known time in the presence of the emanation the rod was removed, and the activity on the portion CD, length 15 cms., determined by the electrometer in the cylindrical testing vessel L, shown in fig. 2 *b*. By this means the excited activity was determined on that portion of the rod where the electric field was sensibly uniform.

Fig. 2 *a*.

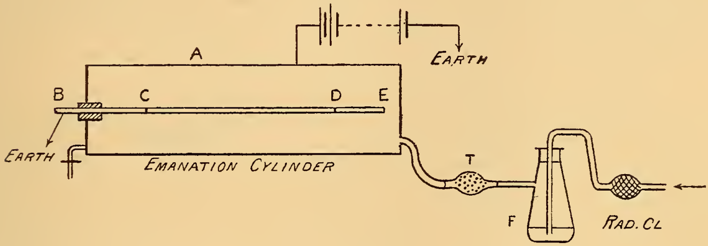
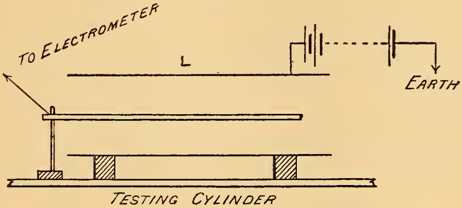


Fig 2 *b*.



In most of the experiments the emanation was introduced into the vessel A a day or two before observations were taken. This ensured a uniform distribution of the emanation throughout the cylinder by the process of diffusion. If observations were required soon after the introduction of the emanation, the emanation was uniformly mixed with the air by means of a stirrer not shown in the figure.

Some experiments were made with this apparatus on the amount of excited activity on the central rod when positively charged for different voltages. For the purpose of comparison, the results are expressed in terms of the percentage amount on the same electrode exposed for the same time when negatively charged with 300 volts between the electrodes. The rod was exposed in the presence of the emanation for 15 minutes, then removed and a fresh rod introduced. In the course of three or four hours' work, the amount of excited activity, obtained for a given time of exposure, diminished about 20 per cent. This was partly due to the decay of the radiating power of the emanation during the interval, and partly to a slight escape of the emanation in removing and replacing the central rod. By determining the ratio of excited activity at the beginning and end of the experiments, a correction was readily made for this diminution.

Table of distribution on anode, diameter 8·3 mms.

Voltage.	Percentage.
−300	100
+300	6
+150	6
+ 50	9
+ 20	10
0	14

It will be seen from the table that the amount on electrode with +300 volts P.D. is 6 per cent. of amount on electrode with −300 volts P. D. The percentage increases with diminution of voltage, rising to 14 per cent. for zero voltage, when the distribution is due to diffusion alone of the carriers to the central electrode. In order to see how much of this amount on the electrode was due to transmission by the electric field and how much to diffusion, the experiments were repeated with the central rod of ·8 mm. diameter instead of 8·3 mms.

−300	100
+300	4
+ 50	7

Now, with a central rod of only about 1/10 of the surface area, it is obvious that the effect due to diffusion must be very much reduced. We may thus conclude from these experiments that a proportion of the excited radioactivity from radium (about 5 per cent.) travels to the positive electrode in an electric field, and the carrier must in consequence have a negative charge.

A special experiment was made to determine the amount of radium excited activity on the anode with an apparatus consisting of parallel plates. For this purpose the emanation vessel of fig. 1 was used, with the plates 1·3 cm. apart. With 300 volts between the plates about 10 per cent. of the total activity was confined to the anode. From the previous experiments we have seen that about 5 per cent. reaches the anode in consequence of transmission by the electric field. The remaining 5 per cent. must thus reach the electrode by other agencies. With such a strong electric field, the effect due to pure diffusion must be very small. It thus seems likely that some of the radioactive carriers have sufficient initial velocity to carry them to the electrode against the electric field.

§ 8. *Velocity of the Carrier.*

Some experiments were made on the velocity of the carrier of excited radioactivity, using the concentric cylinders shown in fig. 2 a. If a and b are the radii of the internal rod and the cylinder, the electric field X at a distance r from the centre, for a P. D. of v volts between the cylinders, is given by

$$X = \frac{V}{r \log_e \frac{b}{a}}.$$

Using the same notations and assumptions as in the case of parallel plates, it can be shown that the velocity K of the carrier of excited radioactivity is given by

$$K = \frac{E_0 + E_1}{E_0(E_0 - E_1)} \frac{(b^2 - a^2) \log_e \frac{b}{a}}{T} . \rho.$$

The following table shows some of the results obtained for different voltages and periods of alternation :—

$E_0 - E_1$.	$E_0 + E_1$.	Alternations per sec.	ρ.	Corrected value of ρ.	K.
205	308	5·7	·35	·32	1·0
205	308	11·2	·24	·20	1·2
205	308	17·2	·19	·13	1·2
205	308	34	·16	?	
385	580	18·3	·30	·27	1·5
385	580	47	·16	?	

The values of the velocity of the carrier determined for the *uncorrected* values of ρ in the above table vary much among themselves. It will be seen, however, that the value of ρ increases with the time of alternation and the voltage, as we should expect from the elementary theory. It was not found possible to reduce the observed value of ρ below about ·16, whether the voltage was diminished or the frequency of alternation increased. This is to be expected, for we have previously shown that the amount of excited activity in the central rod, when diffusion alone is acting, is ·14 of the total; for in cases where the carrier is only able to travel over a small fraction of the distance between the electrodes during a half alternation, only a small amount of the excited radioactivity on the central rod is due to the deposit of positively charged carriers by the electric field. The greater proportion is due to the diffusion of carriers to the electrode and to the carriers which are deposited when the central rod is the anode. The amount of this latter is, as we have shown, about five per cent. of the total. It is difficult to make more than a rough estimate of the amount of excited activity on the electrode in the various cases. For these reasons the corrected values of ρ in the table for the frequencies of 34 and 47 per second are probably not more than about one-third of the observed value ·16.

In the above table a rough correction is made for some of the values of ρ and the resulting velocity calculated.

It will be seen that the values of the velocity of the carrier lie between 1·0 and 1·5 cm. per sec. for a potential-gradient of 1 volt per cm. This is about the same range of values as that obtained for the carrier of thorium excited radioctivity.

From the nature of the results it is not possible to definitely decide whether the carriers of thorium and radium excited activity travel at exactly the same speed. The results, however, indicate that the carriers in the two cases are not very different in speed, and that consequently they do not differ much in size.

We may conclude from these experiments that the greater part of the excited radioactivity from both thorium and radium compounds is due to the deposit of positively charged carriers, produced from the emanations on the cathode, and that these carriers travel at about the same rate as the positive ion produced in the air by Röntgen rays.

When no electric field is acting excited radioactivity is transferred by the diffusion of these carriers to the surface of all bodies immersed in the emanation.

§ 9. *Origin of the Carriers.*

Before discussing the question of the method of production of these positive carriers which cause excited activity, a brief *résumé* is necessary of the physical properties of the emanations from thorium and radium. In the first place the emanations behave in all respects like radioactive gases of high molecular weight. They do not carry with them any charge of electricity, and are consequently unaffected by the presence of an electric field.

In my first paper on the thorium emanation (*loc. cit.*) it was pointed out that the particles constituting the emanation certainly did not move with a velocity greater than ·00001 cm. per sec. for a gradient of 1 volt. per cm. The conclusion was drawn that the emanation itself was initially uncharged. A similar result is true for the emanation from radium ; for the emanation still persists in a closed vessel after several weeks' exposure in a strong electric field. For these reasons the suggestion made by Becquerel*, that the emanations are composed of positive ions directly emitted from radioactive bodies, is untenable ; for if such were the case, the ions would at once be swept to the electrodes by the electric field, and would very rapidly disappear from the gas.

These emanations possess the property of ionizing the gas and of producing from themselves positively charged carriers which cause excited activity in bodies on which they are deposited. This property lasts only a few minutes in the case of the thorium emanation, and for several weeks for the radium emanation.

Two hypotheses may be put forward to account for the origin of these charged carriers :—

(1) The radioactive matter constituting the emanation condenses on the positive ions, produced in the gas by the radiation, and is thus transferred to the cathode.

(2) The particles of the emanation possess the property of expelling from themselves a negatively charged body of some kind. The particle would thus be left with a positive charge, and would be carried to the cathode by the electric field.

It is not easy to decide definitely between these two hypotheses, but the evidence as a whole is strongly in favour of the second.

In regard to (1) it might be supposed that the emanation condensed more readily on the positive than on the negative ion ; on the principle that water and alcohol-vapour condense more readily on the negative than on the positive ion. If this were the case, it would be expected that the emanation would be removed more rapidly if the number of ions were increased in the gas through which the emanation was distributed. There is no evidence that such an effect exists. I have tried the experiment of passing the emanation through a space strongly ionized by radium rays ; but the amount of excited activity in a given time on the cathode, placed in this

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* *Comptes Rendus*, Dec. 9, 1901.

space, was not appreciably altered. I have also tried experiments to see if the radiation from the emanation was affected by exposure in a strong electric field, but with negative results. In order to test this, the thorium was placed in the bottom of a small lead box, and covered with two layers of paper to cut off the direct radiation. The top of the box was tightly covered with a very thin layer of mica. This prevented the escape of the emanation, but allowed the radiation from the emanation to pass through and ionize the gas above the vessel. The amount of this ionization outside the vessel was unchanged if the emanation was exposed to a strong electric field by charging insulated conductors placed inside the vessel.

If the emanation is removed to the cathode in an electric field by condensation on the ion, it is to be expected that it would continue to radiate at the same rate on the electrode as in the gas from which it is removed. On this view the radiation from the cathode should rapidly decrease for the first few minutes after removal from the emanation. Some special experiments were tried to settle this point, but no decrease was observed, although even a minute effect could have been readily detected.

There is thus considerable indirect evidence against the condensation hypothesis; and it has consequently been discarded in favour of (2), which offers a satisfactory explanation not only of the production of positive carriers, but also of the origin of the radiation given out by the emanation itself. On this view the emanation consists of matter in an unstable state, which undergoes further chemical change. The change consists in the expulsion of a negative particle from the neutral molecule. The residual portion of the molecule retains a positive charge, and is carried at once to the cathode in an electric field. This matter again undergoes chemical change, giving rise to the phenomena of excited radioactivity. The experimental data in favour of this view are best considered in the next section (§ 10) on the nature of the radiations.

It has been shown that the carriers of excited activity for both thorium and radium travel at about the same rate as the ions produced in the air by Röntgen rays. From data of the Kinetic Theory of Gases it has been shown that the ion in air is probably large compared with the molecule of oxygen or hydrogen. This has been explained by supposing that the ion, immediately after its production, becomes the centre of a cluster of molecules which move with it. On this view that part of the emanation molecule which retains a positive charge immediately becomes the nucleus of an aggregation of molecules of the surrounding gas. The size of the cluster is probably about the same for the positive ion, since the size is mainly determined by the electric charge which is the same for both. The velocities in an electric field are thus the same for the carriers of excited activity and for the gaseous ion. Since the size of the cluster is large compared with the original nucleus, the velocities of the carriers of thorium and radium excited activity would be about the same, even if the original nuclei were of different masses.

§ 10. *Nature of the Radiations.*

In considering the question of the size of the body expelled from the molecule of the emanation, and of the nature of the radiation from the emanation, it is necessary to take into account the nature of the emanations emitted from all the known radioactive bodies; for there is no reason to suppose that the processes which are taking place in the molecule of the emanation are essentially different in character from those occurring in the other radioactive bodies. It is known that uranium, thorium, and radium emit two types of radiation. One type is not appreciably deviable by a magnetic or an electric field, and is very easily absorbed in matter. These will be called the α rays. The others are deviable and more penetrating in character, and will be called the β rays. In addition I have shown that thorium and radium emit some rays nondeviable in character, but of very great penetrating power. All of the radioactive substances including polonium as well as "excited" bodies and the emanations give out these α rays. Their power of ionizing the gas is very much greater than for the other types of rays emitted; and it is probable that the greater proportion of the energy radiated into the gas is in the form of α rays. The α rays from different radioactive substances, including the emanations of "excited" bodies, do not vary very much in penetrating power. The "excited" radiations for thorium and radium are the most penetrating in character and that of uranium the least.

It has been difficult to offer a satisfactory explanation of the nature of these rays. I have previously shown as untenable the view that they are secondary rays due to the emission of β rays. I have been recently led, by a mass of indirect evidence, to the view that the α rays are in reality charged bodies projected with great velocity. The ionizing effect of the rays is due to the collision of the projected body with the molecules of the gas, in the same way that the cathode rays ionize the gas in their path. Such a projected particle probably produces many thousand ions in its path before its velocity is reduced to the point below which it can no longer ionize the gas. Strutt has put forward the view that the α rays were positively charged bodies since the β rays emitted from the same body carried a negative charge. This view has also been advanced in a recent paper by Sir W. Crookes.

The evidence in favour of the projection nature of the α rays is so far all indirect in character, and is briefly summarized below:—

(1) The absorption of the α rays in matter (like the β rays which we know are projected particles) is approximately proportional to the density of the material. It has been shown that the absorption of uranium, thorium, and radium rays is roughly proportional to the density for air and for aluminium.

(2) The absorption of the α rays by a given thickness of matter *increases* rapidly with the thickness traversed.

I have found that this is a general property of the α radiations not only for the radioactive elements proper, but for the radiations from the emanation and excited bodies. This is to be expected if the rays consist of projected particles, but is difficult to explain if the radiations are æther-waves similar to Röntgen rays.

(3) In the case of the emanations we have direct evidence that a negatively charged particle * is projected. The radiation from the emanation is due to these projected particles which ionize the gas in their path. This satisfactorily explains the experimental observation that the amount of excited activity is directly proportional to the amount of radiation from the emanation. It also serves to explain the fact especially noticeable in the experiments on the radium emanation, that some of the carriers of excited activity have sufficient initial velocity to move against the electric field. This velocity is due to the recoil consequent upon the projection of the charged body.

If these rays are due to projected charged particles they should possess the properties of the α rays of deflectability by a magnetic and electric field.

No deviation of the α rays has so far been detected in a strong magnetic field, but the experiments have not yet been

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* I was at first inclined to suppose that the particle expelled from the emanation was a negative electron, since it is known that both thorium and radium compounds and bodies excited by them, emit some deviable rays. I have, however, made a close examination of the radiation from the emanation by the electrical method, but was unable to detect the presence of any penetrating deviable rays. If such deviable rays are present, they certainly exist in far less proportion compared with the α rays than in the other radioactive substances.

pushed to the necessary limit. The results, however, indicate that if the rays are deflectable, the deviation is minute compared with the β rays. This is to be expected if the mass of the expelled particle is large compared with the electron. If, for example, the projected body had a mass 10 times that of the hydrogen atom, it would require a magnetic field about 10,000 times as strong to produce the same deviation as for the electron moving with the same velocity. There is evidence that large carriers moving with a high velocity are produced in vacuum-tubes. W. Wien * has shown that the "*Canal Strahlen*" of Goldstein are positively charged particles moving with high velocity. These rays are deviated by a magnetic and electric field. When the vacuum-tube is filled with hydrogen the ratio of the charge to the mass, $\frac{e}{m}$, of these carriers is about 10^4, showing that the carriers have the same mass as the hydrogen atom. In an atmosphere of oxygen the size of these carriers is considerably greater than the hydrogen atom.

It is possible that the electric charge on the expelled particle may be different for different radioactive bodies under different conditions. For the emanations of thorium and radium the expelled particles are for the most part negative. It has been shown that some of the radium carriers of excited activity have a negative charge, showing that the expelled body is positive. In addition, Dorn has shown that in a radium solution the excited radioactivity is produced on the anode, and not on the cathode. This shows that the carriers of excited activity in solution have a negative charge, so that the expelled body is positive in sign.

§ 11. *Evidences of Chemical Change.*

In previous papers by Mr. Soddy and myself, the view has been put forward that radioactivity is an accompaniment of continuous chemical change. Taking, for example, thorium, which has been worked out more thoroughly than the other radioactive bodies, it has been shown that a chemical substance Th.X is produced at a constant rate by the thorium compound. This Th.X undergoes further chemical change, one of the products of which is the emanation. This emanation itself is not stable, but expels from itself a negatively charged body. The positively charged portion of the emanation is carried to the electrodes, and this again undergoes further chemical change, giving rise to the phenomenon of excited radioactivity.

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* Drude's *Annal.* No. 6, p. 244 (1902).

There is thus evidence of four distinct changes in each of which the matter produced has distinct chemical properties. For example, Th.X is soluble in ammonia, while thorium and products of the later changes are not. The emanation is not soluble in hydrochloric or sulphuric acid, unlike the matter responsible for excited radioactivity. There is strong evidence also that the chemical changes in the matter responsible for excited radioactivity are complex in character. It has been shown that the excited radiation in a body increases after removal when the body is exposed for a short time in the presence of the emanation. This effect is analogous to the increase of radioactivity of Th.X for the first day after separation, which has been shown to be due to the excited activity produced in the matter constituting the Th.X.

In order to account for the increase in radiating power after removal, one must suppose that the matter which is deposited from the thorium emanation gradually undergoes a chemical change. The transformed matter undergoes a secondary change, the time-rate of which is slower than the primary, but which gives rise to greater radioactivity. From data of § 5 half the matter has undergone change about 1 hour after deposit, while in the secondary change the corresponding time is about 11 hours.

Summary of Results.

(1) Excited radioactivity produced by thorium and radium compounds is due to the deposit of radioactive matter, which is derived from the emanation given out by these bodies.

(2) Excited radioactivity is transmitted by positively charged carriers, produced from the emanation, which travel in an electric field with about the same velocity as the positive ions produced in air by Röntgen rays. This velocity (about 1·3 cm. per sec. for 1 volt per cm.) is about the same for the carriers of thorium and radium excited activity.

(3) These positively charged carriers are due to the expulsion of a negatively charged body from the molecule of the emanation.

(4) Evidence is adduced for the view that the easily absorbed and apparently nondeviable rays of radioactive substance are due to the expulsion of charged bodies at a high velocity. The rays are thus analogous to the *Canal Strahlen* of Goldstein, which Wien has shown to be positively charged bodies projected at a great speed.

In the case of the emanations the expelled particles are for the most part negative in sign.

(5) In the case of radium about 5 per cent. of the carriers

of excited activity are distributed on the anode in a strong electric field.

(6) The excited radiations from thorium due to a short exposure in the presence of the emanation increase in the course of several hours after removal, to three or four times their initial value.

(7) The emanations and the matter which gives rise to excited activity are the result of a succession of chemical changes occurring in radioactive matter. In thorium there is evidence of at least four distinct chemical changes.

Macdonald Physics Building,
McGill University, Montreal.
July 29, 1902.

V. *Effect of Temperature on the Hysteresis Loss in Iron.*

By R. L. Wills, *B.A.*, *A.R.C.Sc.I.*, 1851 *Exhibition Scholar, St. John's College, Cambridge*[*].

IT has been known for some years that for soft iron the magnetic hysteresis, for a given range of magnetic force, diminishes considerably as the temperature is raised. Kunz[†] found that the curve showing the variation of hysteresis with temperature for a specimen of soft iron was practically a straight line, while the corresponding curves obtained by Morris[‡] for a specimen of iron show that the fall of hysteresis is much more rapid as the critical temperature is approached than during the earlier stages of heating.

The present paper gives the results of experiments undertaken at the suggestion of Professor J. J. Thomson, on the effect of temperature upon the hysteresis in iron and a tungsten alloy for which the effect of temperature on the magnetic permeability has already been given[§].

Method.

The method employed is that devised by Mr. G. F. C. Searle[||], the energy dissipated in hysteresis being readily determined by observing the "throw" produced in the movable coil of a sensitive electrodynamometer. Most of the apparatus used was kindly furnished me by Mr. Searle.

The movable coil of the electrodynamometer is connected in series with the secondary coil wound round the specimen,

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[*] Communicated by Prof. J. J. Thomson.

[†] *Electrotechnische Zeitschrift*, 1894, p. 196.

[‡] Phil. Mag. vol. xliv. pp. 213–254 (1897).

[§] R. L. Wills, Phil. Mag. vol. l. pp. 1–21 (1900).

[||] G. F. C. Searle, Proc. Camb. Soc. vol. ix. pp. 2–6 (1895).

the fixed coil of the electrodynamometer being connected in series with the magnetizing coil.

The complete theory of the method will be found in the Trans. Roy. Soc.* and thus it will be sufficient to give here a brief outline of the theory applicable to the present experiments; for convenience in reference the notation employed by Searle and Bedford will be used here.

If the primary and secondary coils are wound closely upon the specimen and if E be the voltage between the ends of the primary coil, then

$$E = RC + NAl\frac{dB}{dt}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C is the primary current, R the resistance of the primary coil, A the sectional area and l the mean circumference of the ring, and N the number of turns per unit of length in the primary coil.

If c be the secondary current we may write

$$0 = Sc + nA\frac{dB}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where S is the resistance of the secondary circuit and n is the total number of turns in the secondary coil.

Now of the work done by E in any time, part is spent in increasing the magnetic energy of the system, and the rest is dissipated in hysteresis and eddy-currents in the specimen and in heating the wires of the primary coil and of the secondary circuit.

When the specimen is subjected to a complete cycle of magnetic changes, the magnetic energy on the whole is unchanged and we have

$$\int ECdt = Al(W + X) + \int RC^2dt + \int Sc^2dt,$$

where W and X represent the space-averages of the energy dissipated per cub. cent. per cycle by hysteresis and eddy-currents respectively. But from equation (1)

$$\int ECdt = \int RC^2dt + NAl\int C\frac{dB}{dt}dt,$$

hence

$$Al(W + X) = NAl\int C\frac{dB}{dt}\,dt - \int Sc^2dt$$

$$= -\frac{NlS}{n}\int Ccdt - \frac{n^2A^2}{S}\int\left(\frac{dB}{dt}\right)^2 dt \text{ from (2).}$$

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* G. F. C. Searle and T. G. Bedford, Phil. Trans. A, vol. 198, pp. 40–52 (1902).

When the whole change is completed in a short time $\int Ccdt$ is proportional to the angular momentum gained by the coil of the dynamometer and this again to the "throw" θ.

By means of an earth-inductor placed in the secondary circuit a known change P in the number of lines of magnetic force passing through that circuit can be suddenly produced while a constant current C' is flowing through the primary. If $-\phi$ be the "throw" of the movable coil and S' the secondary resistance, then

$$-\int Ccdt : C'P/S' = \theta : \phi.$$

Hence

$$Al(W+X) = \frac{NC'PS}{nS'}\frac{l\theta}{\phi} - \frac{n^2A^2}{S}\int\left(\frac{dB}{dt}\right)^2 dt.$$

When the rate of variation of B is so small that dB/dt may be taken as uniform over the section we may write

$$\frac{dX}{dt} = \frac{QA}{\sigma}\left(\frac{dB}{dt}\right)^2$$

where Q is a numerical constant depending on the geometrical form of the section and σ the specific resistance of the material. Searle and Bedford shew that for a circular section $Q=1/8\pi=0{\cdot}03979$, and for a square section $Q=0{\cdot}03512$.

Thus, finally we have

$$W = \frac{NC'PS}{nAS'}\frac{\theta}{\phi} - A\left(\frac{Q}{\sigma}+\frac{n^2}{Sl}\right)\int\left(\frac{dB}{dt}\right)^2 dt$$

$$= \frac{NC'PS}{nAS'}\frac{\theta}{\phi} - \left(\frac{Q}{\sigma}+\frac{n^2}{Sl}\right)16\pi^2N^2A\int\left(\frac{dB}{dH}\right)^2\frac{dC}{dt}\,dC, \quad . \quad (3)$$

if c be neglected in comparison with C in the integral, then dB/dH is a function of C but not of dC/dt. Hence for any given value of C, the contribution to the integral due to the increment dC is proportional to dC/dt.

Using a suitable reversing key we can, as Searle and Bedford show, increase dC/dt in any ratio by increasing the resistance of each of the two parts into which the primary circuit is divided by the key in the same ratio, the battery power being at the same time increased in the same ratio so as to keep the maximum current constant.

Writing U for $NC'PS\theta/nAS'\phi$, we then have

$$W = U - \left(a+\frac{b}{S}\right)R. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where a and b are constants.

The energy dissipated in hysteresis for any induction can therefore be determined by making two measurements of U for different values of R, E being adjusted so as to keep the primary current constant.

The induction was measured by the ballistic method used by Professor Ewing and Miss Klaassen *, and the temperature was measured by a platinum wire as in the previous experiments.

The general arrangement of the apparatus is shown in fig. 1. In the key F, which causes a gradual reversal of the current, *ab* is an arm of insulating material free to turn about its centre over a circular ring consisting of metal strips *c*, *d*, *e*, *f*, *g*, insulated from each other. Resistances *rr* are placed between the strips *f*, *g* and *c*, *d* respectively.

The terminals of the battery circuit containing the small variable resistance R_2 and the Weston amperemeter C are connected to the ends of the arm *ab* which make sliding contact with the strips. In the figure the arm is shown in one of its extreme positions; as it is turned to the other extreme position the current is first diminished by an amount depending on the value of *r*. When the end *b* rests on the insulated strip *e*, the strips *c* and *g* are brought into contact by means of the contact-piece attached to the end *a* of the arm. As the arm is turned further, the current through the magnetizing coil increases again but is reversed in direction, and reaches its original maximum value when the end *b* rests on the strip *g*. Before the contact-piece attached to the end *a* of the arm leaves the strip *g*, the end *b* rests on the strip *f*; it will thus be seen that the primary circuit is never broken during the reversal of the current. A choking-coil L having a very large coefficient of self-induction is inserted in the primary circuit to prevent the current varying too rapidly. The key M is a modification of an ordinary reversing-key, and was used for taking cyclic B-H curves when desired. The terminals *e* and *k* are connected together, and an adjustable resistance R_1 is inserted between the terminals *h* and *k*. By suitably adjusting the resistance R_1 the magnetizing current can be reversed in direction and reduced to any value by a single motion of the rocker.

The reversing-key N is connected to the key M in order that when the resistance R_1 is in the circuit the current may be reversed without altering its value.

The primary current flows through the fixed coils A of the electrodynamometer and passes through the keys M, N to the

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* Ewing 'Magnetic Induction in Iron and other Metals,' 3rd ed. revised pp. 356–370.

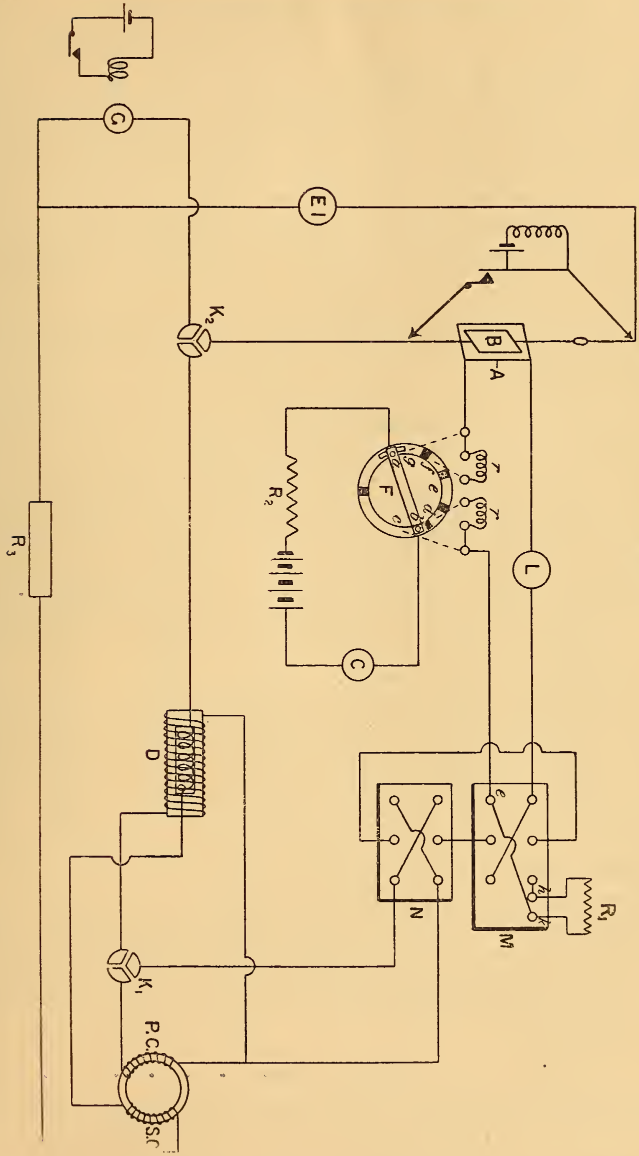

Fig. 1.

primary coil PC wound round the specimen. By means of the two-way key K_2, either the movable coil B of the electrodynamometer or the ballistic galvanometer G is connected in series with the secondary coil SC of the specimen.

The ballistic galvanometer is standardized by means of the solenoid D, the two-way key K_1 being so arranged that the current passes through the primary of the solenoid instead of the coil PC; the secondary coil, wound on a tube inside the solenoid, is connected in series with the secondary coil SC of the specimen, and is kept continuously in the secondary circuit.

The electrodynamometer is standardized by suddenly turning over an earth-inductor EI placed in the secondary circuit, while a known current is passing through the primary circuit, and observing the "throw" produced in the movable coil B.

When measuring hysteresis the earth-inductor is replaced by a coil of the same resistance as the earth-coil but wound non-inductively.

The movable coil is quickly brought to rest by sending a very small current through it, in the right direction, while the primary current is flowing through the fixed coils. This is done by connecting one of its terminals to any point in a closed circuit consisting of a Leclanché cell, a fairly high resistance, and a piece of german-silver wire, and the other terminal through a tapping-key to a suitable point in the german-silver wire. The resistance R_3 is permanently connected in series in the secondary circuit in order to reduce the sensitiveness of the ballistic galvanometer or electrodynamometer when necessary.

If the maximum current be kept constant, but the resistance of each of the parts into which the primary circuit is divided by the key F increased in any ratio by increasing R_1 and R_2 respectively, then dC/dt will be increased in the same ratio. The main part of the variation in the primary resistance was made by varying R_1, the small resistance R_2 being used to adjust the current to any definite value.

The secondary resistance S was varied from about 23 ohms to 523 ohms, and the throws of the dynamometer coil for each induction were, as nearly as could be read, inversely proportional to the secondary resistance; the term bR/S in equation (4) was therefore negligible in comparison with $W+aR$. We thus have

$$W=U-aR. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If, for each value of the maximum magnetizing force, we measure U_1, U_2, U_3, the values of U when the voltages of the battery in the primary circuit are E, 2E, and 3E respectively, and the resistances of the primary circuit are R, 2R, and 3R respectively, then

$$W=2U_1-U_2=3U_2-2U_3.$$

By this means we can ascertain how nearly equation (5) holds for any particular experiment.

The results obtained for a specimen of wrought iron, sectional area 1·56 sq. cm., for E=8, 16, and 24 volts respectively are given in Table I., and are shown also in fig. 2, the curve giving the values of the hysteresis loss being marked A.

The resistance of the portion of the primary circuit between *a*, *b* (fig. 1) containing the battery and ammeter was very small compared with that of the rest of the circuit, so that no appreciable error was introduced by not varying R_2 in any definite manner. The values of W obtained by this means were found to agree within 5 per cent. with the values obtained by calculating from the areas of the cyclic B-H curves.

Table I.

H.	B.	E=8 volts. U_1.	E=16volts. U_2.	E=24 volts. U_3.	$2U_1-U_2$	$3U_2-2U_3$	(Mean) W.	U_3-W Eddy-Current Loss. X.
0.34	194	5·9	7·3	8·8	4·5	4·3	4·4	4·4
0·68	540	32·3	38·2	44·1	26·4	26·4	26·4	17·7
1·02	1205	154	169	185	139	137	138	47·0
1·36	2657	585	655·4	721	514·6	524	519·3	201·8
1·70	4629	1528	1640	1736	1416	1448	1432	304
2·04	6107	2471	2702	2919	2240	2268	2254	665
2·38	7139	3396	3714	4017	3078	3108	3093	924
2·72	8077	4242	4683	5124	3801	3801	3801	1323
3·06	8749	5159	5702	6211	4616	4684	4650	1561
3·40	9332	5940	6551	7161	5329	5331	5330	1831
4·01	10148	7297	8145	8960	6449	6515	6482	2478

We have seen (equation 5) that in these experiments U−W measures the eddy-current loss; in this specimen the eddy-current loss when E=24 volts amounts to more than 30 per cent. of the hysteresis loss. The values of the eddy-current loss for different inductions for E=24 volts are given in the last column of Table I., and are shown graphically in fig. 2 (Curve X.) (p. 124).

The values of U, W, and X are given in ergs per cub. cent. per cycle, X being the space-average of the eddy-current loss.

Experiments on a Wrought-iron Ring.

Mr. W. M. Mordey* has shown that the increase in the magnetic hysteresis which had been noticed in the iron cores

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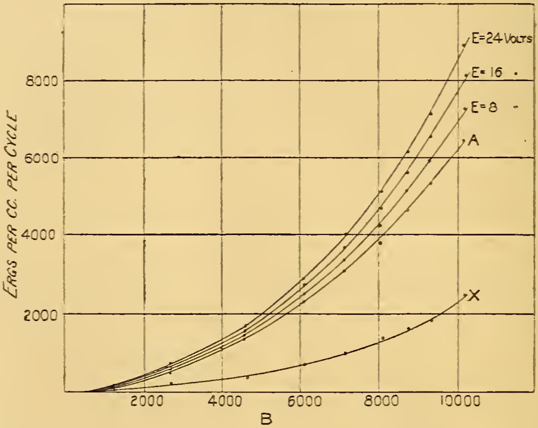
* Proc. Roy. Soc. vol. lvii. Jan. 1895, pp. 224–242.

of transformers is due to prolonged heating at comparatively low temperatures. The experiments of Parshall* and Roget† show that this increase of hysteresis in iron does not always take place, and that in specimens of inferior magnetic quality the rise in hysteresis is much less than in the best specimens of transformer iron.

Fig. 2.



In order to render the values of the hysteresis at different temperatures comparable, the specimen, which when annealed was of inferior magnetic quality, was first heated to about 800° C. and allowed to cool rapidly. In this condition the values of the hysteresis did not sensibly increase by prolonged exposure to any temperature.

The specimen having been demagnetized by reversals values of U_1 for various inductions were first obtained, using a battery of 8 volts, and afterwards a corresponding series of readings for U_2 was taken for the same magnetic forces using a battery of 16 volts. From these two sets of readings the hysteresis losses for different values of the maximum induction were found from the formula $W=2U_1-U_2$ as described above. The results for different temperatures are recorded in Table II., and are shown graphically in fig. 3 (p. 126).

Morris‡ has investigated the effect of temperature on the hysteresis loss of specimens of soft iron for a range of induction of ± 4550; his curves giving the values of the

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* Minutes Proc. Inst. C. E. vol. cxxvi. p. 244 (1896).

† Proc. Roy. Soc. vol. lxiii. pp. 258–267 (1898).

‡ Phil. Mag. vol. xliv. pp. 213–254 (1897).

TABLE II.

Temp. 15° C.			Temp. 202° C.			Temp. 331° C.		
H.	B.	W.	H.	B.	W.	H.	B.	W.
0·34	194	4·4	0·34	26·6	4·3	0·34	368	6·5
0·68	540	26·4	0·68	803	50·4	0·68	1186	76·3
1·02	1205	138	1·02	2085	282	0·88	2072	22·0
1·36	2657	519	1·36	4058	836	1·09	3391	522
1·70	4629	1432	1·70	5664	1484	1·22	4383	771
2·04	6107	2254	2·04	6895	2165	1·36	5072	1044
2·38	7139	3093	2·38	7929	2703	1·70	6648	1648
2·72	8077	3801	2·72	8668	3141	2·04	7683	2151
3·06	8749	4649	3·40	9669	3923	2·72	8869	2802
3·40	9332	5330	...	...	...	3·40	9919	3396
4·01	10148	6482						

Temp. 402° C.			Temp. 460° C.			Temp. 550° C.		
H.	B.	W.	H.	B.	W.	H.	B.	W.
0·34	451	8·6	0·34	610	13·0	0·27	632	13·0
0·54	1012	50·4	0·48	1239	67·7	0·41	1792	102
0·68	1730	134	0·61	2379	186	0·54	3818	344
0·82	2510	298	0·75	3604	407	0·68	5023	601
1·02	4088	637	0·95	5073	753	0·85	6156	827
1·19	5073	873	1·16	6205	1036	1·02	6895	1036
1·36	5811	1162	1·36	7092	1295	1·36	7979	1279
1·70	7141	1609	1·70	8028	1530	2·04	8869	1546
2·04	8077	1924	2·04	8752	1769	2·72	9919	1782
2·72	9102	2434	2·72	9569	2094			
3·40	9978	2787	3·40	10153	2335			

Temp. 620° C.			Temp. 678° C.			Temp. 730° C.		
H.	B.	W.	H.	B.	W.	H.	B.	W.
0·27	1134	36	0·14	464	4·3	0·136	599	13·0
0·34	2565	178	0·20	1256	44·6	0·204	1536	60·6
0·41	3471	252	0·27	2565	145	0·27	2843	151
0·51	4580	391	0·34	3631	243	0·34	3845	241
0·68	5861	633	0·41	4285	320	0·41	4539	312
0·85	6747	799	0·54	5565	447	0·54	5565	402
1·02	7240	929	0·68	6255	527	0·68	6304	497
1·36	8225	1075	1·02	7240	651	1·02	7190	614
2·04	8928	1279	1·36	7929	730	1·70	8126	664
2·72	9453	1389	2·04	8569	785	2·72	8717	755
3·40	9803	1452						

Temp. 748° C.			Temp. 768° C.		
H.	B.	W.	H.	B.	W.
0·136	844	17·4	0·1	700	11
0·204	2194	96·0	0·136	1605	41
0·27	3311	175	0·204	2243	86
0·34	4165	245	0·34	3685	142
0·54	5713	339	0·68	3845	169
1·22	6895	504	1·36	4058	186
2·04	7338	529			

hysteresis at different temperatures show that as the critical temperature is approached the hysteresis falls very rapidly.

Fig. 3.

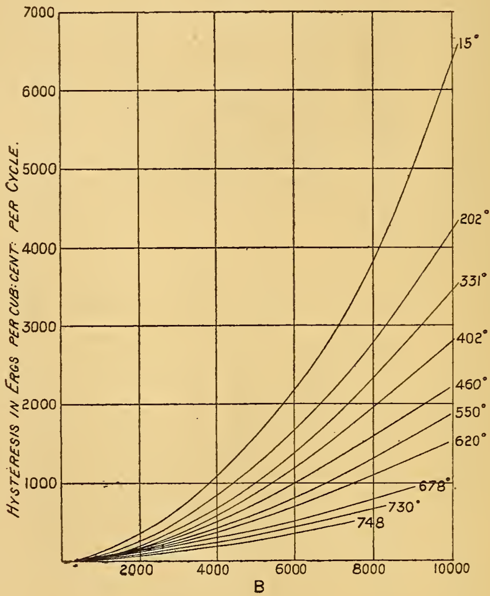
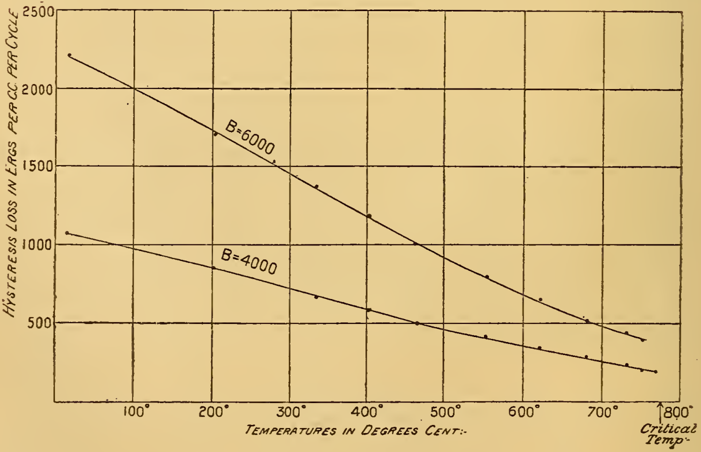


Fig. 4.



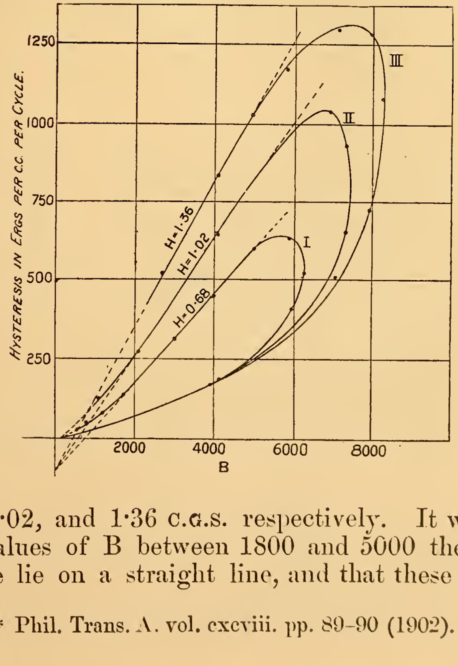
The corresponding curves which I obtained for maximum inductions of ±6000 and ±4000 are given in fig. 4. An induction of 6000 could not be obtained when the temperature had risen above about 750° C., but an induction of 4000 could be reached even when the temperature was only a few degrees below the critical temperature, which in this specimen is about 776° C.

It will be noticed that the fall in hysteresis with rise of temperature decreases as the critical temperature is approached. This is more noticeable in the case of the tungsten alloy, the corresponding curves for which are given in fig. 9.

Searle and Bedford* have studied the effect of strain on the hysteresis loss of iron, and have drawn curves showing the variation of hysteresis with induction for constant ranges of magnetic force. Their curves for any value of H show that through a considerable range of straining the hysteresis is a linear function of the induction. In the case of torsion the hysteresis for this part of the curve is given by $W = aH^{\frac{1}{2}}B - b$, where a and b are constants; for a specimen of soft iron they found that $a = 0·35$, $b = 600$, and for a steel rod $b = 0$.

Corresponding curves can be obtained from the data given in Table II., the hysteresis and induction being varied by heating. Fig. 5 gives three such curves for values of H of 0·68, 1·02, and 1·36 c.g.s. respectively. It will be seen that for values of B between 1800 and 5000 the points for each curve lie on a straight line, and that these lines, when

Fig. 5.



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* Phil. Trans. A. vol. cxcviii. pp. 89–90 (1902).

produced, pass through the same point $b = -100$ on the vertical axis. Within this range of induction, therefore, we have $W = f(H)B - b$. As near as can be determined $W = 0{\cdot}182H^{\frac{3}{4}}B - 100$.

For values of B below about 1800 the values of W are larger than those given by the equation. As the induction is increased beyond 5000 the hysteresis rises less rapidly to a maximum value and then decreases. This is in complete accordance with the experiments of Searle and Bedford, in which the induction is varied by straining. In their experiments, however, it was impracticable to continue the curve much beyond the point of maximum hysteresis. When the induction is varied by heating the curve may be traced until the critical temperature is reached. For low fields we thus get a closed curve, as shown in fig. 5, Curve I.

From the following table, which is obtained from Table II. by drawing curves showing the variation in hysteresis with temperature for constant fields, we see that the smaller the magnetic force the higher the temperature at which the point of maximum hysteresis occurs.

H.	Temperature for maximum hysteresis.	H.	Temperature for maximum hysteresis.
0·34	705° C.	1·36	480° C.
0·68	610 ,,	1·70	355 ,,
1·02	565 ,,	1·90	290 ,,

Experiments on the relation between temperature and magnetizing force in the magnetization of iron have been described in a previous paper*, where a curve is given showing the magnetizing force corresponding to the maximum permeability for different temperatures. A curve very similar to this is obtained by plotting magnetic force as ordinate, and the temperature at which the maximum hysteresis is reached as abscissa, the temperature giving the maximum hysteresis for any magnetic force being, as near as can be determined, the same as that at which the maximum permeability occurs for the corresponding magnetizing force.

"Ageing" of Iron.

The "ageing" of iron by continued heating has been already referred to. Mordey† has examined the effect for

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* R. L. Wills, Phil. Mag. vol. l. pp. 11–14, July 1900.

† Proc. Roy. Soc. vol. lvii. pp. 224–244, Jan. 1895.

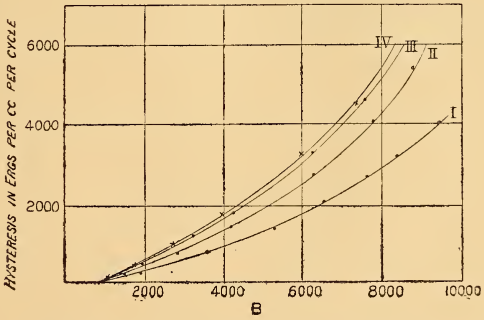
ordinary temperatures, but the later experiments of Roget* deal with temperatures ranging from 50° C. to 700° C. In these experiments the specimens were, however, removed from the oven, and the tests then made at ordinary atmospheric temperature. It appeared desirable to examine the effects produced by prolonged heating when the temperature is maintained constant and the specimen is not cooled for the hysteresis measurement.

Roget continued the heating at the lower temperatures for about a month and found that below 135° C. the hysteresis, for an induction of 4000, during this time increased, at first rapidly, but more and more slowly as time went on. For higher temperatures the hysteresis for the given induction reached a maximum value after a time depending on the temperatures. Then, as the heating was continued, the hysteresis fell, the rate of fall being greater for high than for low temperatures.

In the present series of experiments the specimen was first annealed and then the hysteresis for different ranges of induction measured at intervals, while the temperature was kept as nearly constant as was practicable.

The curves II. III. IV. (fig. 6) show the results of tests made at a temperature of 165° C., after continued heating for 16, 41, and 84 hours respectively; the curve I. gives the initial values of the hysteresis at the same temperature. For longer periods of heating at this temperature the hysteresis remained practically constant. After this constant condition was reached by prolonged exposure to any temperature, the hysteresis measured at that temperature was practically the same as its value after the specimen had been cooled to

Fig. 6.



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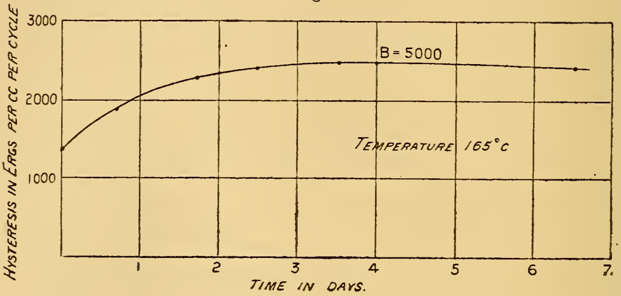
* Ibid. vol. lxiii. pp. 258–267 (1898), and vol. lxiv. pp. 150–156 (1898).

the ordinary temperature of the atmosphere. Reannealing completely restores the iron to its original condition.

Fig. 7 shows the variation of the hysteresis with time by prolonged heating at 165° C. for an induction of 5000. It will be noticed that the hysteresis increases rapidly at first, reaching a maximum value after about four days. Then it decreases slightly to a constant value.

Fig. 7.



Experiments on a Tungsten Alloy.

The rate of change in the permeability of iron as the temperature approaches very near to the critical temperature is so great that, throughout a range of several degrees in this region, only approximate values of the hysteresis could be obtained. Moreover, at such high temperatures the iron is in such a critical state that it was found that the process of demagnetizing by reversals does not entirely wipe out all the effects of previous magnetism, although the residual effect is only noticeable in extremely weak fields.

In the case of a specimen containing 4·5 per cent. tungsten the passage from the magnetic to the non-magnetic condition is much more gradual, and the demagnetizing process, even at the highest temperatures, removed all trace of residual magnetism. The variation of hysteresis loss with temperature in the neighbourhood of the critical temperature can therefore be much more satisfactorily examined with this alloy than with iron.

The results obtained at different temperatures are given in Table III., and hysteresis-induction curves plotted in fig. 8 (p. 132). From these curves the hysteresis-temperature curves shown in fig. 9 have been obtained; the scale of ordinates given applies to the curve for B=6000, the curve for B=2000 is drawn to a scale five times as large. It will be seen that as

TABLE III.

Temp. 15° C.			Temp. 200° C.			Temp. 256° C.		
H.	B.	W.	H.	B.	W.	H.	B.	W.
7·97	1152	293	6·38	1176	436	5·58	1342	500
10·36	3521	5008	8·77	3854	5490	7·97	4826	6373
11·96	5524	10594	10·36	6137	10939	10·36	7868	13495
14·35	8602	21021	15·15	9651	22391	15·15	10018	20900
16·74	10333	30033						

Temp. 315° C.			Temp. 364° C.			Temp. 412° C.		
H.	B.	W.	H.	B.	W.	H.	B.	W.
4·78	1433	639	3·98	1375	376	3·19	1408	300
6·77	4674	5077	5·58	4431	3998	4·78	4674	3585
8·77	7343	10806	6·78	6661	7485	6·38	7291	7233
13·55	9965	16991	9·57	9021	12078	11·16	9913	12411

Temp. 472° C.			Temp. 543° C.			Temp. 604° C.		
H.	B.	W.	H.	B.	W.	H.	B.	W.
2·47	1276	181	1·99	1500	178	1·196	1458	92
3·98	4917	2917	2·79	4992	2179	1·99	4219	1029
5·18	7081	5372	3·59	6556	3464	3·19	6923	2795
7·97	9179	8676	7·17	9126	6830	5·98	8235	3761

Temp. 648° C.			Temp. 670° C.		
H.	B.	W.	H.	B.	W.
1·036	1425	69	3·18	1359	103
1·99	4128	866	7·97	1873	129
6·38	5927	1730			

the temperature is raised the rate of fall of hysteresis increases, reaching a maximum at about 350° C. Then, as the temperature is increased, the hysteresis decreases less rapidly. The curve for B=2000 shows that the rate of fall of hysteresis continues to decrease even when a temperature of 670° C. is reached, which is only about 10° C. below the critical temperature.

Hysteresis-induction curves for constant magnetic forces corresponding to those given in fig. 10 (p. 133) for iron, can be obtained from the results given in Table III. For each magnetic force the values of B at the different temperatures were obtained from the B—H curves and the corresponding values of the hysteresis found from fig. 8.

Fig. 8.

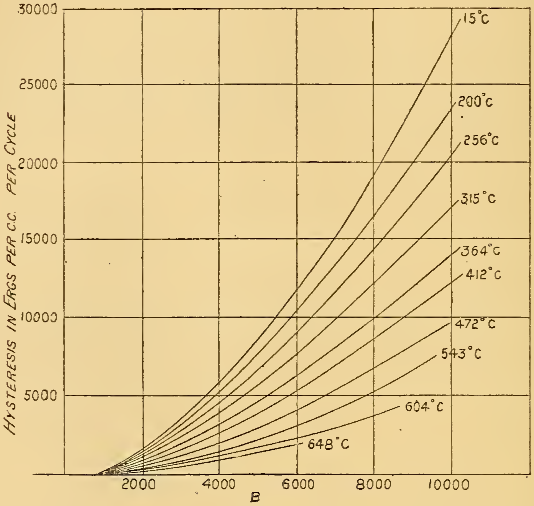
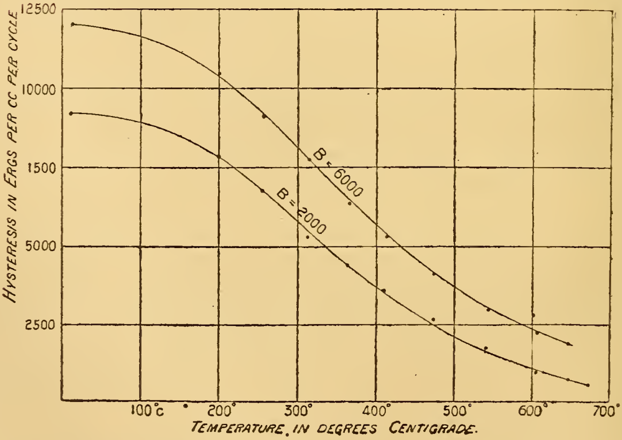
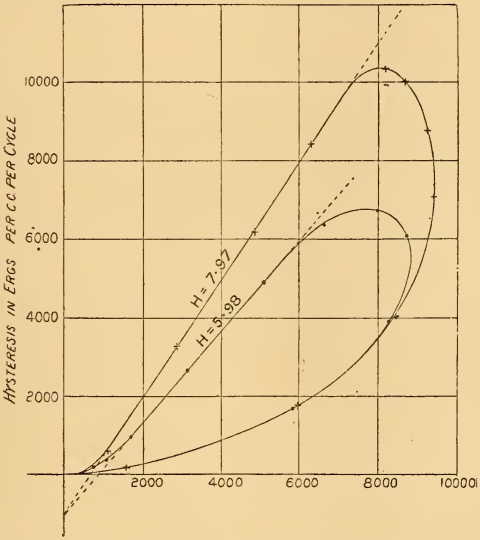


Fig. 9.



Two of these curves for H=5·98 and 7·97 c.g.s. respectively are shown in fig. 10. It will be seen that throughout a considerable range of induction the hysteresis is a linear function of the induction. As in the case of iron, the hysteresis losses, for very small inductions, are larger than those given by the equation, and as the induction increases beyond about 6000 the hysteresis increases less rapidly to a

Fig. 10.



maximum value. Then, as the temperature is raised, the hysteresis falls while the induction is still increasing. Finally, the hysteresis and induction both decrease very rapidly. For the straight part of the curve the equation giving the hysteresis as near as can be determined is $W = \cdot 24 H^{\cdot 88} B - 1000$. The smaller the magnetic force the higher the temperature at which the maximum hysteresis occurs; and, as in the case of iron, this temperature for any magnetic force is practically the same as that giving the maximum permeability with the corresponding magnetic force.

In conclusion I wish to express my thanks to Professor J. J. Thomson for useful suggestions and kindly interest during the progress of the work, and to Mr. G. F. C. Searle for help in the preliminary experiments.

Cavendish Laboratory, Cambridge.

VI. *On the Conditions necessary for Equipartition of Energy.* (*Note on* Mr. Jeans's *Paper*, Phil. Mag. November 1902.)

By S. H. Burbury, *F.R.S.*[*]

MR. JEANS'S conclusions are in substantial agreement with mine, as explained in this Magazine for December 1900, so far as regards the nature of the required conditions. On the question whether these conditions exist in any natural system, there is perhaps difference of opinion.

Mr. Jeans deals, as I also dealt, with two supposed proofs of the law:—(1) that given by Lord Rayleigh interpreting Maxwell in this Magazine for January 1900; (2) the proof given by Boltzmann in the *Vorlesungen über Gas Theorie*. As both profess to prove the truth of the law, the personal authority in favour of it is at first sight overwhelming. If, however, we find on examination that the two proofs are inconsistent with each other, the authority for the law is not the sum, but the difference of two very great magnitudes.

Rayleigh supposes a natural system defined by coordinates and momenta $q_1 \dots q_n$, $p_1 \dots p_n$, which is supposed to move under its own internal forces unaffected by any other body, and therefore to have constant total energy E. With that constant energy it passes in cycle through the phases $\phi_1 \dots \phi_r$. Mr. Jeans prefers to conceive the system as a "point" in a space of $6n$ dimensions. Next we suppose a great number of systems similar in constitution to the first, and each passing in cycle through the same phases $\phi_1 \dots \phi_r$ unaffected by any body external to itself. In that *ensemble* of systems, all having the same energy E, and passing in cycle through the same series of phases, the number of systems in any one of the phases $\phi_1 \dots \phi_r$ at any instant is equal to the number at the same instant in any other of the phases $\phi_1 \dots \phi_r$. This is what Willard Gibbs proves in 'Principles of Statistical Mechanics,' Chapter I.

If $\phi_1 \dots \phi_r$ include *all possible* phases in which the system can be with energy E, the law of equipartition follows. But there are two objections to this result, one namely that according to Mr. Jeans, with whom I agree, no such system exists or can exist in nature, and the other that the motion assumed is cyclic and reversible; whereas Boltzmann appears to me to prove (if only his fundamental assumption be admitted) that the motion in which energy is equally partitioned is irreversible. The two great authorities are thus inconsistent with each other. If the phases $\phi_1 \dots \phi_r$ through

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[*] Communicated by the Author.

which each system passes do *not* include all phases consistent with energy E, the law of equipartition is not proved by this method at all.

We come then to Boltzmann's proof. Here Mr. Jeans begins by saying "we must make Boltzmann's assumption that the gas is in a 'molekular-ungeordnet' state." I do not see the use of making it unless we can reason from it, and that we cannot do till we know what it means. It is possible to believe what we do not understand. It is not possible to reason about what we do not understand. Now Boltzmann gives us no adequate explanation of "molekular-ungeordnet." Nor does Mr. Jeans. Boltzmann makes no use of the assumption in argument. Nor does Mr. Jeans. Unless, indeed, the very definite assumption which they both (as I think) make, and which is stated below, is to be taken as the interpretation of "molekular-ungeordnet." Boltzmann assumes, namely, the independence of the molecular motions. If $FdUdVdW$ be the chance that molecule M shall have velocities $U \ldots U+dU$ &c., and $f\,dudvdw$ the chance that molecule m shall have velocities $u \ldots u+du$ &c.; then he assumes that the chance of the two events happening is $FfdU \ldots dw$. In other words, *the chances are independent at every instant*, and however near M and m be to each other. It is assumed, indeed, only when they are very near to each other, namely, at the point of an encounter. It is right to say that the assumption may be qualified as relating only to molecules approaching encounter. The condition thus assumed I call Condition A.

I understand Mr. Jeans to make precisely the same assumption in his equation (18), using $\rho\rho'$ as Boltzmann uses Ff.

If that assumption be made, the law of equipartition follows from it without any use, or any further use, of "molekular ungeordnet."

If that assumption be, as I maintain, untrue, the product F_f cannot be used as Boltzmann uses it, and the reasoning fails notwithstanding the "molekular-ungeordnet" hypothesis.

I think therefore that the one sufficient and necessary condition for equipartition of energy is that Condition A shall exist at every instant; neither more nor less than this, nor any different thing.

I have said that Mr. Jeans's proof rests on the same assumption as Boltzmann's; and must therefore, like Boltzmann's, stand or fall with the truth of that assumption. It may nevertheless be that a new proof founded on the same assumption is valuable.

VII. *Note on the Theory of the Fortnightly Tide.*

By Lord RAYLEIGH, *O.M., F.R.S.*[*]

AN adequate calculation *à priori* of the tide of fortnightly period—that which depends upon the moon's motion in declination— would be of great interest as affording the means, by comparison with observation, of determining the extent to which the solid earth yields to the tide-generating force. On the assumption that the fortnightly tide over an absolutely rigid earth would be sensibly equal to its "equilibrium value," Prof. G. Darwin[†] has estimated that the actual rigidity must be at least as great as that of steel, in accordance with the earlier surmises of Lord Kelvin.

But is an "equilibrium theory" adequate? The known properties of a system vibrating about a configuration of thoroughly stable equilibrium would certainly suggest an affirmative answer, when it is considered that a fortnight is a long period in comparison with those of the more obvious free oscillations. It is to be remembered, however, that a tidally undisturbed sea is not in equilibrium, and that in virtue of the rotation of the earth the tides are really oscillations about a condition of *steady motion*. In Laplace's theory the rotation of the earth is taken fully into account, but the sea must be supposed to cover the entire globe, or at any rate to be bounded only by coasts running all round the globe along parallels of latitude. The resulting differential equation was not solved by Laplace, who contented himself with remarking that in virtue of friction the solution for the case of fortnightly and (still more) semi-annual tides could not differ much from the "equilibrium values."

The sufficiency of Laplace's argument has been questioned, and apparently with reason, by Darwin[‡], who accordingly resumed Laplace's differential equation in which frictional forces are neglected. Taking the case of an ocean of uniform depth completely covering the globe and following the indications of Lord Kelvin[§], he arrives at a complete evaluation of Laplace's "Oscillation of the First Species." A summary of Darwin's work has been given by Lamb[||] from which the following extracts are taken. The equilibrium

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[*] Communicated by the Author.

[†] Thomson & Tait's 'Natural Philosophy,' 2nd ed. vol. i. pt. ii. p. 460 (1883).

[‡] Proceedings of the Royal Society, vol. xli. p. 337 (1886).

[§] Phil. Mag. vol. l. p. 280 (1875).

[||] Hydrodynamics, § 210, Cambridge, 1895.

value of the fortnightly tide being

$$\overline{\zeta}=\mathrm{H}'(\tfrac{1}{3}-\mu^2),$$

the actual tide for a depth of 7260 feet is found to be

$$\zeta/\mathrm{H}' = \cdot 1515 - 1\cdot 0000\,\mu^2 + 1\cdot 5153\,\mu^4 - 1\cdot 2120\,\mu^6$$
$$-\cdot 2076\,\mu^{10} + \cdot 0516\,\mu^{12} - \cdot 0097\,\mu^{14} + \cdot 0018\,\mu^{16} - \cdot 0002\,\mu^{18},$$

whence at the poles $(\mu = \pm 1)$

$$\zeta = -\tfrac{2}{3}\mathrm{H}' \times \cdot 154,$$

and at the equator $(\mu = 0)$

$$\zeta = \tfrac{1}{3}\mathrm{H}' \times \cdot 455.$$

Again, for a depth of 29040 feet, we get

$$\zeta/\mathrm{H}' = \cdot 2359 - 1\cdot 000\,\mu^2 + \cdot 5898\,\mu^4$$
$$-\cdot 1623\,\mu^6 + \cdot 0258\,\mu^8 - \cdot 0026\,\mu^{10} + \cdot 0002\,\mu^{12},$$

making at the poles

$$\zeta = -\tfrac{2}{3}\mathrm{H}' \times \cdot 470,$$

and at the equator

$$\zeta = \tfrac{1}{3}\mathrm{H}' \times \cdot 708.$$

It appears that with such oceans as we have to deal with the tide thus calculated is less than half its equilibrium amount.

The large discrepancy here exhibited leads Darwin to doubt whether "it will ever be possible to evaluate the effective rigidity of the earth's mass by means of tidal observations."

From the point of view of general mechanical theory, the question at once arises as to what is the meaning of this considerable deviation of a long-period oscillation from its equilibrium value? A satisfactory answer has been provided by Lamb *; and I propose to consider the question further from this point of view in order to estimate if possible how far an equilibrium theory may apply to the fortnightly tides of the actual ocean.

The tidal oscillations are included in the general equations of small vibrations, provided that we retain in the latter the so-called gyrostatic terms. By a suitable choice of coordinates, as in the usual theory of normal coordinates, these

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* Hydrodynamics, §§ 196, 198, 207.

equations may be reduced to the form

$$\left.\begin{array}{l} a_1\ddot{q}_1+c_1q_1 \qquad\qquad +\beta_{12}\dot{q}_2+\beta_{13}\dot{q}_3+\ldots=\mathrm{Q}_1, \\ a_2\ddot{q}_2+c_2q_2+\beta_{21}\dot{q}_1 \qquad\qquad +\beta_{23}\dot{q}_3+\ldots=\mathrm{Q}_2, \\ a_3\ddot{q}_3+c_3q_3+\beta_{31}\dot{q}_1+\beta_{32}\dot{q}_2 \qquad\qquad +\ldots=\mathrm{Q}_3, \\ \ldots\ldots\ldots\ldots\ldots\ldots \end{array}\right\} \quad . \quad . \quad (1)$$

in which

$$\beta_{rs}=-\beta_{sr}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From these we may fall back upon the case of small oscillations about stable equilibrium by omitting the terms in β; but in general tidal theory these terms are to be retained. If the oscillations are free, the quantities Q, representing impressed forces, are to be omitted.

If the coefficients β are *small*, an approximate theory of the free vibrations may be developed on the lines of 'Theory of Sound,' § 102, where there are supposed to be small dissipative (but no rotatory) terms. For example, the frequencies are unaltered if we neglect the *squares* of the β's. Further, the next approximation shows that the frequency of the slowest vibration is *diminished* by the operation of the β's; or more generally that the effect of the β's is to cause the values of the various frequencies to *repel* one another.

To investigate forced vibrations of given period we are to assume that all the variables are proportional to $e^{i\sigma t}$, where σ is real. If the period is very long, σ is correspondingly small, and the terms in $\ddot{q}$ and $\dot{q}$ diminish generally in importance relatively to the terms in q. In the limit the latter terms alone survive, and we get

$$q_1=\mathrm{Q}_1/c_1, \qquad q_2=\mathrm{Q}_2/c_2, \quad \&c. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which are the "equilibrium values." But, as Prof. Lamb has shown, exceptions may arise when one or more of the c's vanish. This state of things implies the possibility of steady motions of disturbance in the absence of impressed forces. For example, if $c_2=0$, we have as a solution, $\dot{q}_2=$ constant, with

$$q_1=-\beta_{12}\dot{q}_2/c_1, \qquad q_3=-\beta_{32}\dot{q}_2/c_3, \quad \&c.$$

In illustration Prof. Lamb considers the case of two degrees of freedom, for which the general equations are

$$\left.\begin{array}{l} a_1\ddot{q}_1+c_1q_1+\beta\dot{q}_2=\mathrm{Q}_1, \\ a_2\ddot{q}_2+c_2q_2-\beta\dot{q}_1=\mathrm{Q}_2; \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

supposing that $c_2=0$ and also that $Q_2=0$, while Q_1 remaining finite is proportional to $e^{i\sigma t}$, as usual. We find

$$q_1=\frac{a_2 Q_1}{a_2(c_1-a_1\sigma^2)+\beta^2}, \qquad \dot{q}_2=\frac{\beta Q_1}{a_2(c_1-a_1\sigma^2)+\beta^2}\,; \quad . \quad (5)$$

so that in the case of a disturbance of very long period when σ approaches zero,

$$q_1=\frac{Q_1}{c_1+\beta^2/a_2}, \qquad \dot{q}_2=\frac{\beta Q_1}{a_2 c_1+\beta^2}. \quad . \quad . \quad . \quad . \quad (6)$$

Since a_2 is positive, q_1 is *less* than its equilibrium value; and it is accompanied by a motion of type q_2, although there is no extraneous force of the latter type.

It is clear then that in cases where a steady motion of disturbance is possible the outcome of an extraneous force of long period may differ greatly from what the equilibrium theory would suggest. It may, however, be remarked that the particular problem above investigated is rather special in character. In illustration of this let us suppose that there are *three* degrees of freedom, and that c_2, c_3, Q_2, Q_3 are evanescent. The equations then become

$$\begin{aligned}(c_1-\sigma^2 a_1)q_1+i\sigma\beta_{12}q_2+i\sigma\beta_{13}q_3&=Q_1,\\ -\sigma a_2 q_2 \quad +i\beta_{21}q_1 \quad +i\beta_{23}q_3 \quad &=0,\\ -\sigma a_3 q_3 \quad +i\beta_{31}q_1 \quad +i\beta_{32}q_2 \quad &=0\,;\end{aligned}$$

whence, regard being paid to (2),

$$q_1\left\{(c_1-\sigma^2 a_1)+\frac{\sigma^2(a_3\beta_{12}{}^2+a_2\beta_{13}{}^2)}{\sigma^2 a_2 a_3-\beta_{23}{}^2}\right\}=Q_1. \quad . \quad (7)$$

When $\sigma=0$, the value of q_1 reduces to Q_1/c_1, unless $\beta_{23}=0$, so that in general the equilibrium value applies. But this is only so far as regards q_1. The corresponding values of q_2, q_3 are

$$q_2=-q_1\beta_{31}/\beta_{32}, \qquad q_3=-q_1\beta_{21}/\beta_{23}\,; \quad . \quad . \quad (8)$$

and thus the equilibrium solution, considered as a whole, is finitely departed from. And a consideration of the general equations (1) shows that it is only in very special cases that there can be any other outcome when the possibility of steady motion of disturbance is admitted.

It thus becomes of great importance in tidal theory to ascertain what steady motions are possible, and this question also has been treated by Lamb (§ 207). It may be convenient to repeat his statement. In terms of the usual polar coordinates Laplace's equations are

$$\frac{du}{dt}-2nv\cos\theta=-\frac{g}{a}\frac{d}{d\theta}(\zeta-\bar{\zeta}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\frac{dv}{dt}+2nu\cos\theta=-\frac{g}{a\sin\theta}\frac{d}{d\omega}(\zeta-\bar{\zeta}), \quad . \quad . \quad . \quad (10)$$

$$\frac{d\zeta}{dt}=-\frac{1}{a\sin\theta}\left\{\frac{d(hu\sin\theta)}{d\theta}+\frac{d(hv)}{d\omega}\right\}, \quad . \quad . \quad (11)$$

where u, v are the velocities along and perpendicular to the meridian, ζ is the elevation at any point, $\bar{\zeta}$ the equilibrium value of ζ, a denotes the earth's radius, n the angular velocity of rotation, and h the depth of the ocean at any point. To determine the free steady motions, we are to put $\bar{\zeta}=0$ as well as du/dt, dv/dt, $d\zeta/dt$. Thus

$$u=-\frac{g}{2na\sin\theta\cos\theta}\frac{d\zeta}{d\omega}, \qquad v=\frac{g}{2na\cos\theta}\frac{d\zeta}{d\theta}; \quad . \quad (12)$$

and

$$\frac{d(h\sec\theta)}{d\theta}\frac{d\zeta}{d\omega}-\frac{d(h\sec\theta)}{d\omega}\frac{d\zeta}{d\theta}=0. \quad . \quad . \quad . \quad (13)$$

If $h\sec\theta$ be constant, (13) is satisfied identically. In any other case a restriction is imposed upon ζ. If h be constant or a function of the latitude only, ζ must be independent of ω; in other words the elevation must be symmetrical about the polar axis. In correspondence therewith u must be zero and v constant along each parallel of latitude.

In the application to an ocean completely covering the earth, such as is considered in Darwin's solution, the above conditions are easily satisfied, and the free steady motions, thus shown to be possible, explain the large deviation of the calculated fortnightly tide from the equilibrium value. What does not appear to have been sufficiently recognized is the extent to which this state of things must be disturbed by the limitations of the actual ocean. Since v must be constant along every parallel of latitude, it follows that a single barrier extending from pole to pole would suffice to render impossible all steady motion; and when this condition is secured a tide of sufficiently long period cannot deviate from its equilibrium value. Now the actual state of things corresponds more nearly to the latter than to the former ideal. From the north pole to Cape Horn the barriers exist; and thus it is only in the region south of Cape Horn that the circulating steady motion can establish itself. It would seem that this restricted and not wholly unobstructed area would fail to disturb greatly the state of things that would prevail, were every parallel of latitude barred. If this conclusion be admitted, the theoretical fortnightly tide will not differ materially from its equilibrium value, and Darwin's former calculation as to the earth's rigidity will regain its significance.

Some caution is required in estimating the weight of the argument above adduced. Though there were no free disturbance possible of *infinitely* long period, it would come to the same, or to a worse, thing if free periods existed comparable with that of the forces, which is itself by hypothesis a long period. On this account a blocking of every parallel of latitude by small detached islands would not suffice, although meeting the theoretical requirement of the limiting case.

It would serve as a check and be otherwise interesting if it were possible to calculate the fortnightly tide for an ocean of uniform depth *bounded by two meridians*. The solution must differ widely from that appropriate to an unlimited ocean; but, although the conditions are apparently simple, it does not seem to be attainable by Laplace's methods. A similar solution for the semi-diurnal tide would be interesting for other reasons.

In any case I think that observations and reductions of the fortnightly tide should be pursued. Observation is competent to determine not merely the general magnitude of the tide but the law as dependent upon latitude and longitude. Should the observed law conform to that of the equilibrium theory, it would go a long way to verify *à posteriori* the applicability of this theory to the circumstances of the case.

VIII. *The Thermomagnetic and Related Properties of Crystalline Bismuth.* By Louis Lownds, *B.Sc.* (*Lond.*), *Ph.D.* (*Berlin*), 1851 *Exhibition Research Scholar, Univ. Coll., Nottingham**.

§ 1. A FORMER paper, published in the Philosophical Magazine for October 1901, gave an account of the Longitudinal and Transversal Thermomagnetic Effects and the Thermoelectric Properties of a Plate of Bismuth cut from a crystal of the metal in the possession of Prof. Groth of München. The present contains an account of the investigation of the change of electrical resistance

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* Communicated by the Author.

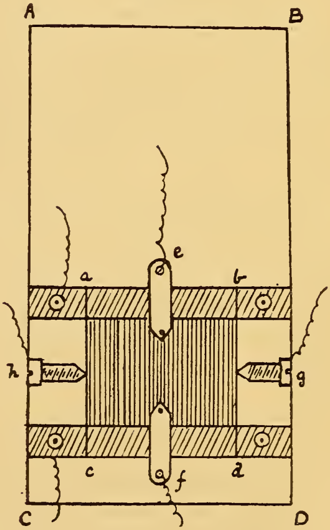
in the magnetic field, the Hall effect, and the conductivity for heat in and out of the magnetic field for the same crystal specimen.

The change of electrical resistance and Hall effect were determined along and at right angles to the chief crystallographic axis and at three different temperatures, viz. (1) at room temperature; (2) at −79° C.; (3) at −186° C. The ratio of the conductivities for heat along and at right angles to the chief crystallographic axis was determined in zero field and in a field of 4980 C.G.S. units.

§ 2. *The Change of Electrical Resistance in the Magnetic Field.*

The crystalline plate *abcd* (fig. 1) was mounted in a small wooden frame ABCD, 4½ cms. long, 2½ cms. wide, and 1 cm. thick. A rectangular piece was cut out at *abcd*, so that the plate fitted exactly, the front surface of the crystal being flush with the surface of the wood. Two such frames were used, according as the effect was to be measured along or at right angles to the chief crystallographic axis. A current was led through the plate by means of wires soldered to the copper strips at *ab*, *cd*. These strips were firmly screwed down on to the crystal, narrow strips of tinfoil being placed between them and the plate in order to ensure good contact and to avoid fracture. Two brass spring-contacts, *e* and *f*, served as electrodes for measuring the difference of electric potential

Fig. 1.



between any two points on the plate. These contacts were adjusted so as to touch two points lying on a line at right angles to the copper strips. A current of known value was then passed through the plate, and the difference of potential between these two points was measured. The field was then excited and the determination repeated, the current through the plate being adjusted to the same value as before. If e_0 is the difference of potential without the field, w_0 the resistance between the points, and I the current strength, e and w the corresponding values with the field, then

$$\mathrm{I} = \frac{e_0}{w_0} = \frac{e}{w}$$

$$\therefore \frac{w}{w_0} = \frac{e}{e_0}$$

$$\therefore \left.\begin{array}{r}\text{Percentage Increase}\\ \text{of Resistance in Field}\end{array}\right\} = 100\,\frac{w-w_0}{w_0} = 100\,\frac{e-e_0}{e_0}.$$

The current was only made momentarily, so that heating effects were avoided. The electromotive force was measured by the compensation method, a D'Arsonval galvanometer being used of resistance 1000 ohms. Induction effects from the current used to produce the fall of potential were avoided by using a key which first made this current, and afterwards closed the galvanometer circuit. The magnetic field being completed the whole time, while observations were being made with field, had no inductive influence. The current I, which was of the order 1 to 2 amperes, was measured by an amperemeter reading to $\frac{1}{2}$ per cent. The electromotive forces were of the order 300 to 600 microvolts and could be determined to at least 1 per cent.

The observations were made :—

(1) At ordinary temperature, the whole plate being immersed in a petroleum bath.

(2) At −79° C. in a mixture of solid carbon dioxide and ether, contained in a silvered Dewar vessel.

(3) At −186° C. in liquid air.

The absolute resistance between the two electrodes e and f, viz., $w_0 = \frac{e_0}{\mathrm{I}}$ enables us to calculate approximately the specific resistance ρ of the plate.

We have

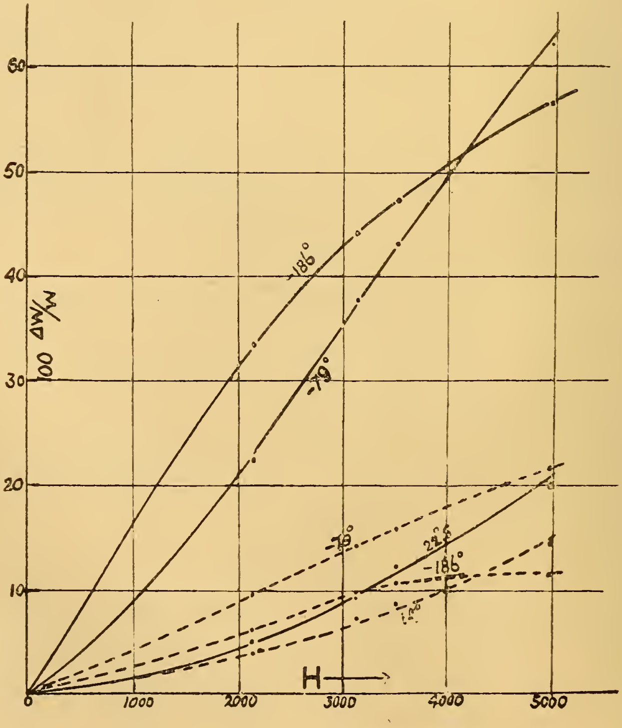
$$\rho = \frac{w_0 \,.\, a}{l},$$

where a is the cross-section of the plate in square centimetres, and l the distance in centimetres between the electrodes. Since l was of the order 5 mms. and slight irregularities existed on the edges of the crystal, this result can only be regarded as approximate. The determination of ρ for any one of the two directions in the plate was made at the three temperatures without altering the positions of the contacts. The results for the percentage change of resistance are given in Table I., and represented graphically in fig. 2. The full-

TABLE I.—Change of Resistance.

	Parallel to Crystallographic Axis.			Perpendicular to Crystallographic Axis.		
Temp. ...	22°·5.	−79°.	−186°.	14°.	−79°.	−186°.
Field.	$100\frac{w-w_0}{w_0}$	$100\frac{w-w_0}{w_0}$	$100\frac{w-w_0}{w_0}$	$100\frac{w-w_0}{w_0}$	$100\frac{w-w_0}{w_0}$	$100\frac{w-w_0}{w_0}$
2120	5·0	22·5	33·5	3·9	9·6	6·1
3120	9·2	37·7	44·2	7·3	14·2	9·7
3500	12·1	43·1	47·4	8·6	15·7	10·6
4980	19·8	62·1	56·5	14·3	21·5	11·4

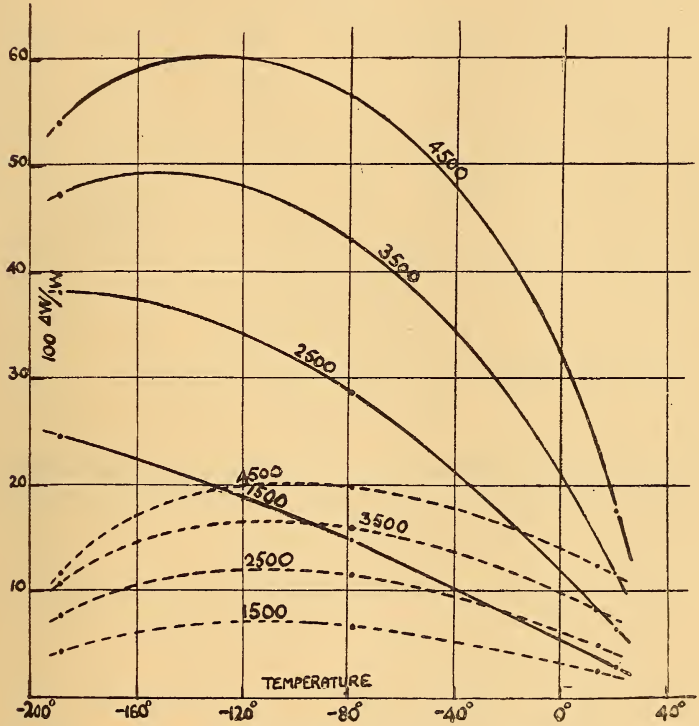
Fig. 2.



line curves refer to the case parallel to the chief crystallographic axis, the dotted curves to the case at right angles to this axis

Fig. 3 is drawn from the values in fig. 2, and coordinates temperature with percentage change of resistance for four different field-strengths. The specific resistances for the two directions and in zero field for the several temperatures are given in Table II., together with values obtained by van Everdingen * at ordinary temperature.

Fig. 3.



According to Everdingen's observations the ratio of the specific resistances for the two directions at 15° C. is as 1 : 1·68, whereas for the crystal plate used by me it is as 1 : 1·78. The ratio of the thermoelectric forces with respect to copper for the two directions parallel and perpendicular to the crystallographic axis was found to be 1 : 1·91 (between 10° C. and 90° C.) †.

[*] E. van Everdingen, Comm. Phys. Lab. Univ. Leyden, lxi. (1900).

[†] L. Lownds, Phil. Mag. October 1901.

TABLE II.

Parallel to Axis.		Perpendicular to Axis.	
Temperature.	ρ.	Temperature.	ρ.
15°	269000 C.G.S.	15°	151000 C.G.S.
− 79	379000	− 79	135000
−186	234000	−186	86000
15°	348000	15°	* 204000 * 229000 * 232000

* Everdingen.

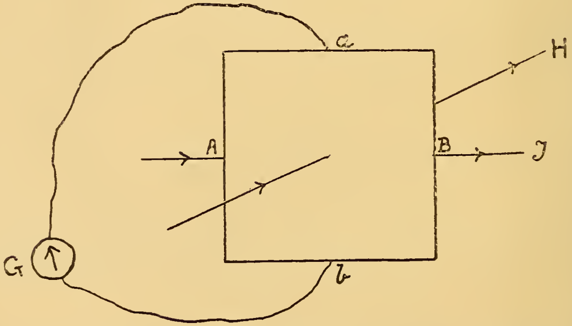
§ 3. *The Hall Effect.*

The Hall constant C is defined by the equation

$$E = C . \frac{\mathfrak{J} . H}{d},$$

where E is the difference of potential between points *a* and *b* in fig. 4 when a current of strength ℑ flows from A to B, the

Fig. 4.



lines of force being at right angles to the plane of the plate. In the above, *d* is the thickness of the plate. Before the magnetic field is excited *a* and *b* are supposed to lie upon an equipotential line. If the current ℑ is from A to B, and the field H in the direction indicated by the arrow, then, when the Hall current is from *a* through the galvanometer G to *b*, the effect is positive. At ordinary temperatures the sign is negative for Bismuth. Two different cases were possible for the measurement of the Hall effect with this crystal plate.

The magnetic field was always at right angles to the plane of the plate, and therefore perpendicular to the crystallographic axis, while the current $\mathfrak{J}$ was either parallel or perpendicular to this axis. This current was led through the plate by means of wires soldered to the copper strips ab and cd. Two small brass screws g and h (fig. 1), which pressed firmly on to the sides of the crystal, were used as electrodes for measuring the Hall electromotive force E. g could be moved in the direction of the length of the crystal, and was adjusted so that when the current $\mathfrak{J}$ passed the electromotive force between g and h was as small as possible. It was found impossible to adjust the contacts so that they lay exactly on an equipotential line, but the error due to this imperfect adjustment makes no perceptible difference in the mean value of the constant. The electromotive force was measured by the compensation method. By this method one is independent of the change of resistance in the plate due to the magnetic field. Before exciting the field a current of known strength was sent through the plate, and the electromotive force between the points g and h measured. The field was then excited, the current $\mathfrak{J}$ adjusted to the same value, and the electromotive force between g and h again measured. The difference between these two readings gave the Hall electromotive force E. The measurements were repeated with the current reversed, and again, for both directions of current with the magnetic field in the opposite direction. The mean of the four values was taken as the measure of the effect. In order to avoid heating of the plate due to the passage of the current $\mathfrak{J}$, the circuit was only closed momentarily. A special key served to close this primary circuit, and immediately afterwards the secondary circuit connecting the Hall electrodes; if the Hall electromotive force was not exactly compensated then a deflexion of the galvanometer was noted. By repeated trials two adjustments could be found, for one of which a deflexion could be obtained in one direction, and for the other in the opposite direction. These adjustments differed from one another by not more than 1 per cent., and the mean was taken as the balance-point. By closing the primary circuit first, induction effects of the primary on the secondary circuit were avoided.

Tables III. and IV. contain the results for the two directions and at the three temperatures, and the curves (fig. 5, p. 150) give a graphic representation. The full-line curves correspond to the case when the current $\mathfrak{J}$ is parallel to the chief crystallographic axis, and the broken-line curves to the case when $\mathfrak{J}$ is at right angles to this axis.

Table III.

Hall Effect.—Primary Current 𝔍 ‖ to the Crystallographic Axis.

H.	𝔍.	Temperature 16°.			Temperature −79°.			Temperature −186°.		
		Hall E.M.F.	E.	C.	Hall E.M.F.	E.	C.	Hall E.M.F.	E.	C.
	Amp.	Mv.	Mv.		Mv.	Mv.		Mv.	Mv.	
+4980	+2	−289	290	−10·3	−109	89	−3·16	+187	222	+7·88
+4980	−2	+302			+107			−188		
−4980	+2	+287			+ 69			−255		
−4980	−2	−284			− 71			+258		
+3500	+2	−227	226	−11·4	−127	117	−5·92	+148	175	+8·85
+3500	−2	+232			+135			−150		
−3500	+2	+222			+104			−203		
−3500	−2	−222			−104			+199		
+3120	+2	−204	200	−11·3	−134	122	−6·92	+137	161	+9·13
+3120	−2	+206			+133			−139		
−3120	+2	+196			+111			−186		
−3120	−2	−196			−110			+183		
+2120	+2	−145	142	−11·8	−122	115	−9·60	+111	125	+10·4
+2120	−2	+146			+124			−109		
−2120	+2	+141			+108			−141		
−2120	−2	−138			−107			+141		

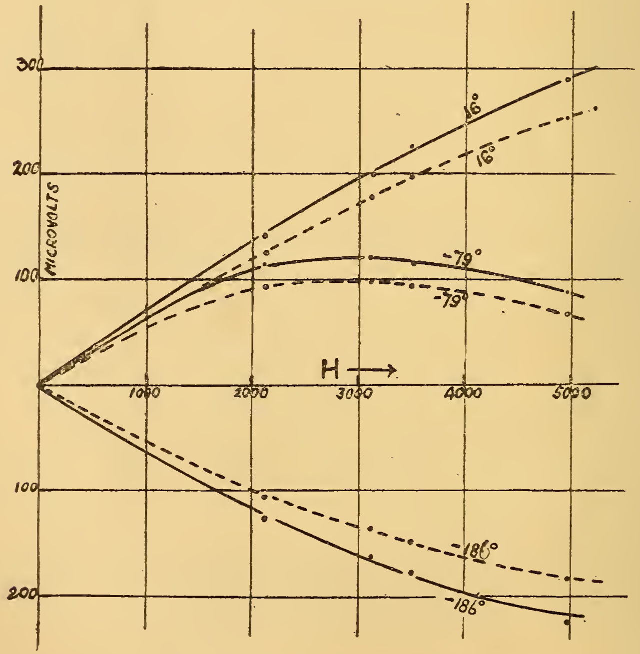
TABLE IV.

Hall Effect.—Primary Current ⊥ to the Crystallographic Axis.

H.	ℑ.	Temperature 16°.			Temperature −79°.			Temperature −186°.		
		Hall E.M.F.	E.	C.	Hall E.M.F.	E.	C.	Hall E.M.F.	E.	C.
	Amp.	Mv.	Mv.		Mv.	Mv.		Mv.	Mv.	
+4980	+2	−256	254	− 9·02	−162	67	−2·38	+100	183	+6·51
+4980	−2	+256			+155			− 99		
−4980	+2	+261			− 20			−271		
−4980	−2	−245			+ 29			+264		
+3500	+2	−194	197	− 9·97	−196	95	−4·81	+ 76	148	+7·51
+3500	−2	+194			+198			− 77		
−3500	+2	+208			0			−225		
−3500	−2	−195			+ 13			+216		
+3120	+2	−178	178	−10·1	−151	99	− 5·61	+ 70	135	+7·62
+3120	−2	+175			+158			− 69		
−3120	+2	+185			+ 43			−202		
−3120	−2	−174			− 44			+198		
+2120	+2	−128	125	−10·4	−148	94	−7·85	+ 58	106	+8·89
+2120	−2	+124			+144			− 59		
−2120	+2	+127			+ 45			−161		
−2120	−2	−123			− 42			+148		

The direction of the current $\mathfrak{J}$ with respect to the crystallographic axis appears to have very small influence on the constant C. This has also been observed by van Everdingen* at ordinary temperature. He found at a temperature of 15° C. and for a field of 4600 C.G.S. units C = −8·0, and for a field of 2600 C.G.S. units C = −10·2, when the current was parallel to the chief axis. In the other case, using three different plates, he found for 4600 C.G.S. field-strength C = −10·6, −8·8, and −8·2, and for the field 2600 C.G.S. C = −12·6, −11·1, and −10·6. These values are of the same order as those found by me. Fig. 6 is obtained from fig. 5 by taking the mean of the values for the two directions of $\mathfrak{J}$.

Fig. 5.



It is to be noted that at ordinary temperature there is very little dissymmetry in the effect for opposite directions of the field. At low temperatures this dissymmetry is more marked. It appears to vary somewhat with the setting up of the crystal, as will be seen from Table V., which contains readings for two different settings up of the crystal.

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* E. van Everdingen, *loc. cit.*

Fig. 6.

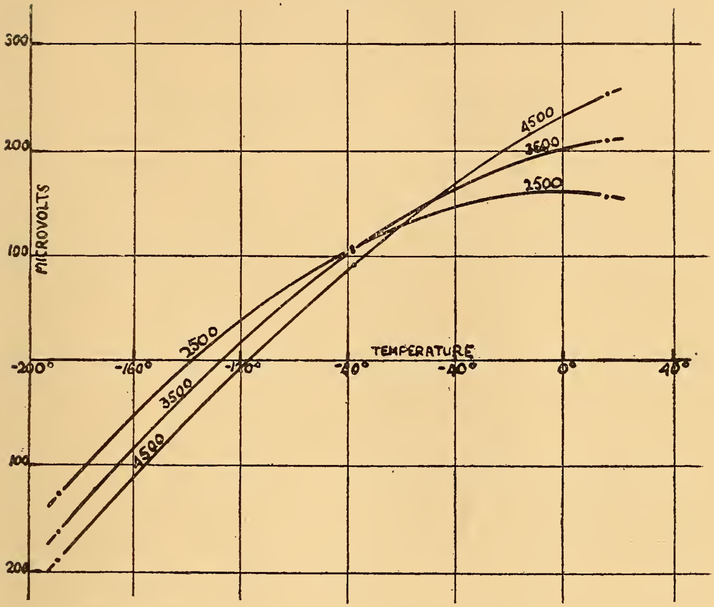

TABLE V.

Hall Effect. Temperature −186°.

H.	ℑ (amp.)	1st setting up.		2nd setting up.	
		E.M.F.	E.	E.M.F.	E.
0	+2	−153	Mv.	−141	Mv.
+4980	+2	− 53	+100	− 34	+107
0	+2	−153		−142	
0	−2	+153		+142	
+4980	−2	+ 54	− 99	+ 36	−107
0	−2	+153		+144	
0	+2	−153		−147	
−4980	+2	−430	−271	−409	−258
0	+2	−166		−156	
0	−2	+166		+156	
−4980	−2	+430	+264	+409	+256
0	−2	+160		+151	
			Mean = 183		Mean = 182

Table VI. shows that the mean Hall electromotive force is not appreciably influenced by the Hall electrodes *g* and *h* not lying exactly upon an equipotential line.

TABLE VI.

Hall Effect. Temperature 16°.

H.	$\mathfrak{J}$ (amp.).	1st Adjustment.		2nd Adjustment.	
		E.M.F.	E.	E.M.F.	E.
0	+2	− 61	v.	+ 9	Mv.
+4980	+2	−317	−256	−228	−237
0	+2	− 61		+ 9	
0	−2	+ 58		− 12	
+4980	−2	+314	+256	+230	+241
0	−2	+ 58		− 11	
0	+2	− 62		+ 9	
−4980	+2	+199	+261	+281	+271
0	+2	− 62		+ 12	
0	−2	+ 52		− 16	
−4980	−2	−193	−245	−269	−253
0	−2	+ 52		− 16	
			Mean = 254		Mean = 250

§ 4. *The Conductivity for Heat.*

The other properties of the crystal, such as change of resistance, Hall effect, &c., have been determined for the two directions and for different field-strengths, and at several different temperatures. The determination of the conductivity for heat, for the two directions, and its variation with temperature, both in and out of the magnetic field, was not possible, since the general methods for the determination of heat-conductivity are not applicable to so small a specimen as we have to deal with in the present. I have sought, however, by the method due to de Senarmont* to get approximate values of the ratio of the conductivities for the two directions in and out of the magnetic field. The crystal was well cleaned and coated with a thin layer of elaidic acid. This has been recommended by Voigt† in preference to the mixture of wax and turpentine used by de Senarmont. On the centre of the crystal plate was pressed the pointed end of a stout copper wire, 1 metre long, which was heated in the middle by means of a Bunsen burner. The isothermal curves on the plate are

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[*] De Senarmont, *C. R.* xxv. pp. 459, 707 (1847).

[†] W. Voigt, *Göttingen Nachricht.* 1896, Heft iii.

in the form of ellipses, the squares of whose axes are proportional to the conductivity in that direction. In the magnetic field the lines of force were at right angles to the plane of the plate. The axes of the ellipses were measured by means of the microscope. The major axis of the ellipse was, both in and out of the magnetic field, at right angles to the chief crystallographic axis of the crystal. The ratio of these axes, without magnetic field, was $\frac{\perp}{\parallel}=1{\cdot}19$, and in a magnetic field of 4980 C.G.S. units $\frac{\perp}{\parallel}=1{\cdot}34$. If we take the squares of these quantities we have the ratios of the heat-conductivities for the two directions. The results are :—

Zero field ...... $\frac{\perp}{\parallel}$ 1·42,
4980 C.G.S. ... $\frac{\perp}{\parallel}$ 1·80.

The corresponding values for the electric conductivity are :

Zero field ...... $\frac{\perp}{\parallel}$ 1·78,
4980 C.G.S...... $\frac{\perp}{\parallel}$ 1·87.

My thanks are due to Prof. E. Warburg for his suggestions throughout the progress of the work.

Physical Institute, Berlin University,
Sept. 4th, 1902.

IX. *The Spectra of Hydrogen, and Reversed Lines in the Spectra of Gases. By* JOHN TROWBRIDGE[*].

IN a previous paper (Phil. Mag. July 1902) I described the spectra produced by powerful condenser-discharges through Geissler tubes filled with hydrogen. A fairly continuous spectrum was obtained between the HH lines and the red end of the spectrum. This spectrum, however, was traversed by reversed lines. In that paper I expressed the hope of being able to obtain quartz tubes. This hope has been realized. Through the kindness of manufacturers[†], working under the direction and according to the method of Professor Shenstone[‡], I have obtained suitable tubes; and the results given by such tubes are so remarkable that they seem worthy of a preliminary paper.

The tubes are 8 centimetres in length, with a capillary 4 centimetres in length and about 2 millimetres in diameter. On account of the difficulty of inserting platinum terminals

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[*] Communicated by the Author.
[†] Baird and Tatlock, London.
[‡] Clifton College.

in quartz, I had the ends of the tubes ground smooth, and the glass-blower of the laboratory prepared glass bulbs in which suitable electrodes were inserted. These bulbs were luted to the ends of the quartz tubes. In certain cases metal plates were luted directly to the ends of the quartz tubes. I employed silicate of soda as a luting agent; and after this had hardened I applied on the outside of the joint a hard preparation of pitch and shellac.

The glass bulbs were covered with other bulbs which allowed a current of water to circulate from the upper end of the tube to the lower; great heat, however, was excited in the capillary of the tube. Quartz prepared by the method of Professor Shenstone possesses the property of resisting changes of temperature in a remarkable manner. One of these quartz tubes can be heated to a white heat and plunged into water without cracking. Such tubes, therefore, are very valuable for the experiments I have been conducting on gases at high temperature.

They also possess the great advantage over end-on tubes of glass provided with quartz windows, that the capillary can be placed close to the slit of the spectroscope, thus giving a very intense light and a broad spectrum; moreover, the quartz is not melted by the intense heat. A photograph of gaseous spectra can be obtained with a single discharge and a very narrow slit; with tubes filled with hydrogen excited by a difference of potential of twenty thousand volts, condenser ·3 microfarads, an extremely intense light is obtained. This light is dazzling white with a bluish cast: it has more than three times the actinic effect of the same quantity of electricity discharged between magnesium terminals. Viewed with a straight-vision spectroscope the spectrum appears continuous; and even photography fails to reveal bright lines between the HH lines and the red end of the spectrum. In the region, however, beyond the limit set by the absorption of the glass Geissler tubes there are both bright lines and dark lines. The principal reversed lines are at wave-lengths—

2889·70
2549·89
2528·60
2524·29
2519·3
2516·21

These lines correspond with the lines of silicon volatilized by the spark in air. It seems that we have in this phenomenon another instance of selective polarization mentioned in my previous paper. The strongest metallic lines or gaseous lines are not those which show the strongest reversal. For instance, my previous photographs show the calcium line at approximately 4227 to be strongly reversed, while the stronger 3968, 3933 do not show a reversal except with much stronger and longer continued discharges.

A careful inspection of the negatives shows that the reversals of the metallic lines occur when they fall on bright gaseous lines or bands. In the same way a bright gaseous line falling on a continuous spectrum can show a similar reversal. We can express this in symbolic language as follows. Let A represent the intensity of the line and B the amount of the previous action of light on the photographic plate; then the reversal appears to be proportional to AB.

It seems probable that there are similar reversed lines running through the solar spectrum. I hope to detect them.

This investigation shows that the presence of dark lines in the spectra of stars does not imply, necessarily, the presence of reversing layers of a colder state of the gases; for such reversal may arise from photographic action on the plates which are used. Moreover, a gas may show a continuous spectrum to the eye, or even when photography is employed with glass tubes and glass lenses, while with quartz tubes such as I have employed a large region in the ultra-violet is shown to be traversed by both dark and bright lines and bands.

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Cambridge, U.S.

X. *A Graphical Method of Determining the Nature of the Oscillatory Discharge from a Condenser through a Coil of Variable Inductance.* *By* E. W. Marchant, *D.Sc., late Granville Scholar of the University of London, Lecturer in Electrotechnics, University College, Liverpool*[*].

THE method which is described below is an extension of the one originated by Dr. Sumpner (Phil. Mag. June 1887).

In this paper he describes a graphical construction for determining the rate of increase of current in a coil having an iron core. The problem is stated generally as the determination of the increase of current through a coil with a

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[*] Communicated by the Author.

variable self-induction when an E.M.F. is suddenly applied to it. The results obtained by him were of very great interest, as he clearly demonstrated both by experiment and calculation the fact that with an iron core coil, such as that of a large electromagnet, the current first increases very slowly until the knee of the magnetization curve is reached, and that it then increases with much greater rapidity. It appeared that this method might be applicable to the case of the oscillatory discharge from a condenser. We have as the fundamental equation

$$\frac{d(\mathrm{L}i)}{dt}+\mathrm{R}i+\frac{\mathrm{Q}}{\mathrm{C}}=0,$$

with the condition that just before the discharge takes place there is a P.D. = E volts between the plates of the condenser.

Li denotes the number of lines of force linked by the coil when a current i is flowing through it. (With iron in the circuit L (of course) is a function of i. With an "air core" self-induction L will represent the self-induction of the coil as ordinarily understood.)

R denotes the resistance of the circuit in ohms.

C the capacity of the condenser in farads.

Q denotes the quantity of electricity on the plates of the condenser at any instant.

i denotes the instantaneous value of the current.

The first term may be written

$$\frac{d(\mathrm{L}i)}{dt}=\mathrm{L}\frac{di}{dt}+i\frac{d\mathrm{L}}{di}\frac{di}{dt}=\frac{di}{dt}\left(\mathrm{L}+i\frac{d\mathrm{L}}{di}\right)=\mathrm{L}'\frac{di}{dt}.$$

We have therefore

$$\frac{di}{dt}=\frac{-\left\{\mathrm{R}i+\left(\frac{\mathrm{Q}}{\mathrm{C}}\right)\right\}}{\mathrm{L}'}=\frac{-i-\frac{\mathrm{Q}}{\mathrm{RC}}}{\frac{\mathrm{L}'}{\mathrm{R}}}.$$

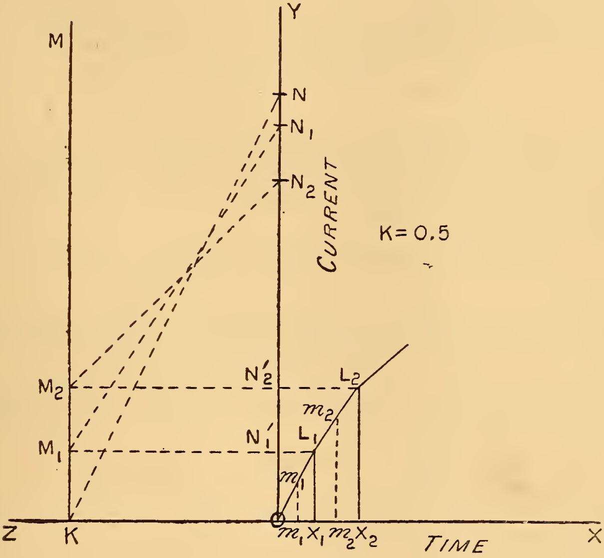
It now remains to show how the value of $\frac{di}{dt}$ may be obtained from this equation.

It will be well first to take the simplest case where L is a constant quantity. The equation then reduces to

$$\frac{di}{dt}=\frac{-\left(i+\frac{\mathrm{Q}}{\mathrm{RC}}\right)}{\frac{\mathrm{L}}{\mathrm{R}}}.$$

Let OX (fig. 1) be the axis of time, OY the axis of current. Just before the discharge there is quantity $Q_0 = E_0 C$ on the plates of the condenser.

Fig. 1.



The quantity at any instant T after the discharge has occurred is therefore $= -Q_0 + \int_0^T idt$, where i is considered positive when it tends to diminish the quantity of electricity on the plates of the condenser, and Q_0 must therefore be considered negative.

$$\frac{di}{dt} = \frac{\frac{Q_0}{C} - \left(Ri + \frac{\int idt}{C}\right)}{L} = \frac{\frac{Q_0}{RC} - \left(i + \frac{\int idt}{CR}\right)}{\frac{L}{R}} = \frac{\left(\frac{Q_0 - \int idt}{RC}\right) - i.}{\frac{L}{R}}$$

Plot along OZ a length proportional to $\frac{L}{R}$, and on OX to the same scale, time in seconds.

If $OK = \frac{L}{R}$ in seconds draw KM parallel to OY.

Along OY take a length $ON = \frac{Q_0}{RC}$ in amperes to the proper scale.

At time 0, $i=0$, and consequently

$$\frac{di}{dt}=\frac{\frac{Q_0}{RC}}{\frac{L}{R}}=\tan(NKO).$$

From O therefore draw a short line OL, parallel to KN, this will be the beginning of the current-curve since

$$\tan(L'OX)=\tan(NKO)=\frac{di}{dt}.$$

It will be convenient to take a time-interval such that dt is numerically some simple multiple of CR. Thus $dt=k\text{CR}$. The exact time-interval is unimportant, provided it be sufficiently small. Since

$$\int idt=\text{area of } OL_1X_1=m_1m_1\times OX_1=m_1m_1\times dt,$$

$$\frac{\int idt}{RC}=m_1m_1\times\frac{dt}{RC} \text{ and } \frac{dt}{RC} \text{ being}=k,\ \frac{\int idt}{RC}=k\times m_1m_1.$$

Plot downwards from N, therefore, a length $k\times m_1m_1$ to N_1, and from L_1 draw L_1N_1' parallel to OX to meet ON in N_1.

$$\text{Then } N_1N_1'=\frac{Q_0}{RC}-k(m_1m_1)-i=\frac{Q_0}{RC}-\frac{\int idt}{RC}-i.$$

Producing L_1N_1' to meet KM in M_1 and joining M_1N_1, $\tan N_1M_1N_1'=\frac{N_1N_1'}{M_1N_1'}=\frac{di}{dt}$ therefore, from the equation above.

Draw from L_1 therefore a line L_1L_2 parallel to M_1N_1. This represents the increase of current during the second time-interval X_1X_2. To determine the value of $\frac{di}{dt}$ at the time corresponding to L_2 draw the mean ordinate m_2m_2 of the trapezium L_1X_1 L_2X_2; the area $=X_1X_2\times m_2m_2$, and is as before $=\int idt$ from X_1 to X_2; the value of $\frac{\int idt}{RC}$ for this interval $=k\times m_2m_2$ as before. And plotting this length downwards from N_1 to N_2 the length NN_2 = the value of $\frac{\int idt}{RC}$ from the beginning of the discharge. Continuing the construction as before and joining M_2N_2 the slope of this line represents the value of $\frac{di}{dt}$ at the instant X_2.

Curves have been plotted for discharges through a circuit having a capacity = 1 m.f. and a self-induction = 1 henry with three different values of the resistance, and these agree to within 1 per cent. with calculation.

Exactly the same method of procedure is adopted when plotting the discharge through a coil of variable inductance, the straight line KM being replaced by a curve drawn to

Fig. 2.—Curve showing the Discharge of a Condenser of 1·25 m.f. Capacity through a Coil having a Core of Soft Iron Wire.
P.D. before Discharge = 9400 volts.
Time for Half-Oscillation = $2{\cdot}9 \times 10^{-5}$ secs.
Experimental value = $3{\cdot}2 \times 10^{-5}$ secs.

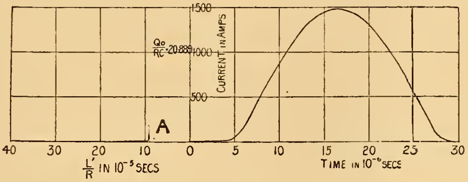


Fig. 3.—Curve showing the Discharge of a Condenser of 1·25 m.f. Capacity through a Coil having a Core of Soft Iron Wire.
P.D. before Discharge = 2350 volts.
Time for Half-Oscillation = 51×10^{-5} secs.

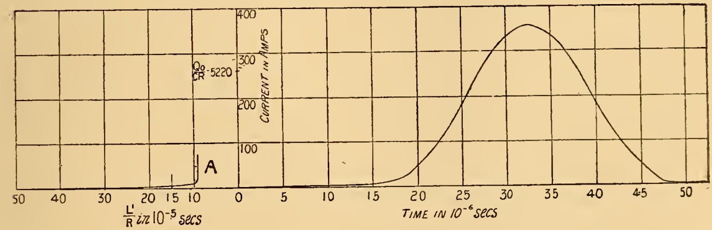
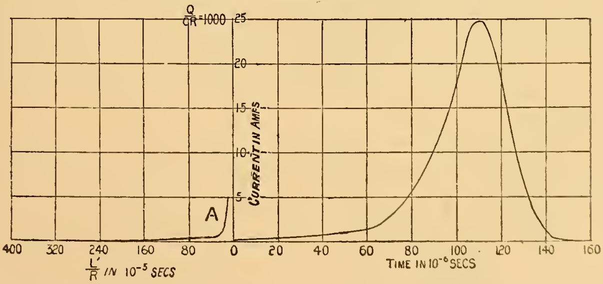


Fig. 4.—Curve showing the Discharge of a Condenser of 1·25 m.f. Capacity through a Coil having a Core of Soft Iron Wire.
P.D. before Discharge = 450 volts.
Time for Half-Oscillation = $15{\cdot}2 \times 10^{-5}$ secs.



represent the variation in the value of $\frac{L'}{R}$ with current. Such curves are shown at A A in figs. 2, 3, and 4.

The chief difficulty that arises is in the drawing of the earlier part of the curve, when the current is just starting, and to do this accurately a supplementary curve is first drawn, a very much larger scale of current being employed.

A curve of the same character may be drawn for the end of the first half wave when the current has fallen to 20 amperes. The shape of the curve is, however, not exactly similar on account of hysteresis. The actual case taken was that of a coil on which a certain number of experiments had been made. The coil was in the shape of a square with about 90 turns of No. 18 g.p. wire on each limb. The self-induction of this coil was measured without the core, and found to be $4{\cdot}1 \times 10^{-5}$ henry. A core of soft-iron wire was used in the experiment, and from the known permeability of the soft iron for different magnetizing forces the curves shown at A A were calculated.

A series of curves has been drawn showing the shape of the current-wave through the coil when the discharge from a condenser of 1·25 micro-farads capacity flows, the condenser being charged with (1) 9400 P.D. (2) 2350 P.D. (3) 450 volts P.D. It is interesting to notice the complete difference in shape of the discharge curves. In the first case, that in which the P.D. is 9400 volts, the current increases very slowly until saturation is attained, that is, when the magnetizing force is about 300, after which the discharge curve becomes nearly sinusoidal. For the smallest voltage saturation is hardly reached, so that the curve becomes peaked; the effects of hysteresis in this curve are clearly shown. The method is of course adaptable to any kind of discharge, the curves in question having been plotted to illustrate its working, and because experimental values of the actual time occupied by the discharge have been obtained. It will be noticed that the agreement between graphical and experimental results is fairly good. Exact agreement would hardly be expected on account of the disturbing effects due to eddy-currents, which are very powerful (at this frequency) with the finest laminations.

It is instructive to notice the increase in the time for a half-oscillation when the P.D. before discharge is decreased. The table below is taken for the voltages considered.

P.D. before Discharge.	Time for 1st Half-Oscillation.
9400	$2{\cdot}9 \times 10^{-5}$
2350	5×10^{-5}
450	$15{\cdot}2 \times 10^{-5}$

It is clear, therefore, that with a discharge such as we are considering, which is rapidly damped, the time for a half-oscillation would increase as the discharge died away, a result experimentally obtained and published in a letter written to 'Nature' by the author in August 1900.

An interesting application of the method is the determination of the deflexion that would be attained by a ballistic galvanometer when a discharge passes through it which cannot be assumed to have ceased flowing before the needle has moved. In this case the value of $\frac{E_0}{R}$ would be variable, and the subtraction would have to be repeatedly performed from a variable point.

In conclusion I wish to express my indebtedness to Mr. G. W. Worrall, B.Sc., for working out some of the values of the self-induction under varying currents which have been used in plotting the curves given above.

University College, Liverpool.

XI. *A Sensitive-strip Spectropolariscope.*

By Professor D. B. Brace *.

THE conditions for maximum sensibility of the eye in making comparisons with the polariscope are the same as those of a photometer. The entire displacement, except in technical work, of photometric comparisons with ordinary light by spectral photometric observations, which the growing demands in photometry for exact data on specific colours have produced, illustrates the corresponding condition in polariscopic work. The importance, both theoretical and practical, of determining, on the one hand, the relative distribution of intensities subjectively and objectively in any radiant and, on the other, the relative transmission of any absorbent for different periodicities, has necessitated the highest instrumental refinements.

It is now possible to obtain settings for the mean spectral colours with a probable error of less than one-fifth per cent. † and on some occasions with a carefully trained eye as low as one-tenth per cent. This has been brought about by improving the viewing screen so that the bounding lines between the comparison fields should be perfectly sharp and vanish with equal illumination of the fields, the colour of course becoming the same over the entire field of view. In

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* Communicated by the Author. Read before the American Physical Society at its Pittsburg meeting, July 1902.

† Phil. Mag. [5] xlviii. p. 420 (1899).

the spectrophotometer the best results have been obtained by means of a silver strip. The photometer is subject to the further restriction in its use of measuring the quantities of light. This element, as a difficulty, is really negligible in the polariscope, but the former difficulty does not seem yet to have been overcome.

In a polariscope it is necessary to vary the so-called sensibility as the amount of light varies. This condition should obtain too for all colours. For the greatest efficiency, the polarizing and analysing elements should not displace the ray when placed in its path, as this would generally affect the position of the image for any one wave-length. The bounding lines between the fields should also vanish for any colour and sensibility and that too whether a broad or a narrow radiant is the source of light. Some of these conditions have been realized in the types already devised, but no one embodies them all.

In the biquartz of Soleil a vanishing line is partially realizable, but as the tint of passage is used white light is required ; and further the sensibility cannot be varied. In a double rotary element, such as that of Poynting rotating differentially in the same direction, a vanishing line is also partially realizable; but its use over a finite portion of the spectrum of sufficient breadth to give a proper intensity will make initial settings of different tints in the different parts of the field, owing to the differential rotation. The neutral position of the analyser will also vary in different parts of the spectrum for similar reasons. This form and the modified form of the biquartz with a small angle of rotation which is used for monochromatic light do not admit of a practical variation in the sensibility. Furthermore, the added rotation of any medium under examination increases the differential rotation of one portion of the field over the other, thus intensifying the difference of tint in the two fields, which diminishes the sensibility in setting. In the polariscopes of Savart, Babinet, Nodot and others a vanishing and a displacement of interference-bands take place. The settings which can be made with these forms are far less accurate than those already mentioned and in some of them very fatiguing to the eye. In the system of Laurent, with a half-wave plate, much used in saccharimetry at the present time, a vanishing line is attainable and the sensibility can be varied, but light of only one colour can be used. In the half-shade polarizer of Jellet any colour may be used, but it is impossible to vary the sensibility and also to eliminate the dark line between the two halves of the field. In the half-shade polariscope of Lippich, in which the field is either bisected or trisected, we have the most adaptable and sensitive instrument which has been devised. This form embodies the very essential feature of a variable sensibility, and, *with a sufficiently broad source*, a nearly vanishing line is possible. However, in most forms of nicols, since it is the extraordinary ray which is used, there is a displacement of its path. This of course can be avoided if the ray enters normally a nicol with the optic axis in the intersection of its face with its diagonal plane. Most nicols are also found to be slightly prismatic. The ray will usually receive a further displacement on its passage through the second nicol which covers a part of the field of the first one. The two ray systems thus give separate images, which, in spectral work, is a serious difficulty in obtaining a perfect match over the field. In setting for any one colour a rotation of either polarizer or analyser should not displace the image. To avoid this, care must be exercised to eliminate the errors due to displacement mentioned above. It does not seem possible to produce a vanishing line between the different parts of the field except with a source of sufficient breadth. With such a radiant at a focus conjugate to the image at the analyser, when the lens is just before the polarizing nicol, there is a great number of bundles of rays which thus produce uniform illumination over the entire field. When, however, the source is very narrow and we have approximately a single bundle of rays, the case is different and we generally observe a decided dark or bright line between the fields, which greatly reduces the delicacy of perception of the eye. This is evidently an irremedial effect since the polished side of the second nicol, usually several centimetres long, will reflect internally or externally any rays striking it, and it is thus impossible to obtain a continuous system of rays across this bounding face, particularly if the rays within it are displaced as described above. In several of the most sensitive half-shade combinations obtainable this defect existed to a greater or less extent. In spectral work, except with bright-line radiants or with absorption cells which never give sufficient homogeneity, a narrow source or slit is essential. Hence the Lippich form of instrument does not seem to be available for general colour observations over successive portions of the spectrum. The amount of light obtainable from a bright-line radiant, *e.g.* an Aron's lamp, was found to be far below that obtained from the direct rays of the same colour from the sun after passing through a spectral system as is usually desirable, *e.g.* absorbing media which have anomalous rotary effects. Other defects usually found are imperfect polishing and figuring of the nicols themselves. These are usually only observed in work with spectral colours from a narrow source giving approximately a single bundle of rays. The scratches and ridges here become at once evident and any variation in the curvature of the face manifests itself in a variation of intensity of the field, producing a shaded or mottled appearance. This is a well-known appearance[*] in spectrophotometry when the ray system is not coaxial with the lenses or when their curvature is not uniform.

In the nicol prism a total reflexion of the ordinary ray takes place at the internal diagonal faces which are cemented with balsam or with evaporated turpentine-oil or linseed-oil, whose indices are less than that for the ordinary ray. This allows a part when balsam, or practically all when these oils are used, of the extraordinary ray to pass through. The reflected ray is absorbed by the sides of the nicol but not completely. When an intense source like the sun is used the diffused light is so large as to produce a decided effect on the hue when colours of very low intensity reach the eye. This of course is a difficulty which the optician can eliminate by proper casing and diaphragming.

It is not a difficult matter mechanically and optically to reverse the conditions of reflexion with the optical media now available. For example, we have as the index of the ordinary ray of spar for the D-line 1·6584, while for the same line the value for α-monobromonaphthaline is 1·6582. Schott and Co., of Jena, also cast a glass the value of which is $n_{\mathrm{D}}=1{\cdot}6527$. The dispersion of each of these is of course different, but for the mean colours of the spectrum the indices are almost the same. It has seemed heretofore impossible to obtain glass so free from strain as to produce no observable depolarization. The use of liquids, however, has been found perfectly practicable and efficient. Solutions of carbon disulphide may be used giving almost any convenient index from a low value with balsam to an index greater than $1{\cdot}7_{\mathrm{D}}$ with phosphorus.

The well-known optical fluid α-monobromonaphthaline is, however, much superior, as it remains nearly colourless if sealed up and not subjected to actinic action by continuous exposure to light. Its index is the same as that of spar for the mean portions of the spectrum. If now the cementing film and the prisms of spar are interchanged, we should have an interchange of the extraordinary and ordinary rays. Thus a plate of spar placed diagonally at the proper angle within a

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[*] Tuckerman, Astrophys. Journ. xvi. p. 145.

cylinder of glass or of this fluid would totally reflect the extraordinary ray and transmit almost completely, and without any displacement as is usually the case in nicols, the ordinary ray. A second cylinder containing a narrow thin strip of the spar would give us a bisected or trisected field with a vanishing line.

In cutting* the spar for both the first polarizer and for the sensitive strip, two directions in the crystal have been tried. In the first system the longest axis of the plate lies in a principal plane through the optic axis, making an angle of 70° with it. The first plate was cut about 2 mm. thick and in the form of an ellipse with its edges ground away so as to fit within the cylindrical cell containing the liquid. The dimensions of this ellipse were 44 mm. by 15 mm. over one face, thus giving a clear circular aperture of 15 mm. with an angle of incidence of 70°. The sensitive strip was cut in the same plane but only 5 mm. by 44 mm., and rectangular in shape. The thickness was 0·15 mm. and its lateral edges perfectly sharp and square with its faces. Experience with plates of these dimensions and thicknesses show that they may be safely reduced to 0·1 mm. or less in thickness. In the second system the plates were all cut rectangular and to the same dimensions as those of the first. Their direction within the crystal, however, is different, their faces being principal planes through the optic axis which is perpendicular to the longest edge or length of the plate. More difficulty was experienced in grinding these as they fractured more readily and a thickness of 0·5 mm. was found practicable. More material was also required for this system.

In order to obtain total reflexion of the extreme red rays, an angle of incidence of 65° is necessary. To provide for total reflexion of a cone of rays, 68° to 70° is required. The angle of incidence adopted is 70°. This gives a length of 40 mm. for a cell of 15 mm. clear aperture. The cost of a plate itself is about one-third that of a nicol of the same aperture. The ellipse or first plate is mounted within a cell of about twice the diameter of the aperture in order to provide for sufficient fluid and effective diaphragming. There are five of these diaphragms fixed to a concentric tube and they are slightly slotted along a diagonal so as to admit and retain the polarizing plate. This latter is cemented slightly at its ends to the blackened tube with fish-glue (Le Page's), mixed in four parts with two of glycerine and five of water. Care is exercised in avoiding any strain as depolarization will

* The plates were cut and polished by Bernhard Halle, Steglitz-Berlin.

be present under the slightest effect induced by the cement or otherwise. Thin cover-glasses are carefully selected and cemented on the brass caps or end-pieces which screw into the tube. No moisture or acid used on the metal must be allowed to reach the plate. The liquid itself shows no action on spar. As it is quite volatile the cell is closed tight, with a bubble of air remaining in to compensate for expansion. The sensitive strip may be mounted in the same cell, but in order to vary the sensibility one of the plates must be capable of a slight displacement. The mechanical difficulties are greater in such a system; but higher efficiency is possible. On the other hand, greater simplicity is obtained by mounting the strip in a separate cell and then placing the two cells in a common tube and rotating the first, as is usually done in the mounting of the Lippich system. With such thin strips of spar, of course care must be exercised in mounting them so that they will not fracture or suffer strain. This was done by cutting away a slight portion in the inner circumference of the caps of the tube and cementing the ends of the strip to these with the cement mentioned. Thin cover-glasses were then cemented over the ends of the blackened brass cell and the liquid inserted through a small opening which was later sealed up. However, such a strip might at the outset show no trace of depolarization, and later not give perfect blackness owing, manifestly, to the setting of the cement and the induced strain in the strip. This was obviated by cementing one end only and leaving the other slightly free within retaining contacts. When these precautions are taken and the system examined in the ordinary way with analyser and telescope, the surprising sharpness between the fields is at once observed and, with a neutral setting, as perfect a vanishing line is obtained as with the most delicately adjusted strip in the best spectrophotometer. This system, properly mounted with parallel end-plates, when placed in any ray system will give a single image and cause no deviation of the axis of the ray system. The sensibility of the system can be varied easily and a vanishing line obtained. It may also be used for any colour and the neutral setting will not vary for different parts of the spectrum. When the liquid is freed from suspended particles by filtration no diffused light emanates from the polarizer and a perfectly black field is obtainable even with direct sunlight. These conditions are not so quickly obtained as with the system of Lippich, but when they are, a greater sensibility is possible. For a single bundle of rays or such as would emanate from a narrow source or slit, it is evident that, on account of the narrow edge of the strip as compared with the long polished side of the second nicol in the Lippich form, a much more continuous system of rays is possible and hence a far sharper bounding or a vanishing line between the fields.

Various systems have been tried for obtaining different monochromatic light of sufficient intensity. As mentioned above, the intense system of Aron gives only definite wavelengths and hence cannot be used for all purposes. Any one of the mercury lines was also found to be much less intense than a corresponding portion of the spectrum sufficiently narrow to give, within the limits of observation, the same rotation of all its components in the experiments tried. Absorption cells are not sufficiently monochromatic for many observations and are of course restricted in the colours available. Except in the sensitive-strip system here described, a broad diffusing source is necessary. Here too sunlight gives the best results; but in order to use it as such, a diffusing plate, *e.g.* a ground-glass or milk-glass plate, must be inserted. This is found to reduce the available light by 95 per cent. to 98 per cent. Owing to the sensibility of the system any arbitrary spectral arrangement will not suffice. No light should be allowed to enter the polarizing system which is not used in the immediate observations. The spectral system adopted must fulfil these conditions. The most obvious arrangement and one used largely is to place a slit at a focus conjugate to the analyser and with the lens immediately at the polarizer, a dispersing prism being placed immediately before or after the lens. A spectrum is thus formed in the plane of the analyser and by a proper diaphragm or slit in this plane, the eye, aided by a telescope or not, will see the field illuminated with a uniform tint. This is owing to the fact that the retina is a conjugate focus to the field aperture, which is a colour radiant, and its lens converges all rays of different colours radiating from one point of the field (dispersing prism) to a common focus on the retina. If, however, a cell of absorbing substance, say for the green, is placed in the path of this beam, the very small amount of green which is transmitted may be largely neutralized by extraneous light or by the smallest fraction of red and blue which is diffused from the faces of the prisms or from internal reflexions of the system, which thus becomes a radiant. This has been found to give apparent rotations following some regular law predicted on entirely different grounds. To avoid these spurious results, the entire dispersion and separation of the colour should take place outside and beyond the polarizer. This of course may be attained in many ways, several of which have been tried, *e. g.* the dispersion may be obtained by a single optical system and the resulting spectrum formed in the plane of the slit above referred to as conjugate to the analyser. A suitable mirror before the prismatic system may be made to rotate any colour into this slit and maintain the system of rays used homocentric to any axis in the system. It is not easy, however, with such a system to obtain a uniform intensity over the entire field of view. The difficulty from diffusion referred to, however, is eliminated.

The system which has given thus far the best results is a modification of one devised by the writer for colour mixtures and used by Doubt * in his determination of the colour equations for different radiants. This is a reversing colour-system consisting in reality of a double dispersing system. A concave mirror whose radius of curvature is the focal distance of the cone of rays emerging from the prism and lens is placed in the focal plane. The rays of different wave-lengths strike it at the same angle and hence are reflected back and recombined in the prismatic system and brought to a focus at the slit source. Evidently any portion of the spectrum would be recombined here. All screens with such a narrow slit were found to diffuse more or less the remaining colours of the spectrum, so that a single narrow mirror was used to reflect a corresponding portion of the spectrum, the remaining portion being allowed to pass on to the darkened walls of the room. After returning through the prismatic system where all rays were recombined, a mirror reflected the cone of rays through the polarizing system which come to a focus at the analyser. In this way fields of perfectly uniform tint with vanishing lines for a neutral setting were obtained, and, using the sun's rays, a sensibility for the mean colours greater than that which had previously been possible with the Lippich form using white light. The accompanying table (p. 169) gives a series of successive settings taken at random by Mr. Bates, Fellow in Physics, to whom is due much credit for the perfection of this arrangement and the elimination of the spurious effects in anomalous dispersive substances observed by the other experimenters.

These give the deviation of a single setting from the mean of from one two-hundred-and-fiftieth to approximately one two-hundreth of a degree for these three wave-lengths.

In natural rotative substances this system needs no special mounting, but in the study of magnetic rotation it must be free from the action of the field. This has been accomplished,

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* Phil. Mag. [5] xlvi. p. 216 (1898).

C-line.	D-line.	E-line.
·075°	·095°	·1575
·075	·095	·1575
·0775	·100	·1600
·075	·1025	·1550
.075	·095	·1550
·075	·0975	·1550
·070	·0975	·1575
·075	·0975	·1575
·075	·0975	·1525
·075	·1000	·1550
·075	·095	·1525
	·095	
	·095	
	·095	
	·095	

when it is near the system, by housing it in a thick iron cylinder of suitable length which becomes at once the containing tube for the cells. Attention should also be called to the further fact that when the rotation is measured immediately by the analyser the different elements of the field sometimes show a slight difference in tint if the rotation is considerable. This is due to the fact that the light is not strictly homogeneous, and the different components are rotated by different amounts. This could be wholly or partially avoided by using a rotary compensator, *e. g.* quartz wedges.

For perfect adaptability to any wave-length there is no doubt that systems giving channeled spectra are preferable, but on this account only, as their sensibility is far less than the half-shade or sensitive-strip instruments. A rotation equal to the amount observable in the system described and referred to in the table above means a displacement of only one forty-thousandth of the distance between two black bands in a channeled spectrum. It is very doubtful indeed whether a setting in channeled spectra closer than one degree can be made with the same certainty as one two-hundredth of a degree with this system. This means one two-hundredth of a band, which ordinarily is very high indeed. However, some observers have claimed settings as accurate as from ten to three one-hundredths of a degree or one six-thousandth of a band. Experienced observers in repeating such observations with similar apparatus have never been able to set, with certainty, closer than one or two degrees. Such a realizable sensibility would truly be an immense step in advance, as a channeled spectrum is really the only true representation of dispersive gradation. Until this can be unquestionably demonstrated, the use of the sun with the sensitive-strip system must be relied upon on account of its greater sensibility and adaptability for any spectral study.

Physical Laboratory,
University of Nebraska, Lincoln.

XII. *Notices respecting New Books.*

Naturlehre. Von Dr. Alois Lanner. Mit 377 Figuren, einer Spectraltafel und 4 meteorologischen Karten in Farbendruck. Wien: Verlag der Jos. Roth'schen Verlagsbuchhandlung. 1902. Pp. 377.

The task of writing an elementary text-book of reasonable size which should contain a brief account of all the branches of physics (including the elements of astronomy) and chemistry is a somewhat formidable one, and we must congratulate the author on its successful accomplishment. Wisely abstaining from trying to confront his reader with an unmanageable mass of facts, the author makes a careful selection of such phenomena as serve to illustrate and bring home to the mind of the student the leading principles of modern science.

In spite of its elementary nature, the book is thoroughly up to date, and the interest of the reader is maintained by frequent references to the numerous practical applications of the principles dealt with in the book.

There is a peculiar interest attaching to this work. It has been written along the lines laid down by the Austrian Ministry of Education for the guidance of teachers in the State secondary schools or "gymnasia." A boy who has mastered the contents of this book has certainly obtained a good insight into physical science, and is splendidly equipped for the subsequent training in a technical college or university. One cannot help thinking how much easier the work of higher technical education would become in England, if only every secondary school were to put its pupils through some such course as that contained in the book under review.

XIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. iv. p. 520.]

May 28th, 1902.—Prof. Charles Lapworth, LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. 'The Red Sandstone-Rocks of Peel (Isle of Man).' By William Boyd Dawkins, M.A., D.Sc., F.R.S., F.G.S., Professor of Geology in Owens College (Victoria University), Manchester.

The Red Sandstone Series, ranging along the coast from Peel to Will's Strand, is faulted into the Ordovician massif of the Isle of

Man. It has been referred to the Old Red Sandstone, the Calciferous Sandstone, the basement Carboniferous, and to the Permian. The series consists of red sandstones containing irregular conglomerates and breccias, more or less chemically altered, known in the Lake District as 'Brockram.' Sections at Ballagnane, Creg Malin, and at the Gob and Traie Fogog, are described in detail; the rocks are classified, and their range to the north-east and inland is described. It is pointed out that the rocks are different in many respects from the basement Carboniferous rocks of Langness and elsewhere, and a list of the materials contained in the 'Brockrams' is given. All these materials have been derived from rocks similar to those which form the Lower Carboniferous Series in the Lake District, with the exception of one or two types which might belong to any other pebble-beach. The fossiliferous pebbles in the rocks in question are described, and their fossil contents determined. The whole group of fossils is Lower Carboniferous and Ordovician, and centres mainly in the Carboniferous Limestone. A comparison is instituted with the Permian rocks of Barrowmouth, the Vale of Eden, and elsewhere. The rocks are much sheared and faulted; the planes of shearing intersect the bedding-planes, and divide the rock into lenticular and diamond-shaped masses, which are scored and slickensided. The earth-movement to which this is due took place in the interval between the latest Palæozoic and earliest Mesozoic deposits. The iron in the rocks was probably derived from the destruction of the Carboniferous shales.

2. 'The Carboniferous, Permian, and Triassic Rocks under the Glacial Drift in the North of the Isle of Man.' By William Boyd Dawkins, M.A., D.Sc., F.R.S., F.G.S., Professor of Geology in Owens College (Victoria University), Manchester.

The whole of the Isle of Man, north of a line drawn due west from Ramsey, is covered with a thick mantle of Glacial Drift. South of this line rises the ice-worn Ordovician massif. Six borings carried out under the advice of the author have elucidated the geological structure of the Drift-covered area. The borings at Lhen Moar, Ballawhane, Knock-e-Doony, Ballaghenny, and two at the Point of Ayre are described in detail, and the rocks classified. The first shows Carboniferous Limestone under Drift; the second and third, Trias, Permian, Yoredale, and Carboniferous Limestone: the fourth, Trias, Permian (thin), and Yoredale: the fifth and sixth, Trias, with gypsum and 76 feet of rock-salt. The rocks all dip in natural order towards the north, and constitute a plateau of marine erosion sloping to the north and east covered with Drift, which is in places not less than 450 feet thick.

3. 'Note on a Preliminary Examination of the Ash that fell on Barbados, after the Eruption at St. Vincent (West Indies).' By John Smith Flett, M.A., D.Sc., F.R.S.E., F.G.S. With an Analysis of the Dust by William Pollard, M.A., D.Sc., F.G.S.

Two samples of the material were sent by Dr. D. Morris, of the Imperial Agricultural Department for the West Indies, to Prof. J. W. Judd, who forwarded them to the Director of the Museum of

Practical Geology. The fine grey powder is gritty to the touch, and it all passed through a sieve with 30 meshes to the inch. It contains plagioclase-felspar (generally idiomorphic labradorite) coated with a thin film of glass, hypersthene and monoclinic brownish augite, both frequently in perfect crystals, magnetite, apatite, possibly zircon, and fragments of a brown glass. Among the finest débris there is much felspar in the form of minute chips. The perfect crystalline form of many of the constituents of the dust and the small amount of glass adherent to them, indicate that at the time of projection the glassy magma must have been very fluid, and it must have been to a large extent wiped off the crystals by friction. From Dr. Morris's account, the minerals of high specific gravity appear to have fallen first; the order being magnetite and pyroxenes first, next the felspars. and finally the glass threads and minute felspar-débris. Dr. Pollard's analysis is as follows:—$SiO_2 = 52{\cdot}81$, $TiO_2 = {\cdot}95$, $Al_2O_3 = 18{\cdot}79$, $Fe_2O_3 = 3{\cdot}28$, $FeO = 4{\cdot}58$, $MnO = {\cdot}28$, $(CoNi)O = {\cdot}07$, $CaO = 9{\cdot}58$, $MgO = 5{\cdot}19$, $K_2O = {\cdot}60$, $Na_2O = 3{\cdot}23$, $P_2O_5 = {\cdot}15$, $SO_3 = {\cdot}33$, $Cl = {\cdot}14$, $H_2O = {\cdot}37$; Total 100·35.

June 11th.—Prof. Charles Lapworth, LL.D., F.R.S.,
President, in the Chair.

The following communications were read:—

1. 'A Descriptive Outline of the Plutonic Complex of Central Anglesey.' By Charles Callaway, D.Sc., M.A., F.G,S.

The central complex of Anglesey was originally composed of diorite, felsite, and granite. The gneiss and granitoid rock of the area, formerly regarded as sedimentary in origin, are now known to be plutonic masses. The diorite undergoes numerous modifications, into hornblende-gneiss, chlorite-gneiss, micaceo-chloritic gneiss, and kersantite and biotite-gneiss. The felsite has not been found in its original state, but is converted into 'hälleflinta,' quartz-schist, mica-schist, and mica-gneiss; granite and quartz-felsite are intrusive into the diorite and felsite, and the two former are regarded as derived from the same magma. They are not foliated, and were intruded subsequently to the modification of the diorite and felsite into gneisses and schists. The diorite, originally a xenolith surrounded and injected by granite, has been modified into an elliptical dome of dark gneiss: into simple gneisses by pressure. and into complex gneisses by pressure *plus* granitic intrusion. This intrusion has often produced fusion at the contact, sometimes with the generation of biotite in the diorite. In addition to this, the diorite possesses an imperfect fluxion-structure.

2. 'Alpine Valleys in Relation to Glaciers.' By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S.

The author discusses some hypotheses about the formation of Alpine valleys which have been advanced by Prof. W. M. Davis, but has left the Ticino Valley, on which the latter lays much stress, to Prof. Garwood, who has very lately visited it. Prof. Davis maintains that the upper and wider parts of Alpine valleys were excavated in pre-Glacial times, the lower and narrower portions during the Great Ice-Age. The author tests this hypothesis by applying it first to the valley of the Visp, of the eastern arm of which, and of the 'hanging valley' like a gigantic corrie, where Saas Fee is situated, he gives a description, pointing out that all parts are so connected that any separate explanation of their form is impossible.

To obtain an idea of the condition of the Alps in Middle and Later Tertiary times, we may consider the effect of alterations of temperature, on the assumption (which, as he shows, is not likely to be seriously incorrect) that the altitude of the Alps during the greater part of their existence has remained unchanged. A rise of temperature of from 6° to 7° Fahr. would have the same effect as lowering the district by 2000 feet; a rise of 10° would correspond with 3000 feet. In the latter case the Pennine chain about the headwaters of the Visp would be comparable with the range from Monte Leone to the Ofenhorn. With a rise of 14° glaciers would almost vanish from the Alps, for the snow-line would then be at 12,000 feet above sea-level. Thus glacial action in the Oligocene and Miocene ages would be a negligible quantity, and it would gradually become sensible during the Pliocene; but glaciers would not invade valleys now free from them until the temperature was some degrees lower than it is at present—in other words, can have occupied these during only a small portion of their existence.

The author passes in review a number of other Alpine valleys, which lead to the same conclusion. He calls attention once more to the connexion of cirques with valleys, to the impossibility of referring the former to glacial action, and to the unity exhibited by all parts of the Alpine valleys, touching upon some structural difficulties which Prof. Davis has been content to meet with hypotheses. Alpine valleys in all parts, as the author shows, indicate by their forms meteoric agencies other than glaciers, which can only have acted for a comparatively short time and have produced little more than superficial effects.

3. 'The Origin of some "Hanging Valleys" in the Alps and Himalaya.' By Prof. Edmund Johnstone Garwood, M.A., F.G.S.

Lateral valleys which enter the main valley marked by discordant grades in the Jongri district of the Sikhim Himalaya have been attributed by the author to Pleistocene elevation and super-erosion of the main valley by water. Similar valleys in the Val Ticino have recently been attributed to overdeepening of the main valley by ice. The author shows that there is no real proof of this in fact the evidence seems strongly to point to fluviatile, and not glacial erosion of the main valley. This is shown by the overlapping profiles and river-gorges situated both above and below some of these 'hanging valleys,' and by the fact that a greater relative amount of erosion has taken place towards the upper end of the main valley than at the lower, where the mouths of the 'hanging valleys' are less elevated. The overdeepening of the main valley is attributed to an epeirogenic uplift in Pleistocene times, consequent on the melting-away of the ice-cap, the lateral valleys being merely tilted sideways. This effect is intensified by the protection accorded to the high lateral valleys by ice, which even nowadays still lingers there. Examples from the Maloja district of the Engadine are cited as confirmatory of this. The best-preserved of these 'hanging valleys' in three districts examined by the author all face north-eastward, and show protection by ice; others not so protected have begun to cut back their gorges to an accordant grade with the main valley. Examples of other types of 'hanging valleys' not due to the overdeepening of the main valley are given, and proofs of the greater power of water to excavate over ice are assigned.

June 18th.—Prof. Charles Lapworth, LL.D., F.R.S.,
President, in the Chair.

The following communications were read:—

1. 'The Great Saint-Lawrence-Champlain-Appalachian Fault of America, and some of the Geological Problems connected with it.' By Henry M. Ami, M.A., D.Sc., F.G.S.

The extent, earth-movements, and striking characteristics of this fault-line and of the geological formations which occur along this line of weakness in the earth's crust, with special reference to the formations in British North America, were discussed.

Recent investigations in the succession of faunas and geological formations in Eastern Canada have emphasized the fact that those formations which occur to the south and south-east of this great dislocation are strikingly like the geological formations referable to the same geological systems in Great Britain and Western Europe. The fault, as it is traced to-day, appears to divide the geological formations of the Maritime Provinces and Canada into two distinct geological provinces—one, east of the fault, in which the several formations resemble both lithologically and palæontologically the British succession; the other, to the west of this great fault, where there occurs the typical American or epicontinental type of succession.

2. 'The Point-de-Galle Group (Ceylon): Wollastonite-Scapolite-Gneisses.' By Ananda K. Coomáraswámy, Esq., B.Sc., F.L.S., F.G.S.

The chief rock-types vary from basic pyroxene-sphene-scapolite-rock, through intermediate rocks composed of pyroxene, scapolite, and wollastonite, with felspar and quartz subordinate or abundant, to acid types made up of orthoclase-microperthite or coarse-grained quartzo-felspathic rocks. They differ from the normal types belonging to the Charnockite Series in their somewhat coarser grain, in the presence of wollastonite, scapolite, and sphene, the existence of definite dykes and segregation-veins crossing the foliation, and in the absence of garnet, hypersthene, original mica, and hornblende; but they resemble the series in the variability of chemical and mineralogical composition, in the conspicuous foliation, the common strike, the petrological character of the acid types, and in the local tendency to graphic structures. The foliation, dykes, weathering, and relationship to the Charnockite Series are described; and an account is given of the more important of the minerals. The rocks must be classed as orthogneisses, and the wollastonite and scapolite are original minerals. Possibly the richness in lime is due to the absorption of a mass of limestone by a portion of the Charnockite Series. If this be the case, the lime-silicates must be regarded as endomorphic contact-minerals. On the other hand, the local richness in lime might be due to an original variation in the constitution of the magma. The rocks show a progressive differentiation from basic to acid types, the coarse segregation-veins being the last product of the process. That the rocks have not suffered from earth-movement since their complete consolidation is evidenced by their microscopic characters, while the interlocking of the minerals at the junction of the segregation-veins with the matrix shows that the veins are of contemporaneous character.

3. 'On the Jurassic Strata cut through by the South Wales Direct Line between Filton and Wootton Bassett.' By Prof. Sidney Hugh Reynolds, M.A., F.G.S., and Arthur Vaughan, Esq., B.A., B.Sc., F.G.S.

In this section a thin bed of typical Cotham Marble is followed by the 'White Lias,' and that by the Lower Lias, which in this district attains a thickness of about 200 feet. The following zones are represented:—(1) the *Planorbis*-beds, containing the *Ostrea*-beds and the *Cidaris*-shales; (2) the *Angulatus*-beds, including the *Conybeari* sub-zone; (3) probably the *Bucklandi*-bed; (4) the *Turneri*-shales; (5) the *Oxynotus*-beds; (6) the *Armatus* and *Jamesoni*-beds; and (7) the *Capricornus*-zone. The strata are remarkably shaly, limestone being predominant only at the base. The typical ironshot Marlstone is only a few feet thick, and the Upper Lias is reduced to a thickness of about 10 feet. The latter consists of a compact, cream-coloured marl with *Ammonites falcifer*, a compact marly limestone with *Amm. communis*, and a pyritic bed containing *Amm. bifrons*. The Cotteswold Sands are 185 feet thick, and contain, at several horizons, hard marly beds with *Amm. striatulus*. They are capped by the Cephalopod-Bed, in which Mr. S. S. Buckman has recognized four ammonite-zones.

The Inferior Oolite has at its base a rock on the horizon of the 'Pea-Grit' followed by oolitic limestones and '*Trigonia*-Grit.' It is succeeded by an oolitic limestone of considerable thickness containing fossils of the Fullers' Earth type, and forming a passage between the Inferior Oolite and the Fullers' Earth, which comes next in succession. Above this are sandy limestones, passage-beds, with *Amm. gracilis*, a form found in the Stonesfield 'Slate.' The Great Oolite consists of white oolitic limestones with a *Pholadomya*-bed below, and an upper series of wedge-bedded oolitic limestones containing lenticular patches of clay and sand with a Bradford-Clay fauna. The Forest Marble, which is of great thickness and monotonous character, consists chiefly of shales, with bands of sandy, shelly, and oolitic limestones. It is followed by the Cornbrash. The Oxford Clay with the usual zones, and the Corallian clays and pisolite close the sections. Fossil lists and palæontological notes on each subdivision are given.

XIV. *Intelligence and Miscellaneous Articles.*

ANOTHER HODGKINS GOLD MEDAL AWARDED.

IN March last, Secretary Langley of the Smithsonian Institution appointed a Committee to consider whether any discovery had been made since the award of the first Hodgkins Gold Medal in 1899, under the general terms of the gift, "The increase and diffusion of more exact knowledge in regard to the nature and properties of atmospheric air in connection with the welfare of man," which would render it proper that such a medal should be again awarded. This Committee consisted of the following distinguished men of science:—Mr. Richard Rathbun, Assistant Secretary of the Smithsonian Institution, Chairman; Doctor A. Graham Bell, for Electricity; Doctor Ira Remsen, for Chemistry; Doctor Charles D. Walcott, for Geology; Professor E. C. Pickering, for Astronomy; Doctor Theodore N. Gill, for Biology; Professor Cleveland Abbe, for Meteorology; Mr. William H. Holmes, for Anthropology; and Mr. S. W. Stratton, for Physics.

Owing to the absence of Mr. Rathbun, Doctor Remsen served as Chairman at a meeting of the Committee held at the Smithsonian Institution in Washington, April 15th, 1902. At this meeting the following resolution was unanimously adopted:—

> "That the Committee recommend to the Secretary of the Smithsonian Institution that it is desirable that one of the Hodgkins Gold Medals be struck, and that it be awarded to J. J. Thomson, of Cambridge, England, for his investigations on the conductivity of gases, especially on the gases that compose the atmospheric air."

The finding of the Committee being approved by the Secretary, steps were at once taken to have the second Hodgkins gold medal struck, under the personal supervision of its designer, Monsieur J. C. Chaplain, of Paris. The medal (shown in the accompanying photographic illustration *) has recently been received by the Institution, and has been despatched to Professor Thomson through the Department of State.

* [We regret that want of space prevents our reproducing the beautiful photograph sent.]

LANDOLT-BÖRNSTEIN, PHYSIKALISCH-CHEMISCHEN TABELLEN.

WE are requested by Professor Börnstein to inform our readers that he and Prof. Meyerhoffer are preparing a new edition of the *Physikalisch-chemischen Tabellen* (edited by Landolt and Börnstein, 1883 and 1894), and would like to receive from English physicists and chemists any corrections, emendations, or additions, in order to render the new edition more perfect.

Professor Börnstein's address is: Wilmersdorf b. Berlin. Landhausstrs. 10.

Professor Meyerhoffer's address is: Berlin W. Uhlandstrs. 162.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

FEBRUARY 1903.

XV. *The Magnetic and Electric Deviation of the easily absorbed Rays from Radium.* By E. RUTHERFORD, *M.A., D.Sc., Macdonald Professor of Physics, McGill University, Montreal*[*].

RADIUM gives out three distinct types of radiation:—

(1) The α rays, which are very easily absorbed by thin layers of matter, and which give rise to the greater portion of the ionization of the gas observed under the usual experimental conditions.

(2) The β rays, which consist of negatively charged particles projected with high velocity, and which are similar in all respects to cathode rays produced in a vacuum-tube.

(3) The γ rays, which are non-deviable by a magnetic field, and which are of a very penetrating character.

These rays differ very widely in their power of penetrating matter. The following approximate numbers, which show the thickness of aluminium traversed before the intensity is reduced to one-half, illustrate this difference.

Radiation.	Thickness of Aluminium.
α rays	·0005 cm.
β rays	·05 cm.
γ rays	8 cms.

In this paper an account will be given of some experiments which show that the α rays are deviable by a strong magnetic and electric field. The deviation is in the opposite sense to

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[*] Communicated by the Author.

that of the cathode rays, so that the radiations must consist of positively charged bodies projected with great velocity. In a previous paper* I have given an account of the indirect experimental evidence in support of the view that the α rays consist of projected charged particles. Preliminary experiments undertaken to settle this question during the past two years gave negative results. The magnetic deviation, even in a strong magnetic field, is so small that very special methods are necessary to detect and measure it. The smallness of the magnetic deviation of the α rays, compared with that of the cathode rays in a vacuum-tube, may be judged from the fact that the α rays, projected at right angles to a magnetic field of strength 10,000 C.G.S. units, describe the arc of a circle of radius about 39 cms., while under the same conditions the cathode rays would describe a circle of radius about ·01 cm.

In the early experiments radium of activity 1000 was used, but this did not give out strong enough rays to push the experiment to the necessary limit. The general method employed was to pass the rays through narrow slits and to observe whether the rate of discharge, due to the issuing rays, was altered by the application of a magnetic field. When, however, the rays were sent through sufficiently narrow slits to detect a small deviation of the rays, the rate of discharge of the issuing rays became too small to measure, even with a sensitive electrometer.

I have recently obtained a sample of radium† of activity 19,000, and using an electroscope instead of an electrometer, I have been able to extend the experiments, and to show that the α rays are all deviated by a strong magnetic field.

Magnetic Deviation of the Rays.

Fig. 1 A shows the general arrangement of the experiment. The rays from a thin layer of radium passed upwards through a number of narrow slits, G, in parallel, and then through a thin layer of aluminium foil ·00034 cm. thick into the testing vessel V. The ionization produced by the rays in the testing vessel was measured by the rate of movement of the leaves of a gold-leaf electroscope B. This was arranged after the manner of C. T. R. Wilson in his experiments on

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* Phil. Mag. Jan. 1903, p. 113. It was long ago suggested by Strutt (Phil. Trans. Roy. Soc. 1900) that the α rays consist of positively charged particles projected from the active substance. The same idea has lately been advanced by Sir Wm. Crookes (Proc. Roy. Soc. 1900).

† The sample of radium of greater activity than that usually sold was obtained from the Société Centrale de Produits Chimiques, through the kindness of M. P. Curie.

the spontaneous ionization of air. The gold-leaf system was insulated inside the vessel by a sulphur bead C, and could be

Fig. 1 A.

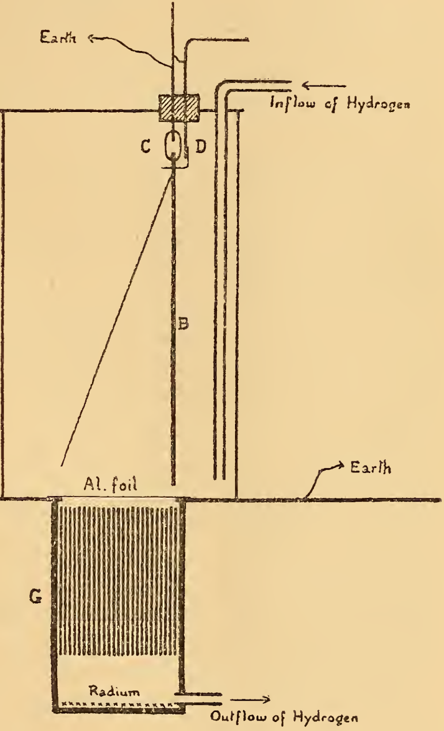


Fig. 1 B.

charged by means of a movable wire D, which was afterwards earthed. The rate of movement of the gold-leaf was observed by means of a microscope through small mica windows in the testing vessel.

In order to increase the ionization in the testing vessel, the rays passed through 20 to 25 slits of equal width, placed side by side. This was arranged by cutting grooves at regular intervals in side-plates into which brass plates were slipped. A cross section of the system of metal plates and air-spaces is shown in fig. 1 B.

The width of the slit varied in different experiments between ·042 and ·1 cm.

The magnetic field was applied perpendicular to the plane of the paper and parallel to the plane of the slits.

The testing vessel and system of plates were waxed to a lead plate P so that the rays entered the vessel V only through the aluminium foil.

It is necessary in these experiments to have a steady stream of gas passing downwards between the plates in order to prevent the diffusion of the emanation from the radium upwards into the testing vessel. The presence in the testing vessel of a small amount of this emanation, which is always given out by radium, would produce large ionization effects and completely mask the effect to be observed.

For this purpose a steady current of dry electrolytic hydrogen of 2 c.c. per second was passed into the testing vessel, streamed through the porous aluminium foil, and passed between the plates, carrying with it the emanation from the apparatus.

The use of a stream of hydrogen instead of air greatly simplifies the experiment, for it *increases* at once the ionization current due to the α rays in the testing vessel, and (at the same time) greatly *diminishes* that due to the β and γ rays.

This follows at once from the fact that the α rays are much more readily absorbed in air than in hydrogen, while the rate of production of ions due to the β and γ rays is much less in hydrogen than in air. The intensity of the α rays after passing between the plates is consequently greater when hydrogen is used; and since the rays pass through a sufficient distance of hydrogen in the testing vessel to be largely absorbed, the total amount of ionization produced by them in hydrogen is greater than in air.

With the largest electromagnet in the laboratory I was only able to deviate about 30 per cent. of the α rays. Through the kindness of Professor Owens, of the Electrical Engineering Department, I was, however, enabled to make use of the upper part of the field-magnet of a 30 kilowatt Edison dynamo. Suitable pole-pieces are at present being made for the purpose of obtaining a strong magnetic field over a considerable area; but with rough pole-pieces I have been enabled to obtain a sufficiently strong field to completely deviate the α rays.

The following is an example of an observation on the magnetic deviation:—

Pole-pieces 1·90 × 2·50 cms.

Strength of field between pole-pieces 8370 units.

Apparatus of 25 parallel plates of length 3·70 cms., width ·70 cm., with an average air-space between plates of ·042 cm.

Distance of radium below plates 1·4 cm.

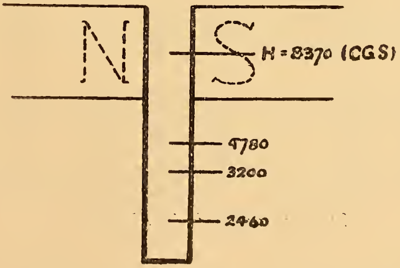
	Rate of Discharge of Electroscope in volts per minute.
(1) Without magnetic field	8·33
(2) With magnetic field	1·72
(3) Radium covered with thin layer of mica to absorb all α rays ...	0·93
(4) Radium covered with mica and magnetic field applied	0·92

The mica plate, ·01 cm. thick, was of sufficient thickness to completely absorb all the α rays, but allowed the β and γ rays to pass through without appreciable absorption. The difference between (1) and (3), 7·40 volts per minute, gives the rate of discharge due to the α rays alone; the difference between (2) and (3), 0·79 volt per minute, that due to the α rays not deviated by the magnetic field employed.

The amount of α rays not deviated by the field is thus about 11 per cent. of the total. The small difference between (2) and (4) includes the small ionization due to the β rays, for they would have been completely deviated by the magnetic field. It is probable that the ionization due to the β rays without a magnetic field was actually stronger than this; but the residual magnetic field, when the current was broken, was large enough to deviate them completely before reaching the testing vessel. (4) comprises the effect of the γ rays together with the natural leak of the electroscope in hydrogen.

In this experiment there was a good deal of stray magnetic field acting on the rays before reaching the pole-pieces. The distribution of this field at different portions of the apparatus is shown graphically in fig. 2.

Fig. 2.

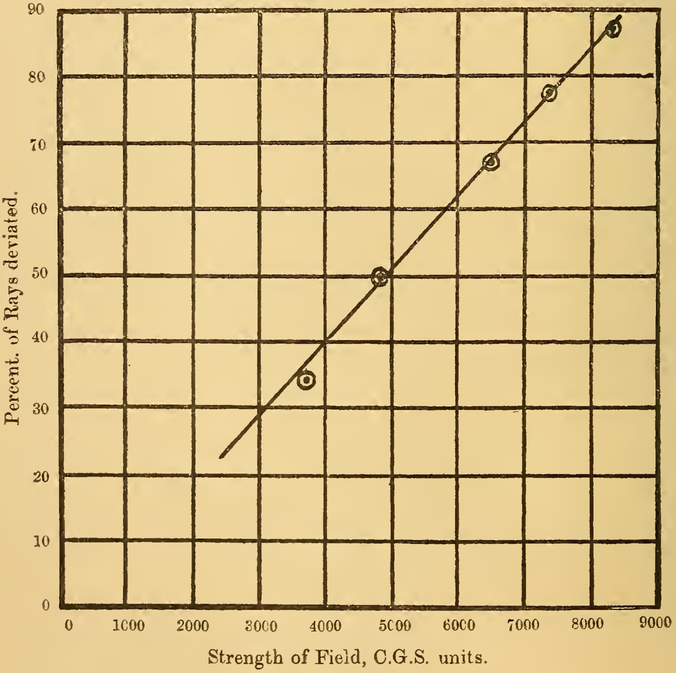


The following table shows the rate of discharge due to the α rays for different strengths of the magnetic field. The maximum value with no magnetic field is taken as 100. These results are shown graphically in fig. 3.

Magnetic field between pole-pieces.	Rate of discharge due to *a* rays.
0	100
3720 C.G.S. units	66
4840 " "	50
6500 " "	33
7360 " "	23
8370 " "	11

The curve (fig. 3) shows that the amount deviated is approximately proportional to the magnetic field.

Fig. 3.

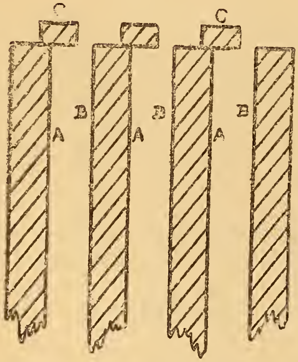


With another apparatus, with a mean air space of ·055 cm., the rays were *completely* deviated by a uniform magnetic field of strength 8400 units extending over the length of the plates, a distance of 4·5 cms.

Direction of the Deviation of the Rays.

In order to determine the direction of the deviation, the rays were passed through slits of 1 mm. width. Each slit was about half covered by a brass plate in which air-spaces were cut to correspond accurately with the system of parallel plates. Fig. 4 represents an enlarged section of three of the plates, with the metal plate C half covering the slit AB. If a magnetic field is applied, not sufficiently great to deviate all the rays, the rate of discharge in the testing vessel when the rays are deviated in the direction from A to B should be much greater than when the magnetic field is reversed, *i. e.* when the rays are deviated from B to A. This was found to be the case, for while the rate of discharge was not much diminished by the application of the field in one direction, it was reduced to about one quarter of its value by reversal of the field.

Fig. 4.



In this way it was found that the direction of deviation in a magnetic field was *opposite* in sense to the cathode rays, *i. e.*, the rays consisted of positively charged particles.

Electrostatic Deviation of the Rays.

The apparatus was similar to that employed for the magnetic deviation of the rays with the exception that the brass sides, which held the plates in position, were replaced by ebonite.

Twenty-five plates were used of length 4·50 cms., width 1·5 cm., and average air-space of ·055 cm. The radium was ·85 cm. below the plates. Alternate plates were connected together and charged by means of a battery of small accumulators to a potential-difference of 600 volts. A current of hydrogen was used as in the case of the magnetic experiment.

With a P.D. of 600 volts, a consistent difference* of 7 per cent. was observed in the rate of discharge due to the α rays with the electric field off and on. A larger potential-difference could not be used as a spark passed between the plates in the presence of radium.

The amount of deviation in this experiment was too small to determine the direction of deviation by the electric field.

Determination of the Velocity of the Rays.

It is difficult to determine with certainty the value of the curvature of the path of the rays in a given magnetic field from the percentage amount of rays deviated, on account of the fact that some of the rays which strike the sides of the parallel plates are deviated so as to pass into the testing vessel.

From data obtained, however, by observing the value of the magnetic field for *complete deviation* of the rays, it was deduced that

$$H\rho = 390{,}000.$$

where H = value of magnetic field,

ρ = radius of curvature of path of the rays.

This gives the higher limit of the value $H\rho$.

By using the usual equations of the deviation of a moving charged body it was deduced that the velocity V of the rays was given by

$$V = 2{\cdot}5 \times 10^9 \text{ cms. per sec.},$$

and that the value $\frac{e}{m}$, the ratio of the charge of the carrier to its mass, was given by

$$\frac{e}{m} = 6 \times 10^3.$$

These results are only rough approximations and merely indicate the order of the values of these quantities, as the electric deviations observed were too small for accurate observations. The experiments are being continued with special apparatus, and it is hoped that much larger electrostatic deviations will be obtained, and in consequence a more accurate determination of the constants † of the rays.

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[*] In later experiments, which are not yet completed, I have been able to deviate about 45 per cent. of the α rays in a strong electric field.

[†] The α rays are complex, and probably consist of particles projected with velocities lying between certain limits; for the radiations include the α radiations from the emanation and excited activity which are distributed throughout the radium compound.

The α rays from radium are thus very similar to the *Canal Strahlen* observed by Goldstein, which have been shown by Wien to be positively charged bodies moving with a high velocity. The velocity of the α rays is, however, considerably greater than that observed for the *Canal Strahlen.*

General Considerations.

The radiations from uranium, thorium, and radium, and also the radiations from the emanations and excited bodies, all include a large proportion of α rays. These rays do not differ much in penetrating power, and it is probable that *in all cases* the α radiations from them are charged particles projected with great velocities.

In a previous paper* it has been shown that the total energy radiated in the form of α rays by the permanent radioactive bodies is about 1000 times greater than the energy radiated in the form of β rays. This result was obtained on the assumption that the total number of ions produced by the two types of rays when completely absorbed in air, is a measure of the energy radiated. The α rays are thus the most important factor in the radiation of energy from active bodies, and, in consequence, any estimate of the energy radiated based on the β rays alone leads to much too small a value.

Experiments are in progress to determine the charge carried by the α rays, and from these it is hoped to deduce the rate of emission of energy in the form of α rays from the active substances.

The projection character of the α rays very readily explains some of their characteristic properties. On this view the ionization of the gas by the α rays is due to collisions of the projected masses with the gas molecules. The variation of the rate of production of the ions with the pressure of the gas and the variation of absorption of the rays in solids and gases with the density at once follows. It also offers a simple explanation of the remarkable fact that the absorption of the α rays in a given thickness of matter, when determined by the electrical method, *increases* with the thickness of matter previously traversed. It is only necessary to suppose that as the velocity of the projected particles decreases in consequence of collision with the molecules of the absorbing medium, the ionizing power of the rays decreases rapidly. This is most probably the case, for there seems to be no doubt that the positive carrier cannot ionize

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* Rutherford and Grier, Phil. Mag. Sept. 1902.

the gas below a certain velocity, which is very great compared with the velocity of translation of the molecules.

It is of interest to consider the probable part that the *α* rays play in the radioactive bodies on the general view of radioactivity that has been put forward by Mr. Soddy and myself in the Phil. Mag. Sept. and Nov. 1902. It is there shown that radioactivity is due to a succession of chemical changes in which new types of radioactive matter are being continuously formed, and that the constant radioactivity of the well known active bodies is an equilibrium process, where the rate of production of fresh active matter is balanced by the decay of activity of that already produced. Some very interesting points arose in the course of these investigations. It was found that the residual activity of uranium and thorium when freed from UrX and ThX by chemical processes consisted entirely of *α* rays. On the other hand, the radiation of UrX* consisted almost entirely of *β* rays, while that of ThX † consisted of both *α* and *β* rays. Similar results probably hold also for radium, for the Curies have shown that radium dissolved in water and then evaporated to dryness temporarily loses to a large extent its power of emitting *β* rays.

It thus appears probable that the emission of *α* rays goes on quite independently of the emission of *β* rays. There seems to be no doubt that the emission of *β* rays by active substances is a secondary phenomenon, and that the *α* rays play the most prominent part in the changes occurring in radioactive matter. The results obtained so far point to the conclusion that the beginning of the succession of chemical changes taking place in radioactive bodies is due to the emission of the *α* rays, *i.e.* the projection of a heavy charged mass from the atom. The portion left behind is unstable, undergoing further chemical changes which are again accompanied by the emission of *α* rays, and in some cases also of *β* rays.

The power possessed by the radioactive bodies of apparently spontaneously projecting large masses with enormous velocities supports the view that the atoms of these substances are made up, in part at least, of rapidly rotating or oscillating systems of heavy charged bodies large compared with the electron. The sudden escape of these masses from their orbit may be due either to the action of internal forces or external forces of which we have at present no knowledge.

It also follows from the projection nature of the *α* rays that the radioactive bodies, when inclosed in sealed vessels

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* Soddy, Proc. Chem. Soc. 1902.

† Rutherford and Grier, Phil. Mag. Sept. 1902.

sufficiently thin to allow the α rays to escape, must *decrease in weight*. Such a decrease has been recently observed by Heydweiler* for radium, but apparently under such conditions that the α rays would be largely absorbed in the glass tube containing the active matter.

In this connexion it is very important to decide whether the loss of weight observed by Heydweiler is due to a decrease of weight of the radium itself or to a decrease of weight of the glass envelope; for it is well known that radium rays produce rapid colourations throughout a glass tube, and it is possible that there may be a chemical change reaching to the surface of the glass which may account for the effects observed.

McGill University,
Montreal, Nov. 10, 1902.

XVI. *On Vector Differentials.* *By* Frank Lauren Hitchcock.—Second Paper †.

1. THE calculus of Quaternions enables us to represent a vector, or directed quantity, by a single symbol, and to work with it easily and compactly. We are not obliged to resolve into components, nor do we arbitrarily introduce any lines or planes of reference.

One of the simplest vectors is that of a point in space, represented by the symbol ρ. If we have a vector function of ρ continuously distributed throughout a portion of space, we may differentiate it: the result is a linear and vector function of $d\rho$, closely analogous, in a mathematical sense, to a homogeneous strain. Any such strain is fully determined if we know the roots of the strain-cubic, and the three directions which correspond to them.

In an introductory paper on this subject (Phil. Mag. June 1902, p. 576) it was shown that if ν be a vector of unit-length normal to any family of surfaces, and if its differential be $\chi d\rho$, then one of the roots of the cubic in χ is always zero.

The other two roots give directions tangent to the lines of curvature. For a line of curvature may be defined as one such that normals at contiguous points intersect, that is, such that the three vectors ν, $\nu + d\nu$, and $d\rho$ are coplanar; but because ν is a unit-vector $d\nu$ is at right angles to ν, and therefore parallel to $d\rho$. Accordingly $(\chi - g)d\rho = 0$, g being a root of the strain-cubic.

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* *Phys. Zeit.* 1902.

† Communicated by the Author.

If we take ϵ a unit-vector along this direction, and η another unit-vector such that $\epsilon\eta=\nu$, it is legitimate to write

$$\nabla\nu=\nu\chi\nu+\epsilon\chi\epsilon+\eta\chi\eta\ ;$$

the vector part of $\nabla\nu$ is equal to the term $\nu\chi\nu$, a result of the paper referred to above; $V\epsilon\chi\epsilon=0$ by the last paragraph; whence $V\eta\chi\eta$ also vanishes and η gives the other root of the strain-cubic.

2. To illustrate further these fundamental facts, take Dupin's theorem that "each member of one of three families of orthogonal surfaces cuts each member of each of the other families along its lines of curvature."

Let the unit-normals be ν ν_1, and ν_2. Then

$$\nabla\nu_1=\nabla(\nu_2\nu)=\nabla\nu_2\,.\,\nu-\nu_2\nabla\nu-2\chi\nu_2.$$

Operate by $S\nu_1$, remembering that

$$S\nu\nabla\nu=S\nu_1\nabla\nu_1=S\nu_2\nabla\nu_2=0;$$

we thus have at once

$$S\nu_1\chi\nu_2=0,$$

that is, $\chi\nu_2$ is at right angles to ν_1. But $\chi\nu_2$ is already known to be at right angles to ν, and is therefore parallel to ν_2. This proves the proposition.

3. In order to study certain quantities related to the second differential of the vector ν we may adopt the notation

$$dV\nabla\nu=\psi d\rho,$$

and remembering that $\chi\nu$ and $V\nabla\nu$ have the same tensor we may put

$$\chi\nu=c\lambda\ ;\ V\nabla\nu=c\mu.$$

Thus λ, μ, and ν form a rectangular unit system. Differentiation with regard to these three directions may be represented by $\frac{d}{dl}$, $\frac{d}{dm}$, and $\frac{d}{dn}$ respectively. Here λ and μ are not the same as the ϵ and η of Art. 1, except in certain cases, of which families of cylinders are among the simplest.

The constituents of ψ may be arranged according to the following skeleton:—

$$\left.\begin{aligned}\psi\lambda&=P\lambda+r\mu+q'\nu\\ \psi\mu&=r'\lambda+Q\mu+p\nu\\ \psi\nu&=q\lambda+p'\mu+R\nu\end{aligned}\right\},$$

in which if we interchange p and p', q and q', r and r', we shall change ψ into ψ'.

To build up this function notice first that the quantity c is the absolute curvature of the orthogonal trajectories of the given surfaces. If c_1 be the tortuosity of these curves then

$$\frac{d\mu}{dn}=c_1\lambda\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

cf. Tait's 'Quaternions,' §§ 299, 300. Hence

$$\begin{aligned}\psi\nu&=\frac{d(c\mu)}{dn}\\&=\frac{dc}{dn}\mu+c\frac{d\mu}{dn}\\&=cc_1\lambda+\frac{dc}{dn}\mu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)\end{aligned}$$

which gives definite values for q and p', and shows that R vanishes. Again

$$\begin{aligned}dc&=d\mathrm{TV}\nabla\nu\\&=-\mathrm{S}\mu\psi d\rho, \text{ by Tait, § 140 (1)}\\&=-\mathrm{S}d\rho\psi'\mu,\end{aligned}$$

so that

$$\begin{aligned}\nabla c&=\psi'\mu\\&=\frac{dc}{dl}\lambda+\frac{dc}{dm}\mu+\frac{dc}{dn}\nu, \quad . \quad . \quad . \quad . \quad . \quad (3)\end{aligned}$$

giving values for Q and r. Next take

$$\begin{aligned}\psi d\rho&=d\mathrm{V}\nabla\nu\\&=d(\nu\chi\nu)\\&=-\mathrm{V}\chi\nu\chi d\rho+\mathrm{V}\nu\phi d\rho, \text{ say ;}\end{aligned}$$

then by taking conjugates,

$$\psi'd\rho=\chi'\mathrm{V}\chi\nu d\rho-\phi'\mathrm{V}\nu d\rho,$$

whence by putting ν for $d\rho$ and remembering that $\chi\mu=\chi'\mu$,

$$\begin{aligned}\psi'\nu&=-c\chi\mu\\&=c\lambda\mathrm{S}\lambda\chi\mu+c\mu\mathrm{S}\mu\chi\mu, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)\end{aligned}$$

giving values for p and q'.

Furthermore, because $\nabla^2\nu$ is a vector,

$$\begin{aligned} S\nabla V\nabla\nu &= 0 \\ &= S(\lambda\psi\lambda + \mu\psi\mu + \nu\psi\nu) \\ &= -(P + Q + R) \\ &= -(P + \frac{dc}{dm} + 0), \text{ by (2) and (3),} \end{aligned}$$

whence we have for the value of P,

$$P = -\frac{dc}{dm}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It remains to get an expression for r'. Identically we have

$$\nabla V\nabla\nu = (p-p')\lambda + (q-q')\mu + (r-r')\nu\,; \quad . \quad . \quad (6)$$

operate by $S\nu$ and put for r its value from (3),

$$S\,.\,\nu\nabla(c\mu) = r' - \frac{dc}{dl},$$

but by the ordinary expansion

$$S\,.\,\nu\nabla(c\mu) = cS\nu\nabla\mu - \frac{dc}{dl}\,;$$

whence by equating values

$$r' = cS\nu\nabla\mu. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

To sum up results,

$$\left.\begin{array}{l} \psi\lambda = \quad -\dfrac{dc}{dm}\lambda + \dfrac{dc}{dl}\mu + c\nu S\lambda\chi\mu \\ \psi\mu = cS\nu\nabla\mu\,.\,\lambda + \dfrac{dc}{dm}\mu + c\nu S\mu\chi\mu \\ \psi\nu = \qquad cc_1\lambda + \dfrac{dc}{dn}\mu \end{array}\right\}, \quad . \quad . \quad . \quad (8)$$

or more compactly

$$\psi d\rho = \lambda S d\rho\left(\frac{dc}{dm}\lambda - cS\nu\nabla\mu\,.\,\mu - cc_1\nu\right) - \mu S d\rho\nabla c + c\nu S d\rho\chi\mu.$$

The quantity r' may be expanded thus

$$\begin{aligned} r' &= cS\nu\nabla\mu \\ &= cS\nu\nabla(-\lambda\nu) \\ &= -cS\nu(\nabla\lambda\,.\,\nu - \lambda\nabla\nu - 2\chi\lambda) \\ &= c(S\nabla\lambda - c). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9) \end{aligned}$$

4. Quantities such as $S\nabla\lambda$ involve operating on ν by both ∇ and d. These operators are not always commutative. In fact if P be any scalar, and σ and τ any vectors, whose differentials we may call $\phi d\rho$ and $\theta d\rho$, we shall have

$$\nabla S\tau\nabla P = S\tau\nabla\,.\,\nabla P - \theta'\nabla P, \text{ by (5) of the first paper,}$$
$$= S\tau\nabla\,.\,\nabla P + iS\theta i\nabla P + jS\theta j\nabla P + kS\theta k\nabla P,$$

and this extended to a vector by the usual method gives

$$\nabla\phi\tau = -S\tau\nabla\,.\,\nabla\sigma + i\phi\theta i + j\phi\theta j + k\phi\theta k. \quad . \quad (10)$$

This equation may be obtained in a quite different way. Write

$$d\phi\tau = d\phi\,.\,\tau + \phi d\tau,$$

where $d\phi\,.\,\tau$ indicates the result of differentiating $\phi\tau$ as if τ were a constant vector. With this understanding

$$d\phi\tau = Sd\rho\nabla\,.\,S\tau\nabla\,.\,\sigma + \phi\theta d\rho$$
$$= S\tau\nabla\,.\,Sd\rho\nabla\,.\,\sigma + \phi\theta d\rho,$$

provided we do not substitute for $d\rho$ any but constant vectors. If now we call the two terms on the right $\phi_1 d\rho$ and $\phi_2 d\rho$, we shall obtain from each a part of $\nabla\phi\tau$. The first term gives

$$q_1 = iS\tau\nabla\,.\,Si\nabla\,.\,\sigma + jS\tau\nabla\,.\,Sj\nabla\,.\,\sigma + kS\tau\nabla\,.\,Sk\nabla\,.\,\sigma$$
$$= S\tau\nabla\,.\,(iSi\nabla\,.\,\sigma + jSj\nabla\,.\,\sigma + kSk\nabla\,.\,\sigma)$$
$$= -S\tau\nabla\,.\,\nabla\sigma,$$

and the second term gives

$$q_2 = i\phi\theta i + j\phi\theta j + k\phi\theta k,$$

leading to the same result as before.

5. From (10), by putting ν for τ and χ for ϕ,

$$\nabla\chi\nu = \frac{d}{dn}\nabla\nu + \lambda\chi^2\lambda + \mu\chi^2\mu + \nu\chi^2\nu. \quad . \quad . \quad (11)$$

Here the first term on the right is the same as $\psi\nu - \frac{dm_2}{dn}$; and because for any direction at right angles to ν

$$\chi^2 - m_2\chi + m_1 = 0, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

it follows that

$$\begin{aligned}\lambda\chi^2\lambda+\mu\chi^2\mu&=\lambda(m_2\chi-m_1)\lambda+\mu(m_2\chi-m_1)\mu\\&=2m_1+m_2(\lambda\chi\lambda+\mu\chi\mu)\\&=2m_1+m_2\mathrm{S}(\lambda\chi\lambda+\mu\chi\mu+\nu\chi\nu)\\&=2m_1-m_2^2\,;\end{aligned}$$

the last term of (11) may be written $c\nu\chi\lambda$; therefore

$$\left.\begin{aligned}\mathrm{V}\nabla\chi\nu&=\psi\nu+c\nu\chi\lambda\\\mathrm{S}\nabla\chi\nu&=2m_1-m_2^2-\frac{dm_2}{dn}\end{aligned}\right\}. \quad . \quad . \quad . \quad (11a)$$

$\mathrm{S}\nabla\chi\nu$ may also be expanded thus

$$\begin{aligned}\mathrm{S}\nabla\chi\nu&=\mathrm{S}\nabla(c\lambda)\\&=c\mathrm{S}\nabla\lambda-\frac{dc}{dl},\end{aligned}$$

which by comparison gives

$$\mathrm{S}\nabla\lambda=\frac{1}{c}\left(2m_1-m_2^2-\frac{dm_2}{dn}+\frac{dc}{dl}\right), \quad . \quad . \quad (13)$$

and so from (9)

$$r'=2m_1-m_2^2-\frac{dm_2}{dn}+\frac{dc}{dl}-c^2. \quad . \quad . \quad . \quad (14)$$

6. Because $d(c\mu)=dc\,.\,\mu+cd\mu$ and μ is a unit-vector, it is clear we may write the value of $d\mu$ by inspection of (8), dropping the component along μ and dividing the rest by c. This gives

$$d\mathrm{UV}\nabla\nu=\lambda\mathrm{S}d\rho\left(\frac{1}{c}\,\frac{dc}{dm}\lambda-\mathrm{S}\nu\nabla\mu\,.\,\mu-c_1\nu\right)+\nu\mathrm{S}d\rho\chi\mu. \quad (15)$$

The differentials of $\chi\nu$ and $\mathrm{U}\chi\nu$, that is of $c\lambda$ and λ, are easily expressed in terms of ψ and χ. For

$$d\chi\nu=d(\mathrm{V}\nabla\nu\,.\,\nu)=c\mathrm{V}\mu\chi d\rho-\mathrm{V}\nu\psi d\rho\,;$$

the first term on the right is the same as $c\nu\mathrm{S}\lambda\chi d\rho$ and the last term is the same as $-\lambda\mathrm{S}d\rho\psi'\mu+\mu\mathrm{S}d\rho\psi'\lambda$: therefore

$$d\chi\nu=-\lambda\mathrm{S}d\rho\nabla c+\mu\mathrm{S}d\rho\psi'\lambda+c\nu\mathrm{S}\lambda\chi d\rho. \quad . \quad (16)$$

For $d\mathrm{U}\chi\nu$ we have only to drop the component of $d\chi\nu$ along λ, and divide the rest by c. This gives

$$d\mathrm{U}\chi\nu=\frac{1}{c}\,\mu\mathrm{S}d\rho\psi'\lambda+\nu\mathrm{S}d\rho\chi'\lambda. \quad . \quad . \quad . \quad (17)$$

7. As an application of some of these expressions, let us examine the criterion that the state of affairs contemplated in Dupin's theorem may exist: in other words, find the differential equation which must be satisfied by the unit-normal to a family of surfaces in order that there may be two other orthogonal families.

One form of the condition is that $S\epsilon\nabla\epsilon$ and $S\eta\nabla\eta$ shall both vanish, ϵ and η having the same meaning as in Art. 1. Furthermore,

$$\begin{aligned}\nabla\epsilon &= \nabla(\eta\nu)\\ &= \nabla\eta\,.\,\nu - \eta\nabla\nu - 2\chi\eta,\end{aligned}$$

and by operating with $S\epsilon$ we obtain for *all* families of surfaces

$$S\epsilon\nabla\epsilon = S\eta\nabla\eta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Hence, if the condition just mentioned is fulfilled,

$$S\epsilon\nabla\epsilon + S\eta\nabla\eta = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19a)$$

It is here not essential that ϵ and η shall be of constant length. We may, therefore, put for them any other vectors to which they are respectively parallel. If g and g' be the roots of the quadratic equation

$$\chi^2 - m_2\chi + m_1 = 0,$$

so that $(\chi - g)\epsilon = 0$ and $(\chi - g')\eta = 0$, and if we operate on any vector at right angles to ν with $\chi - g'$ and with $\chi - g$, the two results will be parallel, in order, to ϵ and to η. Choosing as a convenient operand the unit-vector μ, that is $UV\nabla\nu$, we shall have

$$S(\chi - g')\mu\nabla(\chi - g')\mu + S(\chi - g)\mu\nabla(\chi - g)\mu = 0, \quad . \quad (19b)$$

and by expanding and rearranging

$$S(2\chi - m_2)\mu\nabla\chi\mu + S(m_2{}^2 - 2m_1 - m_2\chi)\mu\nabla\mu - S\mu\chi\mu\nabla m_2 = 0. \quad (19c)$$

From (10), by writing χ for ϕ and μ for τ and $d\mu = \theta_\mu d\rho$,

$$\nabla\chi\mu = \frac{d}{dm}\nabla\nu + \lambda\chi\theta_\mu\lambda + \mu\chi\theta_\mu\mu + \nu\chi\theta_\mu\nu.$$

The form of (19*c*) shows that we are concerned only with that part of $V\nabla\chi\mu$ lying in the tangent plane. The vector part of $\frac{d}{dm}\nabla\nu$ is $\psi\mu$; the terms $\lambda\chi\theta_\mu\lambda$ and $\mu\chi\theta_\mu\mu$ have no tangential component; the term $\nu\chi\theta_\mu\nu$ equals $c_1\nu\chi\lambda$, by (1) or by (15). Thus the first term of (19*c*) becomes

$$\mathrm{S}(2\chi\mu-m_2\mu)(\psi\mu+c_1\nu\chi\lambda);$$

multiplying, and noticing that $\mu\nu=\lambda$ while $\mathrm{S}\nu\chi\lambda\chi\mu=-m_1$,

$$\mathrm{S}(2\chi-m_2)\mu\psi\mu-2c_1m_1-c_1m_2\mathrm{S}\lambda\chi\lambda$$

is the product. We next obtain from (15)

$$\nabla\mu=\lambda\mathrm{S}\mu\chi\mu+\mu(c_1-\mathrm{S}\lambda\chi\mu)-\nu\frac{r'}{c}\quad . \quad . \quad . \quad (20)$$

and here again we are not concerned with the normal component. Thus the second term of (19*c*) equals

$$\begin{aligned}&\mathrm{S}[(m_2{}^2-2m_1)\mu-m_2\chi\mu][\lambda\mathrm{S}\mu\chi\mu+\mu(c_1-\mathrm{S}\lambda\chi\mu)]\\&=-c_1m_2{}^2+m_2{}^2\mathrm{S}\lambda\chi\mu+2c_1m_1-2m_1\mathrm{S}\lambda\chi\mu-c_1m_2\mathrm{S}\mu\chi\mu.\end{aligned}$$

The third term of (19*c*) is the same as $\frac{dm_2}{dn}\mathrm{S}\lambda\chi\mu$. Collecting results and noticing that $\mathrm{S}(\lambda\chi\lambda+\mu\chi\mu)=-m_2$, we find that all the terms containing c_1 cancel out, and the result is

$$\mathrm{S}(2\chi-m_2)\mu\psi\mu+\mathrm{S}\lambda\chi\mu\left(m_2{}^2-2m_1+\frac{dm_2}{dn}\right)=0, \quad (19d)$$

which by (11*a*) may be written

$$\mathrm{S}(2\chi-m_2)\mu\psi\mu-\mathrm{S}\lambda\chi\mu\mathrm{S}\nabla\chi\nu=0. \quad . \quad . \quad (19e)$$

Again, because of the identity

$$(\psi-\psi')\mu=\mathrm{V}(\nabla\mathrm{V}\nabla\nu)\mu$$

we shall have the following expansions:—

$$\begin{aligned}\mathrm{S}(2\chi-m_2)\mu\psi\mu&=\mathrm{S}(2\chi\mu-m_2\mu)(\psi'\mu-\mu\nabla\mathrm{V}\nabla\nu)\\&=\mathrm{S}(2\chi-m_2)\mu\psi'\mu+2\mathrm{S}\mu\chi\mu\nabla\mathrm{V}\nabla\nu\\&=\mathrm{S}(2\chi-m_2)\mu\psi'\mu+2\mathrm{S}\lambda\chi\mu\mathrm{S}\nu\nabla\mathrm{V}\nabla\nu\\&=\mathrm{S}(2\chi-m_2)\mu\psi'\mu+2\mathrm{S}\lambda\chi\mu(\mathrm{S}\nabla\chi\nu+\mathrm{V}^2\nabla\nu),\end{aligned}$$

and by using this result in (19*e*),

$$\mathrm{S}(2\chi-m_2)\mu\psi'\mu+\mathrm{S}\lambda\chi\mu(\mathrm{S}\nabla\chi\nu+2\mathrm{V}^2\nabla\nu)=0. \quad . \quad (19f)$$

Finally, by adding (19*e*) and (19*f*)

$$\mathrm{S}\mu(\psi+\psi')(2\chi-m_2)\mu+2\mathrm{S}\lambda\chi\mu\mathrm{V}^2\nabla\nu=0, \quad . \quad (19g)$$

where the only operation involving the second differential of the unit-normal is the pure strain $\psi+\psi'$. Thus the equation is of the first order with regard to $V\nabla\nu$.

8. In the paper referred to in Art. 1 it was proved that if P be a scalar such that $\nabla^2 P=0$ the unit-normal to the equipotential surfaces satisfies the equation

$$V\nabla(\nabla\nu\,.\,\nu)=0, \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

of which various expansions were given. If ν be given satisfying this condition P is determined by the equation

$$\log T\nabla P=\nabla^{-1}(\nabla\nu\,.\,\nu), \quad . \quad . \quad . \qquad (22)$$

of which the solution is very direct and obvious. We may thus write, as a set of equations defining orthogonal isothermal surfaces

$$\left.\begin{array}{l} S\nu\nabla\nu=0 \\ S\mu(\psi+\psi')(2\chi-m_2)\mu+2S\lambda\chi\mu V^2\nabla\nu=0 \\ V\nabla(\nabla\nu\,.\,\nu)=0 \\ \log T\nabla P=\nabla^{-1}(\nabla\nu\,.\,\nu) \end{array}\right\}, \quad . \qquad (23)$$

where the first two equations are to be satisfied by one unit-vector in order that there may be three orthogonal families of surfaces, the third equation must be satisfied by each of the three unit-normals in order that these surfaces may all be isotherms, and the last equation serves to determine the three potentials. *Cf.* § 336 of Tait's 'Quaternions.'

9. In studying special cases we have evidently at our disposal a great variety of methods. Equations like (19) appear to be chiefly useful in general investigations. In testing whether any given family of surfaces satisfies the condition discussed in Art. 7 it will usually be easier to find a vector corresponding to one of the non-vanishing roots of the strain-cubic, say parallel to η, and operate on it with $S.\eta\nabla$,—though indeed the nature of the surfaces may be such that (19*g*) takes a very simple form. As a brief example, let a family of rings be denoted by the scalar function

$$P=T^4 q\, S^{-1}\rho\phi\rho,$$

where $q=ix+jy+kz+a$ and $\phi\rho=-(ix+jy)$. Then

$$dTq=-T^{-1}q\, S\rho d\rho,$$

so that by differentiating the given function,

$$dP=-4T^2 q\, S^{-1}\rho\phi\rho\, S\rho d\rho-2T^4 q\, S^{-2}\rho\phi\rho\, Sd\rho\phi\rho,$$

and because $dP=-Sd\rho\nabla P$,

$$\nabla P=4\rho T^2 q\, S^{-1}\rho\phi\rho+2\phi\rho T^4 q\, S^{-2}\rho\phi\rho.$$

Then by taking a unit along $\nabla \mathrm{P}$,

$$\nu = \mathrm{U}\nabla\mathrm{P} = (2\rho\mathrm{S}\rho\phi\rho + \phi\rho\mathrm{T}^2 q)(\mathrm{T}^4 q\ \mathrm{S}\rho\phi\rho - 4a^2\mathrm{S}^2\rho\phi\rho)^{-\frac{1}{2}},$$

$\mathrm{T}^2\phi\rho$ being here the same as $\mathrm{S}\rho\phi\rho$. In differentiating again it will be well to put, for brevity, $\mathrm{T}^2 q = t^2$ and $\mathrm{S}\rho\phi\rho = s^2$, so that we have $\mathrm{T}^2\rho = t^2 - a^2$. The result is

$$d\nu = \chi d\rho = \{d\rho(2t^4s^4 - 8a^2s^6) + 4s^4t^2\rho\mathrm{S}\rho d\rho + \phi\rho\mathrm{S}d\rho\phi\rho(8a^2s^2t^2 - t^6)$$
$$+ \phi d\rho(s^2t^6 - 4a^2s^4t^2) + 2s^2t^4\rho\mathrm{S}d\rho\phi\rho + 8a^2s^4\phi\rho\mathrm{S}\rho d\rho\}\{s^2t^4 - 4a^2s^4\}^{-\frac{3}{2}}.$$

This linear and vector function contains six vector terms, of which all but the last two are self-conjugate, and therefore contribute nothing toward $\mathrm{V}\nabla\nu$. The last two terms give

$$\begin{aligned}\mathrm{V}\nabla\nu &= (2s^2t^4 - 8a^2s^4)\mathrm{V}\rho\phi\rho(s^2t^4 - 4a^2s^4)^{-\frac{3}{2}}\\ &= 2\mathrm{V}\rho\phi\rho(s^2t^4 - 4a^2s^4)^{-\frac{1}{2}}.\end{aligned}$$

If this last expression be substituted for $d\rho$ in $\chi d\rho$ above, all the terms vanish except the first and the fourth, giving

$$\chi\mathrm{V}\nabla\nu = (4s^2\mathrm{V}\rho\phi\rho + 2t^2\phi\mathrm{V}\rho\phi\rho)(s^2t^4 - 4a^2s^4)^{-1}.$$

But bv an elementary transformation (Kelland and Tait's 'Introduction to Quaternions,' p. 190, *r*), since ϕ is self-conjugate, we have

$$\phi\mathrm{V}\rho\phi\rho = -2\mathrm{V}\rho\phi\rho - \mathrm{V}\rho\phi^2\rho,$$

and also $\phi^2\rho = -\phi\rho$, whence

$$\chi\mathrm{V}\nabla\nu = 2\mathrm{V}\rho\phi\rho(2s^2 - t^2)(s^2t^4 - 4a^2s^2)^{-1},$$

which is a scalar multiple of $\mathrm{V}\nabla\nu$. Thus $\mathrm{V}\rho\phi\rho$ is a vector parallel to η and

$$\mathrm{S}\eta\nabla\mathrm{V}\rho\phi\rho = \mathrm{S}(iy - jx)\nabla(iy - jx) = 2\mathrm{S}k(iy - jx) = 0.$$

It is clear also that (19*g*) reduces to

$$\frac{dc}{dm} = 0,$$

a general property of surfaces of revolution, provided the axis is the same for all members of the family.

The following may be taken as further illustrations:—

1. If $\mathrm{S}\sigma\nu = 0$, $\chi\sigma$ differs from $\chi'\sigma$ by a normal vector.

2. When applied to a vector in the tangent plane the operator $\chi[\nu\chi\{\nu(\ )\}]$ or $(\chi\mathrm{V}\nu)^2$ is equivalent to a scalar.

3. If two vectors at right angles to each other and to the normal be operated on with $2\chi - m_2$ they will still be at right angles.

4. If $\chi\epsilon = g\epsilon$ and $\chi\eta = g'\eta$, then $g = -S\eta\nabla\epsilon$ and $g' = +S\epsilon\nabla\eta$.

5. With the notation of Art. 4, it may be proved that

$$-S\tau_2\nabla \,.\, \phi\tau_1 = -S\tau_1\nabla \,.\, \phi\tau_2 + \phi\theta_1\tau_2 - \phi\theta_2\tau_1.$$

6. Putting a for $S\mu\chi\mu$ and b for $S\lambda\chi\mu$, while $d\chi\lambda = \phi_\lambda d\rho$, we may establish these six results:

$$(a)\quad \phi'_\lambda\nu = -\chi'\chi\lambda = \lambda(m_1 - m_2{}^2) - m_2\nu\chi\mu - c\nu(a + m_2);$$

$$(b)\quad \phi_\lambda\nu = -\chi'\chi\lambda + \lambda\left(\frac{dc}{dl} - c^2\right) + \mu\frac{dc}{dm} - c_1\chi\mu;$$

$$(c)\quad \phi'_\lambda(2\chi - m_2)\lambda = \frac{bm_2}{c}\psi\lambda + \nabla m_2(a + m_2) - \nabla m_1;$$

$$(d)\quad S\nabla\chi\lambda = \left(c - \frac{d}{dl}\right)m_2 - \frac{a}{c}(r' - c^2) + \frac{b}{c}\frac{dc}{dm};$$

$$(e)\quad V\nabla\chi\lambda = \psi\lambda - \frac{\nu}{c}\left(a\frac{dc}{dm} + b\overline{r' + c^2}\right) - c_1\nu\chi\mu - c^2\mu;$$

$$(f)\quad \frac{dm_1}{dn} = \left(ac + 2b\frac{d}{dm} - a\frac{d}{dl}\right)c - m_2m_1 - (a + m_2)r':$$

from which may be deduced the eighteen constituents of $d\chi\lambda$ and $d\chi\mu$.

7. If ν, ν_1, and ν_2 are unit-normals to three orthogonal families of surfaces, so that $\chi\nu_1 = g\nu_1$ and $\chi\nu_2 = g'\nu_2$, with similar expressions for g_1, g_1' and g_2, g_2', $d\nu$ may be expressed in terms of the three normals and the six g's (see Ex. 4).

8. If $S\rho(\phi + P)^{-1}\rho = -1$, where ϕ is self-conjugate with constant constituents, $U\nabla P$ satisfies (21). Thence may be found the distribution of electricity on an ellipsoid by means of (22). (In differentiating we may treat $\phi + P$ like a scalar, that is

$$d[(\phi + P)^{-1}\rho] = (\phi + P)^{-1}d\rho - (\phi + P)^{-2}\rho dP).$$

9. Of $\phi d\rho$ and $\phi' d\rho$ only one can be integrable.

XVII. *Animal Thermostat.* *By* Lord Kelvin [*].

A THERMOSTAT is an apparatus, or instrument, for automatically maintaining a constant temperature in a space, or in a piece of solid or fluid matter with varying temperatures in the surrounding matter.

Where and of what character is the thermostat by which the temperature of the human body is kept at about 98°·4 Fahrenheit? It has long been known that the source of heat drawn upon by this thermostat is the combination of food with oxygen, when the surrounding temperature is below that of the body. The discovery worked out by Lavoisier, Laplace, and Magnus still holds good, that the place of the combination is chiefly in tissues surrounding minute tubes through which blood circulates through all parts of the body, and not mainly in the place where the furnace is stoked by the introduction of food, in the shape of chyle, into the circulation, nor in the lungs where oxygen is absorbed into the blood. It is possible, however, that the controlling mechanism by which the temperature is kept to 98°·4 may be in the central parts, about, or in, the pumping station (the heart); but it may seem more probable that it is directly effective in the tissues or small blood-vessels in which the combination of oxygen with food takes place.

But how does the thermostat act when the surrounding temperature is anything above 98°·4 and the atmosphere saturated with moisture so that perspiration could not evaporate from the surface? If the breath goes out at the temperature of the body and contains carbonic acid, what becomes of the heat of combustion of the carbon thus taken from the food? It seems as if a large surplus of heat must somehow be carried out by the breath: because heat is being conducted in from without across the skin all over the body; and the food and drink we may suppose to be at the surrounding temperature when taken into the body.

Much is wanted in the way of experiment and observation to test the average temperature of healthy persons living in a thoroughly moist atmosphere at temperatures considerably above 98°·4: and to find how much, if at all, it is above 98°·4. Experiments might also, safely I believe, be tried on healthy persons by keeping them for considerable times in baths at 106° Fahr. with surrounding atmosphere at the same temperature and thoroughly saturated with vapour of water. The

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[*] Communicated by the Author; having been read before Section A of the British Association at Belfast.

temperature of the mouth (as ordinarily taken in medical practice) should be tested every two minutes or so. The temperature and quantity and moisture and carbonic acid of the breath should also be measured as accurately as possible.

P.S., December 5, 1902.—Since the communication of this note my attention has been called to a most interesting paper by Dr. Adair Crawford in the 'Philosophical Transactions' for 1781 (Hutton's 'Abridgments,' vol. xv. p. 147), "Experiments on the Power that Animals, when placed in certain Circumstances, possess of producing Cold." Dr. Crawford's title expresses perfectly the question to which I desired to call the attention of the British Association; and, as contributions towards answering it, he describes some very important discoveries by experiment in the following passage, which I quote from his paper:—

"The following experiments were made with a view to determine with greater certainty the causes of the refrigeration in the above instances *. To discover whether the cold produced by a living animal, placed in air hotter than its body, be not greater than what would be produced by an equal mass of inanimate matter, Dr Crawford took a living and a dead frog, equally moist, and of nearly the same bulk, the former of which was at 67°, the latter at 68°, and laid them on flannel in air which had been raised to 106°. In the course of twenty-five minutes the order of heating was as annexed †.

Min.	Air.	Dead Frog.	Living Frog.
	°	°	°
In 1	......	70½	67½
„ 2	102	72	68
„ 3	100	72½	69½
„ 4	100	73	70
„ 25	95	81¼	78¼

"The thermometer being introduced into the stomach, the internal heat of the animals was found to be the same with that at the surface. Hence it appears that the living frog acquired heat more slowly than the dead one. Its vital powers must therefore have been active in the generation of cold.

[*] Observations by Governor Ellis in 1758; teachings of Dr. Cullen prior to 1765; very daring and important experiments by Dr. Fordyce on himself in heated rooms, communicated to the Royal Society of London in 1774.

[†] In the two following experiments the thermometers were placed in contact with the skin of the animals under the axillæ.—*Orig.*

"To determine whether the cold produced in this instance depended solely on the evaporation from the surface, increased by the energy of the vital principle, a living and dead frog were taken at 75°, and were immersed in water at 93°, the living frog being placed in such a situation as not to interrupt respiration *.

Min.	Dead Frog.	Living Frog.
In 1	85°	81°
„ 2	88½	85
„ 3	90½	87
„ 5	91½	89
„ 6	91½	89
„ 8	91½	89

"These experiments prove, that living frogs have the faculty of resisting heat, or producing cold, when immersed in warm water; and the experiments of Dr. Fordyce prove, that the human body has the same power in a moist as well as in a dry air: it is therefore highly probable, that this power does not depend solely on evaporation.

"It may not be improper here to observe, that healthy frogs, in an atmosphere above 70°, keep themselves at a lower temperature than the external air, but are warmer internally than at the surface of their bodies; for when the air was 77°, a frog was found to be 68°, the thermometer being placed in contact with the skin; but when the thermometer was introduced into the stomach, it rose to 70½°. It may also be proper to mention, that an animal of the same species placed in water at 61°, was found to be nearly 61¼° at the surface, and internally it was 66½°. These observations are meant to extend only to frogs living in air or water at the common temperature of the atmosphere in summer. They do not hold with respect to those animals, when plunged suddenly into a warm medium, as in the preceding experiments.

"To determine whether other animals also have the power of producing cold, when surrounded with water above the standard of their natural heat, a dog at 102° was immersed in water at 114°, the thermometer being closely applied to the skin under the axilla, and so much of his head being uncovered as to allow him a free respiration.

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* In the above experiment the water, by the cold frogs and by the agitation which it suffered during their immersion, was reduced nearly to 91½°.—*Orig.*

In	5	minutes	the dog was	108°,	water	112°	
„	6	„	„	109,	„	112	
„	11	„	„	108,	„	112,	the respiration having become very rapid.
„	13	„	„	108,	„	112,	the respiration being still more rapid.
„	30	„	„	109,	„	112,	the animal then in a very languid state.

“Small quantities of blood being drawn from the femoral artery, and from a contiguous vein, the temperature did not seem to be much increased above the natural standard, and the sensible heat of the former appeared to be nearly the same with that of the latter.

“In this experiment a remarkable change was produced in the appearance of the venous blood; for it is well known, that in the natural state, the colour of the venous blood is a dark red, that of the arterial being light and florid; but after the animal, in the experiment in question, had been immersed in warm water for half an hour, the venous blood assumed very nearly the hue of the arterial, and resembled it so much in appearance, that it was difficult to distinguish between them. It is proper to observe, that the animal which was the subject of this experiment, had been previously weakened by losing a considerable quantity of blood a few days before. When the experiment was repeated with dogs which had not suffered a similar evacuation, the change in the colour of the venous blood was more gradual; but in every instance in which the trial was made, and it was repeated six times, the alteration was so remarkable, that the blood which was taken in the warm bath could readily be distinguished from that which had been taken from the same vein before immersion, by those who were unacquainted with the motives or circumstances of the experiment.

“To discover whether a similar change would be produced in the colour of the venous blood in hot air, a dog at 102° was placed in air at 134°. In ten minutes the temperature of the dog was 104½°, that of the air being 130°. In fifteen minutes the dog was 106°, the air 130°. A small quantity of blood was then taken from the jugular vein, the colour of which was sensibly altered, being much lighter than in the natural state. The effect produced by external heat on the colour of the venous blood, seems to confirm the following opinion, which was first suggested by my worthy and ingenious friend Mr. Wilson, of Glasgow. Admitting that the sensible heat of animals depends on the separation of absolute heat from the blood by means of its union with the phlogistic principle in the minute vessels, may there not be a certain temperature at which that fluid is no longer capable of combining with phlogiston, and at which it must of course cease to give off heat? It was partly with a view to investigate the truth of this opinion that Dr. Crawford was led to make the experiments recited above."

These views of Dr. Crawford and "his worthy and ingenious friend Mr. Wilson*, of Glasgow," express, about as well as it was possible to express before the chemical discoveries of carbonic acid and oxygen, the now well-known truth that oxygen carried along with, but not chemically combined with, food in the arteries, combines with the carried food in the capillaries or surrounding tissues in the outlying regions, and yields carbonic acid to the returning venous blood: this carbonic acid giving the venous blood its darker colour, and being ultimately rejected from the blood and from the body through the lungs, and carried away in the breath. Crawford's very important discovery that the venous blood of a dog which had been kept for some time in a hot-water bath at 112° Fahr. was almost undistinguishable from its arterial blood proves that it contained much less than the normal amount of carbonic acid, and that it may even have contained no carbonic acid at all. Chemical analysis of the breath in the circumstances would be most interesting; and it is to be hoped that this chemical experiment will be tried on men. It seems indeed, with our present want of experimental knowledge of animal thermodynamics, and with such knowledge as we have of physical thermodynamics, that the breath of an animal kept for a considerable time in a hot-water bath above the natural temperature of its body may be found to contain no carbonic acid at all. But even this would not explain the *generation of cold* which Dr. Crawford so clearly and pertinaciously pointed out. Very careful experimenting ought to be performed to ascertain whether or not there is a surplus of oxygen in the breath; more oxygen breathed out than taken in. If this is found to be the case, the *animal cold* would be explained by deoxidation (unburning) of matter within the body. If this matter is wholly or partly water, free hydrogen might be found in the breath; or the hydrogen of water left by oxygen might be disposed of in the body, in less highly oxygenated compounds than those existing when animal heat is wanted for keeping up the temperature of the body, or when the body is dynamically doing work.

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* Who, no doubt, was Dr. Alex. Wilson, first Professor of Astronomy in the University of Glasgow (1760–1784); best known now for his ingenious views regarding sun-spots.

XVIII. *On the Existence of a Relationship between the Spectra of some Elements and the Squares of their Atomic Weights.*

By W. MARSHALL WATTS, *D.Sc.*, *F.I.C.**

IT is well known that the spectra of some allied elements exhibit certain resemblances; so that in the spectrum of one element we have, as it were, the spectrum of another shifted through a certain distance. This has been made clearer by the resolution of the lines of certain spectra into groups by Kayser and Runge, who have shown that in many cases the wave-lengths of the lines of a spectrum can be calculated with considerable accuracy by means of a formula based upon that applied with such striking success by Balmer to the spectrum of hydrogen. In a general way it may be said that an increase in atomic weight produces a shift towards the red end of the spectrum, and the amount of the shift seems in many cases to admit of simple expression in terms of the squares of the atomic weights.

There appear to be two distinct kinds of connexion between the spectra of allied elements. In one class of cases, of which the family of zinc, cadmium, mercury, and that of gallium and indium furnish the best examples, the differences between the oscillation-frequencies of certain lines of the one element are to the differences between the oscillation-frequencies of the corresponding lines of the other element as the squares of their atomic weights; so that, if it be admitted that the lines *do* correspond, it is possible to calculate the atomic weight of the one element from that of the other by means of the spectra.

In the other class of cases, of which the families potassium, rubidium, and cæsium, and calcium, strontium, and barium offer the best examples, the element of greater atomic weight has the smaller oscillation-frequency, and three elements are so related that the differences of oscillation-frequency between the elements, in comparing corresponding lines in their spectra, are proportional to the differences between the squares of the atomic weights; so that we can calculate the atomic weight of one element from the atomic weights of two other elements of the same family by means of their spectra.

In the spectra of lithium, sodium, potassium, rubidium, and cæsium Kayser and Runge distinguish a principal series and two secondary series, the lines of each series being connected

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* Communicated by the Physical Society: read October 31, 1902.

together by a formula of the form

$$\frac{1}{\lambda}=\mathrm{A}[1-\mathrm{B}n^{-2}-\mathrm{C}n^{-4}],$$

where A, B, C are constants, and n receives the values 1, 2, 3, 4, &c.

The lines in each series, therefore, approach closer and closer together towards the violet, coming to a limit at the oscillation-frequency given by the value of A, which is termed the convergence-frequency. The values of the constants for the principal series of the elements named are :—

	A.	B.	C.
Lithium	43584·73	3·06688	25·24012
Sodium	41536·81	3·12939	19·33950
Potassium	35086·55	3·61914	17·82216
Rubidium	33762·11	3·71781	16·65343
Cæsium	31501·56	3·97050	15·55107

Here the differences of convergence-frequency of potassium, rubidium, and cæsium are nearly proportional to the differences in the squares of the atomic weights; but the same does not hold between lithium, sodium, and potassium. The convergence-frequency of sodium, calculated from those of lithium and potassium on this hypothesis, would be about 40810.

The two rules stated above are probably only approximations to the truth—the results of the calculations made would agree more closely with the known values if the actual law were not more complicated than that assumed.

The numbers given below will show what amount of accuracy may be expected.

Example 1. From the atomic weight of cadmium, 111·83, to calculate that of zinc (64·9).

The following are the oscillation-frequencies of the lines assumed to correspond :—

	Cadmium.		Zinc.	
(*a*)	30654·4	10 *r*	32500·0	8 *r*
(*b*)	30734·9	8 *b*	32540·1	10 *r*
(*c*)	31905·5	8 *b*	32928·7	10 *b*
(*d*)	32446·8	6 *b*	33118·6	8 *b*
(*e*)	36023·7	6 *b*	34310·8	4
(*f*)	37334·5	8	34791·3	6
(*g*)	38851·1	4	35285·7	8 *r*
(*h*)	39280·5	2 *n*	35408·9	6
(*i*)	43690·5	10 *r*	36934·7	6
(*j*)	44086·7	4 *r*	37059·2	2 *b*
(*k*)	44630·0	6 *r*	37242·2	8 *b*
(*l*)	45550·6	1	37548·1	8

From these numbers we get for the atomic weight of zinc by combining—

(*a*) & (*c*) 65·44
(*a*) & (*d*) 65·69
(*a*) & (*f*) 65·48
(*a*) & (*g*) 65·17
(*a*) & (*h*) 64·93
(*a*) & (*i*) 65·28
(*a*) & (*j*) 65·15
(*a*) & (*k*) 65·12
(*a*) & (*l*) 65·16
(*b*) & (*e*) 64·69
(*c*) & (*e*) 64·77 and so on.

	Cadmium.		Zinc.	
(*m*)	19655·8	10 *r*	21170·0	10 *r*
(*n*)	20826·7	10 *r*	21591·6	8 *b*
(*o*)	28840·2	10 *r*	24371·4	2
(*p*)	30301·9	4	24869·7	4

(*m*) & (*n*) 67·08
(*n*) & (*o*) 65·38
(*n*) & (*p*) 65·76
(*m*) & (*p*) 65·98

	Cadmium.		Zinc.	
(*q*)	27669·1	8 *r*	29885·1	10 *r*
(*r*)	29370·4	10 *r*	30456·0	8 *r*

(*q*) & (*r*) give 64·78 for the atomic weight of zinc.

Example 2. From the atomic weight of mercury, 119·71, to calculate the atomic weights of cadmium and zinc.

The following are the lines assumed to correspond :—

	Mercury.		Cadmium.		Zinc.	
(*a*)	16250	10	......		21359·5	10 *r*
(*b*)	18366·4	10 *r*	20826·7	10 *r*	21591·6	8 *b*
(*c*)	20156·3	2 *b*	21368·7	10 *r*		
(*d*)	20334·0	6 *b*	21440·4	8 *b*		

(*a*) & (*b*) give 66·13 for zinc.
(*b*) & (*d*) give 111·45 for cadmium.
(*b*) & (*c*) give 109·89 for cadmium.

(*e*)	20334·0	6 *b*	27669·1	8 *r*	29885·1	10 *r*
(*f*)	24037·4	4 *b*	28840·2	10 *r*	30265·9	8 *r*
					30269·2	8 *r*
(*g*)	25578·2	1 *n*	29370·4	10 *r*	30456·0	8 *r*
(*h*)	29828·1	4 *b*	30654·4	10 *r*		
(*i*)	30245·9	1 *b*	30734·9	8 *b*		

(*e*) & (*i*) give 111·06 for cadmium.
(*e*) & (*g*) ,, 113·7 for cadmium and 65·9 for zinc.
(*e*) & (*f*) ,, 112·3
(*e*) & (*h*) ,, 110·1

Example 3. From the atomic weight of indium, 113·7, to calculate that of gallium (69·9).

The following lines are assumed to correspond:—

	Indium.		Gallium.	
(*a*)	22159·3	10 *r*	23961·1	20 *r*
(*b*)	24371·8	8 *r*	24787·3	10 *r*

(*a*) & (*b*) give 69·47.

(*c*)	30701·5	10 *r*	33954·1	1 *n*
(*d*)	32890·5	10 *r*	34780·8	2 *n*

(*c*) & (*d*) give 69·87.

Example 4. From the atomic weight of barium, 136·76, and that of calcium, 39·99, to calculate the atomic weight of strontium (87·37).

The lines assumed to correspond are:—

	Barium.		Strontium.		Calcium.	
(*a*)	15387	6 *r*	19388	10	21617	1 *b*
(*b*)	17873	4 *n*	22061	6	24390	4 *b*
(*c*)	21951	10 *r*	26976	6 *n*	29736	8 *b*
(*d*)	22979	8 *r*	28177	6 *n*	30991	4 *b*
(*e*)	24201	8 *r*	29399	1 *n*	32229	1 *n*

From (*a*) we get 87·85 for the atomic weight of strontium.
(*b*) 87·82
(*c*) 87·54
(*d*) 87·22
(*e*) 87·34

Example 5. From the atomic weight of cæsium, 132·7, and that of potassium to calculate the atomic weight of rubidium (85·2).

The following lines are assumed to correspond:—

	Cæsium.		Rubidium.		Potassium.	
(*a*)	12469	6	13742	4	14465	7
(*b*)	21764	6*r*	23714	6*r*	24700	6*r*
(*c*)	21945	8*r*	23791	8*r*	24719	8*r*
(*d*)	25707	4*r*	27833	4*r*	28998	6*r*
(*e*)	25787	6*r*	27868	6*r*	29006	8*r*
(*f*)	27638	2*r*	29832	2*r*	31068	4*r*
(*g*)	27678	4*r*	29852	4*r*	31073	6*r*

(*a*) gives 86·87
(*b*) 83·24
(*c*) 83·11
(*d*) 84·51
(*e*) 84·93
(*f*) 85·52
(*g*) 85·51

And the convergence-frequencies 31502, 33762, and 35086 give 86·02.

Mitscherlich, so long ago as 1864, pointed out the similarity in the spectra of the chloride, bromide, and iodide of barium, and endeavoured to trace a connexion with the atomic weights of these compounds.

Lecoq de Boisbaudran in 1869 called attention to the spectra of the metals of the alkalies and alkaline earths, remarking that the spectrum of cæsium is like that of potassium shifted bodily towards the red. Hartley in 1890 showed that three triplets in zinc corresponded with three triplets in cadmium, and that in each of these spectra the triplets had their lines similarly spaced if mapped on the scale of oscillation-frequency. Kayser and Runge in 1891 confirmed this statement, and point out many more triplets similarly related, for which they found a connecting formula of the form

$$\frac{1}{\lambda}=\mathrm{A}(1-\mathrm{B}n^{-2}-\mathrm{C}n^{-4}).$$

They further call attention to the fact that the differences in oscillation-frequency in the triplets increase with increase of atomic weight; and that they are nearly as the squares of the atomic weights. They also remark that in the spectra of potassium, rubidium, and cæsium the mean differences of the close pairs are nearly proportional to the squares of the atomic weights.

Ramage (Proc. Roy. Soc. 1901) has discussed many of these relationships, and gives two diagrams with oscillation-frequencies as abscissæ, one with atomic weights as ordinates, the other with the squares of atomic weights as ordinates. He points out that in the second of these two diagrams, the lines connecting corresponding points are nearly straight in the case of potassium, rubidium, and cæsium; and in the case of calcium, strontium, and barium. He remarks also that "curious results were obtained by observing the points in which the converging lines, drawn through corresponding members of doublets and triplets, intersected. It was difficult to determine these points accurately, and the results have since been regarded more as coincidences."

In a more recent paper (June 5th, 1902) on the spectra of potassium, rubidium, and cæsium Ramage confirms his previous results, and says that the lines connecting corresponding members of homologous doublets do actually intersect on the line of zero atomic weight.

XIX. *Theory of the Connexion between the Energy of Electrical Waves or of Light introduced into a System and Chemical Energy, Heat Energy, Mechanical Energy, &c. of the same.* By MEYER WILDERMAN, *Ph.D., B.Sc.* (*Oxon.*)*.

IN the Philosophical Transactions of the Royal Society, October 1902, the author published a paper "On Chemical Dynamics and Statics under the Influence of Light," in the appendix of which he indicated that the laws found experimentally and communicated there find their rational basis and explanation in thermodynamics. Here the author would like to consider the subject in a more general and detailed manner, not limiting himself to the results communicated there.

A. *General condition of Equilibrium of a System exposed to Light or to Electrical Waves.*

The following considerations, the author believes, apply to electrical waves and light simultaneously, for the reason that both are æther waves with a great number of properties in common. White light, as known, consists of light of different wave-lengths, and though the action of light of different wave-lengths upon a chemical system is different in a quantitative sense, the rays of different wave-lengths do not differ from one another from the qualitative aspect. We do not strictly speaking subdivide the different waves of the spectrum according to their lengths into "chemical" and "heat" rays. They all act "chemically," and all produce heat effects, and as far as the "chemical" effect is concerned the maximum and minimum "chemical" effect will fall into different places of the spectrum, depending not only upon the wave-lengths of the light, but also upon the nature of the chemical system itself. Sir William Abney showed that even the red and ultra-red parts of the spectrum also possess the property of producing chemical decomposition †. In the same way, from the standpoint of the electromagnetic theory of light, electrical waves are not to be separated into a special category different from the light-waves — both being æther-waves of the same fundamental nature. We may safely expect that electric waves when introduced into a chemical system are, as well as light-waves, capable of producing phenomena connected with a variation of the chemical potential, even if phenomena of chemical dissociation or association, &c., may not be directly observed, and that it will only be a matter of the proper choosing of the

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* Communicated by the Author.

† Phil. Trans. Roy. Soc. 1880, ii. p. 653.

region of the phenomena and of proper methods to illustrate this successfully.

In this communication the author will chiefly give his consideration to the phenomena he dealt with in the above experimental research, leaving the consideration of other regions to be dealt with by subsequent investigations.

The condition of equilibrium of a homogeneous system (in the dark) is the following :

$dE = td\eta - pdv + \mu_1 dm_1 \ldots + \mu_n dm_n \geqq 0$ (Gibbs' equation 12).

Let us now assume that the above homogeneous system with independent variables (*i. e.*, in which the substances do not act one upon another chemically) is in equilibrium in the dark. Let this system be now exposed to some constant source of light, say to the light emitted by a perfectly black body when it is heated up to the temperature necessary for its beginning to emit light, or to the light from any other source, having the same intensity and the same composition, or to a constant source of the æther vibration of electric waves. Let us also assume that the system is always removed from the source of light by the same distance, which may be chosen *ad libitum*, so that the intensity of the light falling on the system always remains the same. Let us further assume that the layer of the homogeneous system is only taken very thin, or that the absorption of the light by the given system is so small that the intensity of the light falling upon the system in the different planes which are in a vertical position to the propagated rays of light, practically remains the same.

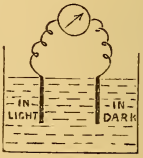
When the system with independent variables is exposed to light, in the first instance it always absorbs more or less light energy. Since no energy can be lost in nature the light absorbed must of necessity transform in the system into some other form of energy. As the light absorbed does not transform into heat (molecular action) alone, even when no visible chemical reaction takes place, it must of necessity transform into some form of kinetic energy of the atoms in the molecules as well. From a molecular mechanical point of view this will mean that under the influence of light the amount of work present in the molecules in the form of energy of the atoms will increase.

Since every system, including those in which light produces no chemical change, continues to absorb light as long as it is exposed to it ; since the absorption-coefficient of a substance is independent of the time of its exposure to the light, and since no energy can be lost in nature, we further arrive at the following conclusion : Either the system is able to store an infinite amount of energy coming from any source of light, if it is only infinitely long exposed to it, which is an impossibility—or, when light transforms into heat and into the new kinetic energy of the atoms, the ratio of the amount of light transformed into heat to that transformed into atomic motion is not constant. This further leads us to the conclusion that having a system with independent components, *i. e.*, which do not act one upon another chemically, the new energy of vibrations of the atoms in the molecules, as caused by the light, will for the given conditions gradually arrive at a *maximum*, after which the light will exert no further additional strain upon the atoms, and the total amount of light which is further absorbed by the system will completely transform into heat.

This maximum value of the new kinetic energy, stored in the system at given conditions of equilibrium, is thus for each substance *a perfectly definite one. It is for each substance of the system directly proportional to its quantity or mass in the system, and each of the substances gets its own peculiar new properties of motion, a new additional potential.*

The above conception being most general and fundamental, it requires experimental evidence of an immediate kind: it ought not to depend upon results obtained in a more remote manner only—such as velocity of chemical combination, &c. The author succeeded in procuring such evidence; two plates of the same metal (fig. 1) connected with the galvanometer and immersed in a conducting liquid, are specially prepared and treated so that the electromotive force in the dark is almost zero. One of the plates is then exposed to the light, while the other is kept in the dark. A deflexion of the galvanometer is obtained (Becquerel, Minchin, Bose, and my own experiments). These phenomena seemed to be of a very complicated nature, more in the nature of an electrical disturbance, because as many different curves in shape and form were obtained as experiments were made; but after much trouble the author succeeded by more careful arrangement of the experiments, and especially owing to the fortunate possession of a constant source of light, in reducing the apparently numerous forms of the curves to two forms only, which in reality constitute one, and thus in arriving at the much needed general law, giving their meaning and content. These confirm the above conceptions formed first in order to explain the laws of chemical statics and dynamics in light in all their details, namely:—(1) There is not only an electrical disturbance created by the light which shows itself in all sorts of ways and then, apparently, often dis-

Fig. 1.



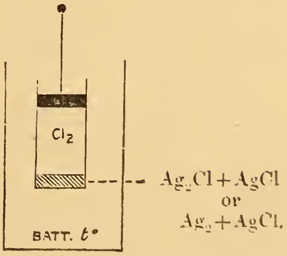
appears, *but the plate in the light always gradually assumes (passing through an induction period) constant new properties; a constant new electromotive force is created, which is to be seen on the photographed curve, from a line parallel to the line in the dark.* Dozens of photographed curves obtained with different metals establish this generalization. (2) *The electromotive force is directly proportional to the intensity of light and is a function of its composition.*

Thus in the above equation (12) new terms $\lambda_1 dm_1$, $\lambda_2 dm_2 \ldots \lambda_n dm_n$ will be added to indicate the new kinetic energy stored by light in the different components of the system.

Further reflection leads to the conclusion that this variation in the energy of the system under the action of light cannot remain without effect upon the entropy of the system. In the general equation (12) $td\eta$ is the thermal energy of the system, and since the same consists not only of molecular but also of atomic motion, it cannot, therefore, remain the same when the atomic motion in the different molecules of the system changes under the influence of light. We are also able to give evidence for this *à priori* conception; we shall carry out for this *a cyclic process at a constant temperature*, making use of the following system: Ag_2 (or Ag_2Cl) + Cl_2 = $2AgCl$. It is known that Ag_2 (or Ag_2Cl) and Cl_2 combine in the dark completely to AgCl. It is also known that AgCl decomposes under the action of light either into Ag_2 and Cl_2 or into Ag_2Cl and Cl_2 (this point is undecided yet); and consequently if AgCl is exposed to light in a closed vessel, this decomposition of AgCl will go on for so long until just as much AgCl is formed in the unit of time from Ag_2 (or Ag_2Cl) and Cl_2, as AgCl decomposes under the action of light into Ag_2 (or Ag_2Cl) and Cl_2; the system will then be in a state of equilibrium, *i. e.*,

$$Ag_2(Ag_2Cl) + Cl_2 \overset{\rightarrow}{\underset{\leftarrow}{=}} 2AgCl.$$

Fig. 2.



Let us now assume we have at the temperature t the system Ag_2 (or $ClAg_2$) + Cl_2 = $2AgCl$, exposed to light, in equilibrium. The same is in a cylinder with a piston, which moves without friction, and exerts a pressure upon the gas Cl_2 contained in the same of one atmosphere, the Ag_2 or AgCl or Ag_2Cl and AgCl being solid. Let the quantity of Cl_2 be = 1 gr. molec.; it will occupy the space of 22 litres.

Now we carry out the following isothermal process:—

1. We remove the light from the same: the Cl_2 will combine with the Ag_2 (or Ag_2Cl) giving 2 gr. mol. AgCl. During this process of combination the work done by the piston *against* the system will be $pv = RT$; $Apv =$ very nearly 2 cal., which will be given to the system; the heat of the reaction of the combination in the dark will be W_d, and this will be taken *from* the system.

2. Now we expose the system to light. It will take up energy from the light, and the light-kinetic energy used up during the reaction will be E_l; if L be the light-kinetic equivalent of heat, LE_l is given *to* the system during the reaction in light. During this reaction 1 gr. mol. Cl_2 is formed, which keeps Cl_2, AgCl, Ag_2 (or Ag_2Cl) in equilibrium; the work done *by* the system is $-pv = -RT$; $-Apv = -2$ cal., and the heat of reaction of dissociation in light is W_l and this is given *to* the system. The system is thus again in the same state from which we started, therefore $-W_d + W_l + LE_l = 0$, *i. e., the heat of the same reaction is at the same temperature in light not the same as in the dark.* If W_d is negative, W_l is $< W_d$; if W_d is positive, W_l is $> W_d$. Now in the equation $dE = td\eta - pdv$, $td\eta$ is the heat taken up by the system (positive or negative) when it is passing from one state to another. Therefore at the same temperature t in the light $td\eta'$ or W_l is different from $td\eta$ or W_d in the dark.

Further, the exposure of the system to light cannot very often remain without a change in the mechanical energy pdv of the system, namely, when chemical transformations take place in the same. It is, however, not impossible that this is also the case even when no chemical transformation takes place in the system, however small this change in the value of pdv may be, considering that the pressure of a gas at a constant volume ought to change with the variation of the kinetic energy of the atoms and molecules. Thus our previous equation for equilibrium of a system with independent variables assumes when it is exposed to the light or to the action of electric waves, and when the heat produced by the absorbed light is removed from the system (say by the surrounding bath of a constant temperature t), the following form:—

$$\begin{aligned} dE + dE_1 &= dE' \\ &= t'd\eta' - p'dv' + \left\{ \begin{matrix} (\mu_1'dm_1') + \\ + (\lambda_1'dm_1') + \end{matrix} \right. \left\{ \begin{matrix} (\mu_2'dm_2') \ldots + \mu_n'dm_n') \\ (\lambda_2'dm_2') \ldots + \lambda_n'dm_n') \end{matrix} \right. \geqq 0 \quad \text{(A)} \end{aligned}$$

where E' is the total energy of the system in light, η' its entropy, v' the volume, $t'\eta'$ the thermal energy, $p'v'$ the mechanical energy in light, $(\mu_1'm_1')$, $(\mu_2'm_2')\ldots(\mu_n'm_n')$ is its chemical energy, and $(\lambda_1'm_1')$, $(\lambda_2'm_2')\ldots(\lambda_n'm_n')$ the new kinetic energy stored in the components of the system under the action of light. The connexion between the terms $(\lambda_1' dm_1')\ldots(\lambda_n' dm_n')$ and $(\mu_1' dm_1')\ldots(\mu_n' dm_n')$ now requires special consideration.

What is to be understood by "the energy stored in the atoms of the molecules, when the same are exposed to light"? It is a thermodynamic necessity that the light absorbed by the system (which in this case we assume to represent a thin layer) should transform into some other form of kinetic energy of the atoms, and that at the same time this new energy should be directly proportional to the total mass of each component, *i.e.*, that the new energy created in the system should be of the form $(\lambda_1' dm_1')\ldots(\lambda_n' dm_n')$. This, however, does not disclose the nature of this kinetic energy itself. A glance at the above equation (A) shows that more than one interpretation of the terms $(\lambda_1' dm_1')\ldots(\lambda_n' dm_n')$ is possible, and these interpretations entirely depend upon how the ultimate nature of the energy stored in the atoms of the molecules under the action of light is conceived.

One conception is that the light-kinetic potentials (λ_1'), $(\lambda_2')\ldots(\lambda_n')$ are identical in nature with the chemical potentials (μ_1'), $(\mu_2')\ldots(\mu_n')$. In this case it will mean that the kinetic energy stored in the atoms under the influence of light $(\lambda' dm_1')\ldots(\lambda_n' dm_n')$ is nothing else than chemical energy; it will mean that under the influence of light the chemical potentials of all and the same substances always increase (simply from one value to another). In the light of this conception, when light-energy is absorbed by any system so far as it does not transform into heat it always transforms into chemical energy.

This conception would have the advantage of enabling us, in the consideration of the systems in which the variables are dependent one upon another, at once to see that the laws which must govern the two important regions of chemical statics and dynamics under the action of light, must be those found experimentally by the author and communicated in the Philosophical Transactions. It carries, however, little conviction for systems with independent variables where no chemical transformation is to be perceived. There are important regions of phenomena—such as phenomena of absorption, dispersion, refraction, fluorescence, &c., for which the assumption that the energy stored in the molecules and atoms under the action of light cannot transform into chemical energy alone, but must also generate an energy *sui generis*, becomes almost imperative. In the mechanical kinetic explanation of the above phenomena, Stokes, Helmholtz, Lommel, and others, have to assume that when light is passing through a system it creates new periodically oscillating movements of the atoms or molecules which are similar to those of the æther waves of the light themselves (this kind of new energy can well be called "light-kinetic energy of the atoms or molecules"). Since the theoretical investigations of the above regions of phenomena on the basis of the above mechanical conceptions met no doubt with great success, having found in the quintessence extensive confirmation in the numerous experimental investigations undertaken for their test, it is only expedient that in the consideration of the subject from a thermodynamic or energetic point of view the formed conceptions should be brought into concord, if possible, with the conceptions of Stokes, Helmholtz, and others. The author has been trying to find a more direct experimental decision upon this very fundamental point, and he believes he has succeeded in the following manner:—*If the action of light consisted in the increase in the chemical potential only, then the current generated under the action of light should according to Gibbs' equations, p.* 503, $v''-v'=\alpha_a(\mu_a'-\mu_a'')$ and $v''-v'=\alpha_g(\mu_g''-\mu_g')$ *always go* IN ONE *direction.* The author finds that the same metallic plates give in different mediums, at one time a current from the plate in the light to that in the dark, at another time in the opposite direction, and also that different metallic plates give in the same medium currents in opposite directions.

Thus the author conceives that the new kinetic energy of the atoms, stored in them under the influence of light, does not transform into chemical energy alone, but into chemical energy and into a light-kinetic energy *sui generis* at the same time. In other words, the terms $(\lambda_1'dm_1')\dots(\lambda_n'dm_n')$ must be decomposed into two parts ν_1dm_1', $\nu_2dm_2'\dots\nu_ndm_n'$ (chemical energy), and $\lambda_1'dm_1'$, $\lambda_n'dm_n'$ (kinetic energy *sui generis* for which we may conveniently retain the term "light-kinetic energy," λ_1', λ_2' ..λ_n' being the light-kinetic potentials), which like gravitation is bound on the same components, but is not identical with chemical energy.

The equation for the system in the dark being

$$dE=td\eta-pdv+\mu_1dm_1\dots+\mu_ndm_n\geqq 0, \quad . \quad . \quad (12)$$

it thus transforms in light into another

$$dE'=t'd\eta'-p'dv'+\mu_1'dm_1'+\lambda_1'dm_1'\dots+\mu_n'dm_n'+\lambda_n'dm_n'\geqq 0, \quad (A')$$

where $(\mu_1')+\nu_1=\mu_1'\dots(\mu_n')+\nu_n=\mu_n'$, &c., the values of μ', λ' being a function of the intensity of light and its composition, of the nature of the components of the surrounding medium, &c.

B. *The Effect of Light upon the Induction and Deduction Periods and upon other Properties of Matter*.*

Since now it is the light passing through the system which is producing the new light-kinetic energy of the atoms and the new additional chemical energy of the molecules of the system, and this is a *time process*, it follows that it is a thermodynamic necessity that all the systems without exception (since all system's absorb light), those with independent as well as those with dependent variables of composition, should arrive at their new state of maximum kinetic energy, passing first through a period of gradual approximation to the same. This period is called the "induction" period.

Experimental evidence:—

1. Such an induction period we find when light is acting upon one of the two plates of the same metal, while the other plate is kept in the dark, in the arrangement before mentioned. Here we have a system with *independent* variables of composition, where no chemical reaction takes place in the same under the action of light, though a gradual increase in the chemical and a creation and increase of the light-kinetic energy, no doubt, take place, because if the chemical potential remained the same at the two surfaces of the plates, no electromotive force could be generated. We may call it the induction period of energy.

2. Such a period of induction we find for the system with *dependent* variables of composition, *i.e.*, where a chemical reaction takes place. It was found by the author* that the velocity-constant of chemical combination of CO and Cl_2 gradually increases till it reaches its constant value. Bunsen and Roscoe first observed the phenomenon of "chemical induction" in their investigation of the combination of chlorine and hydrogen under constant conditions. The phenomenon, however, is of a more complicated nature than conceived by Bunsen and Roscoe. Here we have to deal with two periods: one of induction of energy, the other of chemical induction already found by Bunsen and Roscoe. Indeed chemical combination does not usually start at once on exposure to light, but the system first passes through a latent period during which no chemical reaction can be perceived by the most delicate means, but a gradual increase of the stored energy in form of chemical energy and in form of a kinetic energy *sui generis* undoubtedly takes place in the same manner as in the case of the metallic plates mentioned above. When

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* See the author's paper "On Chemical Statics and Dynamics under the Influence of Light," Philosophical Transactions of the Royal Society, October 1902, pp. 378-391.

the stored energy is great enough to shatter the bonds between the atoms in the molecules, a new chemical rearrangement between the atoms takes place—the chemical induction period starts. As the light-energy is further absorbed by the system, the chemical and light-kinetic potentials further increase, the velocity-constant of the reaction increases (period of chemical induction), until as mentioned before no more strain is exerted by light on the atoms in the molecules, and the impulses of the æther-waves prevent the atoms and molecules from losing their state of maximum energy, keeping them up in the same state of maximum kinetic energy. It is well possible to conceive that the ratio of the amount of light-energy transformed into chemical energy to the amount transformed into light-kinetic energy *sui generis* is not always the same, and this may account for the fact that it takes a time before chemical induction starts. But during both periods—the induction period of energy and the chemical induction period—both the chemical and the light-kinetic potentials must change at the same time, as is to be seen from the fact that with metallic plates an electromotive force is instantaneously obtained on exposure of one plate to light.

Besides the period of induction, a period of chemical "deduction" must equally be considered. This, as well as the induction period, is a thermodynamic necessity. When light is removed from the system, and the maximum kinetic energy of the atoms is no longer kept up by the impulses of the æther-waves, the new kinetic energy of the atoms which has been acquired in light will use itself up, *i.e.*, the atoms and the molecules will sooner or later return to their old state which they had in the dark. In what manner will the kinetic energy of the atoms—previously created by light—use itself up in the dark? If the system consists of independent components it will evidently transform into heat. This we find with metallic plates mentioned before; and this period, during which the chemical potential of the plate previously exposed to light gradually assumes its former value, while its light-kinetic potential gradually disappears, may appropriately be called "the deduction period" of energy. If again under the influence of light a reaction was going on in the system which was not going on previously in the dark, then the above-acquired kinetic energy will partly be used up during the reaction as long as it will still continue to go on in the dark, and partly transform into heat. This period of deduction is naturally also *a time process*, as the process of induction is; it represents to some extent the reverse phenomenon to the last, *i. e.*, during this period the kinetic energy acquired under the influence of light gradually falls from its maximum to zero. Experimental evidence for the deduction period is given in the experimental investigation of the velocity of combination of CO and Cl_2*. As in the case of the induction period, here we must also distinguish between the two periods—the "chemical" deduction period at the beginning when light is removed, usually lasting only a short time (the reaction stops), and the much longer "deduction period of energy." Though chemical reaction very soon stops in the system, it is still in another state of energy, and it only gradually returns to its previous state of energy in the dark before the illumination. This was shown by the author on the length of the induction periods on fresh exposures of the system $CO + Cl_2$ to light. As in the case of the induction period, both the acquired new chemical and the light-kinetic energy decrease simultaneously during the two periods of deduction. It may be, however, that the ratio of the newly-acquired chemical energy to that of the newly-acquired light-kinetic energy still remaining in the system on removal of light, is not always the same during the period of deduction. The induction and the deduction period evidently equally concern systems in which chemical reaction goes on both in the light and in the dark, but with different speeds (H_2O_2), or systems in which a reaction goes on in light only ($CO + Cl_2$ or $H_2 + Cl_2$). It further follows that if after the deduction period is completed the system should again be exposed to the light, the system will evidently have to pass again through a period of induction; and if the light should be again removed from the system, a new deduction period will have to follow. Also, that during the induction period, *i. e.*, before the constant maximum of kinetic energy is reached, the longer the system was previously exposed to the induction, the longer will be the deduction period through which the system passes to the old state, and that, after the induction period has passed and the maximum reached, the deduction period will always last the same time, however long the system may have been exposed to the light; so also the less the system reached the old state, *i. e.*, the less the deduction period is completed, the shorter is the induction period when it is again exposed to the light: it is also evident that both the induction and deduction periods must naturally depend upon the chemical composition of the system at the different times, and upon the intensity and

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* Phil. Trans. 199 A, p. 337.

wave-length of the æther-vibrations. All these detailed conclusions, which here follow as a necessity from purely thermodynamic considerations, find their experimental verification in the above-mentioned research, published in the Philosophical Transactions of the Royal Society, Oct. 1902, and will be further given in the author's research with metallic plates, which will be communicated in due course.

Since the introduction of light into the system with independent variables of composition changes in any case their chemical potentials, and with it their chemical energy, it is evident that *all those physical and chemical phenomena which in one way or another are dependent upon the chemical potentials of the components of a system, such as the electromotive force, the surface-tension, &c., will also undergo a variation when the system is exposed to light.* As all these phenomena are either changed or created by the variation of the chemical potentials of the components, they will change under the influence of light in the same manner as the chemical potentials do, *i. e.*, they will all have under the action of light their *induction* and *deduction* periods, with all the properties of the same which were mentioned above, and after the induction period has passed they will all reach *a constant value* corresponding to the maximum variation of the kinetic energy absorbed by the system under the action of light.

C. *Chemical Statics and Dynamics under the Influence of Light**.

It remains to be seen what are the results obtained for equilibrium and for velocity of reaction when each of the components of the system has not only a (new) chemical potential, but also a light-kinetic potential.

If we integrate the equation

$$dE + dE_1 = dE' = t'd\eta' - p'dv' + \mu_1'dm_1' + \lambda_1'dm_1' \ldots \mu_n'dm_n' + \lambda_n'dm_n, \quad \text{(i.)}$$

under the supposition that the quantity of the mass of the given layer or system (under conditions mentioned on p. 209) with independent variables of composition increases from zero to a finite value, while the nature and state of the system remain the same, we get

$$E + E_1 = E' = t'\eta' - p'v' + (\mu_1' + \lambda_1')m' \ldots + (\mu_n' + \lambda_n')m_n'. \quad \text{(ii.)}$$

Differentiating the same in the most general way:

$$dE' = t'd\eta' + \eta'dt' - p'dv' - v'dp' + (\mu_1' + \lambda_1')dm_1'$$
$$+ m_1'd(\mu_1' + \lambda_1') \ldots + (\mu_n' + \lambda_n')dm_n' + m_n'd(\mu_n' + \lambda_n'),$$

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* See author's paper under the same heading in the Phil. Trans. of the Royal Society, October 1902, pp. 376-395.

and subtracting from this equation (i.) we get

$$\eta' dt' - v' dp' + m_1' d\mu_1' + m_1' d\lambda_1' \ldots + m_n' d\mu_n' + m_n' d\lambda_n' = 0. \quad \text{(iii.)}$$

Here we have a connexion between $2n+2$ variables $t', p', \mu' \ldots \mu_n', \lambda_1' \ldots \lambda_n'$. If this connexion is known, the equation concerning η', v', $m_1' \ldots m_n'$, which are functions of the same variables, will be known as well, and we shall have in the total $n+2$ such independent equations. Here, however, $d\mu$ is not independent of $d\lambda$. General considerations of the conditions of equilibrium of a chemical system in light lead to the conclusion that for this the temperature, the pressure, and the sum of the chemical and of the light-kinetic potentials of each of the components must be constant through the whole system. Therefore

$$\mu_1' + \lambda_1' = C_1', \qquad \mu_n' + \lambda_n' = C_n'. \quad . \quad . \quad . \quad (\gamma)$$

Thus we have in the total $2n+2$ equations for the $2n+2$ variables $t', p', \mu_1', \lambda_1' \ldots \mu_n', \lambda_n'$, and these with (ii.) give in total $2n+3$ known equations, while the total number of variables E', η', t', p', v', μ_1', λ_1', $m_1' \ldots \mu_n'$, λ_n', m_n is $3n+5$. If the system consists of one substance only, then equation (iii.) becomes

$$\eta' dt' - v' dp' + m_1' d\mu_1' + m_1' d\lambda_1' = 0.$$

Equations (iii.) and (γ) give the variation of temperature, or of pressure, or of chemical, or of the light-kinetic potential, or of several of them with the variation of one or some of the variables when all the rest of the variables remain constant.

In case of a gas-mixture there is every reason to assume that the energy, pressure, density $\left(i.\ e.,\ E',\ p',\ \text{and}\ \frac{m'}{v'}\right)$, temperature, entropy, potentials of each of the gases separately are the same when they are together as they would be if they were alone, provided that the gases do not act one upon another chemically. This is an extension of Dalton's law applied not only to pressures but to all other thermodynamic factors of the same. Thus the variation of temperature or of the chemical potentials and of the light-kinetic potentials of each of the gases in dependence upon the variation of all the rest will be the same as if the system consisted of the given gas alone.

Making use of functions ψ', χ', ζ', introduced by Gibbs in his treatment of heterogeneous systems when no light-energy is stored in the same, we ultimately get, putting $E + E_1 - t' d\eta' = \psi'$,

$$-t' d\eta' - v' dp' + m_1' d\mu_1' + m_1' d\lambda_1' \ldots + m_n' d\mu_n' + m_n' d\lambda_n' = 0. \quad \text{(iv.)}$$

Putting $E+E_1+p'v'=\chi'$, we get

$$\eta' dt' + p' dv' + m_1' d\mu_1' + m_1' d\lambda_1' \ldots + m_n' d\mu_n' + m_n' d\lambda_n' = 0. \quad \text{(v.)}$$

Putting $E+E_1-t'\eta'-p'v'=\zeta'$, we get

$$-t' d\eta' + p' dv' + m_1' d\mu_1' + m_1' d\lambda_1' \ldots + m_n' d\mu_n' + m_n' d\lambda_n' = 0 \quad \text{(vi.)}$$

Equations iii., iv., v., vi. are Gibbs' modified fundamental equations of condition, when each of the conponents contains two potentials.

From equation (i.) we further get

$$\mu_1' + \lambda_1' = \left(\frac{dE + dE_1}{dm_1'}\right)\eta', v', m_2' \ldots m_n', \quad . \quad . \quad \text{(i.)}$$

i. e., if we assume that to a given homogeneous mass an infinitely small quantity of m_1' is added, while the mass remains homogeneous, and its entropy in light, volume, and the rest of the substances remain constant; then the sum of the chemical and of the light-kinetic potentials of the introduced substance is equal to the ratio of the increase in the energy E and in the energy E_1 (stored by light in the system), caused by this introduction of the substance m_1', to the introduced quantity of dm_1' *.

It is further evident that if an equation of chemical reaction exists between the units of the substance of the system

$$n_1 A_1 + n_2 A_2 \ldots = m_1 A_1 + m_2 B_2 \ldots, \quad . \quad . \quad . \quad \text{(i'.)}$$

where $A_1, A_2, \ldots B_1, B_2 \ldots$ are the units of the different substances, and $n_1, n_2 \ldots m_1, m_2 \ldots$ numbers, then if the reasoning given by Gibbs in the case of one potential be further applied to our case with two potentials, we have also

$$n_1(\mu_{A_1}' + \lambda_{A_1}') + n_2(\mu_{A_2}' + \lambda_{A_2}') \ldots = m_1(\mu_{B_1}' + \lambda_{B_1}') + m_2(\mu_{B_2}' + \lambda_{B_2}') \ldots \quad \text{(i''.)}$$

Let us now return to the consideration of the equation (iii), first when the system consists of one gaseous substance only. It assumes in the first instance the torm

$$\eta' dt' - v' dp' + m_1' d\mu_1' + m_1' d\lambda_1' = 0.$$

Here $\eta' dt'$, $v' dp'$, $m_1' d\mu_1'$, $m_1' d\lambda_1'$, are the variations in the

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* In the same manner we have

$$\mu_1' + \lambda_1' = \left(\frac{d\psi'}{dm_1'}\right) t', v', m_2' \ldots m_n',$$

$$\mu_1' + \lambda_1' = \left(\frac{d\chi'}{dm_1'}\right) \eta', p', m_2' \ldots m_n',$$

$$\mu_1' + \lambda_1' = \left(\frac{d\zeta'}{dm_1'}\right) t', p', m_2' \ldots m_n'.$$

thermal, mechanical, chemical, and light-kinetic energy of the total mass of the system. We can naturally express the mass in any unit we may desire to adopt. Let this unit be the gram-molecule of the gas, because this will allow a simple use of the gaseous laws and will also be in conformity with the form and content of the equations for chemical reaction which for many reasons were finally adopted by the chemist. Let the total mass of the gas be m_1' gram-molecules. Then we have: the total chemical energy is $\mu_1' m_1'$, and the above variation in the same $m_1' d\mu_1'$; the total light-kinetic energy is $m_1'\lambda_1'$, and the variation in the same $m_1' d\lambda_1'$; the total mechanical energy of the mass is $p'v' = m_1'\mathrm{R}t'$, or nearly $= m_1'. 2$ cal., since $(\rho_1' v_1')$ of 1 gr.-mol. $= \mathrm{R}t'$, and the above variation in the same is $v'dp' = v'd\left(\frac{m_1'\mathrm{R}t}{v'}\right)$, where v' is the volume of the gas; the total η' of the mass $= m_1'\left(\frac{\mathrm{H}'}{t'} + \mathrm{K}_1'\right)$, when $(d\eta')$ of 1 gr.-mol. $= \frac{d\mathrm{H}' \text{ (of 1 gr -mol)}}{t'}$, and (η') of 1 gr.-mol. $= \frac{\mathrm{H}'}{t'} + \mathrm{K}_1'$, where K_1' is an integration-constant.

Thus we get instead of (iii.)

$$m_1'(d\mu_1' + d\lambda_1') = m_1'\mathrm{R}dt' + \mathrm{R}t'dm_1' - m_1'\mathrm{R}t'd\lg v' - m'\mathrm{H}'d\lg t' + \mathrm{K}'dt'$$

and $$\mu_1' + \lambda_1' = \mathrm{R}t' + \mathrm{R}t'\lg\frac{m'}{v'} - \mathrm{H}'\lg t' + \mathrm{K}_1't' + \mathrm{K}_1'',$$

where K_1'' is another integration-constant.

Now we are entitled to assume that in the case of a gaseous mixture Dalton's law will hold good in the wider sense, namely, not only for $\mathrm{E} = \Sigma(\mathrm{E})$, $p = \Sigma(p)$, $\eta = \Sigma(\eta)$, $\psi = \Sigma(\psi)$, $\chi = \Sigma(\chi)$, as indicated by Gibbs, but also for the chemical and the light-kinetic potentials of each gas in the gas-mixture.

Having now a chemical equation of reaction expressed in gram-molecules,

$$n_1 \text{ gr.-m. of } \sigma_1 + n_2 \text{ gr.-m. of } \sigma_2 = n_3 \text{ gr.-m. of } \sigma_3,$$

and $$n_1(\mu_1' + \lambda_1') + n_2(\mu_2' + \lambda_2') = n_3(\mu_3' + \lambda_3'),$$

we thus get

$$n_1\left[\mathrm{R}t'\lg\frac{m_1'}{v'} + (\mathrm{R} + \mathrm{K}_1')t' - \mathrm{H}_1'\lg t' + \mathrm{K}_1''\right]$$
$$+ n_2\left[\mathrm{R}t'\lg\frac{m_2'}{v'} + (\mathrm{R} + \mathrm{K}_2')t' - \mathrm{H}_2'\lg t' + \mathrm{K}_2''\right]$$
$$= n_3\left[\mathrm{R}t'\lg\frac{m_3'}{v'} + (\mathrm{R} + \mathrm{K}_3')t' - \mathrm{H}_3'\lg t' + \mathrm{K}_3''\right],$$

or

$$\lg \frac{\left(\frac{m_1'}{v'}\right)^{n_1} . \left(\frac{m_2'}{v'}\right)^{n_2}}{\left(\frac{m_3'}{v'}\right)^{n_3}}$$

$$= \frac{1}{\mathrm{R}t'}\left[(n_3\mathrm{K}_3' - n_1\mathrm{K}_1' - n_2\mathrm{K}_2')t' - (n_2 + n_1 - n_3)\mathrm{R}t' \right.$$

$$\left. + (n_1\mathrm{H}_1' + n_2\mathrm{H}_2' - n_3\mathrm{H}_3')\lg t' + (n_3\mathrm{K}_3'' - n_1\mathrm{K}_1'' - n_2\mathrm{K}_2'')\right]. \quad (\Omega)$$

i. e., the fact that each of the components has two potentials instead of one does not therefore affect the form of the equation obtained for chemical equilibrium.

Here $\left(\frac{m_1'}{v'}\right)^{n_1} . \left(\frac{m_2'}{v'}\right)^{n_2} : \left(\frac{m_3'}{v'}\right)^{n_3}$ gives the connexion between the concentrations of the gaseous substances expressed in gram-molecules per unit volume acting chemically one upon another under the action of light, which constitutes the law of mass-action in homogeneous systems;

$$(n_1\mathrm{H}_1' + n_2\mathrm{H}_2' - n_3\mathrm{H}_3')\lg t' + (n_3\mathrm{K}_3'' - n_1\mathrm{K}_1'' - n_2\mathrm{K}_2'')$$

the difference between the *thermal energy* of n_1 gram-mol. of $\sigma_1 + n_2$ gram-mol. of σ_2 and the thermal energy of the product of their combination (n_3 gr.-mol. of σ_3) *in light* of a given intensity and composition, i. e., *is the heat of reaction* (let it be denoted by Q_r) *in light*, when n_1 gr.-mol. of $\sigma_1 + n_2$ gr.-mol. σ_2 transform into n_3 gr.-mol. of σ_3; $n_3\mathrm{K}_3'' - n_1\mathrm{K}_1'' - n_2\mathrm{K}_2'' = \mathrm{K}^{\mathrm{iv}}$ is a constant; $-(n_1 + n_2 - n_3)\mathrm{R}t'$ is the work done by the system or against the same during the same transformation in light, and t' is the absolute temperature.

Thus an ordinary consideration of Gibbs' equations under the modified conditions (i. e., *when each component gets under the action of light a light-kinetic potential besides its modified chemical potential*) *shows that the connexion between the logarithm of* $\left(\frac{m_1'}{v'}\right)^{n_1} . \left(\frac{m_2'}{v'}\right)^{n_2} : \left(\frac{m_3'}{v'}\right)^{n_3}$, *or the logarithm of the constant of chemical equilibrium in homogeneous systems in light, the heat of reaction or of transformation of* $n_1\sigma_1 + n_2\sigma_2$ *into* $n_3\sigma_3$ *in light, the external work done by the system or against the same during the reaction, and the absolute temperature remains the same and follows in light the same law as in the dark*,—i. e., *a system which is in equilibrium in the dark, when exposed to light passes under the influence of the same only to a new point of equilibrium, has a new constant of* *equilibrium, new heat of reaction, &c., but the connexion between the logarithm of the constant of equilibrium, the heat of reaction, absolute temperature, will always, nevertheless, be governed by the same law.* Since different intensities and different wave-lengths differently affect the values of the chemical and light-kinetic potentials, &c., they will evidently also differently change the values of the different parts of the equation (Ω).

Thus, having a reversible system $n_1\sigma_1 + n_2\sigma_2 \overset{\rightarrow}{\underset{\leftarrow}{=}} n_3\sigma_3$, and an equation $n_1(\mu_1' + \lambda_1') + n_2(\mu_2' + \lambda_2') = n_3(\mu_3' + \lambda_3')$ in light instead of $n_1\mu_1 + n_2\mu_2 = n_3\mu_3$ in the dark, it will depend upon the values of the individual potentials of all components *in which direction the equilibrium will shift.* The same will be the case when the system is brought from light of one intensity or composition into light of another intensity or composition, the point of equilibrium being for given conditions always a fixed one.

A short notice in a letter from Professor van't Hoff leads me to think *that a general "principle of movable equilibrium" can be established for light, as it was set up by van't Hoff for heat.* I am not sure that this was what van't Hoff meant. In the system $CO + Cl_2 = COCl_2$, $H_2 + Cl_2 = 2HCl$, it is the Cl_2 which absorbs light most. Having a system CO, Cl_2, $COCl_2$ or H_2, Cl_2, HCl in the dark, they do not act one upon another, but on exposure to light $COCl_2$ or HCl is formed, *i. e.*, the system is shifted from the left to the right. Again, in the system $AgCl$ (in light) $= Ag + Cl_2$ (in light), it is the $AgCl$ which absorbs light most, and the light has the effect of forming Ag and Cl_2 from $AgCl$, and not the opposite. Since all substances absorb light, this leads to the conclusion that "*each kind of equilibrium between two states of matter (system) becomes at a constant volume on exposure to light shifted in the direction which is accompanied by the greater absorption of light.*" Van't Hoff's principle for heat, paraphrased, is: "Each kind of equilibrium between two different states of matter (system) becomes at a constant volume on exposure to a higher temperature (heat) shifted in the direction which is accompanied by the absorption of heat."

From the above principle, further conclusions can be drawn about *the influence which the intensity of light and its composition must have upon the point of equilibrium.* The greater the intensity of light, the greater the influence of a given wave-length upon the constituents of the system, the greater is the maximum kinetic energy stored in the atoms and molecules, and it is natural to expect that the substance which absorbs light most has also a greater increase in the values of the potentials, *i. e.*, the greater the increase of the intensity of light, &c., the more the equilibrium will be shifted from the left to the right: more AgCl will be decomposed. In the case of $H_2+Cl_2=2HCl$ and $CO+Cl_2=COCl_2$, since the reaction of decomposition of $COCl_2$ and of HCl in light is in any case infinitely small, this will show itself in an increase of the velocity of combination of CO and Cl_2 or of H_2, Cl_2, as is actually the case. What is the more precise connexion between the constant of equilibrium and the intensity of light? This is a problem which will require long, patient, and most difficult experimental investigation. The author is now endeavouring to approach step by step the solution of this problem. Starting first with the study of one of the simplest cases of equilibrium, namely, with the effect of the intensity of light upon metallic plates of the same kind, mentioned above, the author, being in possession of a constant powerful source of light, was able to establish the fact that *the electromotive force, which in the same manner as the constant of equilibrium gives the maximum work, is directly proportional in this case to the intensity of light.* A more exact investigation of the results obtained and on a larger experimental basis is, however, needed, may to some small extent modify this conclusion, and will be communicated in due time.

Returning to the equation (Ω), we further get that if no work is done by or against the system during the reaction, *i. e.*, at a constant volume $(n_2+n_1-n_3)Rt'=0$, and the total heat-energy of the given gas can be put (approximately at any rate) $=C_st'$, where C_s is the specific heat of the given gas *in light* at a constant volume, and we get, after contracting the constants, instead of equation (Ω),

$$\lg \frac{\left(\frac{m_1'}{v'}\right)^{n_1} \cdot \left(\frac{m_2'}{v'}\right)^{n_2}}{\left(\frac{m_3'}{v'}\right)^{n_3}} = \frac{1}{R}\left(K''' + B \lg t' - \frac{A}{t'}\right), \quad . \quad (\Omega')$$

which, differentiated with respect to t', gives

$$\frac{d\left[\lg \frac{\left(\frac{m_1'}{v'}\right)^{n_1} \cdot \left(\frac{m_2'}{v'}\right)^{n_2}}{\left(\frac{m_3'}{v'}\right)^{n_3}}\right]}{dt'}$$

$$= \frac{(n_3K_3''-n_1K_1''-n_2K_2'')+(n_1C_1+n_2C_2+n_3C_3)t'}{Rt'^2} = \frac{A+Bt'}{Rt'^2};$$

which is van't Hoff's equation, *i. e.*, the variation of the logarithm of the constant of chemical equilibrium in homogeneous (gaseous) systems with the variation of temperature must follow in the light the same law which it follows in the dark.

At a constant temperature equation Ω or Ω' becomes

$$\left(\frac{m_1'}{v'}\right)^{n_1} \cdot \left(\frac{m_2'}{v'}\right)^{n_2} : \left(\frac{m_3'}{v'}\right)^{n_3} = \text{const.}, \quad . \quad . \quad (\Omega'')$$

i. e., *the law of mass-action must hold good for equilibrium in homogeneous systems, when the equilibrium is shifted under the action of light to a new point in the same manner as in the dark. This is exactly what was found to be the case in the experimental part of the paper* "On Chemical Dynamics and Statics under the Influence of Light," Phil. Trans. of the Royal Society, Oct. 1902.

The above equation (Ω'') can in homogeneous systems be decomposed in the usual manner into two equations of two opposite velocities of reaction,

$$\left(\frac{dx}{d\tau}\right)' = \mathrm{C}' \left(\frac{m_1'}{v'}\right)^{n_1} \cdot \left(\frac{m_2'}{v'}\right)^{n_2} \text{ and } \left(\frac{dx}{d\tau}\right)'' = \mathrm{C}'' \left(\frac{m_3'}{v'}\right)^{n_3},$$

which at equilibrium become equal, i. e., *the velocity of a chemical reaction when caused (or influenced) by the light-energy introduced into the system follows in light the same law of mass-action as it follows in the dark, when a reaction is brought about by the intrinsic properties of matter always existent in and inseparable from the same, and which we call chemical affinity or chemical potential. This is just the principal result of the experimental research communicated in the above-mentioned paper.* No law analogous to Faraday's for electrolysis was found to hold good for light introduced into the system.

The experimental results obtained by the author thus led him gradually to believe that the light-energy introduced from an external source into the system does not act upon the same in a manner similar to that of introduced electrical energy; that the above conceptions as to the mode of working of the introduced light upon a system must give the true state of things, the more so as they also furnish a rational and detailed explanation of the phenomena obtained with metallic plates when exposed to light, and of the phenomena of induction and deduction, which otherwise seem to be of a mysterious and complicated nature.

From this result follows further the conclusion, drawn already in the above-mentioned paper in connexion with the *chemical induction* and *chemical deduction* periods (see p. 391):—

Since velocity of reaction follows the law of action of mass, when the molecules taking part in the reaction have attained, under the influence of light, a constant value of their chemical potentials, the same law of mass-action must also be the governing principle for the velocity of reaction at any given moment of the chemical induction and deduction periods, only the velocity constant in the equation for velocity of reaction will vary as the chemical potentials of the reacting substances change.

Davy Faraday Laboratory of the
Royal Institution, November 1902.

XX. *On a Determination of the Ratio of the Specific Heats at Constant Pressure and at Constant Volume for Air and Steam. By* WALTER MAKOWER, *B.Sc., University College, London*[*].

[Plate I.]

1. *Introduction and General Method.*

THE method employed was similar to that used by Lummer and Pringsheim (Smithsonian Contributions to Knowledge, 1898), which consists in allowing the gas under investigation to expand adiabatically and measuring the lowering of temperature caused by such expansion.

In these experiments the initial and final pressures of the gas were measured on a sulphuric acid gauge, and the change of temperature deduced from the variation of the electrical resistance of a fine platinum-bolometer strip immersed in the gas under investigation. The gases experimented upon were air, oxygen, carbon dioxide, and hydrogen, for which the values of the ratio of the two specific heats were found to be 1·4025, 1·3977, 1·2995, 1·4084 respectively.

The chief modifications introduced in the present investigation consist in the substitution of a platinum-thermometer with compensating leads, for the bolometer-strip of Lummer and Pringsheim, who employed a somewhat different device for eliminating errors due to conduction of heat along the leads. Also, at the suggestion of Prof. Callendar, the electrical contacts were made by means of a specially constructed automatic mercury switch, instead of by hand. It was also hoped that it might be possible to use smaller quantities of gas than Lummer and Pringsheim had used, and it was

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[*] Communicated by the Physical Society: read November 14, 1902.

partly with the object of testing this point that the present investigation was undertaken.

If θ_1 and θ_2 be the initial and final temperatures of the gas, and p_1 and p_2 the initial and final pressures respectively, then according to the well-known relation

$$\gamma=\frac{\log(p_1/p_2)}{\log(p_1/p_2)-\log(\theta_1/\theta_2)} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If then the gas be allowed to expand in such a manner that p_1, p_2, θ_1 and θ_2 can be measured, the ratio (γ) of the specific heat at constant pressure to the specific heat at constant volume can be calculated.

In the case of steam, which could not be considered as a perfect gas at the temperatures at which the present experiments were made, the characteristic equation proposed by Callendar (Proc. R. S. lxvii. 1900) was employed. On this assumption the adiabatic relation is still given by equation (1).

PART I.

2. *Experiments with Air.*

The apparatus employed is shown on Plate I. It consisted of a large spherical copper vessel (not shown in the figure) which we will call the "air-vessel," of about 50 litres capacity, connected to a tube C for admitting the air to be experimented with; into the "air-vessel" passed a platinum thermometer by means of which the fall of temperature on expansion of the air at a point near the centre of the vessel was measured. Into the neck of the vessel was soldered a side tube of 1·8 cm. diameter. By withdrawing a rubber stopper fitting tightly into this tube the pressure in the vessel was allowed to fall from a value (p_1) previously adjusted to the atmospheric pressure (p_2). By means of the tube D the "air-vessel" was connected to an oil manometer M which could be placed in communication with the experimental vessel or cut off from it at will by means of the glass tap E. The usual arrangement for measuring the resistance of the platinum thermometer is also shown in the figure. In connexion with the "air-vessel" was a mercury-gauge N which served as an automatic key for closing the battery-circuit at a definite instant after releasing the pressure of the air. The gauge N was connected by rubber r to a T-piece in the tube D, through which passed a platinum wire w, just dipping into the mercury when the pressure inside the apparatus was equal to the pressure of the atmosphere. Dipping into the other arm of the gauge was a wire x passing out through a loosely fitting cork c, through which also passed a glass tube with a platinum wire p sealed through it, electrically connected to w. (This was employed in the chronograph measurements to be described below.) When the pressure in the "air-vessel" was equal to the atmospheric pressure, the wire w was in electrical connexion with the wire x; on raising the pressure the contact between the wire w and the mercury was broken, thus breaking the electric circuit from the wire w through the mercury to the wire x. If the pressure in the "air-vessel" was now suddenly released, contact was made between the mercury and the wire w after a definite time had elapsed. This time (which we will denote by τ) could be varied at will by raising or lowering the limb containing the wire x, and also by means of a screw pinch-cock (not shown in the figure) which served to constrict, to a greater or less extent, the rubber tubing joining the two limbs of the gauge. The two wires x and w were connected respectively to the two terminals of the key K, thus putting the gauge in parallel with this key.

3. *Measurement of Temperature.*

From formula (1) it appears that it is necessary to measure both the temperature (θ_1) before opening the vessel and the temperature (θ_2) to which the gas has fallen, measured at an instant as soon as possible after opening the vessel, as the gas begins to heat up, by conduction from the walls of the vessel, almost at once after releasing the pressure. In order, therefore, to obtain reliable results it is necessary that the thermometer which is used should be able to follow as nearly as possible the variations of temperature of the gas. On this account a platinum thermometer of a pattern similar to that employed by Callendar in his steam-engine experiments of 1895 was constructed.

A piece of pure platinum wire (p) (Pl. I. fig. 2) of diameter ·001 inch was soldered* on to the platinum leads l sealed through one end of the glass tubes g: these in turn were soldered on to the copper leads L, passing out of the glass tubes through the other ends which were left open. Close to the thermometer leads were placed compensating leads to which were soldered a piece of fine platinum wire p' of the

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* In the air-experiments ordinary soft solder was used. In the steam experiments to be described below the fine platinum wires were attached with silver solder.

same diameter as the thermometer wire, but of shorter length, sufficiently long, however, to eliminate any end-effect error due to conduction of heat from the stout platinum leads to the fine platinum-thermometer wire. The four glass tubes were placed closely side by side, and introduced into the "air-vessel" through the stopper B. To measure the resistance of the thermometer, the thermometer and compensating leads were connected to the two arms of the Wheatstone-bridge, as shown in figure 1. In order to keep the heating effect in the thermometer, due to the passage of the electric current, below ·01° C. the current used in the resistance measurements was made sufficiently small, being supplied by one Leclanché-cell through 240 ohms in the battery-arm. The resistances of the two ratio arms were 3 ohms each. To obtain the balance position, a Thomson galvanometer was used, which, however, was rendered astatic to avoid unsteadiness caused by magnetic disturbances.

In all resistance measurements the galvanometer circuit was kept permanently closed, the battery circuit being broken or made by means of the keys. In this way trouble due to thermoelectric E.M.F.'s was avoided.

Measurement of θ_1.—Air was pumped into the "air-vessel" until the pressure inside exceeded that of the atmosphere by a definite amount (about 67 cms. of oil), time being allowed for the air to assume a constant temperature. The resistance of the thermometer was read off by adjusting the resistance R and the sliding contact *s* with sufficient accuracy to give the temperature of the thermometer to ·01° C. The battery circuit was closed by hand by means of the key K.

Measurement of θ_2.—The resistance R was then diminished and the sliding-contact adjusted by judgment nearly to the position where there would be no current through the galvanometer at the instant when the battery circuit was made by means of the automatic gauge-key N. If the sliding-contact was adjusted exactly to the right position, the galvanometer-needle remained at rest for an instant and then gradually moved off as the thermometer heated up again. If, however, the shift was too small the needle gave a kick in the opposite direction to that corresponding to the heating up of the thermometer, came to rest, and then changed the direction of its motion, and gradually moved off as before as the gas heated up. In making the observations that position of the slider was sought for which the kick of the galvanometer just vanished.

To determine the time which elapsed between the instant of removing the stopper *b* and that at which the mercury in the gauge made contact with the wire w, the contact e was disconnected from f and connected to g, thus cutting out the Wheatstone-bridge and placing the gauge-key N in series with a storage-cell S and a chronograph. The platinum point p, which was electrically connected to w, was brought just into contact with the top of the mercury-column, when the air in the "air-vessel" was adjusted to the initial pressure (p_1). On releasing the pressure the chronograph circuit was broken at p and made again through the wire w, after the expiration of a certain time (depending on the rate at which the mercury fell) which was measured on the chronograph to about ·01 second.

This time was varied from ·5 second up to about 5 seconds.

4. *Pressure Measurements.*

The excess pressure ($p_1 - p_2$) in the "air-vessel" before opening to the atmosphere was measured on a manometer M filled with Fleuss pump-oil. The density and coefficient of expansion having been carefully determined the excess pressure could be obtained in centimetres of water by means of the formula

$$\text{density} = \cdot 8826 - \cdot 000644\, t$$

(where t = temperature centigrade)*.

As the oil used was exceedingly viscous some trouble was experienced at first, owing to the long time taken by the oil in running down the sides of the tube when the pressure was altered. For this reason the position of the oil in the manometer was prevented from shifting more than two or three centimetres by closing the tap E immediately before opening the stopper b.

The pressure (p_2) was obtained by reading the barometer.

5. *Observations.*

The following is a series of observations.

The resistances are given in arbitrary units, of which 100 = 1·31 ohms approximately.

The kicks of the galvanometer-needle are given in terms of the micrometer-divisions in the eyepiece of the reading microscope.

By plotting K against r the change of resistance corresponding to no kick of the galvanometer is found to be 10·47.

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* The density and coefficient of expansion of the oil were determined by Mr. N. Eumorfopoulos, of University College, who very kindly supplied me with the oil used in these experiments.

TABLE I.

Resistance (R) before opening vessel.	Resistance (R) after opening vessel.	Kick of galvr. in micrometer divisions. K.	Change of Resistance r.
651·00	640·54	no kick	10·46
651·19	640·84	3	10·35
651·27	641·04	5	10·23
651·38	641·24	10	10·14
651·61	641·44	10	10·17
651·62	651·34	5	10·28
651·82	641·49	4	10·33
651·97	641·54	2	10·43

Barometric pressure = 767·6 mm. mercury at 0° C.
= 1044 cms. of water at 0° C.

Excess pressure = 67·1 cms. oil at 18° C. = 58·3 cms. water. The coefficient of the platinum wire used in the thermometer was ·003835 and its resistance at 0° C. was 610·58. Hence 2·34 units of resistance correspond to 1° pt.; therefore a shift of 10·47 units corresponds to a change of temperature of $4^\circ{\cdot}48$ pt. = $4^\circ{\cdot}43$ C.

$$\therefore \quad \gamma = \frac{\log \dfrac{1102{\cdot}3}{1044}}{\log \dfrac{1102{\cdot}3}{1044} - \log \dfrac{289{\cdot}83}{285{\cdot}4}} = 1{\cdot}396.$$

For this experiment $\tau = {\cdot}76$ second.

6. *Corrections and Results.*

To the value of γ found above there are two corrections to be applied:—

(1) The air in the immediate neighbourhood of the thermometer has risen in temperature by conduction and convection during the time (τ) which elapses between opening the stopper b and closing the battery circuit.

(2) The final temperature as indicated by the thermometer will be higher than the temperature of the air surrounding it on account of direct radiation from the walls of the vessel.

(1) In order to find how much the air had heated up before the battery-circuit was closed by the automatic key, a number of observations were taken similar to those given above, but with different values of τ. A series of values of γ was thus obtained for different values of τ, from which it was possible to deduce the value γ_0 which would have been obtained had

no time been allowed for the air round the thermometer to heat up. For since

$$\log\left(\frac{\theta_1}{\theta_2}\right)=\frac{\gamma-1}{\gamma}\log\left(\frac{p_1}{p_2}\right), \quad . \quad . \quad . \quad . \quad (2)$$

we see, by expanding by the logarithmic series and neglecting all terms except the first, that

$$(\theta_1-\theta_2)=\theta_2\frac{p_1-p_2}{p_2}\frac{\gamma-1}{\gamma}. \quad . \quad \text{(approximately)} \ (3)$$

Hence $\frac{\gamma-1}{\gamma}$ is proportional to the fall of temperature. $\frac{\gamma-1}{\gamma}$ as calculated from (2) was plotted against τ, and by extrapolating back to $\tau=0$ the value of $\frac{\gamma-1}{\gamma}$ corresponding to no heating of the thermometer, due to conduction and convection, was obtained.

In Table II. are given the values obtained:—

TABLE II.

Time of closing circuit in seconds (τ).	γ.	$\frac{\gamma-1}{\gamma}$.
0·76	1·396	·2837
1·12	1·396	·2837
1·90	1·386	·2785
3·33	1·381	·2759
1·83	1·386	·2785
1·45	1·392	·2816
3·00	1·380	·2754
2·30	1·386	·2785
5·00	1·380	·2754
4·01	1·380	·2754
0·95	1·396	·2837
5·15	1·380	·2754
1·90	1·389	·2801
1·65	1·389	·2801
2·13	1·391	·2811
2·15	1·391	·2811

Assuming the variation of $\frac{\gamma-1}{\gamma}$ with τ to be linear over the small range considered, the value of $\frac{\gamma-1}{\gamma}$ corresponding to $\tau=0$ is ·285. Hence $\gamma=1·399$.

(2) The error due to radiation was allowed for by coating the thermometer with platinum black. Assuming that the absorption by a platinum-blacked surface is 15 times as powerful as that of a bright surface*, the error due to radiation could be estimated.

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* Lummer and Pringsheim, *loc. cit.*

The value of γ obtained with a platinum-blacked thermometer was 1·360 for $\tau = 0·86$ second.

Since the value of γ corresponding to $\tau = 0·86$ sec. is 1·394, the correction to be applied for radiation is

$$\frac{1·394 - 1·360}{14} = ·0024.$$

Hence the corrected value of the ratio of the two specific heats of air is $\gamma = 1·401$.

PART II.

7. *Experiments with Steam.*

It will be readily understood that in order to determine the ratio of the two specific heats for steam, the use of vessels of the size employed in the experiments with air just described would be exceedingly inconvenient; and indeed the large size of the vessel does not seem to present the same advantage as in experiments made by the method of Clement Desormes. In the latter method the whole of the gas contained in the vessel is being experimented with, and consequently any error due to the heating of the gas close to the walls produces serious errors in the value of γ obtained; it is therefore desirable to reduce the surface of the vessel compared with its volume. In the present method, however, it is merely with the variation of temperature at the point where the thermometer is situated with which we are concerned, and any heating of gas near the walls of the vessel is unimportant. It therefore seemed likely that results of equal accuracy to those obtained with a large vessel might be obtained with a far smaller one.

To test this point experiments were made with air contained in smaller vessels, and the following apparatus was finally constructed for the steam experiments.

A cylindrical copper vessel with coned ends of about 9·3 litres capacity (Pl. I. fig. 3) was constructed having a wide tap A, by opening which the steam could be allowed to expand adiabatically.

A tube D, provided with a tap through which the vessel could be filled with steam, passed through the lower extremity. On either side of the vessel tubes (B and C) were attached; through B a platinum thermometer was inserted; C communicated through a tap and a fine tube E with a glass tube which was connected to the oil manometer and automatic key. The whole was inclosed in a copper jacket filled with steam maintained at an excess pressure of about half an atmosphere, so that the steam in the inner vessel was superheated about 10° C.

The pressure in the jacket was kept constant by means of an automatic gas-regulator devised by Callendar, which controlled the supply of coal-gas reaching the burner employed for heating the boiler which generated the steam. It was found that by this device the pressure could be kept constant to 1 mm. of mercury. To keep the temperature as constant as possible the whole vessel was packed in cotton-wool.

To prevent the condensation of steam in the tube E a small metal tap T was attached close to the vessel; this tap was not opened until the pressure in the vessel had become constant. By pumping in air the pressure in the tube E was raised slightly above that of the steam in the experimental vessel, so that on opening the tap T a small quantity of air passed into the vessel preventing steam from passing into the tube E and condensing there. In order to roughly determine the pressure of the steam before opening the tap T a small auxiliary mercury gauge was attached to C close to the vessel; when the pressure as registered by this gauge was constant and had been adjusted to about the value required for taking an observation, the tap T was opened, thus putting the oil manometer in connexion with the vessel. As the tube E was fine very little steam diffused into it, and no trouble was experienced from this cause when the experiment was carried out as described. To get rid of any small quantity of moisture which might collect after the apparatus had been working for several hours a T-piece F provided with a drain-tap was attached through which such moisture could be expelled. To carry out an experiment the jacket was filled with steam under pressure, the tap A being open, and the tap D was then opened and steam allowed to enter the vessel, until all the air had been expelled: the taps D and A were then closed. It was found that the pressure in the vessel rose for a short time on account of a small quantity of water carried over by the steam entering through D. The pressure of the steam was then adjusted to a suitable value (about 56 cms. of water above the atmospheric pressure) and allowed to become constant. The tap T was then opened, after which the tap A was quickly opened and the pressures and temperatures registered, as in the experiments with air. The initial temperature (θ_1) was always observed just before opening the tap A, only a few seconds being allowed to elapse between taking this observation and opening the tap. Temperatures were read to ·02° C. and pressures to the nearest millimetre of oil.

Before proceeding to a discussion of the results obtained for steam, the values of γ obtained for air using the same apparatus are given as an indication of its sensitiveness.

TABLE III.

Time of closing the circuit in seconds (τ).	γ.
0·58	1·397
1·21	1·392
2·00	1·392

The value obtained with a platinum-blacked thermometer was 1·374; the correction to be applied for radiation is therefore ·017,

$$\therefore \gamma = 1{\cdot}399.$$

The striking agreement of this value with that obtained with the large vessel demonstrates conclusively that it is possible by the method here employed to work with quantities of gas far smaller than has hitherto been supposed.

8. *Observations and Results.*

The observations were taken in a manner similar to that adopted in the case of air; it was, however, found inconvenient to take all observations between exactly the same pressure limits. The excess pressure was therefore adjusted approximately to the same value in each experiment, and, as in the air-experiments, the sliding-contact was adjusted by judgment *nearly* to the position where there would be no current through the galvanometer at the instant when the battery-circuit was closed; from the initial and final temperatures and pressures a value of $\frac{\gamma-1}{\gamma}$ was calculated, which, as has been shown above, is proportional to the fall of temperature for a constant excess pressure. The kicks of the galvanometer-needle were recorded and a correction applied to the value of $\frac{\gamma-1}{\gamma}$ obtained, in order to allow for the fact that the sliding-contact had not been *exactly* adjusted to the correct position.

In the first series of observations a kick of 1 scale-division corresponded to ·0012 on $\frac{\gamma-1}{\gamma}$; in the second series of observations a kick of 1 scale-division corresponded to ·0016 on $\frac{\gamma-1}{\gamma}$. The observations are given in full below.

TABLE IV.—Series I.

θ_1.	θ_2.	p_1 in cm. water at 0° C.	p_2 in cm. water at 0° C.	Kick of galvanometer in scale-divisions.	$\frac{\gamma-1}{\gamma}$ uncorrected for kick of galv.	$\frac{\gamma-1}{\gamma}$ corrected.
383·30	379·02	1081·2	1028·0	9	·2250	·2358
383·30	378·50	1084·6	1028·0	3	·2349	·2385
383·20	378·37	1084·0	1028·0	no kick	·2395	—
383·50	378·86	1085·4	1030·9	2	·2325	·2349
383·40	378·79	1094·5	1036·0	10	·2200	·2320
383·40	378·69	1091·6	1036·0	no kick	·2367	—
383·40	378·63	1093·5	1036·0	3 or 4	·2314	·2356
383·30	378·53	1092·7	1036·0	no kick	·2349	—
383·30	378·61	1091·6	1036·0	1 or 2	·2355	·2373
383·30	378·79	1090·9	1036·0	3	·2284	·2320
383·30	378·76	1088·4	1035·0	1	·2372	·2384
383·30	378·87	1087·9	1035·0	3	·2331	·2367
383·30	378·83	1090·7	1035·0	17	·2243	·2447
383·30	378·79	1090·4	1035·0	4	·2272	·2320
383·20	378·99	1086·0	1035·0	3	·2296	·2332
383·20	379·02	1086·9	1035·0	2	·2248	·2372
383·20	378·93	1091·0	1035·0	17	·2157	·2361
383·20	378·93	1087·2	1035·0	just a kick	·2308	·2308
383·40	378·82	1090·7	1035·0	7	·2296	·2380
383·40	378·72	1090·3	1035·0	2	·2355	·2379
383·30	378·67	1090·5	1035·0	2 or 3	·2326	·2356
383·10	378·83	1075·8	1021·0	10	·2145	·2265
383·00	378·64	1075·2	1021·0	2	·2212	·2236
383·00	378·46	1077·1	1021·0	5	·2230	·2290
383·00	378·29	1077·7	1021·0	1	·2290	·2302
383·00	378·25	1073·0	1017·0	2	·2331	·2355
383·00	378·21	1073·4	1017·0	1	·2331	·2343
382·90	378·21	1069·4	1015·0	3	·2367	·2403
382·70	377·89	1066·0	1009·0	3 or 4	·2302	·2344
382·70	377·89	1063·8	1009·0	2	·2390	·2414
382·90	378·03	1073·8	1018·0	no kick	·2401	—
383·10	378·23	1076·9	1021·0	no kick	·2395	—
383·40	378·42	1091·2	1035·0	no kick	·2401	---
383·40	378·51	1090·9	1035·0	no kick	·2441	—

For these observations $\tau = 0·67$ second.

Mean value of $\frac{\gamma-1}{\gamma} = ·2349$.

whence $\gamma = 1·307$.

TABLE V.—Series II.

θ_1.	θ_2.	p_1 in cm. water at 0° C.	p_2 in cm. water at 0° C.	Kick of galvanometer.	$\frac{\gamma-1}{\gamma}$ uncorrected for kick of galv.	$\frac{\gamma-1}{\gamma}$ corrected.
383·10	378·49	1084·9	1029·0	6	·2290	·2386
383·20	378·49	1084·2	1029·0	no kick	·2372	—
383·20	378·72	1082·5	1029·0	no kick	·2320	—
383·00	378·48	1091·0	1035·0	4	·2255	·2319
383·00	378·34	1091·6	1035·0	4	·2302	·2366
383·10	378·51	1089·5	1035·0	1	·2349	·2365
383·90	379·47	1098·2	1043·0	1	·2248	·2364
383·90	379·08	1100·4	1043·0	no kick	·2355	—
383·90	379·35	1098·7	1043·0	no kick	·2308	—
383·90	379·50	1099·1	1043·0	3	·2200	·2248
383·90	379·44	1098·9	1043·0	4	·2243	·2307
383·90	379·32	1098·8	1043·0	no kick	·2302	—
383·90	379·22	1099·7	1043·0	1	·2320	·2336
383·90	379·10	1100·6	1043·0	no kick	·2343	—
383·90	379·42	1100·6	1045·0	1	·2266	·2282
383·90	379·38	1100·5	1045·0	1	·2290	·2306
383·90	379·28	1101·5	1045·0	no kick	·2302	—

For these experiments $\tau = 0·50$ second.

Mean value of $\frac{\gamma-1}{\gamma} = \cdot 2328$,

whence $\gamma = 1·303$.

The values of γ obtained in these two series of experiments are given for clearness

	τ in seconds.	γ.
Series I.	0·67	1·307
Series II.......	0·50	1·303

The agreement of these observations was not sufficiently close to necessitate the application of the small correction for radiation applied in the air-experiments (correction (2) above). An attempt was made to apply a correction for the heating up of the steam round the thermometer in the time τ (correction (1) above). The discrepancies were, however, found to be too great to render it possible to plot a curve and extrapolate to the value $\tau = 0$.

It is worthy of mention that the movement of the galvanometer needle was more rapid in these experiments than in those with air, indicating a quicker rate of heating up of the thermometer. This indication was further confirmed by a third series of experiments which was taken, for which τ was

1·14 seconds: the value of γ obtained in this series was 1·291, showing that the thermometer had heated up considerably after 1·14 seconds.

I desire to express my best thanks to Prof. Callendar for his advice and encouragement throughout the course of the work; also to Prof. Porter I am indebted for many valuable suggestions.

XXI. *On the Spectrum of an Irregular Disturbance.*
By Lord RAYLEIGH, *O.M., F.R.S.*[*]

IN my paper "On the Character of the Complete Radiation at a given Temperature"[†], I have traced the consequences of supposing white light to consist of a random aggregation of impulses of certain specified types, and have shown how to calculate the distribution of energy in the resulting spectrum. The argument applies, of course, to all vibrations capable of propagation along a line, and it is convenient to fix the ideas upon the transverse vibrations of a stretched string. Suppose that this is initially at rest in its equilibrium position and that velocities represented by $\phi(x)$ are communicated to the various parts. The whole energy is proportional to $\int_{-\infty}^{+\infty}\{\phi(x)\}^2\,dx$; and it is desired to know how this energy is distributed among the various components into which the disturbance may be analysed. By Fourier's theorem,

$$\pi\phi(x)=\int_0^\infty f_1(k)\cos kx\,dk+\int_0^\infty f_2(k)\sin kx\,dk, \quad . \quad (1)$$

where

$$f_1(k)=\int_{-\infty}^{+\infty}\cos kv\,\phi(v)\,dv, \qquad f_2(k)=\int_{-\infty}^{+\infty}\sin kv\,\phi(v)\,dv. \quad (2)$$

It was shown that the desired information is contained in the formula

$$\int_{-\infty}^{+\infty}\{\phi(x)\}^2\,dx=\frac{1}{\pi}\int_0^\infty[\{f_1(k)\}^2+\{f_2(k)\}^2]\,dk. \quad . \quad (3)$$

As an example, we may take an impulse localized in the neighbourhood of a point, and represented by

$$\phi(x)=e^{-c^2x^2}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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[*] Communicated by the Author.

[†] Phil. Mag. xxvii. p. 460 (1889); Scientific Papers, iii. p. 268.

Equation (1) becomes

$$e^{-c^2x^2} = \frac{1}{c\sqrt{\pi}} \int_0^\infty e^{-k^2/4c^2} \cos kx \, dk, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

while for the distribution of energy in the spectrum by (3)

$$\int_{-\infty}^{+\infty} e^{-2c^2x^2} \, dx = \frac{1}{c^2} \int_0^\infty e^{-k^2/2c^2} \, dk. \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

"If an infinite number of impulses, similar (but not necessarily equal) to (4) and of arbitrary sign, be distributed at random over the whole range from $-\infty$ to $+\infty$, the intensity of the resultant for an absolutely definite value of k would be indeterminate. Only the *probabilities* of various resultants could be assigned. And if the value of k were changed, by however little, the resultant would again be indeterminate. Within the smallest assignable range of k there is room for an infinite number of independent combinations. We are thus concerned only with an average, and the intensity of each component may be taken to be proportional to the total number of impulses (if equal) without regard to their phase-relations. In the aggregate vibration, the law according to which the energy is distributed is still for all practical purposes that expressed by (6)."

The factor $e^{-c^2x^2}$ in the impulse was introduced in order to obviate discontinuity. The larger c is supposed to be, the more highly localized is the impulse. If we suppose c to become infinite, the impulse is infinitely narrow, and the disturbances at neighbouring points, however close, become independent of one another. It would seem therefore from (6) that in the spectrum of an absolutely irregular disturbance (where the ordinates of the representative curve are independent at all points) the energy between k and $k+dk$ is proportional to dk simply, or that the energy curve is a straight line *when k is taken as abscissa.* If we take the wave-length λ (to which k is reciprocal) as abscissa, the ordinate of the energy curve would be as λ^{-2}.

The simple manner in which dk occurs in Fourier's theorem has always led me to favour the choice of k, rather than of λ, as independent variable. This may be a matter of convenience or of individual preference; but something more important is involved in the alternative of whether the energy of absolutely arbitrary disturbance is proportional to dk or to $d\lambda$. In Prof. Schuster's very important application of optical methods to the problems of meteorology, which seems to promise a revolution in that and kindred sciences, the latter is the conclusion arrived at. "Absolute irregularity would show itself by an energy-curve which is independent of the wave-length; *i.e.*, a straight line when the energy and wave-length or period are taken as rectangular coordinates . . ."[*]. It is possible that the discrepancy may depend upon some ambiguity; but in any case I have thought that it would not be amiss to reconsider the question, using a different and more elementary method.

For this purpose we will regard the string as fixed at the two points $x=0$ and $x=l$. The possible vibrations are then confined to the well-known "harmonics," and k is limited to an infinite series of detached values forming an arithmetical progression. The general value of the displacement y at time t is

$$y=\Sigma \sin\frac{s\pi x}{l}\left(\mathrm{A}_s \cos\frac{s\pi a t}{l}+\mathrm{B}_s \sin\frac{s\pi a t}{l}\right) \quad . \quad . \quad (7)$$

in which a is the velocity of propagation and s is one of the series 1, 2, 3. . . . From (7) the constant total energy $(\mathrm{T}+\mathrm{V})$ is readily calculated. Thus ('Theory of Sound,' § 128) if M denote the whole mass, τ_s the period of component s,

$$\mathrm{T}+\mathrm{V}=\pi^2 \mathrm{M} \, . \, \Sigma \frac{\mathrm{A}_s{}^2+\mathrm{B}_s{}^2}{\tau_s{}^2} \quad . \quad . \quad . \quad . \quad , \quad (8)$$

an equation which gives the distribution of energy among the various modes.

The initial values of y and $\dot{y}$ are

$$y_0=\Sigma \mathrm{A}_s \sin\frac{s\pi x}{l}, \qquad \dot{y}_0=\frac{\pi a}{l}\Sigma s\mathrm{B}_s \sin\frac{s\pi x}{l};$$

whence

$$\mathrm{A}_s=\frac{2}{l}\int_0^l y_0 \sin\frac{s\pi x}{l}\,dx; \qquad \mathrm{B}_s=\frac{2}{\pi a s}\int_0^l \dot{y}_0 \sin\frac{s\pi x}{l}\,dx. \quad . \quad (9)$$

If we suppose that $y_0=0$ throughout and that $\dot{y}_0$ is finite only in the neighbourhood of $x=\xi$, we have $\mathrm{A}_s=0$, and

$$\mathrm{B}_s=\frac{2}{\pi a s}\sin\frac{s\pi\xi}{l}\mathrm{Y}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $\mathrm{Y}=\int \dot{y}_0\,dx$. The energy in the various modes being proportional to $\mathrm{B}_s{}^2/\tau_s{}^2$, or to

$$\frac{1}{s^2\tau_s{}^2}\sin^2\frac{s\pi\xi}{l},$$

in which $s^2\tau_s{}^2=\tau_1{}^2$, is thus independent of s except for the factor $\sin^2(s\pi\xi/l)$. And even this limited dependence on s

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[*] "The Periodogram of Magnetic Declination, &c.," Camb. Phil. Trans. xviii. p. 108 (1899).

disappears if we take the mean with respect to ξ. We may conclude that in the mean the energy of every mode is the same; and since the modes are uniformly spaced with respect to their frequency (proportional to s) and *not* with respect to their period or wave-length, this result corresponds with a constant ordinate of the energy curve when k is taken as abscissa.

It is to be noted that the above corresponds to an arbitrary localized *velocity*. We shall obtain a higher and perhaps objectionable degree of discontinuity, if we make a similar supposition with respect to the *displacement*. Setting in (9) $\dot{y}_0=0$ throughout and $y_0=0$ except in the neighbourhood of ξ, we get $B_s=0$ and

$$A_s=\frac{2}{l}\sin\frac{s\pi\xi}{l}Y_1, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $Y_1=\int y_0\,dx$. By (8) the mean energy in the various modes is now proportional to $1/\tau_s^2$ or to s^2. When l is made infinite, so that τ_s may be treated as continuous, we have an energy curve in which the ordinate is proportional to s^2 or k^2, k being abscissa.

We may sum up by saying that if the velocity curve is arbitrary at every point the energy between k and $k+dk$ varies as dk, but if the displacement be arbitrary the energy over the same range varies as k^2dk.

In Schuster's Periodogram, as applied to meteorology, the conception of energy does not necessarily enter, and the definitions may be made at pleasure. But unless some strong argument should appear to the contrary, it would be well to follow optical (or rather mechanical) analogy, and this, if I understand him, Schuster professes to do. If the energy associated with the curve $\phi(x)$ to be analysed is represented by $\int\{\phi(x)\}^2\,dx$, $\phi(x)$ must be assimilated to the *velocity* and not to the *displacement* of a stretched string.

We have seen that when $\phi(x)$ is arbitrary at all points the ordinate of the energy curve is independent of k. In the curves with which we are concerned in meteorology the values of $\phi(x)$ at neighbouring points are related, being influenced by the same accidental causes. But at sufficiently distant points the values of $\phi(x)$ will be independent. Equation (6) suggests that in such cases the ordinate of the energy curve (k being abscissa) will tend to become constant when k is small enough.

Another illustration of the application of Fourier's theorem to the analysis of irregular curves may be drawn from the optical theory of gratings. For this purpose we imagine the aperture of a telescope to be reduced to a horizontal strip bounded below by a straight edge and above by the curve to be analysed, such as might be provided by a self-registering tide-gauge. Any periodicities in the curve will then exhibit themselves by bright lines in the image of a source of homogeneous light, corresponding to the usual diffraction spectra of the various orders. An aperture of the kind required may be obtained by holding the edge of a straight lath against the teeth of a hand-saw. When the combination is held square in front of the telescope, we have spectra corresponding to the number of teeth. When the aperture is inclined, not only do the previously existing spectra open out, but new spectra appear in intermediate positions. These depend upon the fact that the period now involves a sequence of *two* teeth inasmuch as alternate teeth are bent in opposite directions out of the general plane.

The theory of diffraction* shows that the method is rigorous when the source of light is a point and when we consider the illumination at those points of the focal plane which lie upon the horizontal axis (parallel to the straight edge of the aperture).

In order to illustrate the matter further, Mr. Gordon constructed an aperture (cut from writing-paper) in which the curved boundary† had the equation

$$y = \sin 2x + \sin (3x + \tfrac{3}{4}\pi).$$

The complete period was about half an inch and the maximum ordinate about one inch. The aperture was placed in front of a 3-inch telescope provided with a high-power eyepiece. When desired, the plane of the aperture could be considerably sloped so as to bring more periods into action and increase the dispersion.

The light employed was from a paraffin-lamp‡, and it was convenient to limit it by slits. Of these the first was vertical, as in ordinary spectrum work, and it was crossed by another so that at pleasure a linear or a point source could be used. In the latter case the spectrum observed agreed with expectation. Subdued spectra of the first order (corresponding to the complete period) and traces of the fourth and fifth orders were indeed present, as well as the second and third orders alone represented in the aperture-curve. *But along*

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* See, for example, "Wave Theory of Light," *Encyc. Brit.*: 'Scientific Papers,' iii. pp. 80, 87. Make $q=0$.

† Figured in Thomson and Tait's 'Natural Philosophy,' § 62.

‡ Doubtless a more powerful source would be better.

the horizontal axis of the diffraction pattern these subsidiary spectra vanished; so that the absence of all components, except the second and third, from the aperture-curve could be inferred from the observation.

It will be evident from what has already been said that confusion arises when the point-source is replaced by a linear one; and this is what theory would lead us to expect. In a diffraction-grating, as usually constructed, where all the lines are of equal length, the spectra are of the same character whether the source be elongated, or not, in the vertical direction; but it is otherwise here. The inadmissibility of a linear source and the necessity for limiting the observation to the axis seriously diminish the prospect of making this method a practical one for the discovery of unknown periods in curves registering meteorological or similar phenomena; but the fact that the analysis can be made at all in this way, without any calculation, is at least curious and instructive.

It may be added that a similar method is applicable when the phenomena to be analysed occur discontinuously. Thus if the occurrence of earthquakes be recorded by ruling fine vertical lines of given length with abscissæ proportional to time, so as to constitute a grating, the positions of the bright places in the resulting spectrum will represent the periodicities that may be present in the time distribution of the earthquakes. And in this case the use of a linear source of light, from which to form the spectrum, is admissible.

Terling Place, Witham.

XXII. *The Influence of Radiation on the Transmission of Heat.* *By* Arthur Schuster, *F.R.S.**

[Plate II.]

1. THE laws of conduction of heat have been studied in detail, and something has been done to trace the influence of convection on the distribution of temperature; but the effects of radiation on the transmission of heat through partially transparent bodies have been almost entirely neglected. With the solitary exception of a paper by Professor R. A. Sampson †, with which I became acquainted after the greater portion of the results of the present investigation had been worked out, I know of no serious attempt to deal with this problem.

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* Communicated by the Author.

† Memoirs of the Royal Astronomical Society, vol. li.

2. To treat the question in its simplest form I consider, in the first place, a solid which is an absolute non-conductor but capable of radiating and absorbing heat; and I take the flow of energy to be rectilinear, the isothermal surfaces being parallel planes.

If F be the total radiation sent out in unit time in all directions by unit area of the surface of a perfectly black body, the radiation emitted by unit surface of a sheet of thickness dx of a partially transparent body is $\kappa F dx$, where κ is a constant depending on the nature of the substance, the effects of wave-length on κ being for the present neglected.

Let A represent the energy of the stream of radiant heat traversing unit surface of the sheet in unit time from the positive to the negative side, while B represents the flow of energy in the opposite direction. The total absorption of the sheet will be $\kappa(A+B)dx$; and as its radiation towards the two sides is $2\kappa F dx$, it follows that if c be the heat capacity per unit volume, u the temperature, and θ the time,

$$\kappa(A+B-2F)=c\frac{du}{d\theta} \quad \ldots \ldots \quad (1)$$

If we were only considering the radiation normal to the isothermal surfaces as Prof. Sampson has done in the paper already quoted, the law of Balfour Stewart and Kirchhoff would give

$$\frac{dA}{dx}=\kappa(F-A). \quad \ldots \ldots \quad (2)$$

If A represents the total flow in all directions, the equation still holds in the limiting case when the temperature is uniform. For A is then independent of x, and also equal to F.

I shall assume equation (2) to hold also in the case which we are now considering, and shall discuss afterwards how far this assumption invalidates the results.

The corresponding equation for B is

$$\frac{dB}{dx}=\kappa(B-F). \quad \ldots \ldots \quad (3)$$

By combining (2) and (3) we obtain

$$\frac{d}{dx}(A+B)=\kappa(B-A), \quad \ldots \ldots \quad (4a)$$

and

$$\frac{d}{dx}(A-B)=\kappa(2F-A-B). \quad \ldots \quad (4b)$$

Hence, taking account of (1),

$$\frac{d}{dx}(\mathrm{A}-\mathrm{B})=-c\frac{du}{d\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

From (4) and (5) we may deduce

$$\frac{d^2}{dx^2}(\mathrm{A}+\mathrm{B})=\kappa\frac{d}{dx}(\mathrm{B}-\mathrm{A})$$

$$=\kappa c\frac{du}{d\theta};$$

and finally by two differentiations of (1) and elimination of A and B,

$$\left(\frac{d^2}{dx^2}-\kappa^2\right)c\frac{du}{d\theta}+2\kappa\frac{d^2\mathrm{F}}{dx^2}=0. \quad . \quad . \quad . \qquad (6)$$

If the variations of temperature are sufficiently small to allow Newton's law to be applied, we may write $\mathrm{F}=\mathrm{R}u$; so that

$$\left(\frac{d^2}{dx^2}-\kappa^2\right)c\frac{du}{d\theta}+2\kappa\mathrm{R}\frac{d^2u}{dx^2}=0. \quad . \quad . \quad . \qquad (7)$$

This is in essence the equation which Prof. Sampson has deduced in a different manner. Though I am not in agreement with Prof. Sampson as regards the deductions he has made from it, the priority of having established a somewhat important equation belongs to him.

If we adopt Stefan's law, we must write $\mathrm{F}=\mathrm{S}u^4$, so that we obtain the more correct equation

$$\left(\frac{d^2}{dx^2}-\kappa^2\right)c\frac{du}{d\theta}+\kappa\mathrm{S}\frac{d^2u^4}{dx^2}=0.$$

It will be noticed that the equation remains unaltered when $c\rho$, $\kappa\rho$, ρdx is writen for c, κ, dx respectively; so that we may take c to denote the specific heat, κ the coefficient of absorption per unit mass of a thin sheet, and dx the mass per unit surface of the sheet.

3. To consider more particularly the case of steady temperature, I imagine a plate of a non-conducting and partially transparent material placed with its surfaces in contact with two other surfaces which are kept at constant but different temperatures. These surfaces will radiate heat; and if they are black the radiation towards the inside of the plate is known at both boundaries. The surface conditions are (1) for $x=0$, $\mathrm{A}=\mathrm{F}_0$, and (2) for $x=d$, $\mathrm{B}=\mathrm{F}_1$, where F_0 and F_1 are the

radiations corresponding to the temperatures of the bounding surfaces.

When the steady state is reached, (5) leads to

$$B-A=2K,$$

where K is some constant which is to be determined. Putting this value of B − A into equation (4 *a*), we get

$$B+A=2K\kappa x+2c,$$

where c is a second constant. Hence

$$B=K\kappa x+K+c,$$
$$A=K\kappa x-K+c.$$

The values of the constants may now be expressed in terms of the radiations at the surfaces. We find in this way:

$$K=\frac{F_1-F_0}{\kappa t+2};\quad c=\frac{F_0(\kappa t+1)+F_1}{\kappa t+2}.$$

The temperature inside the body is determined from F if the law of radiation is known. In the case considered (1) gives

$$2F=A+B=2K\kappa x+c\quad.\quad.\quad.\quad.\quad.\quad(8)$$

If the temperature variations are comparatively small, Newton's law may be applied, in which case the temperature will be proportional to F, and will vary uniformly in the plate. The important point in the solution of the problem lies in the discontinuities of F, and therefore also of the temperatures at the boundaries.

To calculate the discontinuities we take the values of F at the boundaries, as obtained from (8) after substitution of K and c. We find:

$$F=\frac{F_0(\kappa t+1)+F_1}{\kappa t+2}\quad\text{for } x=0,$$

$$F=\frac{F_1(\kappa t+1)+F_0}{\kappa t+2}\quad\text{for } x=t.$$

But F_0 is the radiation received from the outside when $x=0$; the discontinuity at that surface is therefore

$$F_{(x=0)}-F_0=\frac{F_1-F_0}{\kappa t+2}.$$

The same discontinuity occurs at the other surface. Any radiation I in its passage through the plate is reduced to $Ie^{-\kappa t}$. When κt is large the plate is practically opaque, and the discontinuities are small; but they do not disappear until the plate is of infinite thickness unless the opacity is complete. If, *e. g.*, the opacity of the plate is such that the light is reduced to e^{-10} times its original value, and the temperatures of the bounding surfaces differ by 100°, there would still be a discontinuity of $8\frac{1}{3}°$ at the surfaces.

According to Melloni's experiments, the absorption of heat in rock-salt is independent of the wave-length, a plate of ·26 cm. thick transmitting 92 per cent. of the radiation. From this I calculate the value of κ to be ·032. If we had a plate of rock-salt 1 cm. thick and placed it between black surfaces at temperatures of 100° and 0° respectively, a state of equilibrium would be reached in which, if conduction were entirely absent, the rock-salt in contact with the temperature of boiling water would acquire a temperature of 50°·74, while at the other boundary the temperature would be 49°·26; so that the plate would take up a temperature which nearly throughout its thickness is equal to the arithmetic mean of that of the bounding surfaces.

For the extreme cases the above equations reduce to

$$F=\tfrac{1}{2}(F_0+F_1), \text{ if } \kappa t=0,$$

$$F=[F_0(t-x)+F_1x]/t, \text{ if } \kappa t \text{ is very large.}$$

In the latter case the temperature distribution is the same as that established by conduction.

4. The discontinuities which have been proved to exist when conduction has been neglected show that conduction, however small, must always be taken into account. Before doing so we may extend our calculations to the case that the bounding surfaces are partly reflecting. The surface conditions are then:

$$A=(1-\sigma)F_0+\sigma B \quad \text{for } x=0,$$

$$B=(1-\sigma)F_1+\sigma A \quad \text{for } x=t,$$

where σ is the reflecting power, which must be taken to be one for perfect reflectors.

The same reasoning which previously determined K and c now gives the equations:

$$[(\kappa t+2)-\sigma(\kappa t-2)]K=(1-\sigma)F_1-F_0,$$

$$[(\kappa t+2)-\sigma(\kappa t-2)]c=(1+\sigma)F_0+(1-\sigma)(\kappa tF_0+F_1).$$

The discontinuities of F at both boundaries are

$$(F_1-F_0)(1+\sigma)/[\kappa t(1-\sigma)+2(1+\sigma)].$$

For perfect reflectors $\sigma=1$, and the discontinuities are

$$\tfrac{1}{2}(F_1-F_0);$$

and hence the more perfectly the boundaries reflect the more nearly will the plate assume a uniform temperature, which is halfway between the temperatures of the bounding surfaces.

5. If conduction be taken into account, equation (1) becomes

$$\kappa(A+B-2F)+\lambda\frac{d^2u}{dx^2}=c\,\frac{du}{d\theta}, \quad . \quad . \quad . \quad . \quad (9)$$

λ being thermal conductivity of the body.

Differentiating twice and substituting equations ($4a$) and ($4b$),

$$\begin{aligned}\frac{d^2(A+B)}{dx^2}&=\kappa\frac{d}{dx}(B-A)\\&=\kappa^2(2F-A-B).\end{aligned}$$

This equation and (9) allow A+B to be eliminated, giving the differential equation

$$2\kappa\frac{d^2F}{dx^2}+\left(\frac{d^2}{dx^2}-\kappa^2\right)\left(c\,\frac{du}{d\theta}-\lambda\frac{d^2u}{dx^2}\right)=0. \quad . \quad . \quad (10)$$

When the temperature is steady and its variations across the plate are sufficiently small to admit of the interchange of radiation between two bodies to be proportional to the difference in their temperatures, the equation becomes

$$(2\kappa R+\kappa^2\lambda)\frac{d^2u}{dx^2}=\lambda\frac{d^4u}{dx^4};$$

or, say,

$$\alpha^2\frac{d^2u}{dx^2}=\frac{d^4u}{dx^4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The distribution of temperature in the plate is here not a linear function of the distance. This is a curious result. Radiation alone or conduction alone would cause the slope of temperature in the plate to be uniform; but the combination of both effects destroys the uniformity. The explanation of the apparent paradox is found in the consideration that although the distribution of temperature due to radiation varies uniformly with the distance across the plate, it is not identical with the distribution of temperature due to conduction, owing to the tendency of radiation to cause discontinuity at the surfaces, as has been explained in § 3.

The solution of (10) may be put into the form:

$$u = \mathrm{P}e^{\alpha x} + \mathrm{Q}e^{-\alpha x} + ax + b. \quad . \quad . \quad . \quad . \quad (12)$$

P, Q, a, and b are four constants, and α satisfies the equation

$$\alpha^2\lambda = 2\kappa\mathrm{R} + \kappa^2\lambda. \quad . \quad . \quad , \quad . \quad . \quad . \quad (13)$$

The constants are determined from our knowledge of u_0 and u_d at the ends of the plate and the conditions which hold there as regards radiation.

The heat (H) transmitted in unit time through any isothermal plane in the negative direction is

$$\mathrm{H} = \lambda\frac{du}{dx} + \mathrm{B} - \mathrm{A}.$$

From the original equations

$$\frac{d(\mathrm{A}+\mathrm{B})}{dx} = \kappa(\mathrm{B}-\mathrm{A}),$$

and

$$\kappa(\mathrm{A}+\mathrm{B}) = 2\kappa\mathrm{F} - \lambda\frac{d^2u}{dx^2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$\therefore \quad \kappa^2(\mathrm{B}-\mathrm{A}) = 2\kappa\frac{d\mathrm{F}}{dx} - \lambda\frac{d^3u}{dx^3}. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Substituting F = Ru, the heat transmitted takes the form

$$\mathrm{H} = \frac{\lambda}{\kappa^2}\left(\alpha^2\frac{du}{dx} - \frac{d^3u}{dx^3}\right).$$

From equation (17) we deduce

$$\frac{d^3u}{dx^3} = \alpha^2\left(\frac{du}{dx} - a\right);$$

so that finally for the heat transmitted we have the simple expressions

$$\mathrm{H} = a\frac{\alpha^2\lambda}{\kappa^2} = \left(\frac{2\mathrm{R}}{\kappa} + \lambda\right)a. \quad . \quad . \quad . \quad . \quad (16)$$

In this equation R is a constant such that the excess of heat radiated from unit area of an infinite plane black surface of temperature u_1 over that received from a similar surface placed parallel to it and of temperature u_0 is $\mathrm{R}(u_1 - u_0)$; κ is a quantity such that the radiation falling on a plate of thickness $1/\kappa$ is by absorption within the plate reduced in the ratio $e : 1$: λ is the thermal conductivity, and a is a quantity which must be determined from the conditions of the problem.

If $\mathrm{U} = u_t - u_0$ be the difference in temperature between the two sides of the plate at which x is t and 0 respectively, equation (12) gives

$$U=P(e^{\alpha t}-1)+Q(e^{-\alpha t}-1)+at. \quad . \quad . \quad . \quad (17)$$

Two further equations are required to determine the constants P, Q, and a. These are obtained by considering the relations which hold between A and B at the two surfaces. The radiation A leaving the surface $x=0$ is made up partly by the reflexion of the incident radiation B_0 which we may put equal to σB, and partly by the radiation of the surface itself which is $(1-\sigma)Ru$. Hence A_0, B_0, u_0, the values of A, B, u for $x=0$,

$$A_0-\sigma B_0=(1-\sigma)Ru_0. \quad . \quad . \quad . \quad . \quad (18a)$$

Similarly at the second surface where $x=t$

$$B_t-\sigma' A_t=(1-\sigma')Ru_t. \quad . \quad . \quad . \quad (18b)$$

For surfaces which are black $\sigma=0$, for surfaces which are totally reflecting $\sigma=1$. Substituting the values of F and u in (14) and (15) we find for $x=0$ and $x=t$

$$\left.\begin{aligned}
\kappa(B_0+A_0)&=2\kappa Ru_0-\lambda\alpha^2(P+Q),\\
\kappa(B_0-A_0)&=2aR-\alpha\kappa\lambda(P-Q),\\
\kappa(B_t+A_t)&=2\kappa Ru_t-\lambda\alpha^2(Pe^{\alpha t}+Qe^{-\alpha t})\\
\kappa(B_t-A_t)&=2aR-\alpha\kappa\lambda(Pe^{\alpha t}-Qe^{-\alpha t})
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (19)$$

The four last equations determine A_0, B_0, A_t, B_t in terms of a, P, Q, and hence by substitution in (18 a) and (18 b) the two relations which together with (17) allow the three constants of the equation to be calculated. The calculation of these constants is simplified when $\sigma=\sigma'$, so that the two surfaces have equal reflecting properties. Symmetry shows in that case that the temperature at the centre of the plate must be $\frac{1}{2}(u_0+u_t)$. Applying (12) we obtain the equation

$$\tfrac{1}{2}(u_t+u_0)=\tfrac{1}{2}P(1+e^{\alpha t})+Q(1+e^{-\alpha t})+\frac{at}{2}+b,$$

and for $u=\frac{t}{2}$

$$u=Pe^{\frac{\alpha t}{2}}+Qe^{-\frac{\alpha t}{2}}+b.$$

Equating the two expressions we derive

$$Pe^{\alpha t}+Q=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Hence (17) becomes

$$U=2P(e^{\alpha t}-1)+at. \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Only one further equation is necessary, which is obtained by combining the two first equations of (19) with (18). We then find

$$2aR(1+\sigma)=\lambda\alpha[\kappa(1+\sigma)(P-Q)-\alpha(1-\sigma)(P+Q)]. \quad (22)$$

I will consider the two extreme cases $\sigma=0$ and $\sigma=1$ in greater detail. For $\sigma=0$:

$$2aR=\lambda\alpha[\kappa(P-Q)-\alpha(P+Q)], \quad (22\,a)$$

for $\sigma=1$:

$$2aR=\lambda\alpha\kappa(P-Q). \quad (22\,b)$$

The values of P and a, as found from the combination of (20), (21), and either (22 a) or (22 b), are as follows :—

For $\sigma=0$:

$$a=\frac{U\lambda\alpha[\kappa(e^{at}+1)+\alpha(e^{at}-1)]}{(4R+\lambda\alpha^2 t)(e^{at}-1)+\lambda\alpha\kappa t(e^{at}+1)} \quad (23\,a)$$

$$P=-Qe^{-at}$$

$$=\frac{2RU}{(4R+\lambda\alpha^2 t)(e^{at}-1)+\lambda\alpha\kappa t(e^{at}+1)}. \quad (24\,a)$$

For $\sigma=1$:

$$a=\frac{U\lambda\alpha\kappa(e^{at}+1)}{4R(e^{at}-1)+\lambda\alpha\kappa t(e^{at}+1)} \quad (23\,b)$$

$$P=-Qe^{-at}$$

$$=\frac{2RU}{4R(e^{at}-1)+\lambda\alpha\kappa t(e^{at}+1)}. \quad (24\,b)$$

In order to show the characteristics of the temperature variation indicated by (12) I have plotted curves, taking for κ the value of ·64 and putting $\lambda=1{\cdot}3\times10^{-4}$. A body possessing these constants would have the transparency of clear rock-salt, and a thermal conductivity equal to that of cork. I have calculated the appropriate value of R by taking the radiation of a black body per unit surface to be $10^{-12}\times u^4$, where u is the absolute temperature. This is in close agreement with the best observations. Two black parallel surfaces differing in temperature by a small amount du, exchange heat therefore at the rate of $4\times10^{-12}u^3du$. If u is equal to 300° on the absolute scale this will be nearly $10^{-4}\times du$. Hence for temperatures nearly equal to 30° C. we may in the above equations put $R=10^{-4}$.

Curve I. (Pl. II.) gives the temperature change in a plate of a substance having the properties described, the plate being 5 cms. thick and placed between two totally reflecting surfaces, the average temperature being about 30° C. Curve II.

shows the variations in the plate when placed in contact with two perfectly black surfaces. The effect of increased radiation is shown in Curve III., which gives the temperature variation for totally reflecting surfaces, and with a value of $R=10^{-3}$ corresponding to a temperature of about 360° C. The curve for the higher temperature and black surfaces has not been drawn, as it would confuse the figure, being nearly coincident with Curve I. The temperature scale is of course arbitrary. The curves show very clearly that radiation destroys the uniform temperature slope which is obtained when conductivity alone is taken into account, and that the deviations from uniformity are greater when the surfaces are reflecting than when they are black.

To investigate the effects of radiation on the transmittance of heat it is best to take the two extreme cases: one in which the plate is so thin that very little heat is absorbed in it, and the other in which the plate is so thick that very little radiation can traverse its whole thickness. For small thicknesses we may in equations 23 *a* and 23 *b* expand the exponential, retaining only the terms as far as αt in the numerator, and $\alpha^2 t^2$ in the denominator. After the necessary transformations we find for the case of black surfaces

$$a=\frac{\kappa^2}{\alpha^2}\cdot\frac{U}{t}\left(1+\frac{Rt}{\lambda}\right).$$

Hence for the heat transmitted according to (16)

$$H=a\frac{\alpha^2\lambda}{\kappa^2}=\frac{U\lambda}{t}+RU.$$

The first term represents the heat calculated according to the laws of conduction, and the second term gives the effect of radiation. In the case of a very thin plate we are justified therefore in taking the two effects separately and adding the result. A similar calculation shows that for the case of reflecting boundaries the heat transmitted by a thin plate is that calculated from the known laws of conductivity, viz., $U\lambda/t$.

A different result is arrived at when absorption within the plate cannot be neglected. If we transform equations 23, taking $e^{\alpha t}$ as large compared to one, we find for black surfaces

$$H=\frac{U\lambda}{t}\left(1+\frac{2R}{\kappa\lambda}\right)\left(1-\frac{2R}{\kappa^2\lambda t}\right).$$

and for reflecting surfaces:

$$H=\frac{U\lambda}{t}\left(1+\frac{2R}{\kappa\lambda}\right)\left(1+\frac{4R}{\kappa\lambda\alpha t}\right).$$

When t is sufficiently large the reflecting property of the boundary becomes immaterial, and the transmitted heat is

$$H=\frac{U\lambda}{t}\left(1+\frac{2R}{\kappa\lambda}\right). \quad . \quad . \quad . \quad . \quad . \quad (23)$$

The ordinary measurements of thermal conductivity neglect the effects of radiation and would yield incorrect results if $2R/\kappa\lambda$ were appreciable. This will only be the case for transparent bodies possessing very low conductivities. When the measurements are made at the ordinary temperatures, it is the transparency for rays of low refrangibility that comes into play, so that rock-salt and fluorspar are the only bodies which can come into consideration. According to Melloni's experiments the constant κ for rock-salt is ·32, but this must be doubled to make it apply to rays traversing the substance obliquely as well as normally (see § 7). The thermal conductivity of rock-salt according to Lees is ·014. The fraction $2R/\kappa\lambda$ in this case works out to be ·002. The measurements of conductivity are affected by an error of that amount, which is probably beyond the reach of experiment, but if rock-salt possessed a thermal conductivity as low as that of cork, or ·00013, the error committed in measurements of thermal conductivity by neglecting radiation would amount to 20 per cent. That the effects of radiation may be neglected in proportion as the body absorbs the radiations may appear surprising at first sight, but is explained by the fact that in the case of good absorbers any portion of the body is affected only by the radiation coming from other portions in its immediate neighbourhood which possess temperatures nearly equal to its own.

6. The effects of radiation become conspicuous, and more important than those due to conduction of heat, in the case of gases; but the ordinary method of treatment which considers the two effects separately is, according to § 5, sufficient, when the thickness of the layer is not too large, so that a considerable fraction of the heat-radiation may pass through it. This investigation has been undertaken primarily with a view of clearing up the influence of radiation on the temperature distribution inside a large gaseous body, such as we imagine the sun to be. Here we have to deal with a great thickness which ultimately must be opaque. How far very hot gases may be transparent it is difficult to judge, but opaqueness must ultimately result, if only from the scattering of light by molecules, assisted probably to a great extent by internal reflexions taking place at surfaces at which the density or temperature varies very rapidly. We are all

familiar with this kind of opaqueness, due to reflexions within convection currents set up by the solar heating of a valley. It is advisable therefore to extend the foregoing investigation to include the effects of scattering and irregular reflexions.

If $sAdx$ is the proportion of the incident light A which is intercepted by the layer dx, $\frac{1}{2}sAdx$ will pass out of the layer in either direction. Hence A will be diminished by $\frac{1}{2}sAdx$, and B will be increased by the same amount, if B is the radiation in the opposite direction. Adding the effects of absorption, already discussed, we have

$$\left.\begin{aligned}\frac{dA}{dx}&=\kappa(F-A)+\tfrac{1}{2}s(B-A)\\ \frac{dB}{dx}&=\kappa(B-F)+\tfrac{1}{2}s(B-A)\end{aligned}\right\}\quad .\quad .\quad .\quad .\quad (24)$$

from which we obtain an equation corresponding to (4 a) viz.:

$$\frac{d}{dx}(A+B)=(\kappa+s)(B-A),\quad .\quad .\quad .\quad .\quad (25)$$

while (4 b) remains the same.

Proceeding as in § 3, we obtain the differential equation

$$2\kappa\frac{d^2F}{dx^2}+\left(\frac{d^2}{dx^2}-\kappa(\kappa+s)\right)\left(c\frac{du}{d\theta}-\lambda\frac{d^2u}{dx^2}\right)=0.$$

This equation, which includes (10) for the special case $s=0$, is one which can be discussed in the same manner.

For steady temperatures the solution is of the same form as (12), the value of α now satisfying the relation

$$\alpha^2\lambda=2\kappa R+\kappa(\kappa+s)\lambda.$$

It is of interest to deal with the special case when there is no absorption properly speaking. Putting $\alpha=0$ in (12) we may write the solution

$$u=ax+e,$$

which shows that in the absence of absorption but the presence of scattering the temperature gradient is constant.

To determine the effect of radiation on the transmission of heat we use the fact that for $\kappa=0$ equations (4 b) become

$$\frac{d}{dx}(A-B)=0.$$

Putting

$$A-B=c,$$

and hence

$$\frac{d(A+B)}{dx}=s(B-A)=-sc,$$

$$A+B=-scx+d.$$

If the boundaries are at a considerable distance, it cannot matter what their reflecting properties are, and we may take them to be black radiators of temperatures U_0 $(x=0)$ and U_t $(x=t)$. Writing therefore $A=Ru_0$ for $x=0$, and $B=Ru_t$ for $x=t$, the two equations for A and B determine c. It is found that

$$c=\frac{2R(u_0-u_t)}{st+2},$$

or for a great thickness t

$$c=\frac{2R(u_0-u_t)}{st}.$$

The heat transmitted is

$$-\lambda\frac{du}{dx}+A-B=\lambda\frac{u_0-u_t}{t}\left(1+\frac{2R}{s\lambda}\right).$$

Comparing this with (23) it is seen that as regards its effect on the transmission of heat, scattering has the same effect as absorption.

7. It remains to discuss how far the two assumptions made in this investigation may affect the results. In the first place equation (2) is not strictly correct, and the value of κ will not be the same as that obtained by the measurement of the absorption of radiations passing through the plate. Consider unit area of the surface and let the radiation incident on the plate be equal in all directions. The radiation entering unit-area normally will be $Ad\omega$, and that entering in a direction forming an angle θ with the normal will be $A\cos\theta\, d\omega$, where $d\omega$ is a small solid angle which, in the case under consideration, will be $2\pi\sin\theta d\theta$. If dx is a small thickness of the absorbing plate, the length of path of a ray through it will be $dx/\cos\theta$. Hence the total absorption in the plate will be

$$2\pi A\kappa' dx\int_0^{\frac{\pi}{2}}\sin\theta d\theta=2\pi A\kappa' dx,$$

the total incident radiation is

$$2\pi A dx\int_0^{\frac{\pi}{2}}\sin\theta\cos\theta\, d\theta=\pi A.$$

Hence the ratio of absorbed radiation to incident radiation, which in the above investigation has been denoted by κ, is found to be

$$\kappa = 2\kappa'.$$

Here κ' represents the coefficient of absorption of the normal rays. As long as the radiation at any point of a solid is equal or nearly equal to the internal radiation of a body at uniform temperature, the previous results are correct therefore, provided we take κ to be equal to twice the coefficient of absorption of the normally incident rays. But the absorption of the body itself will tend to diminish the intensities of the oblique radiation, and though this diminution is partly made up by the radiation of the absorbing layer, the tendency on the whole will be that the normal radiations will increase relatively in intensity. The effect will be that κ will gradually diminish from its original value to half its amount. As the purpose of our calculation was not the exact numerical calculation of the effects of radiation, but rather the study of its general influence and the determination of the order of magnitude of the effects, the results looked upon in this light will not be affected by the assumption made. The same will apply to the neglect of the dependence of radiation on wavelength. This simplification will introduce an error the character of which will be of the same nature as that just discussed, so that the apparent coefficient of absorption will gradually diminish, only those radiations traversing an appreciable thickness of the plate which are not strongly absorbed by it.

As a matter of experiment it has, however, been found that by a proper adjustment of the constant κ, the total radiation traversing a thickness t of a plate diminishes as $e^{-\kappa t}$, with a near approach to accuracy, which justifies the equation on which our calculations are based. While it is well to draw attention to the approximate nature of the results, in so far as they depend on the assumptions made, the nature of the influence of radiation in the transmission of heat is sufficiently well represented by the equations which have been obtained. It will be the object of a further communication to study effects of radiation on the temperature distribution in large masses of gas in a state of convective equilibrium.

Description of Plate II.

The curves represent the temperature variation within a plate 5 cm. thick, the surfaces being kept at a difference of 1°, the ordinates representing temperatures, and the abscissæ distances across the plate. The material of the plate is supposed to have a coefficient of absorption equal to that of rock-salt and a thermal conductivity equal to that of cork. Curves I. and II. give the distribution of temperature when the average temperature is about 30° C., Curve I. representing the steady state when the boundaries are totally reflecting, and Curve II. when they are black. Curve III. represents the steady state for totally reflecting boundaries when the average temperature of the plate is about 360° C. This curve shows the approach to the steady state, when the transmission of heat is entirely effected by radiation, thermal conductivity being neglected. The temperature distribution in the limiting case being uniform, but discontinuous at the surfaces. The numbers from which the curves are plotted are given in the following Table, which includes also under column IV. the case of black surfaces, with an average temperature of 360°. It is only necessary to give the temperatures near the colder bounding surface, as the distribution is symmetrical at both sides and uniform near the centre of the plate. The columns headed Temperature Differences represent the difference between the temperature at any point and the temperature of the colder surface; the complete temperature change in the plate is supposed to be 1°.

Distance from Colder Boundary in cms.	Temperature Differences.			
	I.	II.	III.	IV
·01	·075	·042	·240	·127
·02	·129	·074	·330	·178
·04	·196	·117	·384	·212
·05	·217	·133	·388	·221
·10	·274	·186	·400	·253
·20	·335	·267	·425	·315

XXIII. *On Screens Transparent only to Ultra-Violet Light and their Use in Spectrum Photography.* *By* R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University*[*].

[Plates III. & IV.]

ANYONE who has repeated Tyndall's beautiful lecture experiment of kindling a pine stick in the dark heat focus of a burning-glass, concentrating light from which the visible radiations have been removed by means of a solution

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[*] Communicated by the Author.

of iodine in bisulphide of carbon, must have wished that we possessed a screen, opaque to visible light and transparent to the ultra-violet.

I have recently succeeded in making a screen quite transparent to these radiations, though a gas flame cannot be seen through it. By combining it with a large condensing-lens and an arc-lamp, it is possible to form a dark focus of ultra-violet light in which a lump of uranium nitrate glows with a vivid green phosphorescence like a great emerald.

Besides giving us the means of performing a most beautiful lecture experiment, these screens make it possible to photograph the ultra-violet lines in grating spectra of higher orders than the first, entirely uncontaminated by the visible radiations which overlie them. Other applications at once suggest themselves, such as the complete removal of the highly actinic blue and violet rays, in certain investigations of the ultra-violet region where the long exposures necessary are apt to produce fogging of the plates. It seems quite possible too, that photographs of the moon, planets, and nebulæ taken by means of ultra-violet light may furnish valuable data, as I shall attempt to show at the end of this paper.

The substance which has made possible the production of such a screen is nitroso-dimethyl-aniline, the remarkable optical properties of which I have already alluded to in a previous paper. As I have already said, a prism formed of this substance yields a spectrum about 30 times as long as a quartz prism of the same angle, the dispersion resembling somewhat that of selenium. I was of the opinion that the absorption, which commences at about wave-length ·0005, would increase continuously from this point down to the end of the spectrum, as was found to be the case with selenium. On commencing a study of the absorption, however, I was astonished to find that it ended abruptly a little beyond the H and K lines, and that from this point on, the substance was transparent even down to the last cadmium line, of wave-length ·0002.

It at once occurred to me that if some substance or substances could be found absorbing the red, yellow, and green, and transparent to the ultra-violet, we could, by combining them with the nitroso compound, produce the long-sought screen.

Very dense cobalt glass, coated with a thin film of gelatine lightly stained with the nitroso, was found to be transparent only to the extreme red and the ultra-violet, and the red was eventually removed by means of a thin sheet of Chance's "signal-green" glass, such as is used for one of the reflectors in the Ives Kromskop.

This combination is wholly opaque to visible light, while freely transmitting everything between wave-lengths 34 and 38. Of course the employment of glass screens limits the ultra-violet transmission, and a screen of this description is useful chiefly for lecture demonstrations. Considerable care must be used in the adjustment of the strength of the solution of the nitroso in gelatine, otherwise the intensity of the ultra-violet light is considerably weakened.

The best strength is such as will be just sufficient to remove the blue and violet light transmitted by dense cobalt glass. Quite a number of trials will be found necessary in adjusting the densities of the three components of the screen to secure the maximum effect, but when the balance is just right, it is possible to form a focus in which a piece of paper is quite invisible, while a mass of crystals of the nitrate of uranium (which I have found superior to anything else) glows with sufficient intensity to be seen from the back of the largest lecture-room.

It is best to exclude carefully all light which does not pass through the screen.

With the assistance of one of our students, I am at the present time investigating the absorption of a large number of substances, which, so far as I know, have not been previously studied, and I hope in time to dispense with glass entirely, and produce an opaque screen which transmits ultra-violet down to the end of the spectrum.

A combination of a tube furnished with quartz ends, on one of which is a thin film stained with nitroso, transmits all of the ultra-violet, and only the extreme red, but it is very inconvenient to work with. For use as a screen in spectrum-photography there is no especial object in removing the red, yellow, and green, the nitroso alone blocking out completely the actinic portions of the visible spectrum, which overlie the ultra-violet in the second and third order spectra, and I shall next consider solutions of the substance in various fluids in connexion with spectrum-photography.

I have found that the best method of quickly securing a record of the absorption of a solution is to bring a prismatic layer of the liquid, contained in a quartz cell, before the slit of a quartz spectrograph, and photograph the spectrum of the cadmium spark. We secure in this way a record of the absorption of the liquid in various thicknesses, in the form of a curve, quite similar to the curves laboriously constructed from the readings obtained with the spectrophotometer*.

The curve obtained with a solution of the nitroso in glycerine is shown in Plate III. figs. 4 and 5.

It will be noticed that after a certain thickness has been passed we begin to get a noticeable absorption in the ultra-violet, the form of the curve in this region being well shown in figs. 3 and 4. The band in the blue and violet is, however, so much heavier that, by employing a film of suitable thickness, we can get complete opacity in this region, combined with almost perfect transparency in the ultra-violet. The nitroso is soluble in water, glycerine, ether, alcohol, bisulphide of carbon, and many other fluids, and the region of heaviest absorption varies somewhat with the nature of the solvent, the shift of the band not, however, following Kundt's rule in every case.

A stained gelatine film on a quartz plate forms a fairly suitable screen, if we do not wish to photograph below the group of cadmium lines at wave-length 2314. It is opaque, however, to waves much shorter than this. The glycerine solution transmits down to the last cadmium line, $\lambda=2147$, and some other solvents appear to work equally well.

In photographing the spectrum of the cadmium-spark in the ultra-violet of the second order, with the fourteen-foot concave grating, I found that the prolonged exposure of the solution in glycerine to the light of the spark resulted in its decomposition. Gas-bubbles formed in the thin quartz cell, and by bridging across the space between the two plates allowed the passage of blue and violet light.

The same thing occurred with pure glycerine under a quartz plate, while glycerine under glass was unaffected, showing that the decomposition was caused by the extreme ultra-violet.

In addition to the formation of bubbles, a gradual bleaching of the solution occurred. To obviate this difficulty I constructed

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* It is my intention to prepare a monograph on the absorption of a large number of the aniline dyes, and other organic compounds such as the nitroso-dimethyl-aniline, which have not been previously investigated. The spectra will be approximately normal, all on the same scale, and will extend from the C-line down to the end of the spectrum. They will be photographed in the manner which I have described, and will, I hope, make it possible for the spectroscopist or physicist to pick out at once the combination necessary to produce any desired result. Preliminary experiments are now in progress to determine the best form to give the apparatus, and the most suitable source of light, and I shall be very glad of any suggestions pertaining either to the apparatus or to particular substances worthy of investigation. [A similar method of studying absorption within the range of the visible spectrum was employed many years ago by the late Dr. Gladstone.—*Ed. Phil. Mag.*]

a small cell of quartz, by cementing two plates together, with a space of about 0·5 millim. between them, the cell thus formed being cemented to the bottom of a small thistle tube with a very small bore. By filling the thistle tube with the glycerine solution a flow took place through the cell at the rate of about a drop every two minutes. This device worked admirably, and gave no trouble at all, the cell being placed close to the slit of the grating camera, in the path of the convergent beam from the quartz lens. Another very satisfactory screen can be made by dissolving celluloid (previously boiled for some time in water) in amyl acetate, adding a little nitroso, and flowing the solution on a quartz plate. It is, however, opaque to the last two cadmium lines.

The use of the screen necessitates considerable increase in the time of the exposure, the amount varying from two to ten or even twenty times, according to the density of the screen.

The strength of the glycerine solution must be adjusted according to the work required of it: a strong solution gives a wider band in the blue and violet, but diminishes the intensity of the ultra-violet as well. In general the best results are obtained when the blue line of wave-length 4799 in the spark-spectrum of cadmium can be just barely discerned.

In Plate III. fig. 1 the wave-lengths of the principal lines in the spark-spectrum of cadmium are given for reference. The action of the nitroso screen is well shown in fig. 2, the spectra being photographed with a small quartz spectrograph made by Fuess. The first seven spectra were taken through the glycerine-nitroso cell which I have just described, with the following times of exposure: 5, 10, 15, 20, 30, 45, and 60 seconds. The cell was then removed, and the following six spectra taken with exposures 2½, 5, 10, 15, 20, and 30 seconds. A study of these spectra enables us to calculate just what can be done with this screen, and the necessary increase in the time of exposure resulting from its use.

In fig 6, which is a negative, we have the absorption spectra of the various components of the screen which I mentioned in the first part of this paper, taken with exposures of 20 seconds each.

The spectra were taken through screens as follows:—

1. Nitroso in gelatine on glass (thin film).
2. ,, ,, ,, (thick film).
3. ,, ,, on cobalt glass (thin film).
4. ,, ,, ,, ,, (thick film) strong ultra-violet absorption.
5. Dense cobalt glass.
6. Turnbull's blue in gelatine.

7. Chance's "Signal-green" glass (two thicknesses).
8. No screen, 3 seconds' exposure.
9. Cyanine in canada-balsam.
11. Aurantia in collodion.
12. Signal-green glass (one thickness).

These photographs were taken on an orthochromatic plate, the yellow and yellow-green being compressed into the small strip which appears alone by itself in No. 11.

The utility of the nitroso screen in photography with the concave grating is very clearly brought out in the photographs of the iron spectrum shown in Plate IV. These were made with a 14-foot grating, with a glycerine nitroso cell before the slit during one of the exposures. Figures 1 and 2 are from the same plate. Strip B in each was made through the screen, and shows the ultra-violet of the third order, uncontaminated by the blue of the second. In strips A, which were made without the screen, the two orders are mixed. Strips C were made through a glass screen, which cut off the third order ultra-violet, leaving the blue of the second. I have marked a few of the wave-lengths to aid in the identification of the lines.

The times of exposure were for strips A and C ten minutes, for B fifty minutes.

The group of cadmium lines in the neighbourhood of wave-length 2314 is, in the second order spectrum, mixed up with a lot of blue air lines of the first order spectrum. The separation of the two by the nitroso screen is well shown in fig. 3, in which the two orders are shown superposed in strips A, and the ultra-violet of the second order in strip B. The exposures in this case were 15 minutes and 2 hours respectively.

Another screen which I believe may prove useful in astrophysical work is made by combining nitroso-dimethylaniline with a small amount of the dye uranine, the latter removing the bluish-green portion of the spectrum which affects the photographic plate. By a proper adjustment of the two in gelatine on glass, a screen can be formed which, when used with an ordinary (*i. e.*, not orthochromatic) plate gives us a photograph made exclusively by ultra-violet light, comprised between wave-lengths 345 and 365, a rather narrow range.

I have made a few photographs with a screen of this description, which have brought out some interesting points. In a photograph of the full moon, taken by ultra-violet light, the contrast between the bright and dark areas is very strongly accentuated, while in photographs of landscapes made in the same way there is almost no contrast at all except between white objects and objects not white. I have also photographed a collection of rocks and minerals with ultra-violet light and with yellow light. In the negative taken by yellow light there is a great deal of contrast and detail, especially in the marbles and conglomerates, while in the negative taken by ultra-violet light all this is absent, the white specimens coming out very black, with everything else of a thin and almost uniform grey. I hope in the near future to have an opportunity of making some lunar photographs on a large scale, the only instrument at my disposal at the present time being the nine-inch equatorial of the University. Photographing by ultra-violet light appears to diminish the contrast between all objects not white, and to increase the contrast between white objects and those not white. I do not wish to be hasty in drawing conclusions, but it appears to me to be probable that the more luminous portions of the lunar surface, if not as white as plaster-of-paris, must at least be much whiter than grey sandstone. In Plate IV. fig. 4 are reproduced two photographs of the same landscape, taken at the same time and under similar conditions of illumination, the one (A) taken on an orthochromatic plate by yellow light through a screen of dense aurantia, the other (B) taken on an ordinary plate by ultra-violet light.

The absence of contrast between the chimneys and walls in B is especially noticeable in the right-hand part of the picture. I tried various times of exposure, and the picture reproduced is the best of the lot. Another curious effect is the almost complete absence of shadows in the ultra-violet picture (it was taken in full sunlight like the other), showing that most of the ultra-violet light comes from the sky, which is what we should expect, though we should hardly anticipate that the effect would be so pronounced. This is best seen on the monument and on the snow in the middle distance. The increase of "atmosphere" in the ultra-violet picture is very marked. It is so strong that under-exposed plates fog in the shadows of objects not over one hundred yards from the camera, a circumstance which shows the great scattering power of the air for these short waves. The two pictures are also interesting as showing that our eyes have developed a maximum sensibility for that region of the spectrum which shows terrestrial objects in strongest contrast. Nitroso-dimethyl-aniline is the only substance, other than the ordinary aniline dyes, that I have examined thus far, and I feel very hopeful of finding, among the large number of allied substances, absorbing media even more transparent to the ultra-violet radiations than the one which I have described in this paper.

XXIV. *How to apply the Resolution of Light into Uniform Undulations of Flat Wavelets to the Investigation of Optical Phenomena.* By G. Johnstone Stoney, *M.A.*, *Sc.D.*, *F.R.S.*[*]

[The letters *ufw* are used throughout the present paper as an abbreviation for *undulation of flat wavelets.*]

Introduction.

1. LIGHT while within a uniform transparent medium, or any other event which the medium can without external assistance propagate forward as waves, may be resolved within that medium in an infinite number of ways, and among them into undulations of convex or of concave or of flat wavelets. That a resolution into uniform flat wavelets is always possible is proved in the October number of the Philosophical Magazine of 1896, p. 335, where this theorem is enunciated and deduced from an already known theorem [†] in optics; and a more direct proof of the resolution by the Principle of Reversal is given in a paper published at p. 570 of the Report of the British Association for 1901. This proof is better than that previously given, because it is more direct and less inelegant, and also because it furnishes additional information which is useful. A third and extremely elegant proof has recently been published by Mr. Edmund Whittaker, Secretary of the Royal Astronomical Society, at p. 619 of the 'Monthly Notices' of that Society issued in September 1902, where he shows that the general solution of the equation

$$\nabla^2 V = \frac{1}{k^2}\frac{\partial^2 V}{\partial t^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

may be made to assume the form

$$V = \int_0^\pi \int_0^{2\pi} F \, . \, d\theta \, d\psi, \quad . \quad . \quad . \quad . \quad (2)$$

where F is an arbitrary function of the three arguments

$$(x \sin\theta \cos\psi + y \sin\theta \sin\psi + z \cos\theta + kt), \ \theta, \text{ and } \psi ;$$

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[*] Communicated by the Author, having been read in September 1902 before Section A of the British Association.

[†] The theorem here referred to is enunciated at the foot of p. 335 (loc. cit.), and illustrated by the diagram on p. 340. It is the theorem by which Fraunhofer's beautiful experiments with crossed gratings, which were then recent, were explained in the University of Dublin when the author was a student of Trinity College in the forties of the last century. There were two proofs of it current—one an analytical proof by Professor, afterwards Provost, Jellett, based on an extension of one of Airy's theorems in his Tract on Light; and the other a proof by the Principle of Reversal, a new and powerful tool of investigation which MacCullagh had then recently introduced.

in other words, the solution is brought into a form which by Fourier's theorem can be expanded into terms each of which represents an undulation of flat wavelets and is also a particular solution of equation (1).

2. Mr. Whittaker's proof has the advantage of deriving the resolution directly from the fundamental differential equation (eqn. (1)) of those wave-motions in which the speed of propagation is constant as regards x, y, z and t—a condition which, as Clerk Maxwell showed, is fulfilled by electromagnetic waves in an isotropic medium whenever we may assume that the product of the two inductive capacities of the medium is independent of the intensity of the alternations of electromagnetic stress, although in dispersing media it is not independent of their periodic time. (See Clerk Maxwell's 'Electricity and Magnetism,' § 786.) This condition is doubtless complied with by those electromagnetic waves that constitute any light that our eyes can see, if we may omit from consideration the absorption of part of the light by the medium, as we legitimately may when dealing with journeys of any length in the open æther, or with journeys of moderate length across transparent media.

3. On the other hand, the proof by the Principle of Reversal has an advantage which is of great value to the physicist, namely, that it not only proves, like the analytical method, that a resolution into flat wavelets exists, but further, exhibits in each individual case details of the resolution and of the relations in which this resolution stands to other neighbouring resolutions: amongst which the most useful are its relations to resolutions into concave or convex wavelets that are nearly flat. It thus furnishes the general solution of eqn. (1) which is presented in eqn. (2); along with details that are of practical value; and further, with what may be regarded as equivalent to a solution of the theorem in the Calculus of Variations which would investigate the relation to one another of the various functional forms which the solution of eqn. (1) can assume: of which functional forms eqn. (2) is one. This great additional insight, and the adaptability of the method to individual instances, offer such assistance to the experimental physicist that it is fortunate that we are in possession of both proofs. We shall be in a better position to appreciate the advantages here spoken of when we come to the experimental verifications. An account of some of these is in preparation, and the author hopes to publish it as a sequel to the present paper.

4. The resolution of a given distribution of light into its component undulations of flat wavelets is *unique* in the same

sense in which resolutions by Fourier's theorem, or into Spherical Harmonics, are unique ; and it has the immense advantage over every other method of resolution that each of the flat wavelet components advances *unaltered* across the medium. When we aim at the most complete theoretical resolution from the purely mathematical point of view, we are to regard each of the component undulations as an uninterrupted train of waves which are all alike—of the same wave-frequency, intensity, and state of polarization throughout—and *each occupying the whole of space for all time.* Nevertheless it is quite permissible, and is for most purposes convenient, to consider separately what happens within a limited space and definite duration. Moreover, we shall presently see that it is legitimate, *when investigating what happens within a limited space*, to divide the whole body of undulations of flat wavelets into little groups and to substitute a single undulation of flat wavelets for each of these groups ; and that, in like manner, *when dealing with a definite time*, it is legitimate to divide the wave-frequencies into little groups and to substitute a single wave-frequency for each group. By these familiar devices we substitute large numbers which can be accepted by the physicist, for the infinite numbers of the mathematician ; and values estimated at a point which falls short of the limit for the limiting values of the mathematician. We thus sweep aside the difficulties which would otherwise result from ponderable matter consisting of molecules, from electricity consisting of electrons, and from the consequent necessity *when dealing with nature* of substituting the puncta of the physicist for the points of the mathematician.

5. The proof by the Principle of Reversal has another advantage, not yet referred to, viz. that it can be applied to doubly refracting as well as to isotropic media. The investigation at p. 570 of the Report of the British Association for 1901, goes with detail only into the resolution of light in isotropic media, as being the case of most practical importance. This having been accomplished, it is easy to modify the investigation so as to embrace both isotropic and doubly-refracting media. To do this it suffices to substitute throughout that proof the term *wave-surface in the medium* for the term *sphere*, when treating of light diverging from or converging towards a punctum. Thus, Theorem I. on p. 573 of the B. A. Report furnishes, when generalized, the following more comprehensive one :

THEOREM I., extended.

All light traversing a uniform medium whether isotropic or doubly refracting is susceptible of being resolved into undulations of uniform flat wavelets sweeping across that medium with speeds in the different directions represented by the lengths of the perpendiculars in those directions from the centre of the wave-surface upon its tangent-planes.

6. In like manner the primary aim of the present paper is to develop a convenient way of applying the flat-wavelet resolution of light to the investigation of the optical problems that arise in isotropic media; but, like the investigation referred to above, it also can with ease be generalized so as to provide for the optical problems that arise in any uniform medium, whether isotropic or doubly refracting (see § 8).

The inquiry which we have in view naturally divides itself into two portions, the first of which deals with what we may call the chamber study of optical phenomena, and the other with their laboratory study—that is, with the making of actual experiments and understanding them. The present writer has made extensive use of the new method of analysis in both branches of the study.

PART I.—*How to employ the resolution of light into flat wavelets in the chamber study of optical phenomena.*

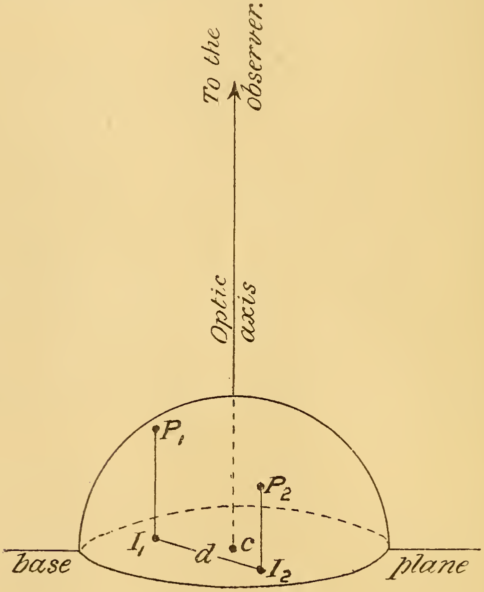
7. If we conceive the light within an isotropic transparent medium to be resolved into its component undulations of flat wavelets, the following will be found a convenient way of dealing with them.

Imagine a straight line in space, which we may call the *optic axis*. In most cases the best position for this line is from the observer to the middle of his field of view. Draw a plane perpendicular to the optic axis, preferably near to the object looked at. This we may call the *base-plane*. With c (the intersection of the optic axis and base-plane) as centre, describe a hemisphere with its convex side towards the observer, and with radii of any assumed length, R. This we may call the *reference-hemisphere*.

8. In doubly-refracting media we have to use half the wave-surface of the medium instead of the simple hemisphere which suffices for isotropic media. But for the present we intend to confine our attention to the latter.

Now (see Theorem I. on p. 573 of the B. A. Report for 1901, or in § 5 above) the light with which we are dealing, whatever it is, might be withdrawn, and undulations of flat wavelets substituted for it, without producing any change in nature. Each one of these u f w's (undulations of flat wavelets) travels in the direction of some radius of the reference-hemisphere, and has its wave-fronts parallel to the tangent-plane at the outer end of that radius We may call undulations *outward-bound* when they travel along the radius from centre to surface of the hemisphere, and *inward-bound* when they travel in the opposite direction.

Fig. 1.



Reference-hemisphere.

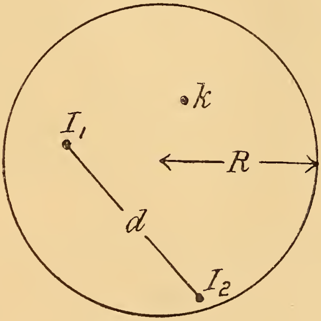
9. Practically, in most real problems, we know beforehand whether we are dealing with outward-bound or inward-bound undulations, so that no appreciable inconvenience results from the circumstance that two undulations—one inward-bound and the other outward-bound—are represented by the same radius cP_1. We may call cP_1 the *guide-radius* of whichever of the two we have to deal with. It may equally well be represented by the point P_1 on the hemisphere (which we may call its *guide-point*); and still better by I_1, the orthogonal projection of P_1 on either the base-plane or some parallel plane (which we may call its *index-point*). For purposes of mathematical investigation it is more convenient

to project the guide-points into index-points on to the base-plane, whereas in experiments the projection is usually exhibited on some parallel plane. The positions of the index-points—*i. e.* of the projections of the guide-points—are the same in the resulting diagram, whether it is formed on the base-plane or on any parallel plane.

10. Accordingly, if u_1, u_2, &c. are the u f w's we have to deal with, then the directions in which they are advancing and the orientations of their wave-fronts, are adequately represented by the index-points I_1, I_2, &c. got by the above construction ; and whether the projection by which we arrive at the index-points is a projection on to the base-plane or on to some parallel plane, they occupy the same positions within a circle in that plane which is the projection upon it of the flat side of the reference-hemisphere, and which, therefore, has R for its radius. This circle and its contents may be called the *Indicator-diagram.*

11. By applying simple geometrical considerations to the foregoing construction, we get the following propositions :—

Fig 2.



Indicator-diagram.

Let u_1 and u_2 be two inward-bound u f w's, consisting of waves similarly polarized and of wave-length λ ; and let I_1 and I_2 be their index-points upon the indicator-diagram. Then a simple geometrical proof furnishes the following elegant theorem.

THEOREM VII.*

The light which these two u f w's throw on the base-plane, or on any parallel plane, is a luminous ruling perpendicular

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* The propositions in this paper are numbered in succession to those in the paper at p. 570 of the B. A. Report for 1901.

to the line d; and the spacing from crest to crest of this ruling is

$$\sigma = \lambda \frac{R}{d}.$$

The position of this ruling will become fully determined if we know the position of any one of the points which the two undulations reach simultaneously in the same phase. We shall use the letter k to designate such a point.

12. Hitherto we have considered only individual u f w's. Let us now consider an entire sheaf of them. By a *sheaf* of u f w's is meant a group of them whose guide-radii form a solid cone. It will be represented either by this cone, which may be called the *guide-cone* of these undulations, or by their *guide-patch* (in which this cone intersects the surface of the hemisphere); or preferably by the projection of this guide-patch upon the indicator-diagram, which we may call the *macula* of the sheaf of u f w's.

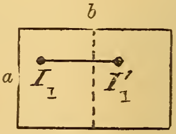
Thus a point on the indicator-diagram represents a single u f w, a macula (or patch on the indicator-diagram) represents a certain sheaf of such undulations.

Let it further be provisionally assumed that the undulations of this sheaf all reach the point k in identical phases at each instant of time, that they are polarized alike, and that they have equal intensities. The point k, which the undulations of the sheaf reach in identical phases, may be either on or off the base-plane. Draw through k a plane parallel to the base-plane, and call it *plane K*; or it may be called the screen K, as we are about to inquire in what way it is illuminated by the light with which we are dealing.

13. The macula of the sheaf may have any shape or size. Let us begin with the simple case where the sheaf of undulations is such that its macula on the indicator-diagram is a rectangle with sides a and b. Bisect this macula, as in the figure, by a line parallel to one of its sides, and let I_1 and I_1' be similarly situated points in the two halves. The line connecting them is parallel to b, and $= b/2$. Hence, by Theorem VII., the two u f w's of which I_1 and I_1' are the index-points would, if they alone were present, produce on plane K a luminous ruling of which one crest passes through k, of which the crests are perpendicular to the line b of fig. 3, and which are spaced asunder by the interval

$$\sigma = \lambda \frac{2R}{b}.$$

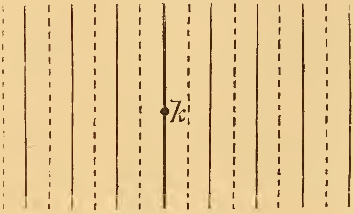
Fig. 3.



A rectangular macula on the Indicator-diagram.

We may represent this by fig. 4, or by the upper strip of fig. 6, in which the continuous lines are the crests of the luminous ruling, and the dotted lines are positions of cipher illumination.

Fig. 4.

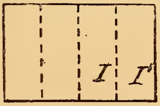


Part of plane K.

All other points, I_2, I_3, I_4, &c. in the left-hand half of fig. 3, have corresponding points in the right-hand half; and each such pair, if acting alone, would produce a ruling on plane K represented diagrammatically by fig. 4, and therefore with cipher illumination along the dotted lines of fig. 4. Accordingly when they are all present, there is cipher illumination along these lines. Moreover, there is maximum illumination at the situation *k*, since we have made the assumption that all the u f w's reach it in identical phases; but elsewhere, wherever light is superposed on light, the resultant illumination will range between cipher and that maximum.

The next step to be taken is to divide the macula into four equal parts by lines parallel to *a*. Then all its points may be grouped in pairs like I and I′, separated by the distance *b*/4 and with the line joining them parallel to *b*. Each such pair of index-points belong to two u f w's which, if acting alone, would produce a luminous ruling on plane K, parallel to the ruling on fig. 4, with one crest passing through *k*, but with its positions of cipher illumination as in strip *β* of fig. 6 (p. 272).

Fig. 5.

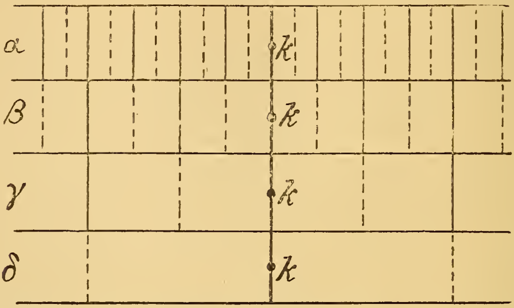


The same macula as in fig. 3.

So, again, by dividing the macula into eight parts, we find that the illumination it produces on plane K is confined to positions which are not on the dotted lines of strip *γ* of fig. 6: and so on.

Finally, by this process, we learn that there is cipher illumination on all the dotted lines of fig. 7, *i. e.* on all the lines dotted or undotted of fig. 4, except the central one.

Fig. 6.



Each strip is the same part of plane K as in fig. 4.

Fig. 7.

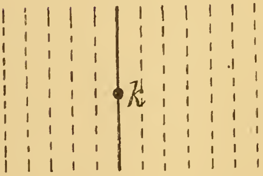


Fig. 8.

The same part of plane K.

By similarly dividing the rectangular macula into 2, 4, 8, 16, &c. equal parts by lines parallel to *b*, we find a second set of dotted lines along which the illumination is cipher, as in fig. 8.

The results we thus arrive at may be summarized as follows :—

THEOREM VIII.

If the sheaf of u f w's represented by a rectangular macula on the indicator-diagram are of the same wave-length, similarly polarized, and of equal intensity; and if they all reach the point k in the same phase ; then, if a flat screen parallel to the indicator-diagram pass through the point k, the illumination produced on it by the u f w's of this sheaf is such that there is maximum illumination at k, where the phases are identical ; considerable brightness close to it, where the phases do not differ much ; cipher illumination along all the dotted lines of fig. 8 ; and probably glimmers of illumination in the interspaces between them.

14. To quite obliterate these glimmers requires, in fact, more light to be thrown upon plane K than is furnished by the undulations of the sheaf, where these are all alike, as we have supposed them to be. The requisite additional light, when resolved into its component u f w's, would furnish on the indicator-diagram certain out-lying and on-lying appendages * to the rectangular macula of the sheaf, of the kind described in a paper "On the Cause of Spurious Double Lines and of Slender Appendages," read at the Oxford Meeting of the British Association (see B. A. Report for 1894, p. 583). But usually the light that is indicated by these appendages in the indicator-diagram is a very small proportion of the total light, and in many practical cases need not be taken into account. Whenever it is legitimate to exclude them from consideration, we may regard the sheaf of undulations as producing illumination upon plane K, only within the central patch of fig. 8, which is shut in by dotted lines.

15. When, as more frequently happens, the macula of a sheaf of undulations is a circular disk or oval instead of a rectangle, the modification of the above analysis is obvious. Airy's investigation of the image of a star in a telescope is a particular case of the above more general theorem, viz. the case where the macula is a circular patch situated exactly in the middle of the indicator-diagram.

16. From Theorem VIII. the following one may with ease be deduced.

Theorem IX.

When light reaches the point k in the same phase &c., from two or more sheafs of u f w's, represented on the indicator-diagram by separate maculæ, then, as before, the illumination of plane K *is chiefly within a central patch surrounding k such as that represented in fig.* 8; *but this central bright patch now consists of a luminous ruling of parallel bands if there are two sheafs, this ruling being finer the more distant the two maculæ are on the indicator-diagram. Similarly, if there are three maculæ not in a straight line, the bright patch of fig.* 8 *is resolved into rows of bright specks; and so on.*

All of these effects can be shown experimentally.

17. When we have occasion to deal with a very small

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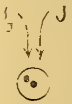
* The demand made by nature for the presence of these appendages is a requirement analogous to the mathematical necessity of substituting a series of sines and cosines of which the arcs are not commensurable for the ordinary Fourier's series, when the series is to represent an isolated event without repetitions: *i.e* when beyond that event the sum of the series is to be everywhere absolutely cipher.

sheaf of u f w's, it is often convenient to substitute a single undulation for the whole of the little sheaf. That this is legitimate when the macula of the sheaf is small enough, may be proved as follows. The guide-cone of the sheaf is, by supposition, a very acute one. Draw a line from its vertex, within the cone. This we may call its axis. Let J be the corresponding point in its little macula. Let u be any one of the undulations of the little sheaf, and let I_1 be its index-point. Along the axis imagine two undulations v_1 and v_1' to be sent, with the same wave-length, state of polarization, and intensity as u_1, but of which v_1 reaches k in the same phase as u_1, and v_1' in the opposite phase. Under these circumstances v_1 and v_1' cancel one another, so that their addition to the system makes no change. Now u_1 and v_1' produce a luminous ruling on plane K of which one of the lines of cipher illumination passes through k, and of which the spacing is

$$\sigma = \lambda \frac{R}{d},$$

where d is the very short distance from I_1 to J. If this distance is short enough the nearest maximum of brightness on either side will be so far from k, that within a limited field of view, such as is seen on looking into an optical instrument, there will be no appreciable light from this ruling. And if so, we may omit u_1 and v_1', and v_1 alone remains. Similar substitutions of v_2, v_3, &c., all of them advancing along the axis, may be made for u_2 u_3, &c., the other undulations of the little sheaf. When this has been done, all these v's may be combined into a single resultant v travelling along the axis. This establishes Theorem X., which is as follows :

Fig. 9.



The small macula.
(Part of indicator-diagram.)

Theorem X.

When dealing with a limited field of view we are at liberty to substitute the resultant v *for any very small sheaf of undulations, and this substitution is legitimate, however unrelated the phases, states of polarization, and intensities of the undulations in the little sheaf may have been.*

This is the first of the two substitutions spoken of above in § 4, which are of the kind that must be legitimate to justify our applying to nature conclusions obtained by mathematics from data which are of necessity almost immeasurably simpler than the complex details that nature everywhere reveals to us when we attempt to pry into her operations at close quarters.

18. The other of the two substitutions spoken of in § 4, may be effected in almost exactly the same way. When two u f w's of wave-frequencies ϕ_1 and ϕ_2 (or of the corresponding wave-lengths λ_1 and λ_2) travel in the same direction, they may, if similarly polarized and of equal intensity, be represented by equations which, by a suitable selection of origin and coordinates, simplify into

$$\left.\begin{aligned} y_1 &= \mathrm{A}\sin\left[2\pi(x-vt)\phi_1\right] \\ y_2 &= \mathrm{A}\sin\left[2\pi(x-vt)\phi_2\right] \end{aligned}\right\} \quad . \ . \ . \ . \ . \ . \ . \quad (3)$$

When both of these undulations are present they produce a resultant effect represented by

$$y_1+y_2=2\mathrm{A}\sin\left[2\pi(x-vt)\frac{\phi_2+\phi_1}{2}\right] . \cos\left[2\pi(x-vt)\frac{\phi_2-\phi_1}{2}\right], \quad (4)$$

which tells us that at each station in space beats occur with a frequency $(\phi_2-\phi_1)/2$, and that the loops between the nodes consist of waves of which the frequency is $(\phi_2+\phi_1)/2$, the phases of the corresponding waves in any two consecutive loops being the reverse of one another.

19. A convenient way to deal with them is to imagine the waves to become stationary and rigid at a given instant of time *, and then to imagine the whole of this rigid system to be borne forward, in a direction perpendicular to the wave-fronts, with the speed v, *i.e.* with the speed of light. It will then sufficiently represent what occurs in nature.

Let us select $t=0$ as the time when the system becomes rigid. The components will thenceforth be represented by the equations

$$\left.\begin{aligned} y_1 &= \mathrm{A}\sin(2\pi\, x\phi_1) \\ y_2 &= \mathrm{A}\sin(2\pi\, x\phi_2) \end{aligned}\right\} \quad . \ . \ . \ . \ . \quad (5)$$

and the resultant by

$$y_1-y_2=2\mathrm{A}\sin\left(2\pi x\frac{\phi_2+\phi_1}{2}\right) . \cos\left(2\pi x\frac{\phi_2-\phi_1}{2}\right), \ . \quad (6)$$

which is a rigid undulation † with loops and nodes, the middles

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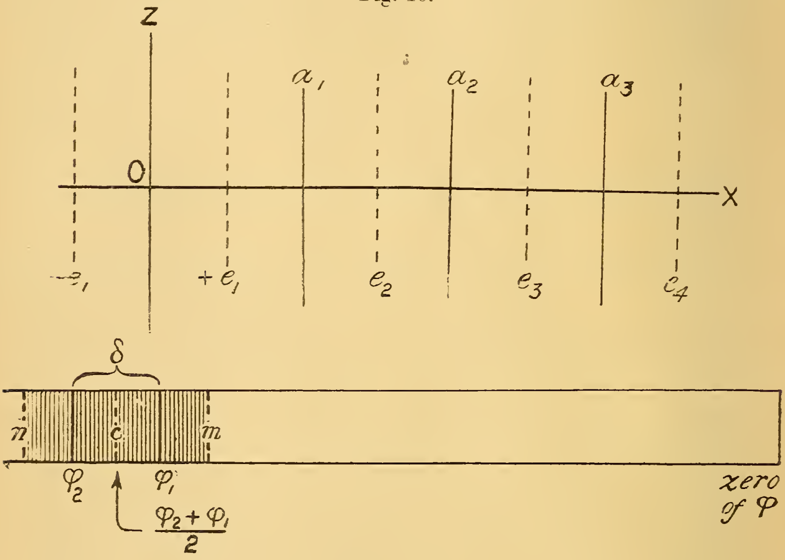
* Another convenient device is to make $x=0$ in eqn. (4), and in this way to ascertain what happens at a given station in space as time flows on. It is quite immaterial which method we employ,: of the two, that in the text is perhaps the more easily handled.

† In speaking of the rigid system it is convenient to continue to use the terms wave, undulation, &c., although there is no motion. They are used in the same sense as when one speaks of an undulating landscape.

of the loops occurring upon the planes where $(\phi_2-\phi_1)x$ (which is of cipher dimensions) is one of the series 0, 1, 2, 3, &c., and with nodes lying upon the planes that are midway between these positions. This may be represented diagrammatically by fig. 10, in which the axis of Y is supposed to be perpendicular to the plane of the paper; and in which the lower figure represents a spectrum of wave-frequencies. Draw the planes a_1, a_2, &c. parallel to the plane YZ and at the distances furnished by the equations

Fig. 10.



$$x=\frac{1}{\delta},\quad x=\frac{2}{\delta},\quad x=\frac{3}{\delta},\quad \&c., \quad . \quad . \quad . \quad . \qquad (7)$$

where δ is an abbreviation for $\phi_2-\phi_1$. Then the middles of the loops of the rigid undulation represented by eqn. (6) are on these planes, and the nodes of that undulation lie on the dotted planes midway between them. These latter planes, e_1, e_2, e_3, &c., are accordingly the situations where the transversal of the waves that form the undulation becomes cipher. The nearest of the dotted planes to plane YZ are the planes e_1 and $-e_1$, viz.:

$$x=\frac{1}{2\delta},\quad \text{and}\quad x=-\frac{1}{2\delta},\quad . \quad . \quad . \quad . \quad . \qquad (8)$$

which, therefore, mark the limits of the central loop.

Let us now indicate upon the spectrum the positions that correspond to the wave-frequencies $\phi_1 - \delta/2$ and $\phi_2 + \delta/2$. Let us suppose that u f w's of all the wave-frequencies between these limits are present, and further assume that they are so related to one another that they are all polarized alike and of equal intensity, and that they had all reached the plane YZ in the same phase when the solidification took place. These would be represented on the spectrum by a band extending from m to n. Let this band be divided into equal parts by the line c. Then the whole of the light can be divided into pairs of rays, one in the left-hand half of the band, and the other in the right-hand half, and with δ as the difference of wave-frequency between the two components of each pair. Every such pair, if it alone were present, would produce the distribution represented in fig. 10, with loops of waves from $-e_1$ to $+e_1$, from e_1 to e_2, and so on, and with their positions of cipher intensity occurring on the dotted planes. Accordingly, as each pair if acting separately would produce cipher intensity on the dotted planes, they all when simultaneously acting produce cipher intensity on those planes. We may make use of strip α of fig. 6 to represent this distribution. And as we are equally at liberty to divide the band mn on the spectrum into 4 parts, or 8, or 16, &c., and thus to group the whole of the light of the band into pairs of rays with a difference of wave-frequency which we can make either $\delta/2$, or $\delta/4$, or $\delta/8$, &c.; we by this process find that when the whole band of light is in action there is cipher intensity on the dotted lines of strip β, and on those of strip γ, &c. of fig. 6, as well as on those of strip α. This means that there is cipher intensity on all the planes, dotted or undotted, that are represented in fig. 10, except the plane YZ. On this plane the intensity is a maximum, because by hypothesis all the u f w's corresponding to the individual rays of the band reached it in the same phase when the solidification took place. Up to the present we have followed the same line of argument as in § 13, and by continuing it to the end, we learn that nearly the whole intensity of what results from the coexistence of all the u f w's is to be found in the central loop between the planes $-e_1$ and $+e_1$, while beyond those limits there may be intensities that correspond to glimmers of light, which become fainter the wider the band mn in the spectrum is, and which, for their total extinction, would require the cooperation of certain appendage rays other than the rays of which we have yet taken account, which appendages, however, in many of the practical cases that arise supply so little light that they may be ignored.

All that remains to be done is to start the rigid system forward in the direction OX with the speed of light. It then represents what occurs in nature, and furnishes the following theorem :

THEOREM XI.

If u f w's of all the wave-frequencies that lie within the band mn in the spectrum travel in the direction OX *; if they are of equal intensities and polarized alike; and if their phases are such that their crests coincide at some one instant of time with any one plane* YZ *parallel to their wave-fronts: then this light produces at each station in space an illumination which lasts for a period* $1/\delta v$, *where* δ *is half the range of wave-frequencies within the band; with perhaps glimmers of illumination before and after that period.*

These glimmers would require for their extinction the simultaneous presence of certain appendage u f w's which, however, in many practical problems represent so small a part of the light that they need not be taken into account.

20. We may also infer the following theorem, which is the converse partly of Theorem VIII. and partly of Theorem XI.

THEOREM XII.

Light that at our station extends over a limited space and lasts for a limited time is theoretically susceptible—*i. e.* would be susceptible if the physical conditions prevailing in nature justified our pursuing a resolution of the kind to its mathematical limit—*of being resolved into u f w's infinite in number and each occupying the whole of space for all time.*

In dealing with the actual problems of nature, a resolution is found to be sufficient which falls short of this extreme, and which is well within what the physical constitution of matter tolerates.

21. We are now in a position to effect the second of the two useful substitutions spoken of in § 4. If we have only to consider what happens at our station within a limited duration which we may call τ, and which may be a second, a minute, an hour, a week, or any other: then we may proceed as follows :—The light with which we are concerned may be of various wave-frequencies extending over either the whole or a part of the spectrum, and the rays of which the spectrum consists may be of any (either the same or different) intensities and states of polarization. They need not be in any way related to one another. We may conceive the spectrum to form a map of wave-frequencies. Then we may divide the length of this spectrum into equal degrees, each of which corresponds to a fixed difference of wave-frequency, which we may call δ, and we may make these degrees large or

small as we please. Let us then make them so small that the duration τ shall be but a small part of the duration $1/\delta\nu$. Then we are at liberty to substitute a single u f w with one definite wave-frequency, for the entire of the little group of u f w's of different wave-frequencies that furnish the rays that fall within any one of the foregoing degrees. To see this it is only necessary to proceed by successive steps which are so exactly analogous to those adopted in § 17, that it is unnecessary to repeat the procedure here. We thereby learn that—

THEOREM XIII.

When we have to consider in any problem what happens within a limited time, it is permissible to divide the wave-frequencies (or the corresponding wave-lengths) *of the light with which we are concerned, into little groups and to substitute light of a single wave-frequency for each of these.*

It is important to bear in mind that this substitution can be effected whatever be the intensities, phases, and states of polarization of the individual undulations of the little group, inasmuch as it depends upon our pairing each member of the group with a *supposed* one which we are at liberty to conceive of as in the opposite phase, in the same state of polarization, and of the same intensity as that member of the group with which it is paired; and this can be effected however unrelated in these respects that member of the group may be to its colleagues.

22. The foregoing theorems (with perhaps a few additions such as the theorem which explains how to resolve a beam or pencil of light into its component u f w's) would be a sufficient foundation on which to proceed with the chamber study of optical phenomena by the new analysis. It will, however, be convenient to continue the study in conjunction with experiments which will afford assistance; and accordingly we intend next to inquire how to exhibit in optical instruments the resolution of light into its component u f w's, and how to employ this resolution as our guide in making and in interpreting experiments.

[To be continued.]

XXV. *The Theory of Electrolytic Dissociation.* *By* W. C. D. WHETHAM, *M.A., F.R.S., Fellow of Trinity College, Cambridge**.

THE theory of the ionic dissociation of electrolytes, chiefly due to Arrhenius, was successful in explaining the electrical properties of aqueous solutions, and in co-ordinating

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* Communicated by the Author.

those properties with the phenomena of osmotic pressure and chemical activity. Hence there followed a general though not universal adoption of the theory, despite the opposition of some chemists. Lately, however, evidence has been offered to show that the general connexion between the properties of electrolytes, which seems to exist in the case of solutions in water, fails when other solvents are used, and that the exact numerical relations between, for example, conductivity and osmotic pressure, which were at one time thought to hold, are inexact at moderate concentrations even for aqueous solutions. It has hence been argued that the fundamental conceptions of the dissociation theory are erroneous, and that it should no longer be accepted as a valid explanation of the electrolytic phenomena. In the present stage of the discussion, it may be of interest to examine the foundations on which the theory rests, and to inquire how far they are affected by such criticism as we have indicated.

The conception of the complete independence from each other of certain parts of the dissolved molecules of electrolytes is attained by two distinct lines of research: (1) the examination of the electrolytic conductivity; and (2) the consideration of the thermodynamic theory of osmotic pressure and allied phenomena.

The appearance of the products of electrolysis at the electrodes, and at the electrodes only, indicates that the opposite parts of the solute must travel in opposite directions through the liquid under the influence of the electric forces, while Faraday's experiments show that the separation of a definite quantity of substance at the electrodes is always associated with the passage through the solution of a definite quantity of electricity, which is proportional to the valency of the ion. We are thus led to conclude that the process of electrolytic conduction is a kind of convection, in which the opposite ions are moved electrically through the liquid, and carry with them definite electric charges. This view of the phenomena was further developed by Kohlrausch, who showed that a calculation of the velocities with which the ions moved under a given electric potential gradient could be made from a knowledge of the conductivity of the solution and of the transport ratio, which had been investigated by Hittorf. The numerical values of the mobilities of different ions obtained by Kohlrausch's theory were confirmed by Lodge, Whetham, Orme Masson, and Steele, who have experimentally determined the velocity of certain ions by tracing their effect on an indicator, or by measuring the rate of motion of the boundary between two different solutions.

It is well known that a finite electromotive force is needed to effect electrolytic decomposition; but, when the process is examined more closely, it is found that the reverse electromotive force of polarization exists only at the electrodes. If this reverse force is eliminated, by the use of alternating currents or otherwise, the conduction proceeds in conformity with Ohm's law, that is, the current is proportional to the electromotive force, so that any force, however small, causes a corresponding current. Thus within the liquid there are no reverse forces of polarization, and consequently no work is done by the current in causing reversible electrolytic separations. The freedom of passage indicated by the facts of electrolysis must therefore exist, whether a current flows or not; the function of the electric forces is merely directive, and the only work expended is done against that frictional resistance to the motion of the ions which is called the ionic viscosity.

So far our results show that under all conditions the ions possess the freedom necessary for their passage through the liquid. That freedom may, however, on the facts enumerated, be secured by a possibility of interchange between the oppositely electrified parts of two dissolved molecules at the instant of collision, or to the successive formation and decomposition of molecular aggregates. Let us trace the consequences of such suppositions.

In accordance with the elementary principles which hold good for the chance encounters of a large number of moving particles, the frequency of collision, or the number of molecular aggregates formed per second, will be proportional to the square of the number of dissolved molecules. Now, on the view suggested, the motion of the ions, and therefore the average ionic mobility, will depend on such chance collisions, and be proportional to the frequency with which they occur. The velocity of the ions under a given potential gradient will thus be proportional, approximately at any rate, to the square of the concentration of the solution. The quantity of electricity conveyed per second under a given electromotive force, that is, the conductivity of the solution, must depend on the product of the relative velocity of the ions and the number of ions per unit volume. It follows that, on any hypothesis of molecular interchanges, the conductivity of a solution will be approximately proportional to the cube of the concentration. This result is quite contrary to observed facts. In dilute solutions, the conductivity is nearly proportional to the first power of the concentration, and, as the concentration increases, the conductivity usually increases at an even slower rate. We are bound to conclude that no process which requires the conjunction of two molecules is involved, and that the ions move independently of each other through the liquid. It should be noticed that migratory independence from each other on the part of the ions is quite compatible with connexion between the ions and the solvent, whether such connexion is of the nature of definite chemical combination or more general physical influence. The electrolytic dissociation theory is quite independent of any particular view we may take of the nature of solution, which may be produced by actions analogous either to physical or to chemical processes.

Many other purely electrical phenomena indicate the same independence of the ions, and receive a ready explanation if that conclusion be accepted. Thus, Kohlrausch's specific coefficients of ionic mobility are definite constants for each ion in dilute solution, and do not depend on the other ion present. Again, when a layer of water is placed on the top of a solution of an electrolyte, owing to the diffusion of the two ions the water takes with reference to the solution a positive or negative potential, according as the positive or negative ion in that solution has the greater mobility. From a knowledge of the osmotic pressures and of the specific coefficients of mobility of the ions, Nernst has shown that it is possible to calculate the observed numerical values both for this difference of potential and for the rate of diffusion of the salt as a whole.

Let us now turn to the second series of observations which led to the development of the dissociation theory. The phenomena of osmotic pressure, and the laws to which those phenomena conform, can be deduced by the application of thermodynamics, either in the manner of van't Hoff and Lord Rayleigh, from the observed relations between the solubility of gases and their pressure, as formulated in Henry's law, or from the fundamental ideas of the molecular theory, as pointed out by Willard Gibbs, von Helmholtz, and Larmor. Adopting the latter method, it is clear that the osmotic pressure which a solution will exert against a solvent is measured by the rate of change of the available energy of the system when solvent is allowed to enter the solution reversibly through a semi-permeable membrane. On the molecular theory, we must imagine the solute to be distributed through the liquid as a number of discrete particles, each of which may affect, either by way of chemical combination or physical influence, a certain minute volume of the solvent lying round it. The nature of this influence is unknown, but, whatever it may be, as soon as the solution becomes so dilute that, except for an inappreciable fraction of the time, these spheres of influence do not in general intersect each other, any further addition of solvent will only increase the separation of the spheres of action; it cannot change the internal condition of one of these spheres or affect the interaction between the solute particles and their surrounding solvent. The change of available energy produced by the entry of solvent must then simply be that due to the dilution of the solute particles, and cannot depend on any interaction between solute and solvent. The rate of change of available energy with dilution, that is, the osmotic pressure, must consequently be independent of the nature of the solvent, and will therefore have the same value if no solvent be present. Thus, in cases where this is possible, that is, for volatile solutes, it follows that the osmotic pressure must be equal to the gaseous pressure corresponding to the same concentration. We thus theoretically establish the gaseous laws for the osmotic pressure of volatile solutes, and, since volatility is probably only a matter of degree, it seems reasonable to extend this result to non-volatile bodies. Whether this extension be regarded as theoretically valid or not, there is abundant experimental evidence that it is practically justified, since the osmotic pressure of solutions of such substances as cane-sugar is well known to have the gaseous value.

When in solutions of electrolytes we examine the osmotic pressure or the correlated effects such as the depressions of the freezing-point, abnormally great values are obtained, and, by the course of reasoning given above, it follows that a number of solute particles greater than that indicated by the chemical formula must exist in the solution; that is, that dissociation must have occurred. To connect this result with the migratory independence of the ions of electrolysis, it is necessary to show that for solutions so dilute that the solute particles are beyond each other's sphere of influence, the number of ions indicated by the electrical behaviour is the same as the number of independent particles required to produce the observed osmotic effects. Thus for a dilute solution of potassium chloride, which yields two electrical ions, potassium and chlorine, the depression of the freezing-point should be twice as great as for a solution of cane-sugar of equivalent molecular concentration. For bodies yielding three ions, such as sulphuric acid or barium chloride, the freezing-point depression should similarly be three times the normal value. When the concentration of the solution is increased, the spheres of influence of the solute particles will intersect, and the thermodynamic deduction of the gaseous value of the osmotic pressure ceases to be valid. Unless we know at what concentration this intersection begins to produce appreciable effects, and what its result will be both on the electrical and on the osmotic properties, we cannot infer that the decrease in equivalent conductivity will proceed in accordance with the decrease in the abnormal excess of osmotic pressure.

It has commonly been assumed, as a necessary consequence of the dissociation theory, that the number of ions indicated by the electrical conductivity must agree with the number of particles producing osmotic pressure both at extreme dilution, when the ionization is usually complete. and also when the concentration is increased to a moderate extent and some of the ions recombine. While it seems likely that the first of these relations should hold in cases where the ionization is known to be complete, it will now be evident that the second relation can only exist if the connexion between the ions. which is produced by increasing the concentration. affects equally both the conductivity and the osmotic properties. Such might be the case were the only result of increasing concentration to cause a certain number of ionic re-combinations to form electrically inactive molecules. each molecule producing the normal osmotic effect; but. if any other appreciable influence arises from ion to ion, it may possibly change the rate of variation of available energy with dilution, that is, the osmotic pressure, before it decreases the ionic mobility. The second relation then can only be expected to hold while the solute particles are beyond each other's sphere of action, and the experimental examination of the relation merely gives a means of estimating at what dilution this condition fails. The conductivity shows that ionization begins to be incomplete at very great dilutions. Even for monovalent salts, such as potassium chloride, the equivalent conductivity begins to diminish at concentrations of about 10^{-3} gram-equivalent per litre. while, with salts containing divalent ions, it is doubtful if complete ionization is more than just reached at the greatest dilution which can be investigated experimentally, namely about 10^{-5} gram-equivalent per litre. Incomplete ionization, however, does not necessarily connote inter-ionic influences except at the moments of collision and in the combined molecules, while for non-electrolytes, the gaseous value of the osmotic pressure is known to extend to much higher concentrations. It is possible. therefore. that the second relation suggested by the theory should hold good for a certain small range of concentration. Nevertheless. as

Dr. Larmor has pointed out to the writer, there is reason to believe that the gaseous laws would fail at much smaller concentrations in solutions of electrolytes than in those of non-electrolytes. If, as is most likely, the forces between the dissolved molecules are electrical in nature, the effect of two non-ionized bipolar molecules on each other will be analogous to that between two short magnets: the force will vary inversely as the fourth power of the distance. On the other hand, with two isolated charged ions, the force will be that between two small electrified bodies, and will vary as the inverse square of the distance. Thus, beyond a certain minute range, the inter-molecular forces will rapidly become insensible, and solutions of non-electrolytes will then conform to the gaseous laws. Electrified ions, however, will produce sensible effects on each other at ranges much beyond these inter-molecular spheres of action, and, even at great dilution, will diverge from the ideal conditions. Such divergence will certainly change the quantity of work done on dilution, and thus affect the osmotic properties. It is not clear, however, that it will also diminish the migratory freedom necessary for electrolysis: the inter-ionic forces will, on the average, be equal in all directions, and may not influence the mobility of the ions under an electromotive force. As a conclusion, then, it follows if we accept the dissociation theory that, in those solutions which are known to be fully ionized at great dilutions, the limiting values of the osmotic properties and of the electrical conductivity should indicate the same number of ions to the molecule; when the concentration increases and the ionization of such solutions ceases to be complete, it is possible, but not necessary, that, throughout a small range, the two methods should give identical values for the coefficient of ionization; the concentration at which such identity ceases should probably indicate the point at which inter-ionic forces begin to prevent further conformity with the gaseous laws; and finally, for the case of solutions in which complete ionization is not shown by the equivalent conductivity, we cannot assume that any exact relation between the two lines of research will be found.

We must now see how far the experimental facts bear out these theoretical conclusions. The equivalent conductivity of electrolytes reaches a definite limit at a dilution which can only be experimentally examined with accuracy in solutions of simple salts, such as potassium chloride, which contain two monovalent ions. In these cases alone, then, can we look for the verification of the ideal relations. At the present time, the best known of the osmotic properties is the depression of the freezing-point, and in Raoult's book on *Cryoscopie* are given the following results obtained by Loomis for the molecular depressions at a concentration of 0·01 gram-molecule of salt in 1000 grams of water, as in themselves trustworthy and in accordance with the best of other results published before the year 1901.

Group I.

Potassium hydrate ...	3·71	Nitric acid	3·73
Hydrochloric acid ...	3·61	Potassium nitrate	3·46
Potassium chloride ...	3·60	Sodium nitrate	3·55
Sodium chloride	3·67	Ammonium nitrate ...	3·58

Group II.

Sulphuric acid	4·49	Calcium chloride	5·04
Sodium sulphate	5·09	Magnesium chloride...	5·08

Group III.

Magnesium sulphate...	2·66	Zinc sulphate	2·90

In the first group are substances which are shown by their electrical properties to yield in solution two monovalent ions. On the dissociation theory, therefore, the osmotic pressure effects should, at high dilution, have double their normal value. The normal value for the molecular depression of the freezing-point is 1·857, calculated from the osmotic theory, and confirmed by experiments on dilute aqueous solutions of non-electrolytes. Twice this value is 3·714, a number to which all the observed molecular depressions of substances in Group I. closely approximate. The electrical behaviour of bodies in the second group similarly indicates dissociation into three ions, which would produce a molecular depression of 5·57. The experimental numbers differ from this value by about 10 per cent., but the error is in the right direction, since the electrical conductivities at the concentrations used show that the ionization is still far from complete in salts with divalent ions. The corresponding error is yet greater in salts of the third group, which give two ions both divalent; the molecular depression should be again 3·714, a number exceeding the observed values by about 30 per cent. All discrepancies are thus of the kind to be expected from a consideration of the electrical phenomena; and the salts of the first group, which are about 95 per cent. ionized at the concentration used in the cryoscopic experiments, yield very concordant results.

Since the date of Raoult's book, the most important and accurate determinations of freezing-points are those undertaken by Dr. E. H. Griffiths by the methods of platinum thermometry. The results as yet obtained were announced to the British Association in the year 1901. From concentrations 0·0005 to 0·02 normal, the molecular lowering of the freezing-point of water produced by cane-sugar was found to be 1·858, while that produced by potassium chloride slowly increased with the dilution, till, in a solution of 0·0003 gram-equivalent per litre, it reached 3·720. Thus the non-electrolyte gave the theoretical result, and the binary electrolyte twice the molecular depression of the non-electrolyte, within extraordinarily narrow limits of experimental error. At this concentration the conductivity indicates that the ionization is about 99·7 per cent. Thus the evidence at present available goes to support the accuracy of the first relation of Arrhenius' theory in the case of aqueous solutions; the observed depressions never appreciably exceed the theoretical values, and the discrepancies in the other direction are readily explicable by incomplete ionization.

Passing to solutions in solvents other than water, we find that sufficient data are not available to decide whether the same relation between the electrical and the osmotic phenomena holds good. The difficulties of experiment are much increased, and no observations on osmotic effects seem to have been made on solutions in which the dilution was carried far enough to secure complete ionization. In many aqueous solutions, such as those of acetic acid and ammonia, complete ionization cannot be experimentally attained; and, without definite evidence, we cannot assume that it is in general reached by possible dilution in another solvent. For reasons already indicated, measurements on stronger solutions are of little use in this connexion. Moreover, for non-aqueous solutions we usually have little knowledge of the general electrolytic behaviour, and of such electrical constants as the transport numbers, so that it is not safe to conclude that the ions are of the same nature as those of the corresponding solutions in water. In alcoholic solutions, at any rate, what little evidence is forthcoming suggests that complex ions are very numerous, even at moderate dilutions, and any such complexity will diminish the number of solute particles and consequently the osmotic effects. Kahlenberg finds that solutions of diphenylamine in methyl cyanide show abnormally low molecular weights, and yet are non-conductors of electricity. Such a result perhaps indicates a dissociation yielding products which are not electrically charged, or a non-electrical double decomposition with the solvent. Until further experiments have been made, it is impossible to say whether or not the first relation suggested by the dissociation theory holds for non-aqueous solutions. In fact, however great be the likelihood of the general similarity of all conduction in solutions, we have not sufficient knowledge of electrolysis in non-aqueous media to conclude that the nature of the process is the same as in aqueous solution. It is not yet certain that we can here apply Faraday's laws, Ohm's law, and Kohlrausch's theory of ionic velocity, though, for alcoholic solutions, a certain amount of evidence in favour of this view has been accumulated.

The second relation enunciated by Arrhenius suggests that, when the dissociation is incomplete, the coefficient of ionization measured electrically should agree with the value calculated from the osmotic effects; but, as we have seen, such a relation can only hold for certain cases, and then only within very narrow limits of concentration. In order to obtain a valid basis for exact comparison with cryoscopic determinations, it is necessary to measure the electrolytic conductivities at the freezing-point. When this is done, it is found that the two values of the ionization, though they approach each other with decreasing concentration, only actually coincide at the most extreme dilution reached in the cryoscopic experiments. Thus, in a full discussion of the subject which will be found in a treatise on the 'Theory of Solution' lately published by the present writer, it is shown that the disturbing causes we have indicated become appreciable at concentrations considerably smaller than hitherto believed; but it is now evident that the discrepancies that then arise are not conclusive evidence against the general truth of the explanations advanced by the dissociation theory. Such discrepancies merely afford useful information about the nature of the disturbing influences, and about the value of the concentration at which these influences begin to be appreciable.

Passing as before to solutions in solvents other than water, we again find the phenomena more complicated, even if the general nature of the conduction should prove to be the same as in aqueous solutions. Complex ions seem to be common, and other disturbing factors appear to be present. Kahlenberg has called attention to cases in which the boiling- or freezing-points of conducting solutions indicate molecular weights equal to or greater than the normal, and this suggests that no dissociation occurs. Until the specific ionic mobilities in these solvents are known, we have no means of estimating what percentage ionization is required to give the observed conductivity; if the mobilities are high, it is possible that a small value would be enough. In any case, such observations may be explained by association of the non-ionized solute molecules, or by the existence of complex ions.

Summing up the results of our inquiry as far as we have gone, we may say that, in those cases for which the theory indicates exact relations, the experimental evidence is in favour of their existence, while all discrepancies are either suggested by the theory itself, or else occur under conditions where the experimental knowledge is too fragmentary for valid conclusions to be drawn.

We must now turn to other deductions from the theory, towards which considerable criticism has lately been directed. In the first place, the mass law of chemical action, which can be established thermodynamically for dilute systems, has been applied to electrolytic dissociation by Ostwald with complete success in the case of aqueous solutions of weak acids; but the law fails when applied to strong acids and other highly ionized electrolytes, and this failure has been regarded as one of the great objections to the dissociation theory. It is probable, however, that the explanation is to be sought in that difference in the law of the variation of the force with the distance which we have already pointed out must exist between solutions containing non-ionized bipolar molecules and those containing dissociated electrified ions. The thermodynamic basis of the mass law is only valid for dilute systems, and, as we have seen, even at small concentration, the forces between dissociated ions may be quite sensible and produce disturbing effects.

The dissociation theory has also co-ordinated the electrical ionization of aqueous solutions and the coefficients of chemical activity. There is no such definite theoretical deduction of this relation as of that between the conductivity and osmotic effects; the connexion of electrical ionization with chemical activity is a matter of observation, and the conclusion that, in the rapid chemical actions characteristic of electrolytes, it is the ions which alone are active, rests on the evidence of this connexion alone. The numerical relations given by Arrhenius, and the many deductions from this hypothesis which have been verified for aqueous solutions, have led to the idea that a similar explanation of the nature of all rapid chemical action might be given, whatever the solvent and whatever the conditions. There seems, however, no valid theoretical reason which necessitates such an extension, and it is possible that, in other solvents and for gaseous systems, rapid chemical change may be brought about by non-electrical double decomposition. This idea is supported by an observation of Kahlenberg on the instantaneous production of a precipitate of copper chloride when hydrochloric acid is passed into a non-conducting solution of copper oleate in benzene. It is evident that such an observation indicates that, in the particular solvent used, chemical action may occur which is not correlated with electrolytic conductivity, but it does not in the least weaken the electrical and osmotic evidence which we have adduced above in favour of the theory of the ionic dissociation of the aqueous solutions of electrolytes.

XXVI. *Notices respecting New Books.*

Annuaire pour l'An 1903, *Publié par le Bureau des Longitudes.* Avec des Notices Scientifiques. Paris: Gauthier-Villars (55 quai des Grands-Augustins). Pp. viii+808. Price 1 fr. 50 c.

THIS important annual contains, besides the usual astronomical, physical, and chemical tables, a number of specially contributed articles, the most important of which are:—"Shooting-Stars and Comets," by R. Radau; "Science and Poetry," by J. Janssen; "On the Work carried out at the Mont Blanc Observatory," by J. Janssen; and the speeches delivered by a number of distinguished French scientists as a tribute to the memory of the late A. Cornu and that of H. Faye.

Compte Rendu du deuxième Congrès International des Mathématiciens, tenu à Paris de 6 *au* 12 *Août* 1900. *Procès-verbaux et Communications, publiés par* E. DUPORCQ. Paris: Gauthier-Villars, 1902.

ALMOST every department of mathematics, pure and applied, is touched on in this volume; and a mere glance through its pages cannot fail to be instructive to mathematicians of all classes. Cantor contributes a paper on the Historiography of the science; Volterra an interesting estimate of the careers and labours of Betti, Brioschi, and Casorati. Hilbert discusses at considerable length the future problems of mathematics; Poincaré the rôle of intuition and logic; and Mittag-Leffler reproduces, with comments, some important letters of Weierstrass to Sophie Kowalewski. Then follow some thirty papers of various lengths upon the theory of numbers, analysis, geometry, dynamics, history, and methods of teaching. At one of the meetings some discussion arose in regard to the proposed adoption of Zamenhof's artificial language *Esperanto* as a universal language in science and commerce; but although the growing disadvantages attending the publication of scientific papers in so many different languages were fully recognized, the motion carried was that of Vassilief, that Academies and Societies study the means for remedying the evil at present existing.

Leçons sur la Théorie des Gaz. Par L. BOLTZMANN, *Professeur à l'Université de Leipzig. Traduites par* A. GALLOTTI. Avec une Introduction et des Notes de M. BRILLOUIN, Professeur au Collège de France. Première Partie. Paris: Gauthier-Villars, 1902. Pp. xix+204.

THE kinetic theory of gases is a subject possessing a peculiar fascination for the mathematical physicist: almost every distinguished member of that body has, at one time or another, devoted a good deal of attention to it. The fascination seems to be largely due to the difficulty of the subject, and to the extremely wary manner in which an investigator must tread on this ground if he is to avoid falling into countless pitfalls. Then, again, a subject so full of delicate and debateable points is sure to be fruitful of controversy; and controversy is always stimulating, and ministers to that lust of battle which, in some form or another, has always dominated the human race.

The results arrived at in the kinetic theory of gases are, however, of much more than purely mathematical interest. As is the case with all really important theories, the kinetic theory has powerfully reacted on experimental science, and stimulated research. To the experimenter, as well as the mathematician, it has yielded a rich harvest of results.

Those students who have neither the time nor the mathematical equipment necessary for a full study of this important yet difficult subject, will probably find the best account of it in a simple form in Meyer's 'Kinetic Theory of Gases,' recently translated by Mr. Baynes. To the advanced student, we can heartily commend the work under review—the first part of a comprehensive treatise on the subject by Professor L. Boltzmann. Few authors could speak with greater authority on this subject, and still fewer could handle it in a manner at once so clear and cautious as that which characterizes Prof. Boltzmann's treatment of it.

The three chapters into which the present volume is divided correspond to three hypotheses regarding the gaseous molecules:—(1) The molecules are elastic spheres; there are no external forces, and no sensible molar movements. (2) The molecules are centres of force; external forces and sensible molar displacements are assumed to exist. (3) The molecules repel one another with a force which varies inversely as the fifth power of the distance.

One cannot help being struck by the evident care which the author has taken to make the reasoning as clear as the nature of the subject will permit, and to point out the exact limitations of the results arrived at, and their connexion with the fundamental assumptions on which they are based.

M. Brillouin contributes an interesting introduction dealing with the historical aspect of the subject, and some valuable notes at the end which embody the results of the most recent investigations.

The Theory of Optics. By Paul Drude, *Professor of Physics at the University of Giessen.* Translated from the German by C. Riborg Mann and Robert A. Millikan, Assistant Professors of Physics at the University of Chicago. London: Longmans, Green, and Co. 1902. Pp. xxi+546.

The English translation of Prof. Drude's important work on Optics must be regarded as one of the most welcome additions to that series of text-books for advanced students which is beginning to supply a long-felt want. Our scientific literature is overloaded with text-books of an extremely elementary kind, while the number of books suitable for the use of the more advanced student is very limited indeed. The late Professor Preston rendered capital service to the cause of English science by the publication of his excellent treatises on Light and Heat; indeed, he may be said to have inaugurated a new era in the history of text-books on physics: and signs are not wanting that his example is likely to be followed by others.

The new work by Drude must take its place as one of the standard treatises on the subject by the side of Preston's 'Theory of Light' and the treatises on Geometrical Optics by Heath and by Herman. It is, in a sense, supplementary to these. Its leading features are the clear and connected account of the principles underlying the construction of optical instruments, and the masterly exposition of modern optical theories, considered from the electromagnetic standpoint. There is no other book in which the reader will find so complete an account of the present state of the electromagnetic theory of light, or in which the various difficulties connected with that theory are dealt with in so clear and painstaking a manner.

The work is divided into three Parts—Geometrical Optics, Physical Optics, and Radiation. The first Part deals with the fundamental laws of geometrical optics, the geometrical theory of optical images, the physical conditions for the formation of an image, apertures and the effects depending on them, and optical instruments. The subjects comprised under Part II. are the velocity of light, interference, Huygens's principle, diffraction, polarization, the mechanical and electromagnetic theories of light, propagation of light in transparent isotropic media, optical properties of transparent crystals, absorbing media, dispersion, optically and magnetically active substances, effects produced by bodies in motion. Part III. is devoted to the consideration of the energy of radiation, the application of the second law of thermodynamics to radiation, and the theory of incandescent vapours and gases.

The translation is well done, with only here and there a suggestion of foreign idiom; the English reader would, no doubt, prefer to see some of the Americanisms in the spelling removed; but that is a small matter in view of the great service rendered by the translators to the English-speaking student. The publishers deserve great credit for the high-class "get-up" of the book.

Fig. 1.

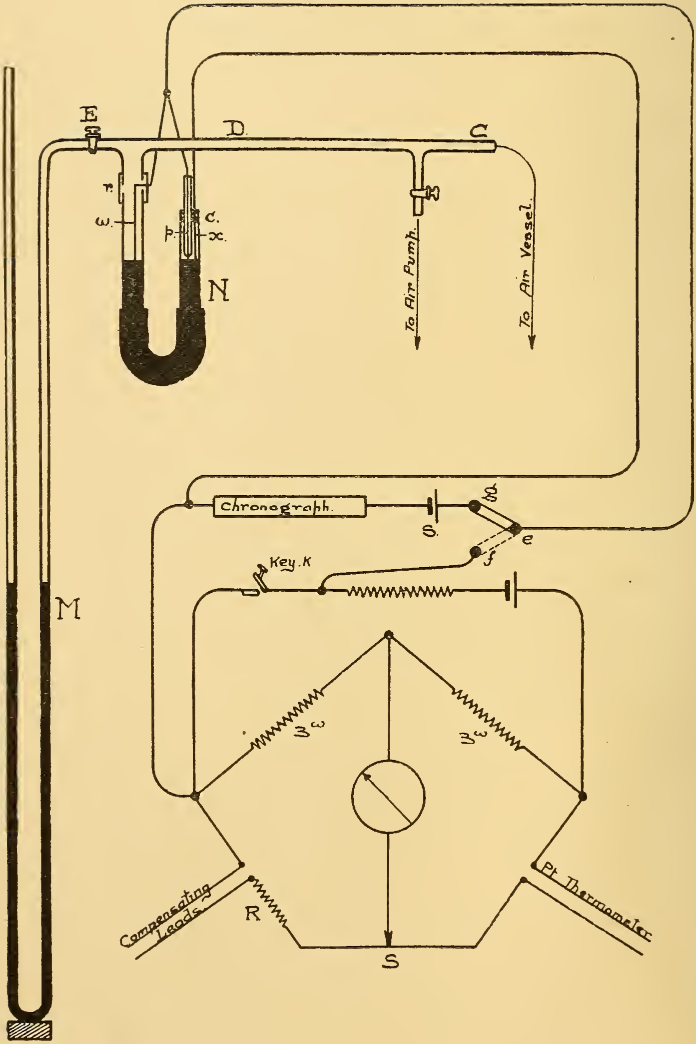
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Fig. 2.

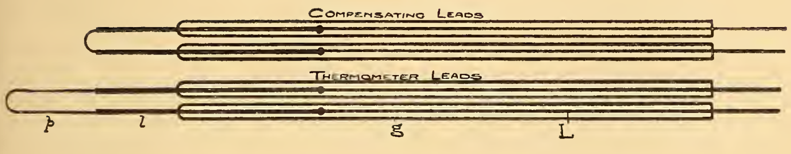
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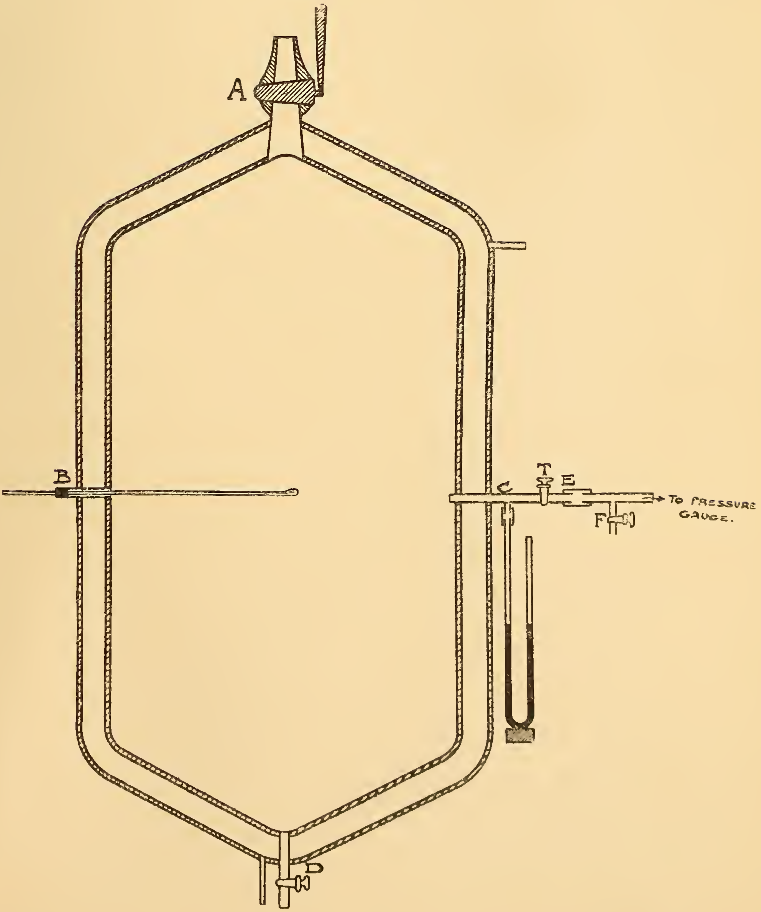
Fig. 3.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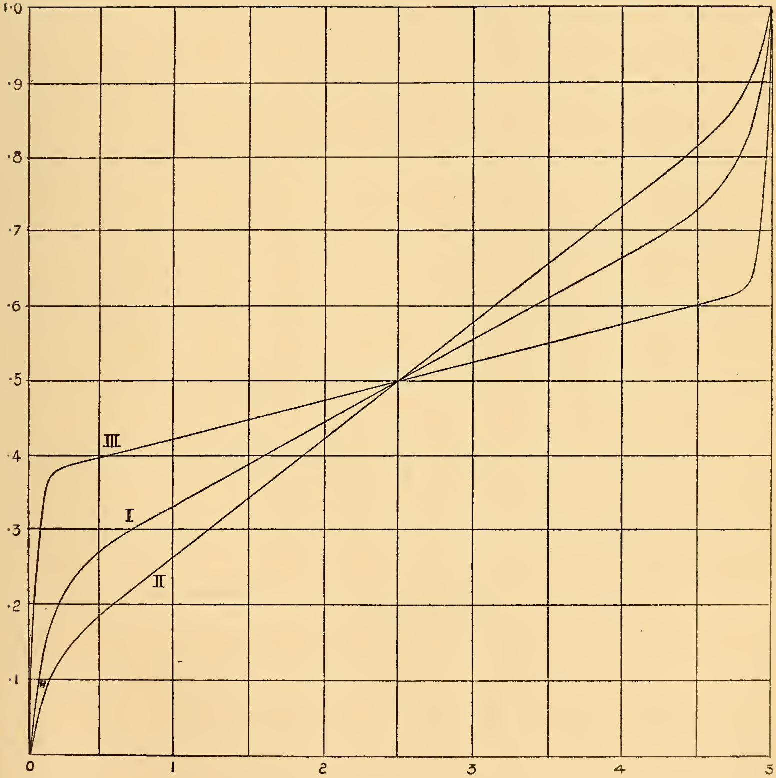
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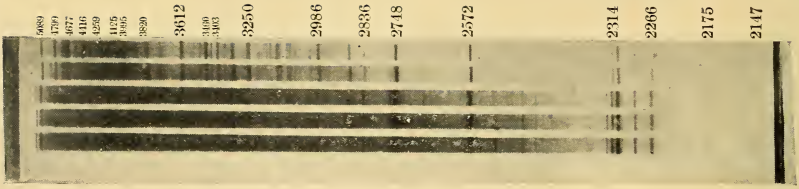

Fig. 1.

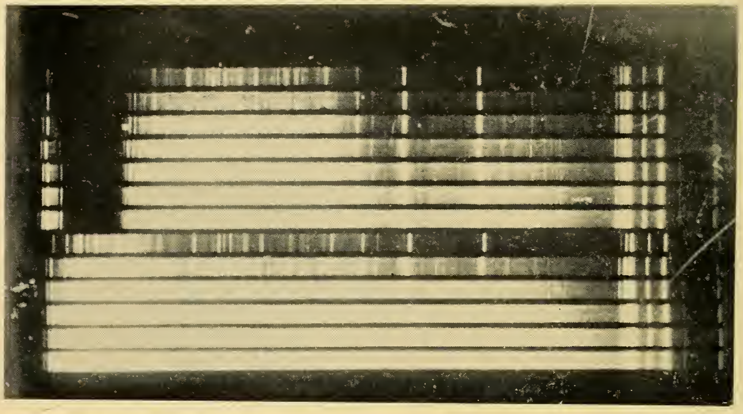

Fig. 2.

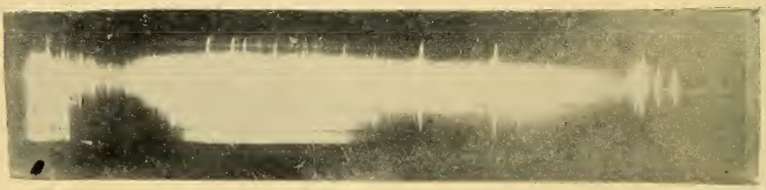

Fig. 3.

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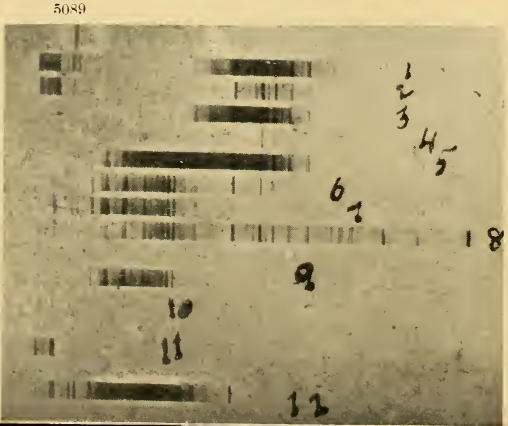

Fig. 6.

Fig. 1.

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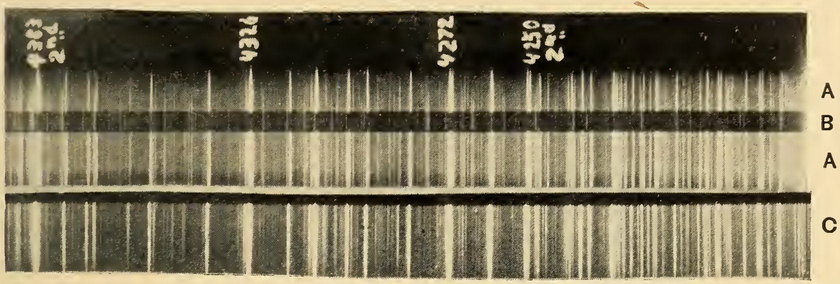

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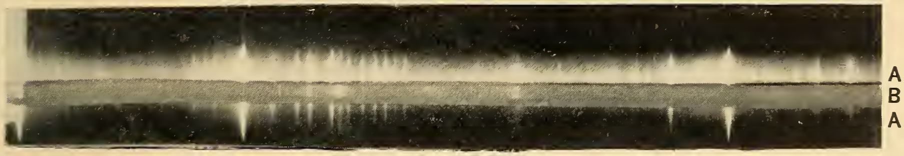

Fig. 4.

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THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MARCH 1903.

XXVII. *On the Free Vibrations of Systems affected with Small Rotatory Terms.* *By* Lord RAYLEIGH, *O.M., F.R.S.*[*]

BY a suitable choice of coordinates the expressions for the kinetic and potential energies of the system may be reduced to the forms

$$T=\tfrac{1}{2}a_1\dot{\phi}_1^2+\tfrac{1}{2}a_2\dot{\phi}_2^2+\ldots, \quad \ldots \quad (1)$$

$$V=\tfrac{1}{2}c_1\phi_1^2+\tfrac{1}{2}c_2\phi_2^2+\ldots. \quad \ldots \quad (2)$$

If there be no dissipative forces, the equations of free vibration are

$$\left.\begin{array}{l} a_1\ddot{\phi}_1+c_1\phi_1+\beta_{12}\dot{\phi}_2+\beta_{13}\dot{\phi}_3+\ldots=0, \\ a_2\ddot{\phi}_2+c_2\phi_2+\beta_{21}\dot{\phi}_1+\beta_{23}\dot{\phi}_3+\ldots=0. \\ \cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \end{array}\right\} \quad \ldots \quad (3)$$

where $\beta_{rs}=-\beta_{sr}$; and under the restriction contemplated all the quantities β are *small*.

If in equations (3) we suppose that the whole motion is proportional to $e^{i\sigma t}$,

$$\left.\begin{array}{l} (c_1-\sigma^2a_1)\phi_1+i\sigma\beta_{12}\phi_2+i\sigma\beta_{13}\phi_3+\ldots=0 \\ (c_2-\sigma^2a_2)\phi_2+i\sigma\beta_{21}\phi_1+i\sigma\beta_{23}\phi_3+\ldots=0 \\ \cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \end{array}\right\}; \quad . \quad (4)$$

and it is known that whatever may be the magnitudes of the β's, the values of the σ's are real. The *frequencies* are equal to $\sigma/2\pi$.

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[*] Communicated by the Author.

If there were no rotatory terms, the above system of equations would be satisfied by supposing one coordinate ϕ_r to vary suitably, while the remaining coordinates vanish. In the actual case there will be *in general* a corresponding solution in which the value of any other coordinate ϕ_s will be small relatively to ϕ_r.

Hence if we omit the terms of the *second* order in β, the rth equation becomes

$$(c_r-\sigma_r{}^2a_r)\phi_r=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

from which we see that σ_r is approximately the same as if there were no rotatory terms.

From the sth equation we obtain

$$(c_s-\sigma_r{}^2a_s)\phi_s+i\sigma_r\beta_{sr}\phi_r=0,$$

terms of the second order being omitted; whence

$$\phi_s:\phi_r=-\frac{i\sigma_r\beta_{sr}}{c_s-\sigma_r{}^2a_s}=\frac{i\sigma_r\beta_{sr}}{a_s(\sigma_r{}^2-\sigma_s{}^2)}, \quad . \quad . \quad . \quad (6)$$

where on the right the values of σ_r, σ_s from the first approximation (5) may be used. This equation determines the altered type of vibration; and we see that the coordinates ϕ_s are in the same phase, but that this phase differs by a quarter period from the phase of ϕ_r.

We have seen that when the rotatory terms are small, the value of σ_r may be calculated approximately without allowance for the change of type; but by means of (6) we may obtain a still closer approximation, in which the squares of the β's are retained. The rth equation (4) gives

$$a_r\sigma_r{}^2=c_r+\Sigma\frac{\sigma_r{}^2\beta_{rs}{}^2}{a_s(\sigma_r{}^2-\sigma_s{}^2)}. \quad . \quad . \quad . \quad . \quad (7)$$

Since the squares of the σ's are positive, as well as a_r, a_s, c_r, we recognize that the effect of β_{rs} is to increase $\sigma_r{}^2$ if $\sigma_r{}^2$ be already greater than $\sigma_s{}^2$, and to diminish it if it be already the smaller. Under the influence of the β's the σ's may be considered to *repel* one another. If the smallest value of σ_r be finite, it will be lowered by the action of the rotatory terms*.

The vigour of the repulsion increases as the difference between σ_r and σ_s diminishes. If σ_r and σ_s are equal, the formulæ (6), (7) break down, unless indeed $\beta_{rs}=0$. It is

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* This conclusion was given in Phil. Mag. v. p. 138 (1903), but without some reservations presently to be discussed. Similar reservations are called for in 'Theory of Sound,' §§ 90, 102.

clear that the original assumption that ϕ_s is small relatively to ϕ_r fails in this case, and the reason is not far to seek. When two normal modes have exactly the same frequency, they may be combined in any proportions without alteration of frequency, and the combination is as much entitled to be considered normal as its constituents. But the smallest alteration in the system will in general render the normal modes determinate; and there is no reason why the modes thus determined should not differ finitely from those originally chosen.

A simple example is afforded by a circular membrane vibrating so that one diameter is nodal. When all is symmetrical, any diameter may be chosen to be nodal; but if a small excentric load be attached, the nodal diameter must either itself pass through the load or be perpendicular to the diameter that does so ('Theory of Sound,' § 208). Under the influence of the load the two originally coincident frequencies separate.

In considering the modifications required when equal frequencies occur, it may suffice to limit ourselves to the case where *two* normal modes only have originally the same frequency, and we will suppose that these are the first and second. Accordingly, the coincidence being supposed to be exact,

$$c_1/a_1 = c_2/a_2 = \sigma_0^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

The relation between ϕ_1 and ϕ_2 and the altered frequencies are to be obtained from the first two equations of (3), in which the terms in ϕ_3, ϕ_4, &c. are at first neglected as being of the second order of small quantities. Thus

$$\left.\begin{array}{l}(c_1 - \sigma^2 a_1)\phi_1 + i\sigma\beta_{12}\phi_2 = 0 \\ (c_2 - \sigma^2 a_2)\phi_2 - i\sigma\beta_{12}\phi_1 = 0\end{array}\right\}, \quad . \quad . \quad . \quad . \qquad (9)$$

in which the two admissible values of σ^2 are given by

$$(c_1 - a_1\sigma^2)(c_2 - a_2\sigma^2) - \sigma^2\beta_{12}^2 = 0. \quad . \quad . \quad . \qquad (10)$$

If one of the factors of the first term, *e. g.* the second, be finite, β_{12}^2 may be neglected and a value of σ^2 is found by equating the first factor to zero; but in the present case both factors are small together. On writing σ_0 for σ in the small term, (10) becomes

$$(\sigma^2 - \sigma_0^2)^2 = \sigma_0^2\beta_{12}^2/a_1a_2, \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

so that

$$\sigma^2 - \sigma_0^2 = \pm\sigma_0\beta_{12}/\surd(a_1a_2), \quad . \quad . \quad . \qquad (12)$$

or

$$\sigma = \sigma_0 \pm \tfrac{1}{2}\beta_{12}/\surd(a_1a_2). \quad . \quad . \quad . \qquad (13)$$

The disturbance of the frequency from its original value is now of the *first* order in β_{12}, and one frequency is raised and the other depressed by the same amount.

As regards the ratios in which ϕ_1, ϕ_2 enter into the new normal modes, we have from (9)

$$\frac{\phi_1}{\phi_2}=\frac{a_2(\sigma_0{}^2-\sigma^2)}{i\sigma_0\beta_{12}}=\pm i\sqrt{(a_2/a_1)}. \quad . \quad . \quad . \quad (14)$$

From (14) we see that in the new normal vibrations the two original coordinates are combined so as to be in quadrature with one another, and in such proportion that the energies of the constituent motions are equal.

The value of any other coordinate ϕ_s accompanying ϕ_1 and ϕ_2 in vibration σ is obtained from the sth equation (4). Thus, squares of β's being neglected,

$$(c_s-\sigma^2a_s)\phi_s+i\sigma\beta_{s1}\phi_1+i\sigma\beta_{s2}\phi_2=0, \quad . \quad . \quad . \quad (15)$$

in which, if we please, we may substitute for ϕ_2 in terms of ϕ_1 from (14).

For the second approximation to σ we get from (15) and the two first equations (4)

$$\left\{c_1-\sigma^2a_1-\Sigma\frac{\sigma^2\beta_{1s}{}^2}{c_s-\sigma^2a_s}\right\}\phi_1+\left\{i\sigma\beta_{12}+\Sigma\frac{\sigma^2\beta_{1s}\beta_{s2}}{c_s-\sigma^2a_s}\right\}\phi_2=0,$$

$$\left\{c_2-\sigma^2a_2-\Sigma\frac{\sigma^2\beta_{2s}{}^2}{c_s-\sigma^2a_s}\right\}\phi_2+\left\{i\sigma\beta_{21}+\Sigma\frac{\sigma^2\beta_{2s}\beta_{s1}}{c_s-\sigma^2a_s}\right\}\phi_1=0,$$

in which the summation extends to all values of s other than 1 and 2. In the coefficients of the second terms it is to be observed that $\beta_{12}=-\beta_{21}$, and that $\beta_{1s}\beta_{s2}=\beta_{2s}\beta_{s1}$; so that the determinant of the equations becomes

$$\left\{c_1-\sigma^2a_1-\Sigma\frac{\sigma^2\beta_{1s}{}^2}{c_s-\sigma^2a_s}\right\}\left\{c_2-\sigma^2a_2-\Sigma\frac{\sigma^2\beta_{2s}{}^2}{c_s-\sigma^2a_s}\right\}-\sigma^2\beta_{12}{}^2=0, \quad . \quad . \quad . \quad (16)$$

terms of the fourth order in β being omitted. In (16) $c_1-\sigma^2a_1$, $c_2-\sigma^2a_2$ are each of the order β. Correct to the third order we obtain with the use of (12)

$$(\sigma^2-\sigma_0{}^2)^2-\sigma_0{}^2\frac{\beta_{12}{}^2}{a_1a_2}\mp\frac{\sigma_0\beta_{12}{}^3}{(a_1a_2)^{\frac{3}{2}}}\pm\frac{\sigma_0{}^3\beta_{12}}{(a_1a_2)^{\frac{3}{2}}}\Sigma\frac{a_1\beta_{2s}{}^2+a_2\beta_{1s}{}^2}{c_s-\sigma_0{}^2a_s}=0. \quad (17)$$

whence

$$\sigma^2-\sigma_0{}^2=\pm\sigma_0\frac{\beta_{12}}{\sqrt{(a_1a_2)}}+\frac{\frac{1}{2}\beta_{12}{}^2}{a_1a_2}-\frac{\frac{1}{2}\sigma_0{}^2}{a_1a_2}\Sigma\frac{a_1\beta_{2s}{}^2+a_2\beta_{1s}{}^2}{c_s-\sigma_0{}^2a_s}. \quad . \quad (18)$$

In (18) β_{12} is supposed to be of not higher order of small quantities than β_{1s}, β_{2s}. For example, we are not at liberty to put $\beta_{12}=0$.

In the above we have considered the modification introduced by the β's into a vibration which when undisturbed is one of two with equal frequencies. If the type of vibration under consideration be one of those whose frequency is not repeated, the original formulæ (6), (7) undergo no essential modification.

In the following paper some of the principles of the present are applied to a hydrodynamical example.

XXVIII. *On the Vibrations of a Rectangular Sheet of Rotating Liquid.* *By* Lord RAYLEIGH, *O.M.*, *F.R.S.*[*]

THE problem of the free vibrations of a rotating sheet of gravitating liquid of small uniform depth has been solved in the case where the boundary is circular[†]. When the boundary is rectangular, the difficulty of a complete solution is much greater; but I have thought that it would be of interest to obtain a partial solution, applicable when the angular velocity of rotation is *small*.

If ζ be the elevation, u, v the component velocities of the relative motion at any point, the equations of free vibration, when these quantities are proportional to $e^{i\sigma t}$, are

$$\left.\begin{aligned} i\sigma u-2nv&=-g\,d\zeta/dx,\\ i\sigma v+2nu&=-g\,d\zeta/dy,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1)$$

and

$$\frac{d^2\zeta}{dx^2}+\frac{d^2\zeta}{dy^2}+\frac{\sigma^2-4n^2}{gh}\zeta=0, \quad . \quad . \quad . \quad . \quad (2)$$

in which n denotes the angular velocity of rotation, h the depth of the water (as rotating), and g the acceleration of gravity. The boundary walls will be supposed to be situated at $x=\pm\frac{1}{2}\pi$, $y=\pm y_1$.

When n is evanescent, one of the principal vibrations is represented by

$$u=\cos x, \qquad v=0; \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and ζ is proportional to $\sin x$, so that

$$\sigma^2=gh. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This determines the frequency when $n=0$. And since by

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[*] Communicated by the Author.

[†] Kelvin, Phil. Mag. Aug. 1880; Lamb, 'Hydrodynamics,' §§ 200, 202, 203.

symmetry a positive and a negative n must influence the frequency alike, we conclude that (4) still holds so long as n^2 is neglected. Thus to our order of approximation the frequency is uninfluenced by the rotation, and the problem is reduced to finding the effect of the rotation upon that mode of vibration to which (3) is assumed to be a first approximation. The equation for ζ is at the same time reduced to

$$\frac{d^2\zeta}{dx^2}+\frac{d^2\zeta}{dy^2}+\zeta=0. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Since v is itself of the order n, the first of equations (1) shows that u, as well as ζ, satisfies (5).

Taking u and v as given in (3) and the corresponding ζ as the first approximation, we add terms u', v', ζ', proportional to n, whose forms are to be determined from the equations

$$i\sigma u'=-g\,d\zeta'/dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$i\sigma v'=-g\,d\zeta'/dy-2n\cos x, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$(d^2/dx^2+d^2/dy^2+1)(\zeta', u', v')=0. \quad . \quad . \quad . \quad . \quad (8)$$

They represent in fact a motion which would be possible in the absence of rotation under forces parallel to v and proportional to cos x. This consideration shows that u' is an odd function of both x and y, and v' an even function. If we assume

$$u'=\mathrm{A}_2\sin 2x+\mathrm{A}_4\sin 4x+\ldots, \quad . \quad . \quad . \quad . \quad (9)$$

the boundary condition to be satisfied at $x=\pm\frac{1}{2}\pi$ is provided for, whatever functions of y A_2, A_4, &c. may be. If we eliminate ζ' from (6), (7), we find

$$\frac{dv'}{dx}=\frac{du'}{dy}+\frac{2n}{i\sigma}\sin x$$

$$=\frac{d\mathrm{A}_2}{dy}\sin 2x+\frac{d\mathrm{A}_4}{dy}\sin 4x+\ldots+\frac{2n}{i\sigma}\sin x;$$

or, on integration,

$$v'=\frac{2ni}{\sigma}\cos x-\frac{d\mathrm{A}_0}{dy}-\tfrac{1}{2}\cos 2x\frac{d\mathrm{A}_2}{dy}-\tfrac{1}{4}\cos 4x\frac{d\mathrm{A}_4}{dy}-\ldots, \quad . \quad (10)$$

$d\mathrm{A}_0/dy$ being the constant of integration. In (10) the A's are to be so chosen that $v'=0$ when $y=\pm y_1$ for all values of x between $-\frac{1}{2}\pi$ and $+\frac{1}{2}\pi$.

From (8) we see that A_2, A_4, &c. are to be taken so as to satisfy

$$\frac{d^2\mathrm{A}_2}{dy^2}-3\mathrm{A}_2=0, \quad \frac{d^2\mathrm{A}_4}{dy^2}-15\mathrm{A}_4=0, \quad \&c.,$$

or, since the A's are odd functions of y,

$$A_2 = B_2 \sinh(\sqrt{3}\,.\,y), \quad A_4 = B_4 \sinh(\sqrt{15}\,.\,y), \quad \&c.$$

Also $$A_0 = B_0 \sin y.$$

In these equations the B's are absolute constants.

The boundary conditions at $y = \pm y_1$ now take the form

$$\begin{aligned} 0 = {} & \frac{2ni}{\sigma} \cos x - B_0 \cos y_1 \\ & - \frac{\sqrt{3}}{2} B_2 \cosh(\sqrt{3}\,.\,y_1)\,.\cos 2x \\ & - \frac{\sqrt{15}}{4} B_4 \cosh(\sqrt{15}\,.\,y_1)\,.\cos 4x - \ldots\ldots, \end{aligned} \qquad (11)$$

which can be satisfied if $\cos x$ be expressed between the limits of x in the series

$$\cos x = C_0 + C_2 \cos 2x + C_4 \cos 4x + \ldots. \qquad (12)$$

By Fourier's theorem we find that (12) holds between $x = -\frac{1}{2}\pi$ and $x = +\frac{1}{2}\pi$, if

$$C_0 = \frac{2}{\pi}, \quad C_2 = \frac{4}{3\pi}, \quad C_4 = -\frac{4}{15\pi}, \quad C_{2m} = -(-1)^m \frac{4}{(4m^2-1)\pi} \qquad (13)$$

The B's are thus determined by (11), and we get

$$A_0 = \frac{2ni}{\sigma} \frac{2}{\pi} \frac{\sin y}{\cos y_1}, \qquad A_2 = \frac{2ni}{\sigma} \frac{2}{\sqrt{3}} \frac{4}{3\pi} \frac{\sinh(\sqrt{3}\,.\,y)}{\cosh(\sqrt{3}\,.\,y_1)},$$

$$A_{2m} = \frac{2ni}{\sigma} \frac{2m}{\sqrt{(4m^2-1)}} \frac{4(-1)^{m+1}}{(4m^2-1)\pi} \frac{\sinh(y\sqrt{4m^2-1})}{\cosh(y_1\sqrt{4m^2-1})}.$$

Hence, finally, for the complete values of u and v to this order of approximation

$$u = \cos x + \frac{2ni}{\sigma} \left\{ \frac{8 \sin 2x}{3\sqrt{3}\,.\,\pi} \frac{\sinh(\sqrt{3}\,.\,y)}{\cosh(\sqrt{3}\,.\,y_1)} + \ldots \right\}, \qquad (14)$$

$$v = \frac{2ni}{\sigma} \left\{ \cos x - \frac{2}{\pi} \frac{\cos y}{\cos y_1} - \frac{4}{3\pi} \cos 2x \frac{\cosh(\sqrt{3}\,.\,y)}{\cosh(\sqrt{3}\,.\,y_1)} + \ldots \right\}. \qquad (15)$$

The limiting values of x have been supposed, for the sake of brevity, to be $\pm\frac{1}{2}\pi$. If we denote them by $\pm x_1$, we are to replace x, y, y_1 in (14), (15) by $\frac{1}{2}\pi\, x/x_1$, $\frac{1}{2}\pi\, y/x_1$, $\frac{1}{2}\pi\, y_1/x_1$. At the same time (4) becomes

$$\sigma^2 = \frac{\pi^2 gh}{4x_1^2} \qquad (16)$$

As was to be expected, the small terms in (14), (15) are in quadrature with the principal term. The success of the approximation requires that the frequency of revolution be small in comparison with that of vibration.

If y_1 be such that $\cos(\frac{1}{2}\pi y_1/x_1)$ vanishes, or even becomes very small, the solution expressed in (14), (15) fails. This happens, for example, when the boundary is square, so that $y_1=x_1$. The inference is that the assumed solution (3) does not, or rather does not continue to, represent the facts of the case as a first approximation.

From the principles explained in the previous paper, or independently, it is evident that in the case of the square (3) must be replaced by

$$u=\cos x, \qquad v=\pm i\cos y, \quad . \quad . \quad . \quad . \quad (17)$$

corresponding to which

$$\zeta=\frac{\sigma_0}{g}(-i\sin x\pm\sin y). \quad . \quad . \quad . \quad . \quad (18)$$

These values satisfy all the conditions when there is no rotation, and $\sigma_0=\surd(gh)$, as in (4). For the second approximation we retain these terms, adding to them u', v', ζ', which are to be treated as small. So far, the procedure is the same as in the formation of (6), (7); but now we must be prepared for an alteration of σ from its initial value σ_0 by a quantity of the first order. Hence, with neglect of n^2,

$$i(\sigma-\sigma_0)\cos x+i\sigma_0u'\mp 2ni\cos y=-g\frac{d\zeta'}{dx} \quad . \quad . \quad (19)$$

$$\mp(\sigma-\sigma_0)\cos y+i\sigma_0v'+2n\cos x=-g\frac{d\zeta'}{dy}. \quad . \quad . \quad (20)$$

These equations are the same as would apply in the absence of rotation if we suppose impressed forces to act parallel to u and v proportional to

$$i(\sigma-\sigma_0)\cos x\mp 2ni\cos y, \quad . \quad . \quad . \quad . \quad (21)$$

$$\mp(\sigma-\sigma_0)\cos y+2n\cos x, \quad . \quad . \quad . \quad . \quad (22)$$

respectively.

The complete solution of (19), (20) to the first order of n would lead to rather long expressions. The point of greatest interest is the alteration of frequency, and this can perhaps be most easily treated by a simple mechanical consideration. The forces given in (21), (22) must be such as not wholly to disturb the initial motion (17) with which they synchronize. Accordingly (21) must be free from a component capable of stimulating a vibration similar to $u=\cos x$, and in like manner (22) must be incapable of stimulating a motion similar to $v = \cos y$. The necessary conditions are

$$\iint \cos x \{(\sigma - \sigma_0) \cos x \mp 2n \cos y\} dx\, dy = 0,$$
$$\iint \cos y \{(\sigma - \sigma_0) \cos y \mp 2n \cos x\} dx\, dy = 0,$$

the integration being taken over the whole area. On account of the symmetry the two conditions coincide; and it is sufficient to integrate for x and y between the limits 0 and $\frac{1}{2}\pi$. Thus

$$(\sigma - \sigma_0) \cdot \tfrac{1}{2}\pi \cdot \tfrac{1}{4}\pi = \pm 2n \cdot 1 \cdot 1,$$

so that

$$\sigma - \sigma_0 = \pm \frac{16n}{\pi^2}. \quad \dots \dots \dots \quad (23)$$

Since n and σ are of the same dimensions, this result holds good, whatever may be the side of the square.

It may be of interest, and serve as a confirmation of the above procedure, to mention that when applied to the principal vibration in a rotating *circular* trough it gives

$$\sigma - \sigma_0 = \pm \frac{2n}{z_1^2 - 1}, \quad \dots \dots \dots \quad (24)$$

where z_1 is the first root of $J_1'(z) = 0$, equal to 1·841, so that

$$\sigma - \sigma_0 = \pm \frac{2n}{2{\cdot}38}. \quad \dots \dots \dots \quad (25)$$

An accordant result may be deduced from the analysis given by Lamb, § 203, by putting $s = 1$, and taking account of the properties of the function J_1. The corresponding value of ζ is given by

$$\zeta = e^{i\sigma t} J_1(kr) \{\cos \theta + i \sin \theta\}. \quad \dots \dots \quad (26)$$

XXIX. *A Suggested Theory of the Aluminium Anode.* By W. W. Taylor, *M.A., D.Sc.,* and J. K. H. Inglis, *M.A., B.Sc.**

ALTHOUGH aluminium is one of the metals which decompose water, it is very slowly acted upon by dilute sulphuric acid, even at moderately high temperatures. With dilute hydrochloric acid the action is violent, and it is found that, if a little hydrochloric acid or soluble chloride (*e. g.*, potassium chloride) be added to dilute sulphuric acid, the action is, to all appearance, as violent as with hydrochloric acid of similar concentration.

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* Communicated by the Physical Society: read November 14th, 1902.

The primary object of this investigation was to find an explanation of this anomalous behaviour of sulphuric acid, and of the effect produced by the addition of chloride. It has long been known * that, when an aluminium electrode is employed as anode in a solution of a sulphate or of sulphuric acid, there is a very great resistance offered to the current, and that this resistance is due to a film which separates the electrode from the solution. If the aluminium is the cathode, or if other acids are substituted for sulphuric acid, this great resistance does not exist. The film cannot merely act as a dead resistance, for the resistance is different according to the direction of the current. It seems probable, then, that the two phenomena are related, and that the film is also the cause of the slow action of sulphuric acid on aluminium. This paper is an attempt to find an explanation which will satisfactorily account for all these phenomena.

Historical Summary.

The behaviour of aluminium as anode in dilute sulphuric acid has been the subject of many investigations, but they have been mainly directed to proving the existence of the abnormalities, and not to finding the cause of them. The earliest measurements appear to have been made by Wheatstone †, who tried to ascertain the position of aluminium in the voltaic series. He found that its position depended on the electrolyte used, and he noticed especially the slight action of nitric acid and of sulphuric acid, and the small current obtained with the latter acid. His experiments were repeated in greater detail by Buff ‡, who observed remarkable peculiarities with dilute sulphuric acid as the electrolyte. He found on electrolysis of dilute sulphuric acid with an aluminium anode and an external battery, that the anode became covered with a dark skin which he supposed to be silicon. Tait § investigated the polarization of the aluminium cell, using a variable polarizing battery. If six Grove's cells formed the polarizing battery, the reverse E.M.F. was 5·20 Daniells ; in this case the polarizing E.M.F. was 10·44 D. As his measurements were made with a Thomson electrometer, they were independent of resistance.

The dark skin first observed by Buff was the subject of several investigations made by Beetz ‖. He at first supposed

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* Buff, Liebig's *Annalen*, cii. p. 269 (1857).

† Phil. Mag. [4] x. p. 143 (1854).

‡ *Loc. cit.*

§ Phil. Mag. [4] xxxviii. p. 243 (1869).

‖ Pogg. *Annalen*, vol. cxxvii. p. 45 ; vol. clvi. p. 464 ; 1877, vol. ii. p. 94.

it to be an aluminium suboxide; but, later, came to the conclusion that it is merely the ordinary oxide or hydroxide. More recently Norden * showed that the film is the ordinary hydroxide, Al $(OH)_3$. Lawrie † had previously come to the conclusion, based on experiments upon the effect of amalgamation on the electrochemical behaviour of aluminium, that the peculiarities are due to a layer of oxide or of suboxide.

The subject has also been investigated by several physicists who endeavoured to explain the physical peculiarities. At first the film of oxide was supposed to act as a layer which protected the electrode from the action of the electrolyte; but Oberbeck ‡ and Streintz § suggested that the film acts as a non-conductor, and that the electrode, the film, and the electrolyte form a condenser; and a condenser consisting of two aluminium plates with a solution of a sulphate as electrolyte has been described by Haagn ‖. In all these cases a neutral sulphate or sulphuric acid solution formed the electrolyte, Streintz especially mentioning that in nitric acid the behaviour of aluminium is quite normal. The question became one of practical importance when Pollak ¶ and Grätz ** independently showed that a cell consisting of one aluminium electrode and one carbon electrode in dilute sulphuric acid could be used to change an alternating current into a direct current, since the phase in which aluminium is the anode is stopped by the cell. Various investigators †† found that currents of 20 volts or even of 100 volts potential can be so transformed. Later researches have not brought to light many new facts, though Wilson ‡‡ showed that the transformation is not complete if the period of alternation is less than $\frac{1}{16}$ second. None of the investigators attempt to explain how this film is produced and maintained. Norden §§, however, gives the following explanation:—When sulphuric acid is electrolysed with an aluminium anode the secondary oxygen produced acts on the anode to form Al $(OH)_3$, which

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* *Zeit. für Elektrochemie*, vi. pp. 159, 188 (1899–1900).

† Phil. Mag. [5] xxii. p. 213 (1886).

‡ Wied. *Ann.* xix. p. 625 (1883).

§ Wied. *Ann.* xxxii. p. 116 (1887); xxxiv. p. 751 (1888).

‖ *Zeit. für Elektrochemie*, iii. p. 470 (1896–97).

¶ *Compt. Rend.* cxxiv. p. 1443 (1897).

** Wied. *Ann.* lxii. p. 323 (1897).

†† *Beiblätter*, xxiii. pp. 108, 502, 564, 650; *Elektrotechn. Zeits.* xxi. p. 913.

‡‡ Electrical Review, 1898, p. 371; Proc. Roy. Soc. vol. lxiii. p. 329 (1898).

§§ *Loc. cit.*

is slowly dissolved by the sulphuric acid or by the aluminium sulphate already in solution, and thus the film is continually renewed on one side and dissolved on the other. If hydrochloric acid be used as electrolyte, the free chlorine acts on the aluminium and forms a soluble salt $AlCl_3$, and not a difficultly soluble oxide.—This explanation is hardly sufficient, for no reasons are given for the formation of secondary oxygen; and, further, aluminium sulphate is a fairly soluble salt. Hence a full explanation is still wanting.

Experimental Results.

Experiments were made, in the first instance, to ascertain in what way the addition of certain salts to the electrolyte affected the aluminium anode. For this purpose the 12 volt storage-battery of the laboratory was used, and in the circuit were a 3 ohm (approximate) resistance, an ammeter which could be read to 0·01 ampere and up to 3·0 amperes, and the electrolytic cell, all in series; a voltmeter reading to 0·05 volt and up to 15·0 volts was also in parallel circuit with the cell. The cell consisted of a beaker containing a 1/1 molar solution of sulphuric acid and the two electrodes, the one of sheet-aluminium, and the other a spiral of thick platinum wire. The procedure was as follows:—The circuit was closed, with the acid alone as electrolyte, and the readings of the voltmeter and ammeter noted as soon as they became constant. To the acid were added successive small quantities of a solution of the salt under investigation; and, after closing the circuit, readings were noted every few minutes until they again became constant. It was found necessary to use a fresh piece of aluminium each time, as, through the continued action of the weak current, the film on the anode became so thick and resisting that addition of even large quantities of potassium chloride had no influence on the current, although a small quantity only was required when a fresh surface was taken. It was therefore necessary to have the surface in as uniform a condition as possible in order that the experiments should be comparable, and this was most easily ensured by using a fresh surface each time.

Effect of Chloride and of Bromide.—The results are given in the following tables.

In the case of ammonium alum solution (Table I.) the effect of potassium bromide was also determined, and after addition of 0·3 c.c. of a 4 molar KBr solution, the current passed freely, though it did not increase so rapidly as after addition of chloride.

TABLE I.

Solution of H_2SO_4=1 molar.
,, KCl =3·9 molar (saturated).

Voltmeter in open circuit.	Electrolyte.	Voltmeter in closed circuit.	Current in Ampères.
11·7 volt.	25 c.c. H_2SO_4....................	11·6	0·01
	,, +0·19 c.c. KCl.	11·6	0·02
	,, +0·25 c.c. KCl.	11·6	0·02
	,, +0·33 c.c. KCl.	11·6	0·03
		falling rapidly to 7·1	rising to 1·50
11·7 volt.	25 c.c. saturated ammonium alum solution......	11·6	$<$0·01
	,, ,, +0·27 c.c. KCl.	9·4	0·76

The experiments were then repeated with more dilute solutions of chloride and bromide.

TABLE II.

Solution of H_2SO_4=1 molar.
,, KCl =0·39 molar.

Voltmeter in open circuit.	Electrolyte.	Voltmeter in closed circuit.	Current in Amperes.
11·7 volt.	25 c.c. H_2SO_4....................	11·65	$<$0·01
	,, +0·97 c.c. KCl.	11·65	0·01
	,, +2·0 c.c. KCl...	falling to 7·0	rising to 0·50
	,, ,, (fresh surface)...	falling rapidly.	rising to 0·80
11·7 volt.	25 c.c. H_2SO_4....................	11·65	$<$0·01
	,, +1·0 c.c. KCl...	11·60	0·025 (rising)
	,, +1·2 c.c. KCl...	11·60	0·02 (rising)
	,, +1·4 c.c. KCl...	11·60	0·02 (rising)
	,, +1·6 c.c. KCl...	......	1·0

In the second of these experiments the currents rose at once to 1·0 ampere after addition of 1·6 c.c. KCl solution, but with smaller concentrations of chloride the current was rather variable, as if the resistance of the film was continually changing. In the case of bromide the current did not increase until 5·0 c.c. of a 0·4 molar KBr solution had been added. It then rose steadily to 0·5 ampere, but the increase was not so rapid as with chloride.

Similar experiments were made with other salts, and the results may be very briefly described.

Nitrate.—A 2·6 molar solution of potassium nitrate was used. After addition of 3·0 c.c. of the solution to 25 c.c. of acid, the current at once rose steadily; considerable irregularity was shown after addition of 2·0 c.c. of the nitrate solution.

Acetate.—Addition of sodium acetate to sulphuric acid had no effect. In order to attain a considerable concentration of acetions, a saturated solution of sodium sulphate was then used instead of sulphuric acid, but this made no difference.

Thiocyanate.—A 2·0 molar solution of potassium thiocyanate was used. Addition of 2·0 to 3·0 c.c. of the solution was found necessary to enable the current to pass readily.

Chlorate.—Addition of potassium chlorate was also found to enable the current to pass readily.

As the presence of aluminium salt might, conceivably, influence the results, several of the above experiments were repeated after 1·0 c.c. of 0·5 molar aluminium sulphate solution had been added to the acid, but no differences were found.

These experiments show that the presence of certain ions, even in small concentration, enables a large current to pass through the cell; and it seemed to us probable that the reason is that the film of aluminium hydroxide with which the anode is covered is permeable to certain ions, but impermeable to others *. If this is so, any anion which can readily pass through the film will enable a current to pass, whilst anions which cannot readily pass through will not enable it to do so. The anomalous behaviour in sulphuric acid would then be due to the impermeability of the film to SO_4'' ions, and also to $Al^{\cdot\cdot\cdot}$ ions. This explanation is also in accord with the fact that reversal of the current immediately causes a current to pass through the cell, this being due to the permeability of the film to H ions, for it is difficult to suppose that reversal of the current immediately removes the film and subsequent reversal immediately restores it.

We next made a series of experiments to determine the relative rates of diffusion of these ions through a film of aluminium hydroxide. The method adopted is one devised by Walden † and consists in forming a film of gelatine containing ammonium chromate over one end of a glass tube, exposing it to daylight, and then washing out all soluble

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* *Cf.* Ostwald, *Zeit. f. Phys. Chem.* vi. p 71 (1890).

† *Zeit. f. Physik Chem.* x. p. 699 (1892).

substances. The tube is then placed in a solution of aluminium salt, and ammonia solution is put inside the tube. In this way a film of $Al(OH)_3$ is formed where the two solutions meet, *i.e.*, in the interior of the gelatine. A solution of the salt under examination is then added to the ammonia solution in the inner tube, and from time to time the outer solution is tested for the salt. From the fact that a film of aluminium hydroxide can be formed in this way, one may conclude that it is impermeable to $Al^{\cdot\cdot\cdot}$ ions, and to OH' ions, as otherwise diffusion would continue until one or other of the salts was completely removed.

Having set up a large number of cells we found that KCl, KBr, KNO_3, $KClO_3$, and KCNS all diffuse through rapidly, though not equally so; $NaC_2H_3O_2$ diffuses slowly, and K_2SO_4 only to a very slight extent. To confirm this result, more cells were set up, and mixtures of KCl and K_2SO_4, KBr and K_2SO_4, were added to the ammonia solution, so that the rates of diffusion through the same film could be observed. The same results were obtained.

It now seemed very probable that the abnormal behaviour of the aluminium anode in sulphuric acid was due to this impermeability. According to Ditte *, the surface of aluminium is covered with a thin film of hydroxide which preserves it from the further action of the air. If, therefore, a piece of aluminium be made the anode in dilute sulphuric acid, the SO_4'' ions are unable to pass from the solution through the film to the anode, and similarly $Al^{\cdot\cdot\cdot}$ ions are unable to pass from the anode into the solution. Hence there are no ions to carry the electricity through the film, and no current can pass. A very slight current does pass, and this may be due to $Al^{\cdot\cdot\cdot}$ ions being formed at the anode, $H^{\cdot}$ ions of the water passing at the same time through the film and thus leaving OH' ions which form $Al(OH)_3$ with the $Al^{\cdot\cdot\cdot}$ ions just formed. This aluminium hydroxide replaces that which may be removed by solution in the acid, and in this way the continuity of the film is maintained.

If Cl', Br', or NO_3' ions are present, they can migrate through the film, thus carrying electricity to the anode where they unite with $Al^{\cdot\cdot\cdot}$ and form neutral salts; and this formation of salt behind the film will break it loose, and so enable the current to pass easily. In this way the results obtained admit of an easy and rational explanation.

If this explanation is correct, it should be possible to

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* *Compt. Rend.* cxxvii. p. 919 (1898).

reproduce the peculiarities of the aluminium electrode with a platinum electrode and a film of aluminium hydroxide. There are various ways in which this might be done, but for practical reasons the following was adopted. The cell consisted of two large pieces of platinum foil as electrodes, an inner porous cell containing ammonia solution (1 molar) and an outer glass beaker containing aluminium sulphate solution ($\frac{1}{6}$ molar). In this way a film of aluminium hydroxide was deposited in the wall of the porous cell.

If the aluminium sulphate solution contained the anode, no current should pass, since $Al^{\cdot\cdot\cdot}$ ions cannot migrate through the film to the cathode, nor OH' ions to the anode. Addition of SO_4'' ions to the ammonia should have no effect on the current, but addition of Cl' ions should cause a current to pass. Reversal of the poles, also, should cause a current to pass, for $NH_4^{\cdot}$ ions can readily pass through the film. With such a cell, and with the 12-volt storage-battery and the same arrangement of apparatus as already described, the following results were obtained :—

Aluminium sulphate solution contained :	Time from closing circuit (minutes).	Voltmeter.	Ammeter.
Anode.	0	11·6	0·20
	60	12·0	0·07
	1140	12·0	0·03
Cathode.	immediately.	11·2	0·20
	45	10·4	0·41
Anode.	10	11·7	0·10
	180	11·95	0·03
Cathode.	1·5	10·8	0·43
Anode.	6	11·7	0·13
Anode.	immediately.	(50 volt current used.)	0·22
	4	,,	0·07
	20	,,	0·04
Cathode.	immediately.	(50 volts.)	0·83 (42 ohms in circuit.)

The small current which passes is due to the low conductivity of ammonia solution ; so a similar experiment was made with a solution of sodium carbonate in the porous cell, as sodium hydroxide might act on the film. The only difference found was that the maximum current was much greater.

Aluminium sulphate solution contained :	Time from closing circuit (minutes).	Voltmeter.	Ammeter.
Anode.	0	11·3	0·22
	13	11·8	0·07
	65	11·95	0·04
Cathode.	immediately.	10·3	0·5
	3	9·6	0·8
	4	9·1	1·0
Anode.	9	11·8	0·09
	19	11·9	0·06

In the next experiment also sodium carbonate solution was used, and after the current had fallen to 0·07 ampere, part of the sodium carbonate solution was replaced by a saturated solution of potassium chloride. The current increased steadily, after 60 minutes it was 0·35 ampere. On reversal, the current rose immediately to over 2 amperes.

In a similar experiment, after the current had fallen to 0·08 ampere, half of the sodium carbonate solution was removed, and a saturated solution of potassium sulphate added ; even after 60 minutes there was no change in the current. Ammonia was also used in the inner cell, and half of it replaced by saturated solution of potassium sulphate after the current had decreased to 0·04 ampere. After 60 minutes the current was 0·05 ampere, and after 20 hours it was constant at 0·10 ampere. On reversal it immediately rose to over 2 amperes.

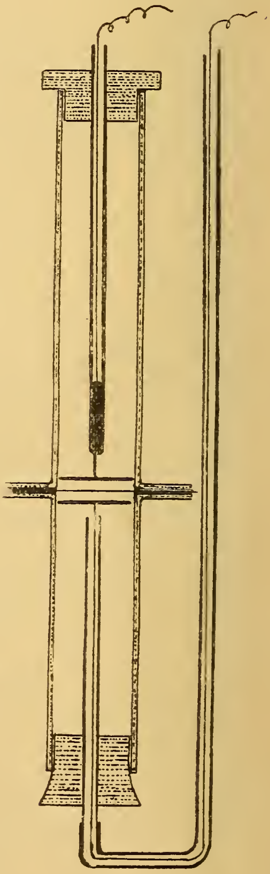
An experiment was also made with solutions of sodium carbonate and aluminium chloride. In this case, after the current had fallen to 0·05 ampere, the poles were reversed and the current increased rapidly (to 0·6 ampere in 1·5 minute) ; but on again reversing, it quickly diminished to its former value.

There is still another way in which the explanation might be tested—by direct measurement of the resistance which the film offers to the passage of different ions. Suppose that solutions of the four salts $Al_2(SO_4)_3$, $AlCl_3$, K_2SO_4, KCl, be prepared so that they have the same conductivity at say 25° C., and that now the two electrodes be separated by a film of $Al(OH)_3$; then the resistances depend upon the rapidity with which the ions can pass through the film, and the four solutions will, in this case, have different conductivities. The differences should, moreover, be of quite a high order.

For in the case of $Al_2(SO_4)_3$, neither ion would pass through the film, and the resistance measured should be high ; in the case of $AlCl_3$, and of K_2SO_4, only one ion could pass through, and the resistances should be of the same order, though much smaller than in the first case. The presence of the film should not make much difference to the resistance of the KCl solution, since both ions can pass through ; this solution should, therefore, have the smallest resistance.

The apparatus which we used consisted of two glass tubes with flanges ground to fit one another. Between the two tubes was placed a piece of filter-paper which had been soaked in a dilute gelatine solution. The flanges were pressed together while the gelatine was hot, so that a close and water-tight junction was made. Dilute solution of aluminium sulphate was poured into one tube which was closed with a rubber stopper provided with an overflow tube; the apparatus was then reversed and a dilute solution of ammonia was poured into the other tube. In this way a film of $Al(OH)_3$ was formed in the gelatinized paper, and after a few hours the whole was carefully washed out with distilled water. One tube was then filled with the solution to be examined, the corresponding electrode adjusted to a definite mark — an overflow tube preventing rupture of the film ; the apparatus was then reversed and the other tube filled with the same solution, and the electrode inserted. The whole was placed in a thermostat at 25° C. and measurements of the resistance made. They were as follows :—

Fig. 1.



$Al_2(SO_4)_3$	289 ohms
$AlCl_3$	259 ohms
KCl	248 ohms.

These differences are very small, especially as we found the error of adjustment of the electrodes to be considerable.

It is doubtful if it is practicable to determine these differences with an alternating current. There can be no migration of the ions (with a high frequency and small current), and therefore a very small amount of certain salts in the film is sufficient to enable a current to pass; and will, in fact, largely determine the conductivity. Now the formation of the film by the interaction of the two salts necessarily produces such a salt in the film; and this, no doubt, is very difficult to remove completely by mere washing[*].

We propose therefore to repeat the experiments with a more suitable arrangement of electrodes, and with special preparation of the film. We also hope to make measurements of the resistances using continuous currents.

The explanation of the peculiarities of aluminium when used as an anode in solutions of sulphates, which has thus been suggested, may be applied to the phenomena observed in the reaction between aluminium and dilute acids. But it seemed desirable to determine by experiment whether the presence of those ions which have so marked an influence on the anode has a similar influence on the rate of solution of aluminium in sulphuric acid. Accordingly, the following rough determinations were made of the rate of evolution of hydrogen from the acid, both alone, and with addition of certain ions.

Preliminary trial showed that at temperatures of 80° C. to 85° C., and with a 2-molar solution of sulphuric acid, the reaction proceeded at a rate which could be conveniently measured. A thermostat was adjusted to 85° C., and all the experiments were made at this temperature. Small flasks of about 80 c.c. capacity, and pieces of sheet aluminium of uniform size and weight (25 mm. square, 0·45 gm.) were used. Each flask contained one piece of the metal and 60 c.c. of a 2-molar sulphuric acid solution, and in addition a known quantity of a concentrated solution of the salt under investigation. The gas evolved was collected in a burette. The salts employed were KCl, KBr, KNO_3, and KCNS. The results are summarized below.

Chloride.—Four experiments were made to determine the effect of chloride, a 3·9 molar solution of potassium chloride

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[*] With a direct current this salt is removed from the film by the action of the current. This is probably the reason why, in the series of experiments last described, the current *at first* is so long (20 hours) in reaching a minimum, although afterwards it reaches the same minimum in much less time (about the same time that had elapsed between the two previous commutations).

being used. The intervals of time required for the evolution of 50 c.c. of hydrogen were

(1)	60 c.c. acid.	180 minutes, diminishing to 150 minutes.
(2)	60 c.c. acid + 1 c.c. KCl.	70 minutes, diminishing to 50 minutes.
(3)	60 c.c. acid + 2 c.c. KCl.	2 minutes.
(4)	60 c.c. acid + 4 c.c. KCl.	2·5 minutes, diminishing to 1·7 minute.

These figures show that chloride has a very decided influence on the velocity of the reaction, but it does not seem to play the part of a simple catalysator. One noticeable feature is that when 2 c.c. of the solution have been added, its maximum effect has been almost reached.

The action may be explained as follows—when a piece of aluminium is put into dilute sulphuric acid, it is covered with a film of hydroxide; this film, being impermeable to SO_4'' ions, is impermeable to $H^{\cdot}$ ions also, for the one ion cannot go anywhere without the other. Thus there is no action between the metal and the acid. The aluminium, however, acts slowly on the water in the film, forming hydrogen and aluminium hydroxide, which maintains the continuity of the film. In this way a slow continuous action takes place. If potassium chloride be added to the acid, $H^{\cdot}$ ions can permeate the membrane, for the Cl' ions can go with them, and the metal thus comes in contact with $H^{\cdot}$ ions. This action breaks up the film and so admits the sulphuric acid to the surface of the metal.

If the concentration of Cl' ions is too small to cause violent action and so destroy the film, they will still have an accelerating influence, but the maximum effect will not be attained.

Bromide.—Addition of bromide appears to have very little influence on the velocity of reaction. Four experiments were made, a 4-molar solution of potassium bromide being used. The times of evolution of 50 c.c. of hydrogen were

(1)	60 c.c. acid	150 minutes.
(2)	60 c.c. acid + 2 c.c. KBr.	160 ,,
(3)	60 c.c. acid + 4 c.c. KBr.	155 ,,
(4)	60 c.c. acid (no. 1) + 1 c.c. KBr.	140 ,,

The fourth experiment was made with the aluminium and acid already used in experiment (1), in order to remove uncertainty as to the uniformity of the surface. Hence the influence of bromide is very slight and the experiments are not sufficient to show whether it accelerates or retards the reaction.

Nitrate and Thiocyanate.—These salts were found to have an accelerating effect. With nitrate the reaction was somewhat irregular, and the gas evolved was found to contain nitric oxide. In the case of thiocyanate, hydrogen sulphide was produced in considerable quantity. The results, consequently, are of no value.

Finally, two experiments were made, with acetic acid, and with a mixture of acetic acid and potassium chloride; for according to the theory, presence of chloride should have an accelerating effect. The acetic acid solution was that of maximum conductivity, and the potassium chloride solution was 3·9 molar. The action was very slow and the curves obtained were irregular. In 30 hours 18 c.c. of hydrogen were evolved when acetic acid alone was used, and in the same time 22 c.c. of hydrogen with a mixture of 2 c.c. KCl and 60 c.c. of acetic acid.

These experiments must be regarded as rough preliminary observations, and we wish to return to the subject at a later date.

Summary.

1. The influence of chloride, bromide, nitrate, acetate, chlorate, and thiocyanate, in varying concentration, on an aluminium anode in sulphuric acid was investigated.
2. A theory to explain the results was brought forward and tested experimentally.
3. The essential peculiarities of an aluminium anode were reproduced by means of a platinum anode and a film of aluminium hydroxide.
4. Some measurements were made to determine the influence of chloride and of bromide, on the reaction between aluminium and sulphuric acid.

Chemical Laboratory,
University of Edinburgh.
October 1902.

XXX. *On Loaded Lines in Telephonic Transmission.*

By GEORGE A. CAMPBELL*.

[Plates V. & VI.]

THE loaded line discussed in this paper is an electrical circuit of two long parallel conducting wires having self-induction coils inserted at regular intervals. An elementary mathematical treatment adapted to engineering

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* Communicated by Prof. Trowbridge.

applications will be given; a second paper will present an engineering study and an account of experimental methods and results.

Vaschy*, Heaviside†, and others have either suggested or unsuccessfully tested the insertion of self-induction coils on actual lines. Heaviside stated in 1893 that there was "no direct evidence of the beneficial action of inductance brought in in this way," and no progress was made till 1899, when the subject was investigated independently by Professor M. I. Pupin‡ and myself. It has been shown that the loaded line affords a practical method of improving the transmission efficiency of long lines employed for telephonic, telegraphic, or other electrical purposes.

An interesting contribution to the general properties of this structure has been made by Mr. Charles Godfrey§ in a paper on wave propagation along a periodically loaded string and I am indebted to that article for equation (18) which furnishes a complete solution of the propagation.

This study has been made with special reference to telephonic applications, and I have limited the mathematical treatment to the forced harmonic steady state, as that furnishes all the theoretical information which we are in position to use in telephony, and practical applications generally, provided only a sufficient frequency range is considered. The range which it is necessary to consider in telephony might be determined by constructing a network which would transmit uniformly all frequencies between certain limits, and then experimentally determining the interval which is just sufficient to preserve the full character of speech. Practical cable transmission shows that speech remains intelligible even when the superior limit is comparatively low. Cable quality is, however, not desirable, and for unimpaired articulation it appears from the tests which have been made that the limit lies well above two thousand cycles per second. Efficient, clear transmission requires a low and constant attenuation, and constant velocity, throughout the telephonic frequency interval, and constant line impedance of negligible reactance is desirable. With an open wire line of heavy copper wire (resistance R, inductance L, capacity C) this is approximately attained, the attenuation-coefficient,

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* *La Lumière Electrique*, January 12, 1889.

† Electromagnetic Theory, i. p. 445 (1893).

‡ Trans. Am. Math. Soc. p. 259, July 1900; Trans. Am. Inst. Elec. Eng. xvii. May 1900.

§ Phil. Mag. xvi. p. 356 (1898).

velocity, and line impedance being respectively—

$$a = \frac{R}{2}\sqrt{\frac{C}{L}},$$

$$v = \frac{1}{\sqrt{LC}},$$

$$k = \sqrt{\frac{L}{C}}.$$

For a loaded line these formulæ apply approximately and the problem taken up in this paper is the determination of the correction factors. This is direct; the approximation of loaded to uniform line shows only indirectly the performance of the loaded line.

I.

A summary must be given of the general transmission formulæ upon uniform lines which will be required. An harmonic electromagnetic steady state is resolvable into a wave propagation with definite velocity and attenuation, but no distortion, throughout each uniform interval of the line, the wave suffering reflexion at points of non-uniformity. This is mathematically an exact and simple analysis of the steady state, but it conforms only approximately to the physical action. It neglects the diffusion or distortion resulting from dissipation which is, in the steady state, not in evidence, except indirectly, as a variation with the frequency of the velocity and attenuation. This variation of the velocity and attenuation furnishes sufficient measure of the distortion at the head of an advancing wave for most practical applications. Except for this head distortion an harmonic steady state is established by pure wave propagation—the line presents a definite line impedance which determines the initial current at the impressed force; the electromagnetic wave originating at the impressed force travels with a definite attenuation and a definite velocity along the line and divides upon reaching a point of non-uniformity into a reflected wave and a transmitted wave. Repeated reflexions establish the steady state.

The equation of a simple current wave upon a uniform line is

$$i = \frac{Ee^{\iota pt}}{k} e^{-\gamma x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the line impedance k, the propagation coefficient γ, the attenuation coefficient a, and the velocity of propagation v, are given by

$$k=\sqrt{J_1J_2}, \qquad (2)$$

$$\gamma=a+\frac{p\iota}{v}=\sqrt{\frac{J_1}{J_2}}, \qquad (3)$$

where, if R, L, C, S are the effective loop-line resistance, inductance, capacity, and leakage conductance at a frequency $p/2\pi$, the series and shunt impedances are

$$J_1=R+Lp\iota, \qquad (4)$$

$$J_2=(S+Cp\iota)^{-1}; \qquad (5)$$

consequently

$$a=\sqrt{\tfrac{1}{2}\sqrt{(R^2+L^2p^2)(S^2+C^2p^2)}+\tfrac{1}{2}(RS-LCp^2)} \qquad (6)$$

$$=\frac{R}{2}\sqrt{\frac{C}{L}}\left(1+\frac{SL}{CR}\right) \text{ for large L and small S} \qquad (7)$$

$$v=\frac{2a}{CR+LS}. \qquad (8)$$

For transmission from one construction of impedance k_1 to a second of impedance k_2 the current reflexion and transmission coefficients are respectively

$$\alpha=\frac{k_1-k_2}{k_1+k_2}, \qquad (9)$$

$$1+\alpha=\frac{2k_1}{k_1+k_2}. \qquad (10)$$

If upon a line of length l with terminal sets of impedances J_s, J_r, at the sending and receiving ends, there is an impressed force $Ee^{\iota pt}$, the current at distance x from the sending set is

$$i=\frac{Ee^{\iota pt}}{k+J_s}\cdot\frac{e^{-\gamma x}+\alpha_r e^{\gamma x-2\gamma l}}{1-\alpha_r\alpha_s e^{-2\gamma l}}, \qquad (11)$$

where the reflexion coefficients are

$$\alpha_r=\frac{k-J_r}{k+J_r}, \qquad \alpha=\frac{k-J_s}{k+J_s}.$$

If the line attenuation is large and the sending and receiving sets are similar, the receiving current is approximately

$$i_r=\frac{Ee^{\iota pt}}{2J_s}\cdot\frac{4kJ_s}{(k+J_s)^2}e^{-\gamma l}, \qquad (12)$$

If terminal transformers are added and the transformer impedances are J_1 for the set side winding, J_2 for the line side winding, and J_{12} between the two windings, then (12) becomes

$$i_r = \frac{Ee^{\iota pt}}{2J_s}\left(\frac{4kJ_s}{(k+J_s)^2}\right)\left(\frac{J_{12}(k+J_s)}{(k+J_2)(J_1+J_s)-J_{12}{}^2}\right)^2 e^{-\gamma l}, \qquad (13)$$

where the four factors are, respectively, the value of the current for a circuit consisting of the two sets alone, the effect of terminal reflexion, the effect of transformers, and the effect of transmission over the line. For transformers of high inductance, negligible resistance, and negligible magnetic leakage (13) becomes

$$i_r = \frac{Ee^{\iota pt}}{2J_s} \cdot \frac{4k\frac{J_1}{J_2}J_s}{\left(k\frac{J_1}{J_2}+J_s\right)^2} \cdot e^{-\gamma l}, \quad . \quad . \quad . \quad (13a)$$

and the transformers are equivalent to a change in the line impedance from k to $k\,J_1/J_2$.

The impedance of a circuit consisting of length l of uniform line $(k\gamma)$ closed through an impedance J_0 at the further end is by formula (11)

$$J = k \cdot \frac{1-\alpha e^{-2\gamma l}}{1+\alpha e^{-2\gamma l}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where $\alpha = (k-J_0)/(k+J_0)$ is the reflexion coefficient from line to terminal impedance.

Diagram I. (Pl. V.) shows the value of the reflexion factor in equation (12). The factor involves the two impedances symmetrically, is a function of their ratio only, and becomes unity if they are equal. Let the absolute value and angle of the impedance ratio be r, θ, and of the reflexion factor be e^{-b}, ϕ, then

$$\frac{k}{J_s} = r \operatorname{cis} \theta,$$

$$\frac{4kJ_s}{(k+J_s)^2} = e^{-b} \operatorname{cis} (-\phi),$$

$$b = \log \left\{ \frac{1}{4}\left(r+\frac{1}{r}\right) + \frac{1}{2}\cos\theta \right\}, \quad . \quad . \quad . \quad (15)$$

$$\phi = \tan^{-1} \frac{\left(r-\frac{1}{r}\right)\sin\theta}{2+\left(r+\frac{1}{r}\right)\cos\theta}, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and (12) may be written

$$i_r = \frac{\mathrm{E}e^{\iota pt}}{2\mathrm{J}_s} e^{-(b+al)} \,\mathrm{cis}\, -\left(\phi + \frac{p}{v} l\right), \quad . \quad . \quad . \qquad (17)$$

where the second and third factors are, respectively, the effective attenuation and the phase lag due to the line. As b can be negative, reflexion may augment the receiving current, but in general the effect is a loss which may be comparable with the attenuation loss. Thus for $k/\mathrm{J}_s = 10$, $b = 1{\cdot}11$, and the range of "easy commercial" telephonic transmission, which requires an effective attenuation coefficient of 3·2 with present instruments, would be reduced 1·11/3·2, or 35 per cent.

By Diagram I. (Pl. V.) the transformer efficiency in equation (13a) is a maximum and completely offsets the reflexion loss when $\mathrm{J}_2/\mathrm{J}_1 = |k/\mathrm{J}_s| = r$. It follows that, by introducing transformers into a line at every point of non-uniformity due to apparatus or a change in line construction, reflexion losses may be entirely eliminated and the effective attenuation made as small as or smaller than the real line attenuation.

The effect of loading a line uniformly is shown by Diagram II. (Pl. V.), which gives the attenuation coefficient for lines having $\mathrm{R}=2$, $\mathrm{C}=1$, and different values of L. Also the velocity, for with these values of the constants the velocity and attenuation coefficient are numerically equal. With no inductance the attenuation curve is a parabola. Any increase in inductance reduces the attenuation and makes it more nearly uniform, and by a sufficient increase in the inductance the attenuation can be reduced to any desired value, but for this it is essential that the leakage be null.

The effect of leakage is added in Diagram III. (Pl. V.), which is plotted for $\mathrm{K}=1$, $\mathrm{L}=1$, $\mathrm{C}=1+\mu$, $\mathrm{S}=1-\mu$, but gives the attenuation coefficient and velocity curves for any uniform line by a change in scales only.

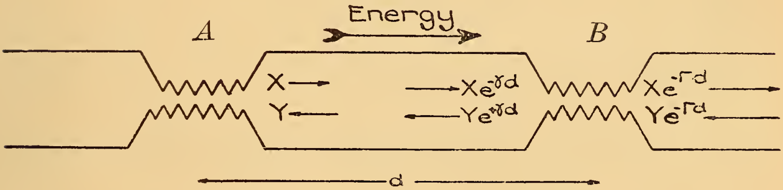
II.

An infinite loaded line will be considered first in order to treat propagation and terminal conditions separately. We might follow in detail the repeated division of the wave by reflexion at loads and the interference of the resulting wavelets which mutually annul each other, with the exception of a group suffering reflexion and transmission in a certain ratio which gives rise to a wave of small attenuation and negligible distortion, although the individual wavelets may be enormously attenuated and distorted by the length of their course back and forth upon the line. The following theorem will, however, lead directly to the solution and avoid the infinite summation.

Upon an infinite line of periodic recurrent structure a steady forced harmonic disturbance falls off exponentially from one periodic interval to the next. The theorem is proven by the consideration that as the line is infinite, there are identical circuits beyond points separated by a periodic interval, and the relative effect upon the disturbance of advancing an interval must be the same for all portions of the line.

Consider a uniform line (k, γ) with loading coils A, B, &c., at the interval d of impedance $\mathrm{H}d$, or H per unit length of line, and we will designate by (K, Γ) the impedance of the loaded line at the middle of a load and the propagation coefficient of the loaded line. Then if X, Y are the direct and reflected current waves at the further side of the loading coil (A), at the next coil (B) the direct and reflected waves are $\mathrm{X}e^{-\gamma d}$, $\mathrm{Y}e^{+\gamma d}$ on the sending side, and $\mathrm{X}e^{-\Gamma d}$, $\mathrm{Y}e^{+\Gamma d}$ on the further side. At a coil the reflexion coefficient is

Fig. 1.



$$\frac{k-(\mathrm{H}d+k)}{k+\mathrm{H}d+k}=-\frac{\mathrm{H}d}{2k+\mathrm{H}d}, \qquad \text{and} \qquad \frac{2k}{2k+\mathrm{H}d}$$

is the transmission coefficient; the equations of condition at B are therefore

$$\mathrm{Y}e^{\gamma d}=-\frac{\mathrm{H}d}{2k+\mathrm{H}d}\mathrm{X}e^{-\gamma d}+\frac{2k}{2k+\mathrm{H}d}\mathrm{Y}e^{-\Gamma d}.$$

$$\mathrm{X}e^{-\Gamma d}=-\frac{\mathrm{H}d}{2k+\mathrm{H}d}\mathrm{Y}e^{-\Gamma d}+\frac{2k}{2k+\mathrm{H}d}\mathrm{X}e^{-\gamma d}.$$

Eliminating X and Y, we have

$$\cosh(\Gamma d)=\cosh\gamma d+\frac{\mathrm{H}d}{2k}\sinh\gamma d. \quad . \quad . \quad . \quad (18)$$

which completely determines the propagation coefficient of the loaded line, including the attenuation coefficient and velocity of propagation*.

To determine the line impedance (K), observe that the impedance is periodic and apply formula (14) to the circuit, beginning at the middle of one coil and extending to the middle of the next coil:—

$$K=\frac{Hd}{2}+k\cdot\frac{1-\dfrac{k-\left(\frac{Hd}{2}+K\right)}{k+\frac{Hd}{2}+K}e^{-2\gamma d}}{1+\dfrac{k-\left(\frac{Hd}{2}+K\right)}{k+\frac{Hd}{2}+K}e^{-2\gamma d}},$$

or

$$K=\sqrt{k^2+\frac{H^2d^2}{4}+Hdk\coth\gamma d}$$

$$=k\sqrt{\left(1+\frac{Hd}{2k}\tanh\frac{\gamma d}{2}\right)\left(1+\frac{Hd}{2k}\coth\frac{\gamma d}{2}\right)}, \quad . \quad (19)$$

which completely determines the loaded line impedance at the middle of a load. The impedance at any other point might be found by the same method.

Substituting the values of Γ and K given by (18) and (19) in equation (11) we have the formula for the current at any load, or substituting in (12), (13), (13 *a*), or (17) we have the value of the receiving current, but the substitution can best be made after numerical values are obtained.

The method which has been employed in deducing (18)

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* For a simpler proof of equation (18), short circuit the loaded line at the middle of the coil B and consider the ratio of the current at A to the current at B. As section A–B may then be considered, either, (1) as a uniform line of constants k, γ, and length d, terminating in an impedance $Hd/2$, or, (2) as a portion of a uniform line of constants K, Γ, and length d, terminating in a short circuit, two values for the ratio of the current at A to the current at B may be obtained, and the two equated give a relation between the two sets of line constants. The two expressions are found on making the proper substitutions in (11) to be identically the right and left hand members of equation (18).

In this proof it is to be noticed that the loaded line is short-circuited at the middle of a load in order that it shall act like a short-circuited uniform line with the constants K, Γ; if the line is not short-circuited at the middle of a load (or at the middle of a line section) a wave traverses on reflexion a line which is not throughout of uniform periodic structure. For the suggestion leading to this proof I am indebted to Dr. A. E. Kennelly. (July 1902.)

and (19) is quite general and has been applied to a variety of cases of interest, such as artificial lines with mutual induction between loads, S. P. Thompson's compensated cable, and periodic lines of two or more different intervals, but these constructions lie outside the scope of this paper.

III.

To give a precise and comprehensive idea of the performance of the loaded line, formulæ (18) and (19) must be reduced to diagrams giving the attenuation coefficient (A), velocity (V), and line impedance (K). The diagrams can best be constructed for the correction factors α, η, κ, defined by the equations :—

$$A=\alpha\frac{R+R'}{2}\sqrt{\frac{C}{L+L'}}, \quad \ldots \quad (20)$$

$$V=\eta\frac{1}{\sqrt{(L+L')C}}, \quad \ldots \quad (21)$$

$$K=\kappa\sqrt{\frac{L+L'}{C}}, \quad \ldots \quad (22)$$

where R, L, C, R′, L′, are the line resistance, inductance, and capacity, and the load resistance and inductance, all per unit of length. We can reduce the number of independent variables from 7 to 4 by introducing in place of R, L, C, R′, L′, d, p, the new variables ω, δ, ρ, λ defined by

$$\omega=\frac{1}{2}pd\sqrt{(L+L')C}, \quad \ldots \quad (23)$$

$$\delta=\frac{R+R'}{2}d\sqrt{\frac{C}{L+L'}}, \quad \ldots \quad (24)$$

$$\rho=\frac{R'}{R}, \quad \ldots \quad (25)$$

$$\lambda=\frac{L'}{L}. \quad \ldots \quad (26)$$

For a discussion of practical applications we may assume that there is no leakage, no line inductance, and that δ is small. While leakage, on a heavily loaded line, seriously increases the attenuation, the effect of small leakage will be given with sufficient accuracy by the correction (7) for uniform lines. The practical effect of distributing a small portion of the total inductance along the line must be to make the line act a trifle more like a uniform line. Its general effect as shown by Godfrey's results will be discussed later.

In cable circuits the inductance is quite negligible, and a moderately loaded open wire circuit would have several times more load than line inductance. δ is the attenuation coefficient for a periodic interval, and will be small if the line is to be efficient.

Substituting (20) to (26) in (18) and (19), and expanding

$$\alpha\delta+\frac{2\omega}{\eta}\iota=\cosh^{-1}\sum_{0}^{\infty}\frac{(2n+1)(1+n\rho)-2\omega^2}{(2n+1)\,!}\left(\frac{4\,\delta\omega\iota}{1+\rho}\right)^n, \quad (27)$$

$$\kappa=\frac{\sqrt{\displaystyle\sum_{n=0}^{n=\infty}\frac{[2(2n+1)(2\omega^2+2n\omega^2\rho-n)-4\omega^4-n\rho(4n^2-1)(\rho n-\rho+2)]\left(\frac{4\,\delta\omega\iota}{1+\rho}\right)^n}{(2n+1)\,!}}}{4\omega^2\displaystyle\sum_{n=0}^{n=\infty}\frac{1}{(2n+1)\,!}\left(\frac{4\,\delta\omega\iota}{1+\rho}\right)^n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

for all values of the variables. As the series converge rapidly these formulæ may be used for general computation by noticing that

$$\cosh^{-1}(x+y\iota)=\cosh^{-1}\frac{\sqrt{(x+1)^2+y^2}+\sqrt{(x-1)^2+y^2}}{2}$$

$$+\iota\cos^{-1}\frac{2x}{\sqrt{(x+1)^2+y^2}+\sqrt{(x-1)^2+y^2}}. \quad (29)$$

In the limiting case $\delta=0$, the formulæ become :—

$$\omega \leqq 1 \left\{ \begin{aligned} \alpha&=\frac{3+3\rho-2\omega^2}{3(1+\rho)\sqrt{1-\omega^2}}, && . \quad . \quad . \quad . \quad (30)\\ \eta&=\frac{\omega}{\sin^{-1}\omega}, && . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)\\ \kappa&=\sqrt{1-\omega^2}, && . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32) \end{aligned} \right.$$

$$\omega > 1 \left\{ \begin{aligned} Ad&=2\cosh^{-1}\omega, && . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)\\ \eta&=\frac{2\omega}{\pi}, && . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)\\ \kappa&=\iota\sqrt{\omega^2-1}. && . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35) \end{aligned} \right.$$

These simple formulæ, which furnish the practical information we require, are reduced to curves in diagrams IV., V., VI. (Pl. V.), which also give a few curves for $\delta=0{\cdot}1$, to show the close approximation with which the (α, η, κ) curves for $\delta=0$ will apply to any practical loaded line, for δ would, perhaps, never approach 0·1 in actual lines, but have a value nearer 0·01.

Inspection of the diagram shows that at $\omega=1$ the character of the propagation changes; that at this point reflexion, *per se*, introduces attenuation. With perfect conductivity ($\delta=0$) there is no attenuation below $\omega=1$, but there is attenuation above this value, and this is due, necessarily, to reflexion. Below $\omega=1$ the attenuation is proportional to the resistance so long as the resistance remains small, while above $\omega=1$ the attenuation is almost independent of the resistances (or may even decrease with an increase in resistance), but increases rapidly with the value of ω. Consequent on this change in the character of the propagation there is an accompanying change in the line impedance from pure resistance below $\omega=1$ to pure reactance for higher values of ω. The velocity curve also changes its direction and character abruptly at $\omega=1$; there are two coils per actual wave-length for $\omega=1$, *i.e.*, the disturbance is in opposite phases at consecutive coils. The critical value $\omega=1$ furnishes the first essential condition for an efficient loaded line, viz.:—

$$\tfrac{1}{2}pd\sqrt{\mathrm{L}'\mathrm{C}}<1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

i.e., there must be more than two coils per actual wave-length, or approximately, π coils per wave-length with the load uniformly distributed. This has long been known for loaded strings[*].

I have made use of these results by employing artificial loaded lines for cutting out harmonics in generator currents. The harmonics may all be cut down as far as desired by the use of a sufficient number of sections, while the attenuation of the fundamental can be reduced at pleasure by decreasing the resistance. The line does not require tuning, and with a small value of ρ the action would be quite independent of the frequency throughout a considerable range. The curves for $\rho=\alpha$ correspond to the case of an artificial line. Combining condensers and inductances, we may make a system which will not only cut out higher frequencies, but also all frequencies below a certain limit, as suggested at the beginning of this article. This system will be an inversion of a model of J. H. Vincent's[†].

The velocity and impedance are approximately independent of the resistances. The attenuation below $\omega=1$ is not only approximately proportional to the total resistance, but the curves also show that the attenuation is reduced by trans-

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[*] Routh, Advanced Rigid Dynamics, p. 260, § 411; Rayleigh, Theory of Sound, i., § 148, pp. 233, 234.

[†] Phil. Mag. xlvi. p. 557 (1898).

ferring resistance from the coil to the line, and that the loaded line attenuation may be less than that for a uniform line of the same total resistance, inductance, and capacity. Inspection of the formulæ shows that this applies to any line of high inductance for which

$$\rho<\tfrac{1}{3},$$

$$\omega<\frac{\sqrt{3(1-3\rho)(1+\rho)}}{2},$$

and that the maximum reduction is for

$$\rho=0,$$

$$\omega=\frac{1}{\sqrt{2}},$$

$$\alpha=\tfrac{2}{3}\sqrt{2},$$

when it amounts to 5·7 per cent.

IV.

To determine the loading for maximum efficiency, the total weight of copper in cable and load being given, we may make use of the following formulæ for the weights of loading coils and cable conductors per unit length of line, the formulæ applying to coils of similar proportions and cables of similar cross-section :—

$$df\mathrm{W}=w'\left(\frac{\mathrm{L}'}{\mathrm{R}'}\right)^{\frac{3}{2}}, \quad . \quad . \quad . \quad . \quad . \quad (37)$$

$$(1-f)\mathrm{W}=\frac{w}{\mathrm{RC}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

where W is the total weight of copper per unit length ; w, w' are constants made a minimum by suitable proportions of coils and cables, respectively ; d is the spacing of the coils ; and f is the proportion of the total copper in the coils. We will assume that the line is to be of high efficiency so that formulæ (30), (31), (32) apply, and suitable terminal apparatus or terminal transformers will be employed to practically annul terminal reflexion. The problem reduces to securing minimum attenuation at the frequency of transmission. Taking the product of equations indicated by (20), $(23)^{\frac{1}{4}}$, (30), $(37)^{\frac{1}{4}}$, $(38)^{\frac{5}{8}}$, and substituting $\mathrm{R}'=\rho\mathrm{R}$, we obtain for the attenuation

$$\mathrm{A}=\frac{3+3\rho-2\omega^2}{6\cdot2^{\frac{1}{4}}\omega^{\frac{1}{4}}\rho^{\frac{3}{8}}f^{\frac{1}{4}}(1-f)^{\frac{5}{8}}(1-\omega^2)^{\frac{1}{2}}}\cdot\frac{w'^{\frac{1}{4}}w^{\frac{5}{8}}p^{\frac{1}{4}}}{\mathrm{W}^{\frac{7}{8}}} \quad . \quad . \quad (39)$$

which takes its minimum value

$$A=1\cdot639(w'^2w^5p^2W^{-7})^{\frac{1}{8}} \quad . \quad . \quad . \quad . \quad (40)$$

for

$$f=\tfrac{2}{7}=\cdot2857,$$

$$\rho=\tfrac{3}{7}=\cdot4286,$$

$$\omega=\sqrt{\tfrac{3}{7}}=\cdot6547,$$

and therefore :—

For a given total weight of copper in cable and load the attenuation of a given frequency is made a minimum by placing 2/7 of the copper in coils having a resistance equal to 3/7 of the line resistance and spacing them $\pi\sqrt{7/3}=4\cdot80$ *per uniform line wave-length,* i. e., $\pi/\sin^{-1}\sqrt{3/7}=4\cdot401$ *per actual wave-length on the loaded line.* These proportions make

$$\alpha=1\cdot058,$$

$$\eta=\ \cdot9171,$$

$$d=2\cdot028\left(\frac{w'^2W}{w^3p^6}\right)^{\frac{1}{8}}, \quad . \quad . \quad . \quad . \quad . \quad (41)$$

$$\frac{L'}{R}=0\cdot695\left(\frac{W^3}{p^2ww'^2}\right)^{\frac{1}{4}}, \quad . \quad . \quad . \quad . \quad (42)$$

$$K=0\cdot488\left(\frac{w^3}{w^2C^8p^2W}\right)^{\frac{1}{6}}, \quad . \quad . \quad . \quad . \quad (43)$$

$$Wl=1\cdot759\left(\frac{w^5w'^2p^2\iota^{15}}{(Al)^8}\right)^{\frac{1}{7}}, \quad . \quad . \quad . \quad (44)$$

The last formula, giving the total weight of copper in a line of length l and attenuation e^{-Al}, shows the relative importance of the different factors. The weight increases as the 2·14 power of the range. Open wire circuits also increase in weight somewhat faster than the square of the length, but cable weights vary as the cube of the range. Loading, therefore, presents the greatest possibilities upon long cable circuits. The weight is evidently comparatively independent of the frequency. The attenuation coefficient comes in approximately inversely as the first power. Of the two specific weights w, that for the cable is far more important than that for the coils w. Thus the total weight Wl will be doubled by changing w to 2·64 w, or w' to 11·3 w'. This shows the comparative importance of the coil weight.

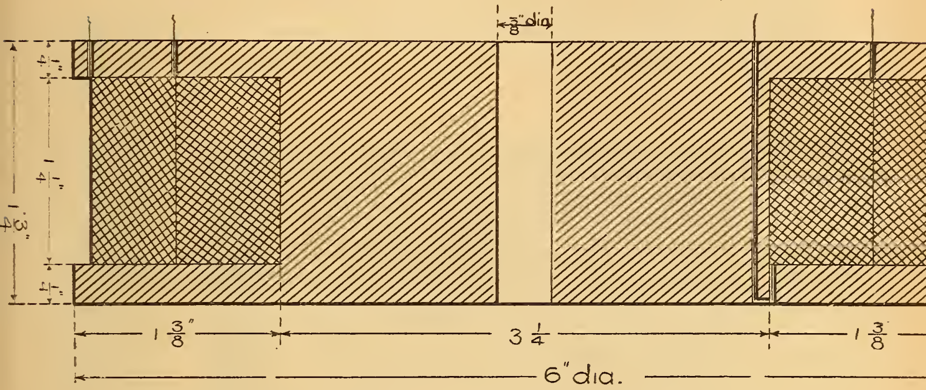
In practical engineering, costs must be substituted for theoretical copper weights, (37) (38) being replaced by the actual relation between gross costs and effective time constants at telephonic frequencies, and a variety of practical requirements are involved which will materially modify the above results. In special cases it may be necessary to connect a loaded line of high impedance directly to an unloaded line or terminal apparatus designed for present lines. Diagram I. (Pl. V.) will give the reflexion loss and reduction in range. From the formulæ already deduced, the proportions may be determined for maximum efficiency with a given total weight of copper and given terminal conditions.

EXPERIMENTAL WORK.

In January 1899, I was assigned the problem of investigating the possibilities of improving the efficiency of cables for telephonic service. After considering some other methods I concluded that the loaded line presented the greatest promise, and, as I felt that more progress would be made by experimental tests than by mathematical work, I immediately planned to have made an artificial line with 100 loading coils on a twenty-mile cable circuit. Before this line was completed, becoming more confident of the success of loading, an experiment on an actual cable was planned, and for these tests three reels of 100-pair telephone cable, commonly known as "Conference Standard" cable, were brought to the laboratory. Each reel contained about 600 feet of cable, so that the entire circuit, when connected back and forth, formed a metallic cable pair thirty-five miles in length, with a resistance of about 87 ohms per mile and a mutual capacity of about ·057 microfarad per mile. For a laboratory test a circuit thirty-five miles in length could not be stretched out to its full length, and we actually used the cable on the reels with the circuit looped back and forth, fifty times through the first cable, then into the second and third cables. The equivalence of a looped circuit of this kind to a straight-away circuit had been shown, provided the circuit was balanced as all telephone circuits must be balanced in order to eliminate cross talk and noise. This point was also carefully tested during the investigation.

For the loading of this cable 300 coils were manufactured. A cross-section of this loading coil, known as the T-14 coil, is shown in fig. 2. On a wooden spool a primary of 578 turns of No. 20 single cotton-covered wire was wound, and a secondary of 465 turns of No. 20 single cotton-covered wire. The turns were so chosen as to give the primary and secondary the same inductance, and they also had approximately the same resistance. The cable circuit, as has been explained, consisted of 300 lengths connected in series. Between each length and the succeeding length a T-14 coil was inserted, the primary in one wire of the pair and the secondary in the other wire of the pair, the connexions being so made as to put the coil into the cable inductively. Each coil added about ·11 henry and 12 ohms to the circuit. To ensure the reliability of the test it was necessary to so place the loading coils that the mutual induction should be negligible. Accordingly they were spread over all the space available, and tests showed that any effect of mutual induction between coils was quite negligible.

Fig. 2.



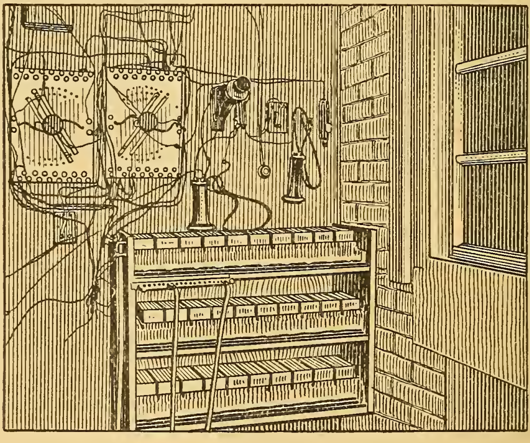
The experimental line is shown in the photograph on Plate VI. The three reels of cable are all visible; one is in plain sight, another is at the extreme left, and the third can be distinguished at some distance to the right. The reel at the extreme right had no connexion with this experiment. The cables were brought out to pot-heads, and each wire terminated in a screw-cup. In this way any combination of connexions could be made. Two of the pot-heads of the middle reel of cable are in plain sight in the photograph. The coils were placed upon shelves—being placed horizontally and on edge on alternate shelves. With this arrangement there was practically no mutual induction except between one coil and the adjacent coil, or two on either side. The four coil terminals were carried underneath the shelf to a distributing board between the pot-heads, and this enabled us to connect in the coils in any desired manner.

An artificial section was also made and loaded with 100 T-14 coils, and this is seen in the right-hand half of the photograph. The coils upon the shelves are plainly visible.

The artificial cable, which consisted of mica condensers and German-silver resistances, does not show conspicuously.

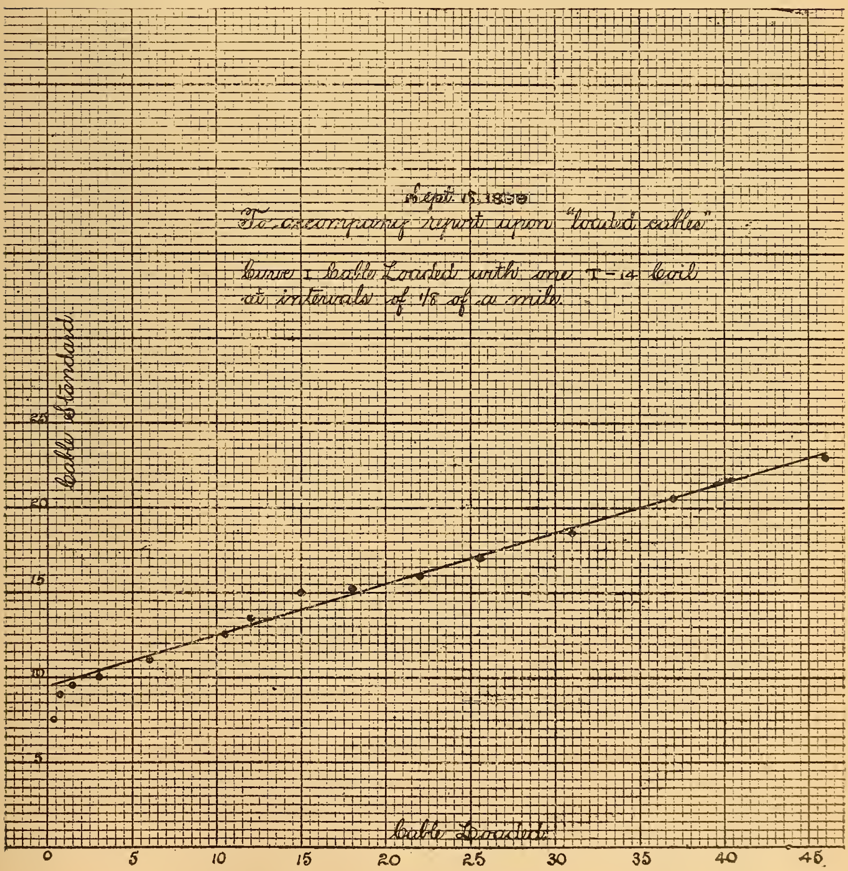
One of the transmitting stations is shown at the left of the photograph. The receiving station is shown in the second photograph. At this station there were switches and an artificial cable, in addition to the telephone set. The artificial cable, known as the "cable standard," consisted of mica condensers and German-silver resistances. The photograph (fig. 3) shows the thirty boxes, each containing ten condensers, and, somewhat indistinctly, the German-silver wires. It also shows a jack strip and two cords and plugs, by means of which any length of cable up to thirty miles, by steps of one mile, could be put in circuit. For lengths greater than thirty miles another artificial cable was added to this.

Fig. 3.



The manner of making the test was as follows:—The cable was connected back and forth without the loading coils and the artificial section was also connected up without the loading coils, and then the whole of this circuit was compared with the cable standard. It was found that the entire cable and artificial section were equivalent to forty-six miles of the cable standard, and shorter lengths were equivalent to corresponding lengths of the cable standard. Next, the coils were introduced into the cable circuit and into the artificial section, making a cable circuit forty-six miles in length with four hundred equally spaced loading coils. The transmission was greatly improved and found equivalent to the transmission over twenty-three miles of cable standard, and in addition the articulation was clearer and sharper. In addition to this the side tone at the transmitting end was reduced so as to be hardly noticeable, so that the result of loading was to increase the receiving-end current while decreasing the sending-end current. Tests were made upon different lengths of the loaded cable and the results of one set of tests are shown in the accompanying diagram (fig. 4). The results were

Fig. 4.



represented fairly well by a straight line which corresponds to the approximate formula (17). This line shows that the initial loss was equivalent to nine miles of standard cable, but on account of the greatly reduced attenuation, the loaded line is better than the unloaded line for all distances greater than fifteen miles. If the line representing the experimental results is to be parallel to itself, lowered nine miles we have the curve for a line with terminal transformers. and for this case the loading is shown by the experiment to nearly treble the distance over which transmission of a given volume is obtained, and it actually accomplishes more than that, for the quality is improved. The tests upon which this diagram is based were made with telephonic transmission and ear estimates at the other end of the line and are, of course, more or less qualitative. since the difference of quality prevents a sharp estimate. At the transmitting end a person talks in a steady, monotonous manner, and it is arranged so that the person listening at the other end can switch instantly from the loaded line to the artificial cable standard, and *vice versâ*, and alter the length of the cable standard to secure an equal volume of transmission over the two. The comparison gave the equivalents of the two circuits for commercial service, which answered the questions which I had before me.

For a complete scientific investigation it is desirable to use a sinusoidal current and make qualitative measurements, and we have made some tests in this way. A great deal of experimental work has been done, both upon this cable with the T-14 and other loading coils with different separations between loads, with iron-cored loading coils and with terminal transformers, also with other cables and with loaded aerial lines several hundred miles in length, but the results are incomplete, and I am not prepared to attempt a discussion of them at present.

Any description of the experimental work must include a discussion of the actual performance of loading coils under periodic currents, which is an extended subject. For the mathematical work it has been assumed that the effective inductance and resistance of the coil is the same for all frequencies, which cannot be assumed in experimental work.

For the extended experimental work which has been done, which has been laborious and most painstaking, I am indebted to Mr. E. H. Colpitts, who has had charge of the experimental tests described above.

June 7, 1901.

XXXI. *The Variation of Potential along a Wire transmitting Electric Waves.* *By* C. A. Chant, *University of Toronto, Toronto, Canada**.

[Plate VII.]

I. *Introductory.*

HERTZ† was the first to explore a wire along which electric undulations were passing. His oscillator consisted of two sheet-brass plates 40 cms. square, connected by a copper wire 60 cms. long, in the middle of which was a spark-gap. Opposite and parallel to one plate was placed another of equal size, from which was led off a copper wire, the first metre of which was curved and the rest of it straight. As a detector he used his circular resonator, 70 cms. in diameter. The nodes were well marked in two wires, the length of the straight portions of which were 5·5 m. and 8 m. respectively. The half-wave-length was determined to be 2·8 m.

These experiments were repeated and extended by Sarasin and de la Rive‡, who somewhat increased the effect by using two wires led off from two plates placed opposite the oscillator plates, the resonator being held between them. These experiments showed very clearly that the apparent wave-length measured along the wire was dependent purely on the size of the resonator, the wave-length being equal to eight times the diameter of the resonator.

Somewhat similar results were obtained by Waitz§, who used a circular resonator to which were attached two wires, one joined near each terminal knob, and led off either parallel to each other or in opposite directions. In the former case, by sliding along a bridge laid across the wires, the sparks between the resonator knobs passed through maximum and minimum intensities; in the latter case, by hanging capacities on the wires and sliding them along, the sparks varied similarly. He worked with plate oscillators of two sizes, as well as cylindrical and spherical ones. He found that his minima depended entirely on the dimensions of his circular resonator.

The conclusion naturally drawn by Sarasin and de la Rive and Waitz from their experiments was that the oscillator

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* Communicated by Prof. Trowbridge.

† H. Hertz, Wied. *Ann.* xxxiv. p. 551 (1888); 'Electric Waves,' p. 106.

‡ E. Sarasin and L. de la Rive, *Archives des Sciences Physiques et Naturelles*, Genève, t. xxiii. p. 113 (1890).

§ K. Waitz, Wied. *Ann.* xli. p. 435 (1890).

emitted waves of various lengths, extending over several octaves; but this hypothesis has been shown to be improbable, a more satisfactory explanation being based on the fact that the oscillations of the oscillator are very rapidly damped, while those of the resonator are very persistent*.

In Lecher's† experiments the exciter consisted of two sheet-metal plates, 40 cms. square, joined by a bent wire 2 m. long, with a spark-gap in the middle of it. Opposite each plate and parallel to it was another of the same size, from which ran long straight parallel wires. On the farther ends of these was laid a vacuum-tube, and across the wires at different points were laid metallic bridges. When these were properly placed, namely, at the potential nodes, the tube at the ends lighted up. The wave-lengths he obtained, however, were not those proper to the exciter, but those of that part of the wire-system on that side of the first bridge next the plates which was in resonance with the rest of the wire-system.

In Cohn and Heerwagen's‡ experiments with Lecher's method a condenser was added to the ends of the wires.

Blondlot§ also experimented with parallel wires, but used an oscillator of quite different construction. In Lecher's arrangement the capacity is large compared to the self-induction; in Blondlot's the reverse is the case. The latter has the advantage that the damping is much diminished.

These "wire-waves" have been the subject of numerous investigations, a notable one being that by Drude‖. He found that the oscillator must be considered as composed of the Blondlot semicircular primary exciter, together with that portion of the secondary wire-system as far as the first bridge; and that when the bridges are properly placed there is resonance between this oscillator and the rest of the system. Very convenient forms of this apparatus are given by Coolidge¶ and Hormell**.

Donle††, who used chiefly the Blondlot oscillator, joined the ends of the parallel wires with a glow-lamp. His aim

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* See Poincaré, *Les Oscillations Électriques*, Art 55 & fol.; J. J. Thomson, 'Recent Researches,' p. 340.

† E. Lecher, Wied. *Ann.* xli. p. 850 (1890).

‡ Cohn and Heerwagen, Wied. *Ann.* xliii. p. 343 (1891).

§ R. Blondlot, *Comptes Rendus*, cxiii. p. 628 (1891).

‖ P. Drude, "Eine bequeme Methode zur Demonstration des electrischen Brechungsexponenten von Flussigkeiten," Wied. *Ann.* lv. p. 633 (1895).

¶ W. D. Coolidge, Wied. *Ann.* lxvii. p. 578 (1899).

** W. G. Hormell, Am. Journ. Science, xii. p. 433 (1901).

†† W. Donle, Wied. *Ann.* liii. p. 178 (1894).

was to diminish the wave-length, which he reduced to 130 cms. Coolidge's smallest wave-length was 12 cms.

In Rubens's experiments the exciter was of the Hertzian form, with plates 40 cms. square. The two opposing parallel plates were but 10 cms. square, though the smaller plates are not quite as efficient as those of equal size*. From these smaller plates the parallel wires went out—in this instance to a distance of 570 cms.—and were explored by a bolometric method. Rubens † found that the oscillations along the wires were not the same as those of the oscillator; in other words, the oscillations were not forced along the wires, but were those natural to them.

These experiments were verified by Rutherford ‡, who substituted a magnetic detector for the bolometer, and found it equally sensitive.

In all these experiments it will be observed that the wave-lengths determined along the wires are not those proper to the oscillator, but are either due to the detector used or to the wires vibrating naturally.

In Birkeland's § and Jones's ‖ researches the reverse seemed to be the case. The wire-systems were both similar to that of Sarasin and de la Rive, but the means of exploration were different. Birkeland examined the potential at various points of his wire, which was 30 m. long, by measuring the length of the spark which leaped from it to an earth connexion, the existence of the spark being indicated by a telephone receiver held to the ear. He obtained minimum points which varied as the period of the oscillator was changed, thus indicating that the measured wave-length depended on its period. These minima were unequally spaced, which irregularity was attributed to the damping of the waves and the loss on reflexion at the ends of the wires; but the explanation does not seem entirely satisfactory ¶.

Jones used a thermal junction inserted at different points of his wire which was 130 m. in length, the effect being indicated by a low-resistance galvanometer in circuit with it. The oscillator was of the usual type, with plates 40 cms. square, but the length of the connexion between the plates is not given. Several well-defined maxima and minima were observed, and the wave-length was determined to be approximately 4·3 m. It is interesting to read that "several

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* Drude, *Physik des Aethers*, p. 446.

† H. Rubens, Wied. *Ann.* xlii. p. 154 (1890).

‡ E. Rutherford, Phil. Trans. A, 1897, vol. clxxxix. p. 1.

§ Kr. Birkeland, Wied. *Ann.* xlvii. p. 583 (1892).

‖ D. E. Jones, Brit. Assoc. Report, 1891, pp. 561–2.

¶ See Poincaré, *Les Oscillations Électriques*, p. 176.

curious results were recorded for which no explanations were forthcoming"[*].

It may be worth while to recall how the wave-length of Hertz's plate oscillator was determined. He obtained it with the aid of his circular resonator, but, as has been already remarked, the wave-length thus found is always eight times the diameter of the resonator. If, then, we could know when the resonator was exactly in unison with the oscillator, the wave-length could be deduced with considerable accuracy. But this is not at all possible; the resonance is far from being sharply defined. Indeed, Hertz says that the same resonator, of diameter 70 cms., was in resonance with three different oscillators. The first consisted of two spheres of diameter 30 cms.. connected by a wire 70 cms. long, with a spark-gap in the middle; the second, of two plates 40 cms. square, joined by a wire 70 cms. long with a spark-gap as before; the third had plates of the same size, but the wire was 60 cms. long[†].

Thus the wave-length emitted by each of these was taken to be the same, namely, 560 cms. Now the period and wave-length of the first oscillator have been found theoretically. Hertz[‡] calculates the period to be 1·26 hundred-millionths of a second, and the wave-length to be 4·6 m., while Drude[§] makes the latter 4·8 m. Both values differ considerably from that obtained by resonance. Again, the second and third oscillators differ considerably in period, though that of the second was found to be the same as that of the first (see below). We must conclude that the wave-length 5·6 m. is not a very close approximation.

In the experiments to be described presently it will be seen that oscillators of the same type may differ decidedly in their behaviour; that some seem able to force their vibrations upon a wire, while others cannot. The wave-length of an oscillator the same as the third of the three just described was concluded to be 5·88 metres.

II. *Experimental Arrangement.*

While engaged during the session 1900–1, in the Jefferson Physical Laboratory of Harvard University, on another

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[*] 'Nature,' vol. xliv. p. 454 (1891).

[†] Hertz, 'Electric Waves,' Art. V. pp. 81–2; Art. VI. pp. 96–7; Art. VII. pp. 108 & 113.

[‡] Hertz, ibid. pp. 51 & 270 (note 6).

[§] Drude, *Physik des Aethers*, p. 397. See also J. J. Thomson, 'Recent Researches,' Arts. 289 & fol.

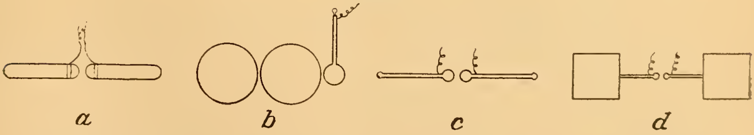
investigation* in which the magnetic detector was used, the fact that an electrical disturbance about a wire parallel to the wings of the detector exerted a strong action on the detector was continuously and painfully evident. Indeed, the effect arising from the connecting wires at first entirely masked the true radiation from the oscillator.

This suggested the possibility of conveniently exploring the field along a wire by shortening the wings of the detector and then placing it close to the wire at various points in its length. The experiment was tried, but the demagnetization of the detector was small. However, on removing one wing and placing the other near the wire the effect was much greater and easily measurable.

But the action with one wing is not at all the same as with two. When the detector with two wings is placed along the wire, the surging in its helix and the consequent demagnetization is greatest at points where the current oscillation is greatest, *i. e.* at a current loop; the effect is least at a current node. With a single wing these results are exactly reversed, the effect is greatest at a current node, which is, of course, a potential loop. This can be explained in the following way:—The little wing and the portion of the wire just beside it act as a miniature condenser, and when there is a maximum variation of potential in the element of wire there will also be a maximum variation in the detector wing, which will cause currents to surge back and forth in the helix, and so to demagnetize the iron core. At a current loop (or potential node) the variation in potential is a minimum, and so the detector when placed there will show minimum demagnetization. Indeed, the indications of the magnetic detector should be precisely similar to those of the bolometer as used by Rubens.

An attempt was then made to force standing waves in a wire, and preliminary experiments seemed to show the possibility of determining the wave-lengths of oscillators in this way. Some measurements were made then, which, since the writer's return to Toronto, have been considerably extended.

Fig. 1.



The oscillators were of four kinds, illustrated in fig. 1.

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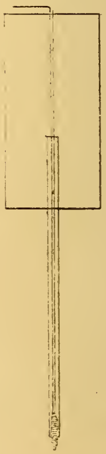
* C. A. Chant, 'An Experimental Investigation into the "Skin"-effect in Electrical Oscillators,' Am. Journ. Sci. xiii. p. 1 (1902); Phil. Mag. [6] vol. iii. p. 425 (1902).

The cylinders of (*a*) were 2·5 cms. in diameter and 12·5 cms. long, with hemispherical ends; the spheres of (*b*) were of two sizes, namely, with diameters of 10 cms. and 30 cms. respectively; the larger spherical ends of (*c*) were 19 mm., the smaller 6 mm., and the straight portion 4·2 mm. in diameter, while the length over all was 12·5 cms.; in (*d*) is shown the ordinary Hertzian plate oscillator.

The sparks were produced by an induction-coil capable of giving sparks 12·5 cm. long, and fed by five accumulators in series.

The interrupter was similar to that used in the other investigation. It consisted in a platinum-tipped rod, which, by means of a motor, was alternately plunged into and withdrawn from mercury, the surface of which was kept clean by a stream of water continually flowing over it. In series with this were a pendulum interrupter and a contact-key. This key was depressed during any desired number of vibrations of the pendulum—usually five swings—during which time the coil was interrupted approximately 60 times. This number, of course, varied somewhat with the speed of the motor, but it did not change much during any series of readings.

Fig. 2.

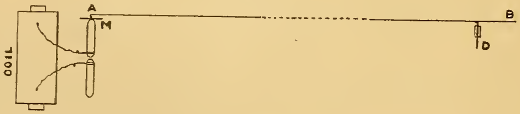


The magnetic detector was the same as that used in the other research. It had twenty pieces of iron, 0·014 cm. in diameter and 1 cm. long, insulated from each other by paraffin, and wound over with 90 turns of fine insulated wire. It was mounted in the end of a glass tube, and all held on a small sheet of hard rubber by means of wax. It is shown one-half of natural size in fig. 2.

The magnetometer and telescope, as well as the method of placing the detector behind the magnetometer, were as described in the former paper.

The manner of producing the oscillations along the wires is shown (for the cylinders) in fig. 3. AB is a long straight wire (0·7 mm. in diam.) ending at A in a small knob 6 mm. in diameter, which was separated from an end of one of the cylinders by a piece of mica, M, usually 0·15 mm. thick. By this means the surgings on the cylinders were impressed

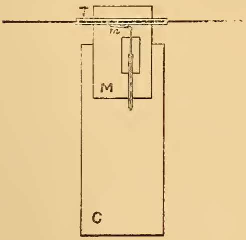
Fig. 3.



upon the wire, which was explored by placing the little detector near it at different points in its length.

Since the magnitude of the effect depends on the distance the detector wing is held from the long wire it was necessary to regulate this accurately. To do so a small glass tube about 4 cms. long, T, fig. 4, with bore just great enough to allow it to slide over the wire, was taken, and to the outside of this was fastened a bit of finely-drawn tubing, *m*, into which the wing fitted snugly. In all the experiments the wing was 1 cm. long.

Fig. 4.



The glass tube was attached to a piece of hard rubber (or mica), M, which, again, was cemented to the top, C, of a carriage which moved along beside the wire.

Thus, to examine any portion of the wire, the carriage was moved along to the required place, the distance of which from the end of the wire was measured by a scale on the ways on which the carriage moved. The detector was magnetized, then placed in its pocket beside the glass tube, and sparks made to pass at the oscillator for a certain length of time. The detector was then removed and examined by the magnetometer. This process was systematically carried out, beginning at the end of the wire and advancing by equal spaces.

For the linear oscillator, shown in fig. 1, *c*, the arrangement was precisely the same as for the cylinders. For the Hertzian oscillators, fig. 1, *d*, a rounded end was given to one of the plates by taking a piece of brass rod 6 mm. in diameter and about 2 cms. long, rounding the ends, and then making a slit in one end, which allowed it to be slipped over the plate. This is shown in fig. 5.

Fig. 5.

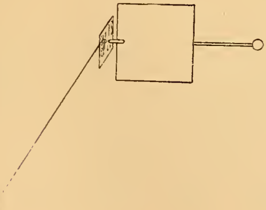
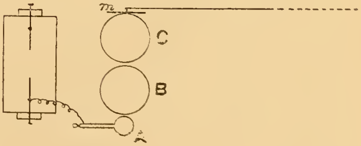


Fig. 6.



The arrangement for the spherical doublet is shown in fig. 6. When the coil was in action sparks passed between

A and B and B and C, and the oscillations on the sphere C were transmitted to the wire across the mica plate, *m*.

The wires used were quite short, ranging from 1 metre to 8·6 metres in length.

III. *Results of Experiments.*

It will be convenient to divide the results into two parts:—A, those obtained with the oscillators *a*, *b*, *c* of fig. 1: and B, those with the Hertzian oscillators.

A. *Cylindrical Oscillator* (fig. 1, *a*).

In Pl. VII. fig. 7, *a*, *b*, *c* are shown curves obtained with the cylindrical oscillator, which was made of sheet platinum on a wooden form with well-shaped hemispherical ends. Here, as always, the greatest variation in potential was at the end of the wire. It gradually fell until a minimum was reached at approximately 20 cms. from the end, and after another rise it dropped again to a minimum at approximately 60 cms. Each of the last two curves gives a half-wave-length of 40 cms., the first one 38 cms., or a mean wave-length for the oscillator of approximately 79 cms.

In every instance the actual readings are shown.

Linear Oscillator (fig. 1, *c*)

Curves obtained with this oscillator are shown in Pl. VII. fig. 7, *d*, *e*. Curve (*d*) is the mean of two sets of readings with five swings of the pendulum. The mean of five sets, each of two swings, gave the same minima, though the curve was not so good. Curve (*e*) is a repetition of the second portion of the readings; it is the mean of two sets of five swings each.

Here three minima are easily seen at 19, 59, and 99 cms. respectively, from the end; and the wave-length is thus approximately 80 cms.

Spherical Doublet (fig. 1, *b*).

Curves for this oscillator are given in Pl. VII. fig. 8. It was much more difficult to get consistent series of readings with it. Curves (*a*) and (*b*) are for the 10-cm. spheres. The half-wave-lengths deduced are respectively 19 and 19·5 cms., with a mean wave-length of 38·5 cms. Curves (*c*) and (*d*) are for the 30-cm. spheres. The half-wave-lengths from these are 61 and 62 cms. respectively, with a mean wave-length of 123 cms.

These curves are not as smooth as the former ones, but are perhaps as good as one should expect with so dead-beat an oscillator.

From the results with the 10-cm. spheres the ratio of wave-length to diameter is 3·85, while with the 30-cm. spheres this ratio is 4·1 *. The theoretical value given by J. J. Thomson † is 3·6. Further exploration of the wire revealed no more minima.

B. *The Hertzian Oscillators.*

With the Hertzian oscillators the results were quite different from those just given, and indeed they differed considerably amongst themselves.

The first oscillator tried had sheet-zinc plates 40 cms. square, with the straight wire between them 60 cms. long; and the wire transmitting the waves was 860 cms. long. One minimum was very well marked, but there were no more clear ones. Then a second oscillator, with 20-cm. plates, and otherwise of just half the size of the former was tried, but the minimum, instead of being half the distance from the end, was much farther from it. This led to the making of additional oscillators, with plates 10, 15, 25, 30, 35, 50 cms. square respectively, and with the wires between of proportional length. The spark-knobs were 19 mm. in diameter, the same knobs being used with all the oscillators.

Using these oscillators, readings were taken with wires from 100 to 860 cms. long; and the results obtained are exhibited in the accompanying table and curves. In the table the positions of the minima are given by stating their distances in centimetres from the free end of the wire. There was always one more marked than the others, and this one, indicated in the table by more prominent type, will be referred to as the *chief* minimum.

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* It may be interesting to compare values of this ratio obtained by other experimenters. Some are given in the following table, taken from a paper by Hull in the 'Physical Review,' vol. v. p. 231, 1897:—

Diam. in mm.	λ. in mm.	λ/Diam.	Experimenter.
80	200	2·50	Righi
37·5	106	2·83	,,
8	26	3·25	,,
7·8	18·4	2·36	Bose
19·3	91	4·71	Hull
9·3	43	4·62	,,
7·9	40	5·18	,,

† J. J. Thomson, 'Recent Researches,' p. 370.

In Pl. VII. fig. 9 are shown readings and curves obtained with the 20-cm. oscillator, with various lengths of wire, and in fig. 10 are similar readings with the oscillator of double the size, *i. e.* with 40-cm. plates; while in fig. 11 is shown a series of three successive curves given by the 20-cm. oscillator with the same length of wire. These illustrate the method moderately well.

Remarks on the Table and the Curves.

A glance at the table will show that the oscillators used can be divided into two distinct groups, the first including the four smaller ones, and the second the three larger ones, while the oscillator with 30-cm. plates lies between the two groups. The results with each group are consistent amongst themselves, while the 30-cm. oscillator behaved in a very irregular manner.

For the first group (the smaller ones) the positions of the minima for any particular length of wire are independent of the size of the oscillator, *i. e.* they depend only on the wire's length. In this case the oscillator does not force its period on the wire.

In the second group, on the other hand, the positions of the minima depend only on the size of the oscillator, not at all on the length of the wire.

The conclusion seems natural that, in this latter case, the distance of the minimum from the free end is one quarter of the wave-length of the oscillating system. The values of this quarter-wave-length deduced from the table are:—

For 35-cm. oscillator... 132·7 cms. (mean of 11 results).
,, 40 ,, ... 147·1 ,, (,, 21 ,,).
,, 50 ,, ... 171·5 ,, (,, 6 ,,).

Now it is possible that the proximity of the wire to the oscillator may have the effect of virtually increasing the size of the oscillator, and if such is the case all the quarter-wave-lengths so determined are too great. According to Poincaré's* deduction from the homogeneity of the fundamental equations, the wave-length of an oscillator or resonator varies directly with its linear dimensions. In fig. 12 the points A, B, C have abscissæ proportional to the dimensions of the three larger oscillators and ordinates proportional to the quarter-wave-lengths given above. It is seen that they lie very approximately on a straight line, but this line does not pass through the origin. Let us now draw a line parallel to it and passing

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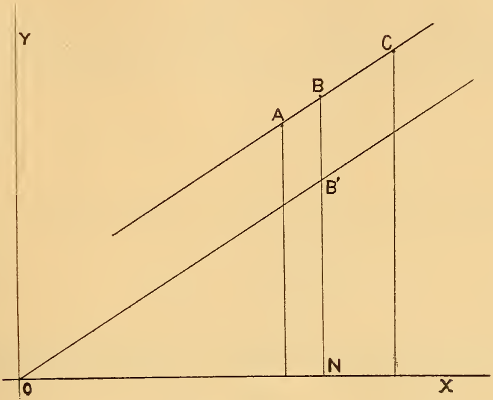
* Poincaré, *Les Oscillations Électriques*, Art. 53.

through the origin. The ordinate B′N of this line, corresponding to the 40-cm. oscillator, has a length of approximately 103 cms. Thus if the principle of direct proportionality, stated by Poincaré, held without limit to its application, the arrangement of the wire as in the experiments, should be equivalent to adding 44 cms. to the quarter-wave-length of each of the three larger oscillators. On the other hand, the fact that varying the length of the wire from 3 m. to 8·6 m. had no effect on the position of the minimum, seems to show that the wire did not act in the manner referred to. In other words, the quarter-wave-lengths given are proper to the oscillators.

Fig. 12.



Experiments with the first and second Hertzian oscillators referred to above, gave the following values for the quarter-wave-length:—

For 40-cm. plates, straight connexion 70 cms.... 154·4 cms.
30 „ spheres, „ „ „ ... 153·9 „

These are practically identical.

For all wires of 3 metres and upwards in length there is a well-defined minimum between 10 and 15 cms. from the end next the oscillator. In figs. 9, 10 (Pl. VII.) is shown a portion of each curve near the oscillator in continuous line, and also in broken line. In this neighbourhood the oscillator exerted a strong action directly on the detector. In order to allow for this, readings were first taken as usual (shown by continuous line); then the wire was removed and readings taken at exactly the same points. These latter were then subtracted from the former, and the broken line shows the

Table of

Size of Oscillator Plates.	Distance, in centimetres, of minima							
	Wire 860 cms.	Wire 850 cms.	Wire 840 cms.	Wire 830 cms.	Wire 820 cms.	Wire 810 cms.	Wire 800 cms.	Wire 790 cms.
10 cms.								*187*...635 ...780 655 ...781 625?...780 *187* *193* 645 ...781
15 cms.								*188*...635 ...780 *185*...618?...780 *182*
20 cms.	*200*	*192*	*182*...710	*190*. .675. .820	*198* *200*	*208*...645 *205*...650	*188*. .620 ?. .790 *190*. .650 ...790	*193*...638 ...780
25 cms.								*180*......... 655...780 *186*......... 630...780 *190*
							MEAN	*187·1*
30 cms.								*130*...230...585...780 *140*...220...620...780 *130*
35 cms.			...					*132*......... 630...775 *135*......... 620...770 *133*
40 cms.	*148*...735?	*150*.. 740?	*145*...750	*150*...745	*150*...720?	*150*...645 *148*...655	*150*...650...790	*150*. .350. .625?. .780 *150*. .345. . —- . .780
50 cms.								

MINIMA.

from free end of wire.						
Wire 700 cms.	Wire 600 cms.	Wire 500 cms.	Wire 400 cms.	Wire 300 cms.	Wire 200 cms.	Wire 100 cms.
	175 178 178 177		197 197 199 203			
	183 178 182 186		148...205 152...197 150...200 203 152			
185......... 540..690 245...345..542..690 170 175	177...460...590 175...480...590 175...450...590 175	207...350 ...490 195...347 ...490 195...365 ...490 188 ? 195 ?	202...390 210...390 206...390	154...290 155...290 152	150 148	85 85
	177 182 184		205 208 207 200			
......	178·8	......	202·6			
	125 142 ? 119...200 ? 136		124...196...260 140...200...262 142...215 125...207...271 127...197...272 122...200...260			
	134 134 132 132		133 132 132 131			
150...360...550...688 142...355?. 550...690 144	154...430 ...590 146...430 ...590 147...430?...590 150...440 ...590	152...355?...490 150...355 ...490 150...335?...490 154	149...387 147...387 149	143...290 150...290 150	140 138	82·5 82
	170 170 172 170	170 177				

result. Here it is assumed that the action of the oscillator and of the wire singly are equivalent to the two together. To examine this minimum more closely readings were taken at intervals of one centimetre. There is no doubt of its existence; it is about 10 cms. from the end for the smaller oscillators and slightly farther for the larger ones. I find it difficult to give the significance of this.

Other minima were found, but they were not so well defined. They are, no doubt, due to natural oscillations of the wire, but they are hard to identify.

For the wires 300 and 400 cms. long the chief minima are at the middle points.

The question of the dependence of the positions of the minima on the detector is interesting and important; and that there is no such connexion was shown in the following way. A second helix, similar to that of the detector, was soldered to the free wire running up beside the one bearing the wing, thus practically doubling the capacity and inductance; but there was no displacement of the minima. The period of the detector must be many times that of the oscillators.

In the near future I hope to apply the magnetic detector to the exploration of much longer wires, in which case the phenomenon of standing waves should be more distinctly shown.

University of Toronto.

XXXII. *On the Spectrum of an Irregular Disturbance.* *By* Arthur Schuster, *F.R.S.*[*]

In the February number of the Philosophical Magazine Lord Rayleigh quotes under the above title the following remark, which I made in a paper on the "Periodogram of Magnetic Declination as obtained from the Records of the Greenwich Observatory during the years 1871–1895:"

"Absolute irregularity would show itself by an energy-curve which is independent of the wave-length, *i. e.*, a straight line when the energy and wave-length or period are taken as rectangular coordinates, while the perfect regularity of homogeneous vibrations would show itself as a discontinuity in the energy-curve."

Discussing the same problem, Lord Rayleigh arrives at the different conclusion that the energy of an arbitrary disturbance is proportional to dk or k^2dk, according as the

[*] Communicated by the Author.

velocity-curve or the displacement-curve is taken to be arbitrary. Here k is the frequency, or the inverse of the period. I arrived at my own conclusion by translating the results of an investigation, in which Fourier's analysis was employed, into what I thought to be its complete optical analogy. The definitions that I gave of what I called the Intensity of the Periodogram are, I think, quite clear and definite, but the optical and mechanical analogy is not as good as I thought. This depends on the fact that I took the periodic time to be the independent variable instead of the frequency. It does not matter which we take, if we deal only with a number of separate periods, each having finite amplitude, the ordinates in that case measuring energy, but if the periods approach each other indefinitely and the energy between any two of them is to be represented by the area included between the corresponding ordinates, the curve and the axis of abscissa, the abscissa must represent frequencies unless some correction is made to the ordinates.

I was therefore wrong, when translating my results into optical language, to compare the ordinate of the periodogram, as I had defined it, with the intensity of a luminous disturbance, and Lord Rayleigh's criticism is quite justified.

It may be desirable to alter my definition so as to make the optical analogy complete, though practical considerations have to be taken into account.

Whether frequencies or periods are best plotted depends on individual cases, but if we take the period we may still preserve the optical analogy which in that case would be with the spectrum of a diffraction-grating. It would only be necessary for this purpose to divide the ordinates by the squares of the periods. This would not involve any additional arithmetical labour, unless the Fourier coefficients are obtained by mechanical means. As Lord Rayleigh points out, meteorological irregularities should be made to correspond to velocities in the mechanical analogy, and this I had realized.

I should like, in conclusion, to refer to a subject intimately connected with the matter under discussion. We constantly meet with the assertion that Röntgen radiations are due to impulses and not to regular oscillations. I have no objection to this statement if its meaning is clearly understood, but generally it is put forward in such a way as to imply that an impulse is something smaller, or even something of a different order of magnitude, than a periodicity of short wave-length. The statement that Röntgen rays are impulses differs from the statement that Röntgen rays are short waves, only in so far that the impulse theory asserts that there are long waves present as well as short ones; but supposing that a violent disturbance, lasting an indefinitely short time, leaves the inner side of a Röntgen tube, where it is generated, it will quickly become modified. Before it has traversed the glass walls, the impulse has already spread out owing to the absorption of some of the periods in the glass, and if this modified impulse is further sent through a screen like a thin sheet of aluminium or black paper, all the visible rays are cut off, and the invisible ones down to at any rate very short lengths. The Röntgen radiation that affects a fluorescent screen or a photographic plate therefore can only contain waves which are either exceedingly short or very long, provided it consists of transverse waves at all.

That an impulsive motion of æther cannot possibly remain an impulsive motion, after traversing media with selective absorption, or media in which dispersion takes place, should be clearly understood. I may, perhaps, in connexion with this, quote a sentence from a letter I wrote to 'Nature' a few weeks after Röntgen's discovery was first announced. At that time there was no theory put forward, except the original one of Röntgen, that the rays were due to longitudinal vibrations. The absence of interference was considered to be an objection to any undulatory theory.

"The absence of interference would not, however, be sufficient to show that the radiation is not of the nature of ordinary light, but only that it does not possess sufficient regularity, or, in other words, that the disturbance is not sufficiently homogeneous. That this is the case is not at all impossible, for the radiation is produced by an impact which, in the first instance, may be an impulsive motion propagated outwards, and, after passing through the screen, would only possess such regularity as is impressed upon it by the absorption of the longer waves"[*].

I think that the theory of impulses, as well as its limitations, is clearly expressed in this passage.

XXXIII. *On the Charge of Electricity carried by a Gaseous Ion. By* J. J. Thomson, *Cavendish Professor of Experimental Physics, Cambridge*[†].

In the Philosophical Magazine for December 1898, I gave a determination of the electric charge carried by an ion in a conducting gas. The method employed in this investigation was as follows:—If n is the number of charged positive and negative ions per unit volume of the

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[*] 'Nature,' vol. liii. p. 268.

[†] Communicated by the Author.

gas, e the charge carried by an ion, u the mean velocity of the positive and negative ion in a given electric field, the current through unit area of the ionized gas in this field will be neu; hence if we measure this current we can determine the value of ne, as u the velocity of the ions in a field of known strength has been determined by Zeleny and Rutherford. The number of ions n was measured by depositing by C. T. R. Wilson's method a cloud on the ions and determining the number of particles of water vapour in unit volume of the cloud.

Since these experiments were made, the progress of our knowledge of the electrical properties of gases has made several improvements in the method possible. The discovery of radium has furnished us with a constant source of radiation very much easier to work with than the variable Röntgen rays, which were the source of ionization in the earlier experiments. The introduction of the Dolezalek electrometer, which can be made to give a deflexion of 20,000 or more scale-divisions for the potential-difference of one volt, makes the determination of the exceedingly small currents passing through the ionized gas much more accurate than was possible with an electrometer of the type used in the earlier experiments, which only gave a deflexion of 50 divisions for a volt; and although the Dolezalek electrometer has a much greater capacity than the older form, the difference is not sufficient to neutralize the advantage gained by the increased sensitiveness.

The consideration which influenced me most in repeating the experiments was the increase in our knowledge of the laws governing the deposition of the cloud round the charged ions. The cloud is made by cooling the air by a sudden expansion. I had noticed in the earlier experiments that when this expansion was increased so that the ratio of the volume of the air after expansion to that before exceeded the value 1·3, there was a noticeable increase in the number of particles in the cloud. Mr. C. T. R. Wilson, who has made (Phil. Trans. cxciii. p. 289) a systematic study of the relative efficiency of negative and positive ions as nuclei for condensation, found that while a cloud begins to be deposited round negative ions when the expansion is 1·25, it is not until the expansion is equal to 1·31 that the positive ions are caught by the cloud; thus if all the particles are caught by the cloud, the number of water particles in the cloud formed with the larger expansion when both positive and negative ions are caught ought to be twice that with the smaller when only the negative ions are caught. In my earlier experiments the increase in the number of particles with the larger expansions, though marked, was not so great as this, pointing to the conclusion that all the positive ions had not been caught by the larger expansion.

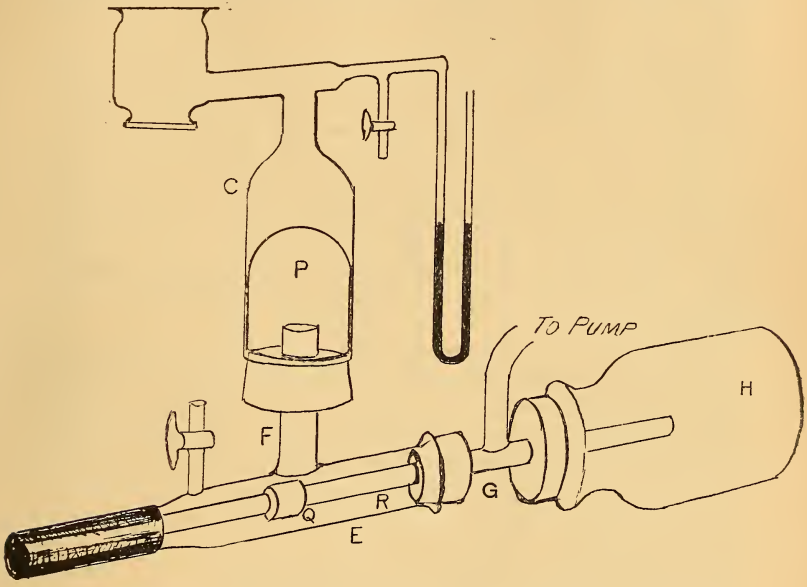
It is obvious that since the moisture begins to deposit first on the negative ions, unless the rate of expansion is very rapid, the drops formed in the earlier stages of the expansion round the negative ions will have time to grow and form convenient nuclei for further condensation, so that as the expansion increases, the tendency will be for the moisture to deposit on the drops already formed rather than to form new drops round the positive ions. Thus with slow expansions we should expect the number of drops formed to be more nearly equal to the number of negative ions than to the sum of the positive and negative ions.

The results of the present experiments show that this was the case in the expansions used in the earlier experiments. The value of n determined in those experiments was but little greater than the number of negative ions; as ne is the quantity determined by the electrical experiments this caused the value of e to be nearly twice its real value.

The results of Mr. C. T. R. Wilson's experiments give us the means of testing whether the expansion is rapid enough to catch the positive as well as the negative ions, for if we determine the number of drops in the cloud when the expansion is less than 1·31, and again for expansions considerably greater than this value, and find that the latter number is twice the former, we may feel sure that the large expansion has been rapid enough to catch the positive ions. This test has been applied throughout the experiments described in this paper.

The apparatus for producing the cloud was of the kind used by Mr. Wilson. The expansion is produced by the motion of a light glass piston P which slides freely up and down the larger tube C, the lower end of the piston is always below the surface of a layer of water at the bottom of the tube. The inside of the piston is put in connexion with a vessel E by means of tube F, which passes up through the layer of water. H is a large vessel exhausted to as low a pressure as possible; H and E are connected by the tube G, the end of this tube in E is closed by an indiarubber pad which can be quickly removed by means of the rod R; when this is done (the piston being at the top of its range) the pressure of the air drives the piston down, and the air in C and the vessels connected with it expand. The amount of this expansion can be adjusted by altering the height to which the piston is raised before the expansion begins.

In order to make the expansion take place with sufficient rapidity the piston was made of very light glass. The vessel H was exhausted until the pressure in it was but little greater than that due to the water vapour, and especial care was taken that all the tubes, through which air had to rush during the expansion, were of as wide a bore as possible and without any constrictions; when these precautions were taken, it was found that the expansion was rapid enough to catch all the positive ions. This is shown by the following results, which are a sample of those obtained in a large number of experiments.



Ionization produced by a sample of radium A placed at a height 10 cms. above the top of the vessel in which the cloud is formed.

Pressure of atmosphere 768 mm. Temperature 19·5.

Expansion.	Time taken by drops in cloud to fall 1 centim.	Number of drops in cloud reckoned per c.c. of the volume of the gas before expansion.
1·346	9·7 sec.	$6·6 \times 10^4$
1·333	9·8 ,,	6·7 ,,
1·32	9·1 ,,	5·7 ,,
1·31	8·25 ,,	4·8 ,,
1·29	7·1 ,,	3·6 ,,
1·28	7·12 ,,	3·6 ,,
1·27	7 ,,	3·55 ,,
1·257	6·5 ,,	2·9 ,,

Thus we see that when the expansion is greater than 1·33, the number of nuclei caught by the cloud does not depend upon the amount of the expansion. When this is between 1·33 and 1·29 this number diminishes, until when the expansion is 1·29 the number caught is only half that at the higher expansions. The number now remains independent of the expansion until this falls below about 1·27; for expansions smaller than this the number of nuclei caught falls off rapidly with the expansion. We conclude from this that for expansions greater than 1·33 all the ions positive as well as negative are caught by the cloud; then when the expansion is smaller than 1·33 and greater than 1·29 some, but not all, of the positive ions and all the negative ions; for expansions from 1·29 to 1·27 all the negative but none of the positive ions are caught in the cloud; and that when the expansion falls below 1·27 only a fraction of the negative ions are caught.

The values of the numbers given in the third column of the preceding table were calculated by the following method: let q be the volume of water deposited through the expansion per unit volume of the expanded gas (this was calculated by the method given in the earlier paper), n' the number of drops per unit volume of the expanded gas, a the radius of one of these drops; then $q = n' \frac{4\pi}{3} a^3$.

If v is the rate at which the drops fall, then

$$v = \frac{2}{9} \frac{ga^2}{\mu},$$

where μ is the coefficient of viscosity of the gas. In the case of air $\mu = 1{\cdot}8 \times 10^{-4}$ and v is therefore equal to $121 \times 10^4 a^2$; hence

$$n' = \frac{3q}{4\pi} 1331 \times 10^6 v^{-\frac{3}{2}}.$$

The number of drops reckoned per unit volume of the gas before expansion is $n' \times$ expansion. The velocity of the drops was determined by measuring the time taken by the top of the cloud to fall through two consecutive centimetres. With the drops used, these times were very approximately equal to each other; with clouds consisting of very fine drops which fall slowly, the time taken to fall through the second centimetre is often considerably greater than that for the first, owing to the diminution produced by evaporation in the size of the drops.

To facilitate the measurement of the velocity the inside of the cloud-chamber was lined with damped black silk, a narrow slit being left to allow the cloud to be observed. The bottom of the chamber was a plane piece of glass, and the fog was illuminated by a vertical beam of light reflected from a mirror. The top of the cloud-chamber was made of sheet aluminium ·3 mm. thick, this allowed the rays from the radium to pass through. Two different samples of radium were used: the one called B was placed at a distance of 15 cms. above the top of the cloud-chamber, the other (a weaker specimen), A, was 10 cms. above it. The radium was spread over surfaces measuring 7 cms. by 5 cms., and was kept in its place by a thin sheet of mica.

The electrical part of the apparatus included a guard-ring condenser, the upper plate of which was a circular piece of aluminium of the same thickness and cut from the same plate as that forming the top of the cloud-chamber; the lower part of the condenser consisted of a circular plate of aluminium 2·47 cms. in radius in one piece of apparatus, 4·55 in another, surrounded by a guard-ring also of aluminium; the distance between the upper and lower plates of the condenser was 1 cm. The radium was placed above the upper plate of the condenser and at the same distance from it as in the cloud experiments, *i. e.* the sample A was placed 10 cms. and the sample B 15 cms. above the plate. The lower circular plate was connected with one pair of quadrants of a Dolezalek electrometer, the wire making the connexion being led through a metal tube connected with the earth. The radium was surrounded by lead guards so as to confine its radiation to the neighbourhood of the condenser. The radium, the guard-ring condenser, and a second condenser used to determine the capacity of the system were placed inside a box lined with metal. The top plate of the condenser was maintained at a constant potential; the lower plate, which was in connexion with the electrometer, was initially put to earth. When the earth connexion was then broken, a current of electricity passed between the plates through the air ionized by the radium; this current charged up the electrometer, and the needle was deflected. Knowing the deflexion of the electrometer produced in a given time, the quantity of electricity received by the lower plate in that time can be calculated, if we know the capacity of the electrometer and its connexions.

If u is the mean velocity of the positive and negative ions under the electric field applied to the air between the plates, n the number of ions (positive and negative) per c.c. of the air, e the charge on an ion, A the area of the lower plate, the quantity of electricity received by the lower plate in unit time is $neuA$. If C is the capacity of the electrometer and its connexions, this quantity of electricity will produce a potential-difference of $neuA/C$ between the quadrants, the deflexion of the electrometer is proportional to this difference of potential; hence to deduce the value of ne from the readings of the electrometer, we require to know the value of C. This was found by connecting with the lower plate of the condenser another condenser of known capacity C′, and again measuring the difference of potential between the plates after the current has been flowing for one second; this is equal to $neuA/(C+C')$; hence if δ_1, δ_2 are the deflexions of the electrometer before and after C′ was inserted, we have

$$\frac{\delta_1}{\delta_2}=\frac{C+C'}{C},$$

or

$$C=\frac{\delta_2 C'}{\delta_1-\delta_2}.$$

The effective capacity of the Dolezalek electrometer depends mainly upon the charge on the needle, and may therefore vary considerably from time to time, thus in these experiments C ranged from 200 to 900 cms.: it is therefore very necessary to determine the value of C for each observation. The proceeding adopted was to take, say, six consecutive readings with the condenser C′ (whose capacity was ·001 microfarad) out (in three of these the upper plate was at a higher potential than the lower plate; in the other three the sign of the potential-difference was reversed); then six with it in, and then another six with it out.

The high effective capacity of the Dolezalek electrometer makes it less sensitive for measuring small quantities of electricity than for potential-differences.

The value of n in the electrical experiments is the number of ions per c.c. of the gas when exposed to the electric field; in the cloud experiments the value found for n is the number when there is no electric field. The electric field tends to drive the ions out of the gas, so that the number in the electric field will be less than the other; when the field is strong the difference is very marked, but with the weak fields (about $\frac{1}{3}$ of a volt per cm.) used in these experiments the difference is inappreciable; we can test whether the field is weak enough to ensure this by measuring the currents under different electric fields: since u the velocity of the ion is proportional to the electric force, if the electrometer deflexion is also proportional to this force, n will be constant, *i. e.* will not alter with the force. The electric force was reduced to one-half its value, *i. e.* $\frac{1}{6}$ of a volt per cm., and the electrometer deflexions again determined: as these were found to be just half the value with the double force, it was concluded that with the weak fields used in these experiments the value of n was sensibly the same as that without fields.

To test whether the secondary ionization due to the incidence of the radiation on the aluminium was appreciable, the observations were repeated with the lower plate covered with wet tissue-paper. It was found, however, that the results obtained with the wet paper were the same as those without.

The following are the results of experiments made to determine the number of ions per c.c. due (1) to a specimen of radium A placed 10 cms. above the top of the chamber in which the cloud was produced, (2) to another specimen (B) placed at a height of 15 cms. above the cloud-chamber. The first table contains the number of positive and negative ions caught by expansions greater than 1·33, the second the number of negative ions caught by expansions less than 1·33.

Expansions greater than 1·33.

Pressure of atmosphere.	Temp.	Difference in pressure be- and after expansion.	Expansion.	Time taken by cloud to fall 1 cm.		Ions per c.c.	
				Radium A.	Radium B.	Radium A.	Radium B.
773	19·5° C.	193	1·343	9·65 sec.	18·6 sec.	$6\cdot3\times10^{4}$	17×10^{4}
753	19	185	1·335	10	...	$6\cdot65\times10^{4}$	
749·5	19	184	1·336	10·25	...	$6\cdot8\times10^{4}$	
761	19	185	1·33	10	18·25	$6\cdot66\times10^{4}$	$16\cdot3\times10^{4}$
772	19	193	1·343	9·5	17·25	$6\cdot3\times10^{4}$	$15\cdot5\times10^{4}$
768	19·5	193	1·344	9·75	18·5	$6\cdot4\times10^{4}$	$16\cdot9\times10^{4}$
					Mean ...	$6\cdot5\times10^{4}$	$16\cdot42\times10^{4}$
Expansions less than 1·33.						Negative ions per c.c.	
768	19·5	163	1·277	7	13	$3\cdot3\times10^{4}$	$8\cdot6\times10^{4}$
773	19·5	163	1·276	6	13·5	$2\cdot6\times10^{4}$	$8\cdot9\times10^{4}$
772	19	167	1·28	7·125	12·5	$3\cdot3\times10^{4}$	$8\cdot2\times10^{4}$
					Mean ...	$3\cdot0\times10^{4}$	$8\cdot5\times10^{4}$

If we take the mean of the results, we find the radium A produces at a distance of 10 cms. $6\cdot25\times10^{4}$ ions per c.c., while radium B produces $16\cdot75\times10^{4}$.

The results of the determinations of ne, where n is the number of ions per c.c., and e the charge in electrostatic measure on an ion, are given in the following table. D is the deflexion of the electrometer in scale-divisions for the potential-difference of 1 volt, C is the capacity of the electrometer and its connexions, δ_1 the mean of the positive and negative deflexions in one minute of the electrometer when there was a potential-difference of $\frac{1}{3}$ of a volt between the plates of the condenser, the gas between the plates being exposed to the radiation from the radium A at a distance of 10 cms., δ_2 the same quantity when the gas was exposed to the radiation from B at a distance of 15 cms. The values of ne are deduced as follows: if A is the area of the plate attached to the electrometer, u the mean velocity of the positive and negative ions under a potential-gradient of a volt per cm., the quantity of electricity given to this plate in unit time under $\frac{1}{3}$ of a volt per cm. is equal to $\frac{1}{3}neu\mathrm{A}$, this produces a potential-difference of $\frac{1}{3}neu\,\mathrm{A/C}$ in electrostatic measure between the plates; the potential-difference in volts is, however, $\delta_1/60\,\mathrm{D}$, hence we have

$$\frac{1}{3}\,\frac{neu\,\mathrm{A}}{\mathrm{C}}=\frac{\delta_1}{60\mathrm{D}}\times\frac{1}{300}.$$

From Zeleny's experiments u for moist air is 1·4 cm./sec., A=19·1; we have thus the data for determining ne:—

D.	C.	δ_1.	δ_2.	ne for radium A.	ne for radium B.
7400	483	63	170	$25{\cdot}2\times10^{-6}$	68×10^{-6}
6550	640	30	...	$20{\cdot}7\times10^{-6}$	
7600	900	25·5	71·5	$19\ \times10^{-6}$	53×10^{-6}
8800	930	28	78	$18{\cdot}5\times10^{-6}$	52×10^{-6}
			Mean ...	$20{\cdot}8\times10^{-6}$	$57{\cdot}6\times10^{-6}$

Thus, since for radium A $ne=20{\cdot}8\times10^{-6}$ and $n=6{\cdot}25\times10^4$, the value of $e=3{\cdot}3\times10^{-10}$:

For radium B $ne=57{\cdot}6\times10^{-6}$ and $n=16{\cdot}75\times10^4$, thus $e=3{\cdot}5\times10^{-10}$.

The mean of these values gives $\mathbf{3{\cdot}4\times10^{-10}}$ as the charge in electrostatic units of the gaseous ion. This is only about half the value $6{\cdot}5\times10^{-10}$ I found in the earlier experiments. The difference is, as I have already explained, due to the expansions in the earlier experiments practically catching only the negative ions; this made the calculated value of n little more than half the true value, while it made the value of e twice as great as it ought to have been.

If we know the value of e, we can at once deduce the number of molecules in a c.c. of gas at 0° C. and 760 mm. pressure. For if N is this number, then, since e is the same as the charge on the hydrogen ion in the electrolysis of solutions,

$$Ne=1{\cdot}22\times10^{10}$$

since $$e=3{\cdot}4\times10^{-10},\quad N=3{\cdot}6\times10^{19}.$$

This number is well within the limits of the various determinations made by the methods of the kinetic theory. The above method for determining N has the advantage of not involving a knowledge of the shape of the molecules, or any assumption as to the nature of the effects produced when two molecules come into collision.

In making the experiments described in this paper, I have had the help of my assistant Mr. Everett.

XXXIV. *On the Effect of Absorption on the Resolving Power of Prism Trains, and on Methods of Mechanically Compensating this Effect.* By F. L. O. WADSWORTH*.

[Plate VIII.]

IN previous investigations † of the resolving-power of prism spectroscopes, it has been generally assumed, 1st, that the illumination is uniform over the wave-front passing

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* Communicated by the Author. The general investigation on resolving-power, of which the present paper forms a part, was begun nearly eight years ago, but the work has been much interrupted and delayed by other more imperative and immediate demands upon the writer's time and attention. The publication of various parts of the work has therefore been more scattered and irregular than might otherwise have been the case. Since this paper was written, Prof. Campbell, with whom I fortunately had an opportunity of discussing it, has called my attention to a paper on the same subject that was published about a year ago by Dr. Reese of the Lick Observatory Staff. On examining this paper (Astrophys. Journ. xiii. p. 199, April 1901) I find that Dr. Reese has deduced the general equation corresponding to (11) of this paper (for $b_1=0$), but has confined his investigations of the effects of absorption to the particular case where the value of β is very small. Hence his conclusion (p. 206) "that the resolving power of the Mills Spectrograph is diminished by less than one half of one per cent. by the absorption of the prisms" is incomplete, and for that reason erroneous and misleading as a general conclusion. I have therefore allowed my own paper to stand as it was originally written, acknowledging Dr. Reese's priority of publication as above.

† See Rayleigh, Phil. Mag. vol. viii. pp. 261–264; vol. ix. pp. 49–56; vol. xlii. p. 167; *Enc. Brit.* vol. xxiv. pp. 430–439; Schuster, *ibid.* vol. xxii. pp. 373–374; also papers by the writer, Astrophysical Journal, vol. i. p. 52; vol. iii. pp. 176 and 321; vol. iv. p. 54; vol. vi. p. 27; vol. xvi. p. 1; Phil. Mag. vol. xliii. p. 317.

through the prism-train; 2nd, that the material of the latter is of the same temperature and refractive index throughout.

The general theoretical results agree so closely with those obtained in practice that it is certain that the error, if any, introduced by either of these assumptions must be small under usual conditions. It is not, however, *a priori* certain that this would be true when the absorption of the glass, or the differential temperature-change in different parts of the prisms, becomes abnormally large, as it may do in certain regions of the spectrum, and under conditions of use of the instrument such as are met with in astrophysical work. The following investigation was undertaken in order to determine the actual magnitude of the effects to be expected from large variations in absorption and optical density over the transmitted wave-front.

The most general expression for the distribution in intensity in the image of a point formed at the focal plane of a telescope is

$$I^2 = \left[\iint \frac{i}{\lambda\rho} \sin \frac{2\pi}{\lambda}(at-\rho)\, dx\, dy\right]^2, \quad . \quad . \quad . \quad (1)$$

where i is the amplitude of vibration of any element dx, dy in the wave-front: ρ is the distance of this element from a point p in the focal plane at which the intensity is desired.

In reducing this general expression to the form usually given*, the following assumptions are made†:—

1st. That the amplitude of vibration is constant, $i=$const.

2nd. That the wave-front passing the diffracting aperture is truly spherical, *i. e.*,

$$x^2+y^2+z^2=f^2.$$

3rd. The light which unites to form the image is strictly monochromatic, *i. e.*, $\lambda=$const.

Under these assumptions (1) may be reduced at once to the form given by Lord Rayleigh,

$$I^2 = \frac{1}{\lambda^2 f^2}\left[\iint \sin\left(\frac{2\pi\xi}{\lambda f} + \frac{2\pi\eta}{\lambda f}\right) dx\, dy\right]^2$$

$$+\frac{1}{\lambda^2 f^2}\left[\iint \cos\left(\frac{2\pi\xi}{\lambda f} + \frac{2\pi\eta}{\lambda f}\right) dx\, dy\right]^2, \quad . \quad (2)$$

where ζ, η are the coordinates of any point in the focal-plane image.

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[*] Rayleigh, article "Wave Theory," *Enc. Brit.* vol. xxiv. p. 430.

[†] See also Popular Astronomy, "Problems Relating to . . . Resolving Power of Telescopes," vol. v. pp. 528–536; and Astrophysical Journal, vol. xvi. pp. 266 *et seq.*

If we retain i as a variable function,

$$i=\phi\,(xy), \qquad \ldots\ldots\ldots \qquad (3)$$

but consider the second and third assumptions as correct, we obtain similarly

$$\mathrm{I}^2=\frac{1}{\lambda^2 f^2}\left[\iint\phi(xy)\sin\left(\frac{2\pi\xi}{\lambda f}+\frac{2\pi\eta}{\lambda f}\right)dx\,dy\right]^2$$
$$+\frac{1}{\lambda^2 f^2}\left[\iint\phi(xy)\cos\left(\frac{2\pi\xi}{\lambda f}+\frac{2\pi\eta}{\lambda f}\right)dx\,dy\right]^2 \quad . \quad (4)$$

In the case of the prism spectroscope the aperture of the prism-train is generally rectangular, and if all parts of the beam of light falling on the first prism-face are of uniform intensity, the diminution in the amplitude of vibration due to the absorption of the glass of the train will be uniform along any line parallel to the refracting edge of the prisms. Along any line at right angles to this the change will be expressed by the law

$$i=i_0 e^{-\frac{\beta}{2}(l-l_0)} \qquad \ldots\ldots\ldots \qquad (5)$$

where i and i_0 are the amplitudes of vibration of the ray after traversing thicknesses of l and l_0 centimetres of glass, and β is the coefficient of absorption.

If we choose the two lines just defined as the axes of y and x respectively we have for $\phi(xy)$ in (3)

$$\phi(xy)=i_0 e^{-\mathrm{B}x} \qquad \ldots\ldots\ldots \qquad (6)$$

since the length of path, $l-l_0$, through any given point in the prism-train is directly proportional to x, the distance of that point from the central ray.

The functin $oe^{-\mathrm{B}x}$ is independent of y, and, for a rectangular aperture, the limits of integration for y in both terms of (4) are constant. Hence we obtain at once for the distribution in intensity along the axis of ξ in the focal plane

$$\mathrm{I}_\xi^2=\frac{i_0{}^2 d^2}{\lambda^2 f^2}\left[\int_{-\frac{b}{2}}^{+\frac{b}{2}} e^{-\mathrm{B}x}\sin\frac{2\pi\xi}{\lambda f}x\,dx\right]^2+\frac{i_0{}^2 d^2}{\lambda^2 f^2}\left[\int_{-\frac{b}{2}}^{+\frac{b}{2}} e^{-\mathrm{B}x}\cos\frac{2\pi\xi}{\lambda f}x\,dx\right]^2$$
$$=\frac{i_0{}^2 d^2}{\lambda^2 f^2}[\mathrm{C}^2+\mathrm{S}^2]. \qquad \ldots\ldots\ldots\ldots\ldots \qquad (7)$$

For convenience put

$$\frac{2\pi\xi}{\lambda f}=k.$$

Then integrating each of the two terms of (7) by parts we obtain

$$\left.\begin{aligned} C &= k\left(e^{\frac{Bb}{2}} - e^{-\frac{Bb}{2}}\right)\cos\frac{kb}{2} - B\left(e^{\frac{Bb}{2}} + e^{-\frac{Bb}{2}}\right)\sin\frac{kb}{2} \\ S &= k\left(e^{\frac{Bb}{2}} + e^{-\frac{Bb}{2}}\right)\sin\frac{kb}{2} + B\left(e^{\frac{Bb}{2}} - e^{-\frac{Bb}{2}}\right)\cos\frac{kb}{2} \end{aligned}\right\}, \quad . \quad (8)$$

and therefore

$$I_\xi^2 = C^2 + S^2 = \frac{e^{Bb} + e^{-Bb} - 2\cos kb}{k^2 + B^2}. \quad . \quad . \quad . \quad (9)$$

Resubstituting for k its value in terms of ξ, and also expressing $\cos kb$ in terms of $\sin\frac{kb}{2}$ we finally obtain

$$I_\xi^2 = i_0{}^2\,\frac{b^2 d^2}{\lambda^2 f^2}\,\frac{e^{Bb} + e^{-Bb} - 2 + 4\sin^2\frac{\pi\xi b}{\lambda f}}{(Bb)^2 + 4\left(\frac{\pi\xi b}{\lambda f}\right)^2}. \quad . \quad . \quad . \quad (10)$$

When the origin of coordinates is not at the centre of the horizontal aperture, and the limits of integration, b_1 and $-b_2$, are unequal, we obtain similarly

$$I_\xi^2 = i_0{}^2\,\frac{d^2}{\lambda^2 f^2 (k^2 + B^2)}\left[e^{-2Bb_1} + e^{2Bb_2} - 2\cos k(b_1 + b_2)\,e^{-B(b_1+b_2)}\right] \quad . \quad . \quad . \quad (11)$$

When there is no absorption $B=0$ and $i=1$, and both (9) and (10) reduce at once to the usual form for rectangular aperture, *i.e.*,

$$I^2 = \frac{b^2 d^2}{\lambda^2 f^2}\,\frac{\sin\frac{\pi\xi b}{\lambda f}}{\left(\frac{\pi\xi b}{\lambda f}\right)^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

For very small values of B the distribution in intensity is practically the same as when there is no absorption. For very large values of B, on the other hand, the term e^{Bb} remains the only one of importance in the numerator, and we have

$$I_\xi^2 = i_0{}^2\,\frac{b^2 d^2}{\lambda^2 f^2}\,\frac{e^{Bb}}{(Bb)^2 + 4\left(\frac{\pi\xi b}{\lambda f}\right)^2}. \quad . \quad . \quad . \quad (13)$$

In order better to show the transition between these two extreme cases, the values of the function I_ξ^2 have been computed for six intermediate values of B as follows :—

$$\begin{aligned} Bb&=0{\cdot}5754,\\ Bb&=1{\cdot}3862,\\ Bb&=2{\cdot}1972,\\ Bb&=2{\cdot}7726,\\ Bb&=4{\cdot}6052,\\ \text{and}\qquad Bb&=7{\cdot}825. \end{aligned}$$

In these computations the quantity $i_0{}^2.\frac{b^2d^2}{\lambda^2f^2}$, whose value is determined simply by the intensity of illumination in the incident wave-front and by the dimensions of the instrument,

TABLE I.

$\pi\frac{a}{a_0}$.	$I^2=\frac{\sin^2 x}{x^2}$	I_a^2 for different values of B*b*.					
		B*b*=·5754.	1·3862.	2·1972.	2·7726.	4·6052.	7·825.
0·00	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
0·10π	·9675	·9681	·9696	·9739	·9766	·9862	·9925
0·20π	·8751	·8769	·8870	·8997	·9100	·9436	·9745
0·30π	·7368	·7411	·7598	·7880	·8114	·8791	·9459
0·4 π	·5754	·5792	·6086	·6535	·6900	·7988	·9079
0·5 π	·4053	·4138	·4527	·5132	·5628	·7102	·8620
0·6 π	·2545	·2646	·3105	·3826	·4416	·6207	·8128
0·7 π	·1353	·1462	·1955	·2732	·3313	·5351	·7599
0·8 π	·0547	·0654	·1140	·1916	·2558	·4624	·7079
0·9 π	·0119	·0217	·0663	·1382	·1989	·4003	·6571
1·0 π	·0000	·0084	·0464	·1089	·1629	·3494	·6079
1·1 π	·0080	·0146	·0452	·0968	·1422	·3087	·5621
1·2 π	·0243	·0292	·0528	·0935	·1303	·2752	·5194
1·3 π	·0392	·0428	·0605	·0923	·1222	·2477	·4798
1·4 π	·0468	·0497	0632	·0886	·1139	·2232	·4432
1·5 π	·0450	·0472	·0587	·0805	·1026	·2008	·4095
1·6 π	·0358	·0381	·0486	·0686	·0889	·1798	·3773
1·7 π	·0229	·0250	·0358	·0554	·0736	·1611	·3495
1·8 π	·0108	·0130	·0239	·0434	·0626	·1441	·3233
1·9 π	·0027	·0049	·0155	·0344	·0529	·1298	·3002
2·0 π	·0000	·0020	·0120	·0297	·0462	·1182	·2789
2·2 π	·0072	...	...	...	·0422	·1011	·2429
2·4 π	·0159	...	...	...	·0402	·0885	·2116
2·6 π	·0136	...	...	...	·0347	·0764	·1871
2·8 π	·0045	...	...	...	·0270	·0651	·1655
3·0 π	·0000	...	...	...	·0210	·0562	·1470
3·2 π	...	...	...	...	...	·049	·1317
3·5 π	...	...	...	...	...	·043	·1169
4·0 π	...	...	...	...	...	...	·0888
5·0 π	...	...	...	...	...	...	·0582
6·0 π	..	...	...	...	...	...	·0413

is so chosen that the intensity I^2_ξ at the centre of the diffraction image, $\xi=0$, is the same (unity) in each case. The abscissæ are expressed in terms of the angular coordinates $\frac{\alpha}{\alpha_0}$ which are determined by the relations

$$\alpha=\frac{\xi}{f}, \quad \alpha_0=\frac{\lambda}{b},$$

and therefore

$$\frac{\pi\xi b}{\lambda f}=\pi\frac{\alpha}{\alpha_0}=x. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The comparative values of I^2_α for values of α ranging from 0 to $6\alpha_0$, and for the values of Bb given above, are tabulated in columns 3, 4, 5, 6, 7, and 8 of Table I. (p. 359) and plotted as full-line curves in fig. 1 (Pl. VIII.). For comparison the value of I^2 for $B=0$ is also tabulated in column 2 of this table, and plotted as a dotted curve in fig. 1.

An inspection of this table, or the corresponding curves of fig. 1, shows that the effect of increasing absorption is to change the form of the curve $I^2=f(\alpha)$, 1st, by gradually obliterating the points of maxima and minima on each side of the centre, and, 2nd, by gradually increasing its apparent width *mm*. We have to consider this change in form (*a*) on the resolving-power of the instrument, (*b*) on the visual or photographic appearance of the spectral lines.

(*a*) The visual criterion for resolving-power is that two lines of equal intensity may be considered as definitely "resolved" when the illumination at the centre of their superimposed diffraction images is not more than 0·81 of the illumination at the centres of the images themselves. In the case of an instrument unaffected by absorption (equation 11), this corresponds to a separation of the two lines by an amount

$$\sigma_0=\alpha_0=\frac{\lambda}{b}$$

as defined by (14).

In the case of two equal lines separated by an angular interval σ the relative intensities in the physical image of the double source at the points corresponding to the centres of the lines themselves and a point midway between them will be

$$\frac{I^2_m}{I^2_c}=\frac{2I^2_{\sigma/2}}{I^2_0+I^2_\sigma}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and the lines will be resolved or not according as I_m^2 is less or greater than $0·81\ I_c^2$.

Applying this criterion to the case of the images I_α^2 shown in fig. 1, we find for a constant separation $\sigma=\alpha_0$ the following values of $\frac{I_m^2}{I_c^2}$:—

For $$Bb=\ ·5754: \quad \frac{I_m^2}{I_c^2}=\frac{8·276}{1·0084}=\ ·82+$$

$$Bb=1·3862: \quad \frac{I_m^2}{I_c^2}=\frac{·9054}{1·0464}=\ ·86+$$

$$Bb=2·1972: \quad \frac{I_m^2}{I_c^2}=\frac{1·0264}{1·1089}=\ ·92+$$

$$Bb=2·7726: \quad \frac{I_m^2}{I_c^2}=\frac{1·1256}{1·1629}=\ ·97-$$

$$Bb=4·6052: \quad \frac{I_m^2}{I_c^2}=\frac{1·4204}{1·3494}=1·05+$$

$$Bb=7·825: \quad \frac{I_m^2}{I_c^2}=\frac{1·724}{1·608}=1·07+$$

which shows that the effect of absorption is to decrease the resolving-power of the instrument by an amount depending both on the value of B and of b.

To find the separation necessary for resolution we must select a value of σ such that

$$\frac{2I^2_{\sigma/2}}{I_0^2+I_\sigma^2}=0·81. \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

If we put

$$e^{Bb}+e^{-Bb}-2=4D,$$

$$(B'b)^2=4F^2,$$

and

$$\frac{\pi}{\alpha_0}\cdot\frac{\sigma}{2}=x,$$

we obtain from (9) and (15)

$$(F^2+x^2)\left[\frac{D}{F^2}+\frac{D+\sin^2 2x}{F^2+(2x)^2}\right]\cong 2·5(F^2+\sin^2 x), \quad . \qquad (17)$$

from which we can determine x and σ necessary for resolution for any given values of Bb. We thus obtain

For	$\mathrm{B}b = \cdot 5754$	$\sigma = 1\cdot007\alpha_0$
	$\mathrm{B}b = 1\cdot3862$	$\sigma = 1\cdot04\alpha_0$
	$\mathrm{B}b = 2\cdot1972$	$\sigma = 1\cdot11\alpha_0$
	$\mathrm{B}b = 2\cdot7726$	$\sigma = 1\cdot18\alpha_0$
	$\mathrm{B}b = 4\cdot6052$	$\sigma = 1\cdot54\alpha_0$
	$\mathrm{B}b = 7\cdot825$	$\sigma = 2\cdot56\alpha_0$

These relative values of Bb and σ are plotted (circles) in fig. 2 (Pl. VIII.). As is there shown, the relation between these quantities can be closely represented by the dotted curve, the equation of which is

$$\sigma = \alpha_0\{1 + \cdot0253\,(\mathrm{B}b)^2\} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

an expression which is simpler and more convenient for computation than the more exact formula (16).

An inspection of the curve in fig. 2 shows that for small values of Bb, *i. e.* for small absorptions, the actual resolving-power of the instrument σ is very nearly the same as the theoretical resolving-power α_0. For large values, however, it is very considerably reduced; nearly one-third for a value of Bb equal to 4.

To obtain a better idea of the physical conditions corresponding to the different values of Bb considered above, it is desirable to express these values in terms of the intensities at the centre and edges of the transmitted wave-front. We have from (5) and (6)

$$\frac{i}{i_0} = e^{-\mathrm{B}x}.$$

Since the intensities at any two points are proportional to the square of the amplitudes of vibration, we have for the centre of the transmitted wave-front $x=0$, and the edge $x=\frac{b}{2}$, the ratio

$$\frac{i_\epsilon^2}{i_0^2} = e^{\mp \mathrm{B}b},$$

and therefore for the different values of Bb already considered

$$\frac{i_\epsilon^2}{i_0^2}=\frac{9}{16}=\left(\frac{3}{4}\right)^2 \text{ for B}b=\cdot 5754$$

$$\frac{i_\epsilon^2}{i_0^2}=\frac{1}{4}=\left(\frac{1}{2}\right)^2 \quad ,, \quad =1\cdot 3862$$

$$\frac{i_\epsilon^2}{i_0^2}=\frac{1}{9}=\left(\frac{1}{3}\right)^2 \quad ,, \quad =2\cdot 1972$$

$$\frac{i_\epsilon^2}{i_0^2}=\frac{1}{16}=\left(\frac{1}{4}\right)^2 \quad ,, \quad =2\cdot 7726$$

$$\frac{i_\epsilon^2}{i_0^2}=\frac{1}{100}=\left(\frac{1}{10}\right)^2 \quad ,, \quad =4\cdot 6052$$

$$\frac{i_\epsilon^2}{i_0^2}=\frac{1}{2500}=\left(\frac{1}{50}\right)^2 \quad ,, \quad =7\cdot 825$$

or for the extreme cases the intensity at the edge of the beam traversing the base of the prism-train is fifty-six per cent. and one twenty-fifth of one per cent. respectively, of the intensity at the centre.

To find the relation between the quantities Bb, $\frac{i_\epsilon^2}{i_0^2}$, and β, the coefficient of absorption of the glass, we have similarly from (5) and (6)

$$\text{B}x=\frac{\beta}{2}(l-l_0).$$

Also from the geometry of the prism-train

$$\frac{x}{l_1-l_0}=\frac{\sqrt{1-n^2\sin^2\phi/2}}{2\sin\phi/2},$$

for a single prism of refracting angle ϕ placed at minimum deviation. For N similar prisms placed *en train* we have similarly

$$\frac{x}{l-l_0}=\frac{x}{\text{N}(l_1-l_0)}=\frac{\sqrt{1-n^2\sin^2\phi/2}}{2\text{N}\sin\phi/2},$$

and therefore in general

$$\text{B}=\beta\text{N}\frac{\sin\phi/2}{\sqrt{1-n^2\sin^2\phi/2}}, \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

from which we can determine the corresponding values of Bb and β for any given spectroscope. Some examples may be of interest.

For the Bruce spectrograph of the Yerkes Observatory, which is one of the largest and most recently constructed instruments of this class, we have for b. ϕ, N, and n the following values* :—

$$b = 5{\cdot}1 \text{ cms.}$$
$$\phi = 63^\circ\ 35' \text{ (mean value).}$$
$$N = 3.$$
$$n = \begin{cases} 1{\cdot}653 \text{ for } \lambda = 5500\dagger \\ 1{\cdot}678 \text{ ,, } \lambda = 4300 \\ 1{\cdot}693 \text{ ,, } \lambda = 3900\dagger. \end{cases}$$

Introducing these values and solving for Bb we find

$$Bb = \beta \times \begin{cases} 16{\cdot}4 \text{ for } \lambda = 5500 \\ 17{\cdot}2 \text{ ,, } \lambda = 4300 \\ 17{\cdot}8 \text{ ,, } \lambda = 3900 \end{cases}$$

The absorption of the glass of which this prism-train is composed (0·102) has been determined by Vögel and Müller‡. The values of β computed from their results are as follows:—

For wave-length 5500, $\beta = {\cdot}021$
,, ,, 4300, $\beta = {\cdot}071$
,, ,, 3900, $\beta = {\cdot}37$

For the visual region of the spectrum, therefore, the value of Bb for this spectroscope is about ·34, and the corresponding value of σ, as given by (18), is less than $1{\cdot}003\ \alpha_0$, *i. e.* the resolving-power is diminished less than one-third of one per cent. by the result of absorption.

In the photographic region of the spectrum, however, the case is quite different. At wave-length $\lambda = 4300$, which is about the middle of the photographic region, the value of Bb for the Bruce spectroscope is $17{\cdot}2 \times {\cdot}071 = 1{\cdot}22$, and the corresponding value of σ is 1·04, *i. e.* the resolving-power at this point in the spectrum is reduced about four per cent. by the result of absorption. At wave-length $\lambda = 3900$ the value of Bb is 6·59, the value of σ is $2{\cdot}10\ \alpha_0$, and the resolving-power is therefore diminished by more than fifty per cent.

For prism spectroscopes of larger size or greater resolving-power than the one above considered the effect of absorption may become serious, even in the visible part of the spectrum,

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* "The Bruce Spectroscope of the Yerkes Observatory," E. B. Frost, Astrophysical Journal, vol. xv. pp. 12–17, Jan. 1902.

† Estimated by exterpolation from the values given by Frost.

‡ Astrophysical Journal, vol. v. p. 82 (1897).

particularly if a denser glass than 0·102 is used. Prism spectroscopes have been constructed having an aperture of from 2·2 cms. to 2·5 cms., and prism-trains of from 10 to 13 dense flint prisms*. These prism-trains have been constructed of very dense flint-glass whose coefficients of absorption are probably considerably higher than those for 0·102, which is unusually white and transparent. Assume the coefficients to be only 33 per cent. (1/3) larger. Then, since the ratio $Bb \div \beta$ is roughly only one-half as large for the Bruce instrument as for the Young and Grubb instruments, we have for the latter:

In the visible spectrum

$$Bb \simeq 1{\cdot}00 \qquad \sigma = 1{\cdot}025\,\alpha_0.$$

In the photographic region

$$\lambda = 4300 \qquad Bb \simeq 3{\cdot}7 \qquad \sigma = 1{\cdot}35\,\alpha_0$$

$$\lambda = 3900 \qquad Bb \simeq 20{\cdot}0 \qquad \sigma = 11{\cdot}0\,\alpha_0.$$

In this last case the resolving-power of the spectroscope is reduced more than 90 per cent. by absorption in the neighbourhood of the H and K lines.

It is evident from these results that it is useless to increase the theoretical resolving-power r of our prism spectroscopes beyond a certain point. For every value of β there will be a certain limiting value of α_0, and hence of r, for which the practical resolving-power of the instrument as affected by absorption (which we will call R_β) will be a maximum. To find this value we must transform equations (18) and (19) so that all variables are expressed in terms of r and R_β.

From the well-known relation

$$r = \frac{m}{\alpha_0} = \frac{\lambda}{\Delta\lambda}$$

we have obviously

$$\frac{R_\beta}{r} = \frac{\alpha_0}{\sigma}.$$

We have also the relation

$$Nb \frac{\sin \phi/2}{\sqrt{1 - n^2 \sin^2 \phi/2}} = \frac{r}{2} \cdot \frac{d\lambda}{dn}^{\dagger} \quad . \quad . \quad . \quad . \qquad (20)$$

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* Young, 'Nature,' vol. iii. p. 110; Grubb, Monthly Notices R. A. S. vol. xxxi. pp. 36–38.

† See Astrophysical Journal, vol. i. p. 55 (1895).

From (18), (19), and (20) we then obtain at once

$$R_\beta = \frac{r}{1 + \cdot 0063\left(\beta r \frac{d\lambda}{dn}\right)^2}, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

which is similar in general form to the expression for the purity of the spectrum with slits of finite width*.

To find the value of r for which R_β is a maximum we have

$$\frac{d}{dr} R_\beta = \frac{1 - \cdot 0063\left(\beta \frac{d\lambda}{dn} r\right)^2}{\left\{1 + \cdot 0063\left(\beta \frac{d\lambda}{dn} r\right)^2\right\}^2} = 0, \quad . \quad . \quad . \quad (22)$$

or for R_β=max.

$$r_m = 12\cdot 59 \frac{1}{\beta} \cdot \frac{dn}{d\lambda}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and for the corresponding maximum value of R_β

$$R_\beta(\text{max.}) = 6\cdot 29 \frac{1}{\beta} \cdot \frac{dn}{d\lambda} = \frac{1}{2} r_m, \quad . \quad . \quad . \quad . \quad (24)$$

that is, the maximum practical resolving-power that can be attained with a prism spectroscope is one-half what we could attain with the same spectroscope if there were no absorption.

For the flint glass 0·102 which we have been considering, the value of the ratio

$$\frac{dn}{d\lambda}$$

for wave-length $\lambda = 3900$ is about 4250. The value of β for the same region is, as we have seen, about ·37. Hence for this glass we have

$$R_\beta(\text{max.}) \cong 72000,$$

for

$$r_m \cong 144000.$$

The relation between r and R_β, as given by (21), is tabulated in Table II. and plotted in Curve 1 of fig. 3 (Pl. VIII.). It will be seen that the increase in R_β is very small (less than 7 per cent. of the maximum) between the points $r = 100000$ and $r_m = 144000$; and it would therefore in general be inadvisable to go beyond the first point, if we proposed to work in the neighbourhood of the H and K lines with a prism spectroscope of dense flint glass. The theoretical resolving-power of the Bruce instrument for this region is about 153000, $\left\{\frac{dn}{d\lambda}(t_1 - t_2)\right\}$, and is therefore

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* See Phil. Mag. vol. xliii. pp. 333–339.

TABLE II.

r.	R_{β}.		
	II.	III.	IV.
25,000	24375		
50,000	44680	48765	49275
75,000	59152		
100,000	67750	90830	95970
125,000	71675		
150,000	72420	122220	137070
200,000	68880	142460	169820
300,000	56760	157140	217830
400,000	46440	152720	239440
500,000	38750	141850	244200
600.000	33060	129420	239160
800,000	25440	107200	217280
1000,000	......	90100	192700

considerably larger than can be used to best advantage. The Young spectroscope has a theoretical resolving-power r of nearly 300000 in the same region of the spectrum, but as will be seen from the Table or the Curve the effect of absorption cuts down the practical resolving-power to about 57000, actually less than that which an instrument of only one-fourth the size would possess.

It is at once evident from these results that if high-power prism spectroscopes are to be used in the investigation of the photographic region of the spectrum, the use of the extra dense flint glass, so commonly employed in the past, must be avoided, not only on the score of light-efficiency, but, as now appears, on the score of photographic resolving-power and purity as well. The use of lighter flint reduces the theoretical resolving-power, r, of any given prism-train by decreasing the value of the dispersion-coefficient $\frac{dn}{d\lambda}$; but this may be easily and even advantageously compensated by increasing the refracting angle ϕ of the prisms. The advantages of this latter construction on the score both of light-efficiency and economy of material were pointed out by the writer several years ago*, and it has been adopted in all the large spectroscopes recently constructed at Allegheny†.

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* Astrophysical Journal, vol. ii. p. 264 (1895).

† Among others may be mentioned the spectroscope of the Philadelphia Observatory, the spectroscope of the Lowell Observatory, and the spectroheliograph of the Philadelphia Observatory (just completed). Prof. Lord, of the Emerson McMillen Observatory, has also recently replaced the battery of dense flint prisms first constructed for his star spectroscope with one of light flint; and I believe Dr. Gill, of the Cape Observatory, is likewise considering this change.

To show the advantage of the lighter glasses on the score of photographic purity the values of R_β have also been computed for the dense flint, 0·93, and the light flint, 0·340, of Schott's table. The constants n, β, and $\frac{dn}{d\lambda}$ for wave-length 3900 for these two glasses are as follows:—

$$0{\cdot}93 \qquad n_{3900}=1{\cdot}66\,; \qquad \frac{dn}{d\lambda}=3500; \qquad \beta\cong{\cdot}14$$

$$0{\cdot}340 \qquad n_{3900}=1{\cdot}61\,: \qquad \frac{dn}{d\lambda}=3100; \qquad \beta\cong{\cdot}08.$$

The values of R_β for these values of $\frac{dn}{d\lambda}$ and β are tabulated in columns III. and IV. of Table II., and plotted as curves II. and III. of fig. 3 (Pl. VIII.). The points of maximum for these curves are found at

$$r_m \cong 315000 \text{ for glass } 0{\cdot}93,$$
$$r_m \cong 488000 \quad ,, \quad ,, \quad 0{\cdot}340.$$

and the corresponding values of R_β (max.) are

157000	for	0·93,
244000	for	0·340.

As in the preceding case the form of the curves is such that it is not desirable to go to the extreme maximum values of of R_β, but to stop at points corresponding to $r\cong 200000$ and $\cong 350000$ respectively.

For the visible portion of the spectrum the values of n, $\frac{dn}{d\lambda}$, and β for the first glass considered, 0·102, are as follows:—

$$n=1{\cdot}653\,; \qquad \frac{dn}{d\lambda}\cong 1150, \qquad \beta={\cdot}021.$$

$$\therefore \quad \beta\frac{d\lambda}{dn}={\cdot}000018:$$

$$r_m\cong 740000;$$

$$R_\beta \text{ (max.)} \cong 370000.$$

The above results show that while the Bruce spectroscope is quite efficient for the visible part of the spectrum, it is quite otherwise for the photographic region in the neighbourhood of the H and K lines. Such an instrument would not be well suited, therefore, for solar work, particularly of a spectroheliographic nature.

For regions of the spectrum lying below wave-length 3900, materials having a smaller coefficient of absorption than light flint or even crown-glass must be used. In the case of glass, indeed, we soon reach a limit beyond which a further reduction in density will be actually disadvantageous. As will be seen from (21) and (23) we reach an absolute maximum for R_β when the quantity

$$\beta \frac{d\lambda}{dn}$$

becomes an absolute minimum. For the various flint glasses already considered, the absorption-coefficient β decreases more rapidly than the dispersion-coefficient $\frac{dn}{d\lambda}$; hence the quotient of these two coefficients decreases with diminishing index of refraction.

But as we pass from the flints to the crowns the reverse takes place, and the value of β decreases less rapidly than the dispersion. Hence we soon reach a point at which the quotient

$$\beta \frac{d\lambda}{dn}$$

is an absolute minimum for glass. Thus for the crown 0·203 examined by Vogel we have in the neighbourhood of the H line

$$n_{3900} \cong 1{\cdot}532, \qquad \frac{dn}{d\lambda} \cong 1650, \quad \text{and} \quad \beta \cong {\cdot}054.$$

Hence for crown 0·203

$$\beta \frac{d\lambda}{dn} = 0{\cdot}000032,$$

which is nearly 25 per cent. larger than the corresponding quantity (0·000026) for the light flint 0·340. Hence, in spite of its diminished absorption crown-glass would not be as good a material to use for the prisms as light flint.

We might perhaps find a flint for which the quotient of the two coefficients is somewhat less than in the case of 0·340. It is, however, safe to say that the value of this quotient cannot be much reduced, and that the maximum practical resolving-power which we can attain in spectroscopes with glass prisms will not exceed 250,000 units in the photographic region of the spectrum, nor 400,000 in the visual region.

In order to attain still higher resolving-powers we must use other materials than glass. Of those available for this purpose quartz, rock-salt, and fluorite are among the best. Unfortunately I have not been able to find any reliable data on the coefficients of absorption of these materials for different wave-lengths. Although they are considerably less than those for glass for both very short and very long wave-lengths, they are sufficiently large to exercise an appreciable effect on the resolving-power in these ultra-visible portions of the spectrum. It is also necessary to remember that certain kinds of glass, as well as other materials of which prisms may be constructed, frequently show strong selective absorption; and certain regions even in the visible part of the spectrum where this occurs may exhibit a lack of apparent definition in consequence. In fact, in all discussions involving questions of resolving-power, the possibility of the effects of large local or general absorptions must be kept in mind.

(*b*) The second effect of absorption which we have to consider is that on the general form and apparent "width" of the individual spectral lines. This effect is in many respects more pronounced and striking than that on the resolving power just considered; for as will be seen by an inspection of fig. 1 (Pl. VIII.), the apparent width is increased in a much greater ratio than the resolving-power is diminished by increased absorption.

As long as there is a well-marked minimum on each side of the centre, we may consider the edges of the spectral image to be defined by the position of these minima; or, in other words, consider that the apparent "width" of the line is $m_0 m_0$ (fig. 1). For the value $\beta=0$ this width for an infinitely narrow slit and monochromatic radiation is of course $2\alpha_0$. The effect of an increasing absorption is to increase all the ordinates of the diffraction pattern relatively to the central one (for $\alpha=0$); but the ones in the neighbourhood of the first minima are increased proportionally more than the others, so that these points of minima are gradually obliterated, and become indistinguishable for values of Bb greater than 1·5. The edges of the line then become less and less sharply defined and clearly marked. Their apparent position depends somewhat on the absolute as well as the relative intensity at different parts in the diffraction pattern; but in general they may be taken to lie near the limits $\pm m$ defined by the relations

$$f(\pm m) = \mathrm{I}^2_{\pm m} \backsimeq \cdot 04\, \mathrm{I}^2_0\,;$$

i. e. near the points at which the intensity of illumination in the image first falls to less than 4 per cent. of the intensity at the geometrical centre.

Assuming this criterion, we have for the relation between

Bb (or β) and w, the apparent "width," the following values (from Table I. and fig. 1):—

$$\begin{array}{lllll}
\text{For } \mathrm{B}b = & 000 & w = m_0 m_0 & = & 2{\cdot}00\,\alpha_0, \\
\mathrm{B}b = & {\cdot}575 & w & = & 2{\cdot}04\,\alpha_0, \\
\mathrm{B}b = & 1{\cdot}386 & w = m_1 m_1 & = & 2{\cdot}16\,\alpha_0, \\
\mathrm{B}b = & 2{\cdot}197 & w & = & 3{\cdot}66\,\alpha_0, \\
\mathrm{B}b = & 2{\cdot}77 & w = m_2 m_2 & = & 4{\cdot}8\,\alpha_0, \\
\mathrm{B}b = & 4{\cdot}61 & w = m_3 m_3 & \cong & 7{\cdot}6\,\alpha_0, \\
\mathrm{B}b = & 7{\cdot}83 & w & \cong & 13{\cdot}5\,\alpha_0.
\end{array}$$

The apparent width of the line for the last value of Bb is therefore nearly seven times as great as the theoretical width, $2\alpha_0$, for zero absorption. This large increase in w, together with the accompanying reduction in the practical resolving-power, R_β, is quite sufficient to explain the apparent haziness and lack of definition frequently observed in certain portions of a spectrum formed by prisms with strong selective absorption.

The effect of absorption on the form and distribution in intensity in the spectral image, and hence on the resolving-power of the prism-train, may be entirely eliminated by mechanical diaphragming of the prism aperture. By referring to equation (7) we see that the form of the expression for I^2 is the same as would be obtained if the illumination were uniform over the wave-front, and the latter were limited by an aperture whose length (along the x axis) is b, as before, but whose width at any point is the ordinate to the exponential curve

$$y = ae^{-\mathrm{B}x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

If, therefore, we limit the aperture of the prism-train by a diaphragm whose width is y^{-1}, the illumination remaining the same as in (7), we obtain for the distribution in intensity in the image of the spectral line

$$\mathrm{I}_\xi^2 = \frac{i^2 a^2}{\lambda^2 f^2}\left[\int_{-\frac{b}{2}}^{+\frac{b}{2}} e^{-\mathrm{B}x} e^{\mathrm{B}x} \sin\frac{2\pi\xi}{\lambda f} x\,dx\right]^2$$

$$+ \frac{i_0{}^2 a^2}{\lambda^2 f^2}\left[\int_{-\frac{b}{2}}^{+\frac{b}{2}} e^{-\mathrm{B}x} e^{\mathrm{B}x} \cos\frac{2\pi\xi}{\lambda f} x\,dx\right]^2$$

$$= \frac{i_0{}^2 a^2}{\lambda^2 f^2}\left[\int_{-\frac{b}{2}}^{+\frac{b}{2}} \cos\frac{2\pi\xi}{\lambda f} x\,dx\right]^2 = \frac{i_0{}^2 a^2 b^2}{\lambda^2 f^2} \frac{\sin^2\frac{\pi\xi b}{\lambda f}}{\left(\frac{\pi\xi b}{\lambda f}\right)^2}. \quad . \qquad (26)$$

which is the same as obtained with rectangular aperture of height d, unaffected by absorption, save that the absolute intensities at every point in the pattern are diminished in the ratio

$$\frac{I_{00}^2}{I^2}=\frac{i_0^2a^2}{d^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (27)$$

Since the intensity in the transmitted wave-front at the thin edge of the prism is the same as in the incident beam ($l=0$), we have, by making $x=-\frac{b}{2}$ in (6),

$$i_0^2e^{Bb}=1, \quad \text{or} \quad i_0^2=e^{-Bb}. \quad . \quad . \quad . \quad . \quad . \qquad (28)$$

Also if we choose a in (25) such that the greatest width of the diaphragm is equal to d, we have

$$d=ae^{\frac{Bb}{2}},$$

or

$$a^2=d^2e^{-Bb}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29)$$

Hence we have from (27), (28), and (29)

$$\frac{I_{00}^2}{I^2}=e^{-Bb}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (30)$$

For the Bruce spectroscope before considered the value of Bb for wave-length 3900 is, as already computed,

$$Bb\cong 6{\cdot}59\,;$$

$$\therefore \quad \frac{I_{00}^2}{I^2}\cong{\cdot}000\,002.$$

Although so much light is lost in diaphragming the aperture as above described, the intensity in the resultant spectral image will compare somewhat more favourably with that secured under the actual conditions of absorption with full aperture, because the "width" of the line is so much reduced when the diaphragm is used. The intensity at the centre of the diffraction-image with full aperture bd (see 10) is

$$I_0^2=i_0^2\frac{b^2d^2}{\lambda^2f^2}\cdot\frac{e^{Bb}+e^{-Bb}-2}{(Bb)^2}. \quad . \quad . \quad . \quad . \qquad (31)$$

The ratio between this intensity and the intensity of the image formed by the same instrument, unaffected by absorption, will be

$$\frac{I_0^2}{I^2}=\frac{e^{-Bb}}{(Bb)^2}\left\{e^{Bb}+e^{-Bb}-2\right\}. \quad . \quad . \quad . \qquad (32)$$

For the same case considered before for which Bb is $6{\cdot}59$, we have

$$\frac{I_0^2}{I^2} \simeq {\cdot}023.$$

Finally, for the ratio between the intensities with and without a diaphragm we have from (30) and (32),

$$\frac{I_{00}^2}{I_0^2} = \frac{e^{-Bb}(Bb)^2}{e^{Bb} + e^{-Bb} - 2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

which gives us for the Bruce instrument in the H regions

$$\frac{I_{00}^2}{I_0^2} \simeq {\cdot}0001. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33a)$$

The curve bounding the edges of the diaphragm for any given case is given by the equation [see (25) and (29)],

$$y = \pm e^{+\beta N \frac{\sin \phi/2}{\sqrt{1-n^2 \sin^2 \phi/2}}\left(x - \frac{b}{2}\right)} \quad . \quad . \quad . \quad . \quad . \quad (34)$$

For the above case

$$B = \beta N \frac{\sin \phi/2}{\sqrt{1 - n^2 \sin^2 \phi/2}} = 1{\cdot}29,$$
$$b = 5{\cdot}1.$$

If with these values of b and B we make $d = b$ and compute y for different values of x, we shall find the form of the required diaphragm to be that shown in fig. 4 (Pl. VIII.). The widths at the two ends are 0·008 cm. and 5·1 cms. respectively, with the wide end toward the base of the prism.

When so placed this diaphragm will entirely eliminate the effect of the variable absorption, but only, as indicated by (33) and (33*a*), at a very large sacrifice of intensity of illumination. This device can therefore be used only when we have abundance of light. In other cases the only means we have of reducing the effect of absorption for any given material is to decrease the resolving-power of the prism-train either by reducing the aperture or the number of prisms. or both.

General Conclusion.

The results of the preceding investigation show that in the case of prismatic spectroscopes we are confined to certain resolving-powers. We are limited in one direction by the physical properties of the glass now at our disposal, in another by the difficulty, we might almost say impracticability, of obtaining blocks of crystalline minerals of larger than a certain size, and in a third by lack of sufficient illumination.

Our only means of obtaining more powerful instruments seems to lie, therefore, in the further development of the grating-spectroscope. The maximum resolving-powers that have thus far been attained with the latter class of instruments are somewhat less than 400,000 units *, about the maximum which, as we have now shown, is attainable with prismatic spectroscopes in the visible region of the spectrum. As the writer has already shown † instruments having at least three times this resolving-power are not only exceedingly desirable, but absolutely necessary to the successful investigation of certain spectral phenomena. We must therefore aim to ultimately produce gratings at least 40 cms. diameter. A machine designed to rule gratings of this size was begun by the writer seven years ago (1896), but owing to the many interruptions to which reference was made at the beginning of the article, work on it was only recently completed ‡. The construction of a machine of about the same size was begun in 1899 by Professors Michelson and Stratton at the University of Chicago; but work on this has also been much interrupted and delayed by the resignation of Professor Stratton to accept the directorship of the new National Bureau of Standards at Washington. More recently still Jewell, at Johns Hopkins, has been remodelling one of the Rowland dividing-engines to rule 10 in. (25 cm.) gratings.

It is to be hoped, therefore, that through the united efforts of all of those now working on this problem, gratings of a considerably larger size than we now have may soon become a commercial possibility.

Allegheny Observatory, November, 1902.

XXXV. *The Use of Contour Integration in the Problem of Diffraction by a Wedge of any Angle.* *By* H. S. Carslaw, *Professor of Pure and Applied Mathematics in the University of Sydney, N.S.W.*§

IN the Appendix on Diffraction to his Adams Prize Essay ‖ Macdonald gives a discussion of the two-dimensional

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* See paper on "Resolving Power of Telescopes and Spectroscopes for Lines of Finite Width," Phil. Mag. vol. xliii. p. 320, May 1897.

† *Loc. cit.* The large solar grating-spectroscopes of the new Allegheny Observatory are designed for gratings of 25 cms. and 40 cms. aperture Report of Director, 1900.

‡ See Report of the Director, Allegheny Observatory, 1900, p. 22. The final setting up of the new engine has been still further delayed by the delay in the completion of the new Observatory and Laboratories.

§ Communicated by the Author.

‖ 'Electric Waves,' by H. M. Macdonald, Camb. 1902.

problem, where the boundary is formed by two planes inclosing an angle α. As a special case his formula yields the solution given by Sommerfeld[*] for the semi-infinite plane.

The method by means of which Macdonald obtains the solution of this problem depends upon a general theorem, proved earlier in his treatise. I propose in this note to give another demonstration, using the method of contour integrals. This method has been employed with very great success in the theory of potential, by Dougall[†], and the proof which I give here would occur to any one reading his most important and suggestive paper (*cf.* §§ 17, 21).

Taking the origin in the edge of the wedge, which occupies the space $\alpha < \theta < 2\pi$, and considering the case in which the electric force is parallel to the edge of the wedge, the problem reduces to the solution of the equation

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + k^2 u = 0,$$

where, in addition, it is required that u shall vanish at the boundary $\theta = 0$ and $\theta = \alpha$, and that it shall become infinite as $\log\left(\frac{1}{R}\right)$, when $R = 0$, at the point (r', θ').

If the space were unbounded we should take as our solution

$$u = U_0(kR),$$

where

$$R^2 = r^2 + r'^2 - 2rr' \cos(\theta - \theta'),$$

and $U_n(z)$ is the Bessel's function of the second kind, given by the equation

$$U_n(z) = \frac{\pi}{2 \sin n\pi}\left(J_{-n}(z) - e^{-in\pi} J_n(z)\right).$$

The addition formula for $U_0(kR)$ is well known, and will be used later, namely

$$U_0(kR) = J_0(kr') U_0(kr) + 2\Sigma_{n=1} J_n(kr') U_n(kr) \cos n(\theta - \theta')$$

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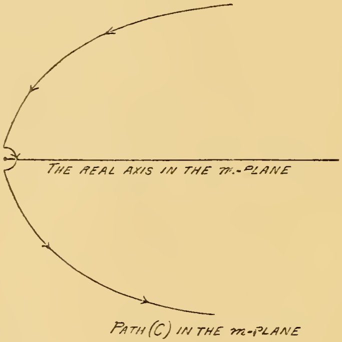
[*] Sommerfeld, "Mathematische Theorie der Diffraction," *Math. Ann.* Bd. xlvii. (1896); *cf.* also a paper by the Author in Proc. Lond. Math. Soc. vol. xxx.

[†] Dougall, "The Determination of Green's Function by means of Cylindrical or Spherical Harmonics," Proc. Edin. Math. Soc. vol. xviii. (1900).

in the case when $r > r'$; while when $r < r'$, r and r' must be interchanged.

The method of this paper consists in obtaining a contour integral for this expression, $U_0(kR)$, *and then adding to it terms which introduce no singularity, and cause the boundary conditions to be satisfied.*

Fig. 1.



Consider the integral

$$\int \frac{\cos m(\pi - \theta + \theta')}{\sin m\pi} U_m(kr) J_m(kr) dm,$$

taken in the m-plane over the path (C) of fig. 1.

When m is large we have the approximate values

$$J_m(z) = \left(\frac{z}{2}\right)^m \frac{1}{\Pi(m)}$$
$$= \left(\frac{z}{2}\right)^m \frac{1}{\sqrt{2\pi m} \, . \, e^{m \log m - m}},$$

using the asymptotic value for $\Pi(m)$*, so that we see that $J_m(z)$ vanishes at infinity, when the real part of m is positive.

In the same way, using the relation,

$$\Pi(m)\,\Pi(-m) = \frac{m\pi}{\sin m\pi},$$

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* *Cf.* Whittaker's 'Modern Analysis,' § 110.

the approximate value of $J_{-m}(z)$ is given by the equation

$$J_{-m}(z)=\left(\frac{z}{2}\right)^{-m}\frac{\sin m\pi}{m\pi}\cdot\sqrt{2\pi m}\,.\,e^{m\log m-m},$$

and this does not vanish at infinity, when the real part of m is positive.

However, since

$$U_m(z)=\frac{\pi}{2\sin m\pi}\left(J_{-m}(z)-e^{-im\pi}J_m(z)\right),$$

the expression for $J_m(z')U_m(z)$ simplifies, and we find its approximate value to be given by

$$J_m(z')U_m(z)=\frac{1}{2m}\left(\frac{z'}{z}\right)^m.$$

Hence this product vanishes at infinity, when the real part of m is positive, provided that $z>z'$.

Further, it is readily shown that

$$\frac{\cos m(\pi-\theta+\theta')}{\sin m\pi}$$

vanishes at infinity, when $0<\theta-\theta'<2\pi$. Thus

$$\frac{1}{2i\pi}\int_C\frac{\cos m(\pi-\theta+\theta')}{\sin m\pi}J_m(kr')U_m(kr)dm,\left(\begin{matrix}r>r'\\\theta>\theta'\end{matrix}\right),$$

over the path (C) of fig. 1 is equal to the sum of the residues of this function. Therefore

$$\frac{1}{i\pi}\int_{C'}\frac{\cos m(\pi-\theta+\theta')}{\sin m\pi}J_m(kr')U_m(kr)dm,\left(\begin{matrix}r>r'\\\theta>\theta'\end{matrix}\right)$$

over the path (C′) of fig. 2 is equal to

$$\frac{1}{\pi}\left[J_0(kr')U_0(kr)+2\Sigma_{n=1}J_n(kr')U_n(kr)\cos n(\theta-\theta')\right],$$

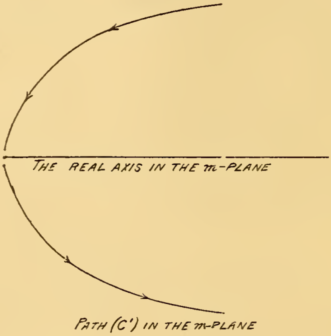
the path (C′) differing from the path (C) by the removal of the small semicircle at the origin.

We have therefore obtained the following expression for $U_0(kR)$ as a contour integral:—

$$\frac{1}{i}\int_{C'}\frac{\cos m(\pi-\theta+\theta')}{\sin m\pi}J_m(kr')U_m(kr)dm,\left(\begin{matrix}r>r'\\\theta>\theta'\end{matrix}\right),$$

while when $r<r'$, or $\theta<\theta'$, we have only to interchange r and r', or θ and θ', in the above expression.

Fig. 2.



To deduce the solution of the diffraction problem, where the boundary is given by the planes $\theta=0$ and $\theta=\alpha$, we have to balance the expression just obtained by the addition of solutions of the differential equation

$$\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+k^2u=0,$$

which remain finite in the space considered, $0<\theta\leqq\alpha$, and cause the boundary conditions to be satisfied.

It will be seen that

$$u=\frac{1}{i}\int_{C'}\left[\cos m(\pi-\theta+\theta')-\cos m(\pi-\alpha+\theta')\frac{\sin m\theta}{\sin m\alpha}\right.$$
$$\left.-\cos m(\pi-\theta')\frac{\sin m(\alpha-\theta)}{\sin m\alpha}\right]\frac{J_m(kr')\,U_m(kr)\,dm}{\sin m\pi}$$

satisfies all these conditions when $r>r'$, and $\alpha>\theta>\theta'$, while when $r<r'$, or $\theta<\theta'$, we shall have only to interchange r and r', or θ and θ', in the above.

To prove this we note first that the different elements of the integral satisfy the differential equation, and that the boundary conditions are satisfied. Further, that no new sources are introduced by the additional terms, since the integrals they give converge for all the values of r and θ in the space considered, unlike that for the first term, which has a singularity at the point (r', θ').

This expression simplifies, and may be written

$$2i\int_{C'}\frac{\sin m(\alpha-\theta)\sin m\theta'}{\sin m\alpha}\,J_m(kr')U_m(kr)\,dm,\left(\begin{matrix}r>r'\\ \alpha>\theta>\theta'\end{matrix}\right),$$

and as there is now no pole at the origin in the m-plane, we may take the path (C) instead of (C′).

Hence we obtain our solution in the form of an infinite series, by the use of Cauchy's residue theorem, this solution being given, for all values of θ in the space $0<\theta<\alpha$, by the equations

$$u=\frac{4\pi}{\alpha}\Sigma\sin\frac{n\pi}{\alpha}\theta\sin\frac{n\pi}{\alpha}\theta'\,U_{\frac{n\pi}{\alpha}}(kr)\,J_{\frac{n\pi}{\alpha}}(kr'),\quad r>r'. \quad .\ (1)$$

$$u=\frac{4\pi}{\alpha}\Sigma\sin\frac{n\pi}{\alpha}\theta\sin\frac{n\pi}{\alpha}\theta'\,U_{\frac{n\pi}{\alpha}}(kr')\,J_{\frac{n\pi}{\alpha}}(kr),\quad r<r'. \quad .\ (2)$$

This result agrees with that given by Macdonald*, and may be compared with the solution of the same equation in the n-fold Riemann's space, given by Sommerfeld†.

This method may be extended to the corresponding three-dimensional problem, and it can also be employed in the cases where the diffraction is caused by a Sphere or Circular Cylinder. Several interesting results in these cases have been already obtained by me, and I hope to publish a full discussion of these problems at a later date.

Glasgow, January 1903.

XXXVI. *Notices respecting New Books.*

The Meteorology of the Ben Nevis Observatories. Part II. *Containing the Observations for the Years* 1888 . . . 1892, *with Appendices. Edited by* Alexander Buchan, *LL.D., F.R.S., and* Robert Traill Omond; forming Volume XLII. of the Transactions of the Royal Society of Edinburgh. 1902. Pp. xiv+552.

A PREVIOUS volume (vol. xxxiv.) of the Edinburgh 'Transactions' gave particulars of the earlier meteorological observations taken on the summit of Ben Nevis and at its base, at the Public School, Fort William, from December 1883 to the end of 1887. The present volume brings down the complete observational record to the end of 1892. During the final years of this period the Fort William data are from the Observatory opened there in July 1890, which possesses a superior set of self-recording instruments.

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* *Loc. cit.* p. 190.

† *Loc. cit.* p. 356 (13).

A short preface, pp. v to x, gives an account of the position and management of the observatories; whilst an introduction, pp. 1 to 8, describes very briefly the instrumental outfit and the nature of the observations. The data for each of the five years 1888 to 1892 are in the first instance treated separately. Thus for 1888 we have for Ben Nevis itself tables for each month, including *hourly* readings of the barometer, wet- and dry-bulb thermometers, rainfall, sunshine, direction and force of wind (scale 0 to 12), and amount of cloud (scale 0 to 10). These tables give also particulars for each day of the mean barometric pressure and cloudiness, the maximum and minimum temperatures, the maximum wind-force, and total amounts of rainfall and sunshine. Following the Ben Nevis tables are corresponding but more restricted tables for Fort William. There is then a summary of mean monthly and annual diurnal variations for Ben Nevis, and a transcript of the entries made during the year in a log-book kept at the summit observatory. The log treats in considerable detail of fogs, auroras, halos, thunderstorms, and other miscellaneous phenomena.

The records for the subsequent years 1889 to 1892 follow similar lines; only, after the institution of the low-level observatory, the Fort William data appear in greater detail, and corresponding tables for the base and the summit stations appear side by side in adjacent pages. The five years' records occupy over 400 pages. They are followed on p. 419 by a table summarizing the snowfall data on Ben Nevis from 1883 to 1892; and after this are a set of rather incomplete records obtained with a Robinson cup-anemometer, a type of instrument difficult to work at the summit. On pp. 436 to 445 are a series of important tables, giving mean diurnal variations of barometric pressure, temperature, &c., for each month of the year, based on the observations of a number of years. From the title of the volume one would have supposed that no data later than 1892 would have been available; but the tables just referred to utilize the observations taken up to the end of 1896.

The remainder of the volume forms an Appendix, consisting mainly of miscellaneous meteorological papers, some apparently new, others abstracts of papers previously published. Only a few of them are exclusively confined to Ben Nevis data. Dr. Buchan and Mr. Omond discuss the differences between the diurnal variations of the barometer in bright and in cloudy weather at some nine stations. Mr. Buchanan has a general discussion of the effects of fog on Ben Nevis meteorology. Mr. Aitken has a report on observations of atmospheric dust. The remaining papers are due to Dr. Buchan and to Messrs. Omond, Rankin, and Mossman. Most are mainly observational or statistical in character, but several—*e. g.* papers by Dr. Buchan on the influence of high winds on the barometer, and by Mr. Omond on differences between the Ben Nevis and Fort William barometers when both are "reduced to sea-level"—are more theoretical.

A table of contents, pp. xiii and xiv, and an index, pp. 551 to 552 make the book easily consulted.

The preparation of the tables in a volume such as this represents an enormous amount of labour of a kind calculated to damp the ardour of any but the most enthusiastic workers, and Dr. Buchan and Mr. Omond well deserve the thanks of meteorologists. They are to be congratulated on the beautifully clear way in which the tables are printed, and on the success of the various devices for guiding the eye to take in the prominent features. The reader of the Ben Nevis "logs" must also bear a tribute to the great zeal shown by the observers at the summit. The freezing-up of instruments, blocking by snow, and other exceptional conditions, render the use of ordinary self-recording apparatus impossible, so that all the hourly records—except those of sunshine—are from eye observations. In the winter months, during high gales and drifting snow, few people would envy the observer whose duty takes him out of doors in the midnight hours. When it comes to a critical estimate of the value of the observations, there is a little more room for doubt. The non-instrumental estimate of such a constantly fluctuating element as wind-force, the record of rainfall or melted snow during storms, the use of the sunshine recorder in alternating clear and snowy or foggy weather, are attended by uncertainties from which the records at low-level stations are comparatively free. Such sources of uncertainty should, however, be largely eliminated when it comes to mean monthly or annual diurnal variations. In the comparison of the data at the base and the summit there are uncertainties arising from the great difference in the environment of the two stations. The station at the base has its wind and even its sunshine record considerably interfered with by surrounding high grounds; whilst some of the records at the summit are influenced by the want of symmetry in the shape of the mountain, there being an enormous precipice on one side of the observatory, at no very great distance. This want of symmetry must add to the difficulty of judging how far meteorological conditions at the summit are comparable with those that would exist at the same level in the free atmosphere if the mountain were non-existent. In some of the discussions in the latter part of the volume evidence of greater familiarity with physical principles and results, and with the theory of instruments, would give the reader more confidence that the point of view selected is the one most likely to lead to a clear issue. There seems a slight slip in the theory of the table on p. 545 for eliminating from diurnal variations any "non-cyclic" change taking place progressively. The table ascribes to an interval of 23 hours the change that really answers to 24. The consequent error would, however, very seldom be of practical moment. C. C.

Franges d'Interférence et leurs Applications Métrologiques. Par J. Macé de Lépinay, *Professeur à la Faculté des Sciences de Marseille.* Paris: C. Naud. 1902. Pp. 101. ("Scientia" Series, No. 14.)

In this interesting and up-to-date brochure the author gives a comprehensive account of the production of interference-fringes, their properties, and application to the exact measurement of length. The last chapter in the book gives a brief account of some determinations of the mass of a cubic decimetre of distilled water at 4° C.; and perhaps no better evidence of the value of optical methods of measuring lengths could be obtained than the following concordant results of three recent determinations of this quantity:—

Macé de Lépinay	999·954 grammes
Fabry, Macé de Lépinay and Perot ..	999·974 ,,
Chappuis	999·976 ,,

L'Électricité Déduite de l'Expérience et Ramenée au Principe des Travaux Virtuels. Par M.-E. Carvallo. Paris: C. Naud. 1902. Pp. 91. ("Scientia" Series, No. 19.)

This little book—one of the latest additions to the well-known "Scientia" series—forms an excellent introduction to some of the more difficult portions of Maxwell's great treatise. It is mainly concerned with the application of Lagrange's dynamical equations to electrical problems. The principle of virtual work is employed by the author to establish Lagrange's equations, and the treatment of this subject appears to us to be clearer than any we remember having seen elsewhere. The discussion of the applicability of Lagrange's equations to electrical problems is very thorough, and the interesting case of Barlow's wheel, to which the equations are not applicable, is fully discussed.

United States Magnetic Declination Tables and Isogonic Charts for 1902. *By* L. A. Bauer, *Chief of Division of Terrestrial Magnetism U.S. Coast and Geodetic Survey.* Washington, 1902. Pp. 405, with 2 Charts.

Terrestrial Magnetism has long formed part of the work of the U.S. Coast and Geodetic Survey, but it has recently been constituted a separate division of the survey under the supervision of Dr. Bauer, well known as the Editor of the journal 'Terrestrial Magnetism.' Judging by the present volume—the first drawn up under Dr. Bauer's regime—there is every prospect of increased activity in magnetic work in the United States. The first part of the volume gives a lengthy historical account of the origin and progress of the subject, commencing with a *résumé* of what is believed to have been known by the Chinese and early Greeks and Romans, and following the course of discovery down to the present day. On pp. 28 to 30 is a summary of old observations of declination, taken prior to 1600 at different parts of the world, including an observation by Frobisher at a somewhat mysterious "Fair Island (S.W. of Scotland)." Dr. Bauer has many complimentary references to early English observers, including Norman and Gellibrand; but he evidently thinks (*cf.* p. 35) that so far as Terrestrial Magnetism is concerned Gilbert's work has been overrated. The latter part of the historical introduction gives tables and curves of secular change in all parts of the world, also particulars as to diurnal and annual inequalities of declination at various stations in America and elsewhere, and includes a brief discussion of magnetic storms. Under the heading of "Magnetic Observatories," pp. 56–61, we have an illustrated account of the new American Magnetic Observatory at Cheltenham, Maryland; this includes a full description of the elaborate arrangements for securing small diurnal variation of the temperature. The equipment of this observatory comprises magnetographs both of the Adie (Kew) and Eschenhagen patterns. Several of the photographic traces obtained at Cheltenham in 1902 are reproduced, including one which shows a magnetic disturbance whose beginning is supposed to synchronize with the eruption of Mt. Pelée (Martinique) on May 8th. Following this, pp. 62–65, are some small scale magnetic charts, including early ones by Hansteen, Halley and Duperrey, others by Neumayer, and some by the British Admiralty for the epoch 1905. There is also a general description of magnetic surveys, including that of the United Kingdom by Rücker and Thorpe, with a reference to the proposed Norwegian expedition under Amundsen during the present year to the neighbourhood of the north magnetic pole.

The remainder of the volume deals more directly with the special work of the U.S. Coast and Geodetic Survey. It describes the Survey's type of magnetometer-theodolite, contains instructions as to the taking of observations, and gives many particulars as to secular change of declination in the United States and outlying territories. These secular change data are used in reducing to the epoch Jan. 1, 1902, an enormous mass of observations of declination in America—some in British territory,—particulars of which occupy pp. 117–266. Then follows a minute description of the position of all stations occupied between 1881 and midsummer 1902. At the end of the book are two isogonic charts for the epoch Jan. 1, 1902, one for the United States proper, with adjacent regions in Canada and Mexico, the other for Alaska.

C. C.

XXXVII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 175.]

November 5th, 1902.—Prof. Charles Lapworth, LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'The Fossil Flora of the Cumberland Coalfield, and the Palæobotanical Evidence with regard to the Age of the Beds.' By E. A. Newell Arber, Esq., M.A., F.G.S.

2. 'Some Remarks upon Mr. E. A. Newell Arber's Communication: On the Clarke Collection of Fossil Plants from New South Wales.' By Dr. F. Kurtz, Professor of Botany in the University of Córdoba, Argentine Republic.

3. 'On a new Boring at Caythorpe (Lincolnshire).' By Henry Preston, Esq., F.G.S.

This boring, after piercing Northampton Sands, passed through 199 feet of Upper Lias, 19 feet of Marlstone, and into the Middle Liassic Clays. With the aid of other shallow wells in the Lincolnshire Limestone, the author shows that this rock has a decided dip to the west down the face of the escarpment, as though it had settled down upon the eroded surface of the Upper Liassic Clay. This settlement is probably the cause of a continuous spring flowing from the junction, and it has given rise to an underestimate of the thickness of the Upper Lias.

November 19th.—Prof. Charles Lapworth, LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. 'The Semna Cataract or Rapid of the Nile: a Study in River-Erosion.' By John Ball, Ph.D., F.G.S., A.R.S.M., Assoc. M.Inst.C.E.

Inscriptions placed on the rocks at Semna, between the second and third cataracts, under the 12th and 13th dynasties, serve as a means of gauging the local changes due to river-erosion during a period of about 4200 years. Horner, in 1850, came to the conclusion that

> 'the only hypotheses which could meet the requirements of the facts observed, would be either the wearing away of a reef or barrier at the place in question—a process requiring too long a period,—or the existence at some distant period of a dam or barrier, formed perhaps by a landslip of the banks, at some narrow gorge in the river's track below Semna.'

The author is in favour of the former explanation. The river, above and below the Kumna and Semna temples, has a width of 400 metres, but between the two temples a narrow band (200 metres wide) of hard red and grey gneiss contracts the river at low Nile within a central channel about 40 metres wide. Through this deep channel not less than 400 cubic metres of water pass per second. The gneiss itself, dykes of syenite-porphyry, hornblende-schists, and augitite are described; and it is shown that the foliation of the gneiss is parallel to the channel, and probably accounts for the direction of the latter. Rapid erosion with the formation of pot-holes is observed to be now taking place; and the author calculates that if 200 cubic metres (approximately 500 tons) of rock per year has been removed from the barrier, the lowering of it would amount to 2 millimetres a year, or in 4200 years 7·9 metres, the depth of the present river below the lowest group of inscriptions dating from the time of Amenemhat III. The yearly discharge of the Nile past Semna is nearly 100,000 million tons of water; and the author considers that the removal of 500 tons of rock under existing conditions in a year is not only not impossible, but highly probable, as all this erosion only amounts to 5 milligrams of rock per ton of silt-laden water. This erosion is compared with the classic instance of the River Simeto in Sicily. At Assuan and Silsilla the river has suffered considerable lowering within geologically recent times, probably brought about by the removal of long pre-existent hard barriers. The sluices of the new dam at Assuan may in the future give a quantitative determination of silt-erosion in granite, and it would appear to be not difficult to ascertain at Semna the rate of pot-holing. The formation of new pot-holes 1½ feet deep, in an artificial channel in rock in Sweden, has been observed to take place in 8 or 9 years, and the author hopes in future to attempt some measurements of this kind at Semna.

2. 'Geological Notes on the North-West Provinces (Himalayan) of India.' By Francis J. Stephens, Esq., F.G.S., A.I.M.M.

The country examined extends in a north-westerly direction across the line of strike, from the borders of Nepal and South-eastern Kumaon to north of the Alakmunda River in the vicinity of Badrinath, and the Marra Pass. The foothills consist of Tertiary clays and sandstones, the snowy ranges of gneissose, granitic, and metamorphic rocks of various descriptions. 'Between the snowy ranges, or rather the most southerly range of the Himalàya chain, a band of hills extends, for nearly 50 miles on an average, to the foothills.' These have hardly been explored, though roughly mapped on geological maps of India as belonging to a 'Transition Series.' The whole area is rich in minerals. The author gives a brief description of various rocks, met with mainly in this third belt. They include slates with vein-quartz; mica- and graphite-schists;

dykes of dolerite; granites; clay-slates, sandstones, and schists, with copper, lead, and tin; limestones, serpentines, and hornblendic rocks, with talc, steatite, etc.; various schists, quartzites, and limestones. The summary of the author's observations leads him to

'suppose that there are at least three distinct limestone or calcareous series in Kumaon and Garhwal, and that schists and quartzites, with several isolated patches of granitic rock, form a large part of the remaining formations.'

3. 'Tin and Tourmaline.' By Donald A. MacAlister, Esq., F.G.S.

Cassiterite hardly ever occurs without tourmaline, though the latter is found without the former; hence it appears that tourmaline-producing constituents and influences are of wider range than are those of cassiterite. Boron-trioxide is an extremely common accompaniment of volcanic action, and there can be no doubt that it has acted powerfully in changing such original minerals as the micaceous and felspathic ingredients of crystalline rocks. From a comparison of formulæ representing tourmaline and felspar, it is evident that the act of tourmalinization has been accompanied by a loss of soda. The excess of this soda will combine with boric acid, forming metaborate and pyroborate of soda. The former, acting on disseminated tin-ore, might result in the production of sodium-metastannate and borax. The metastannate is soluble, and capable of being leached out of the magma, and, by a new reaction, tin-oxide may be precipitated and concentrated, while sodium-metaborate may be liberated. According to the cooling-curve of solutions, in all probability deposition of the oxide of tin would take place more rapidly at a certain stage in the process of cooling than at others.

December 3rd.—Prof. Charles Lapworth, LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. 'On some Well-sections in Suffolk.' By William Whitaker, Esq., B.A., F.R.S., F.G.S.

Notes of thirty-one new wells have accumulated since 1895, some of them giving results which could not have been expected. A trial-boring for the Woodbridge Waterworks Company gave a depth of 133¾ feet down to Eocene beds, and a thickness of Crag about double of any before observed in the neighbourhood. An analysis of the saline, hard, water yielded is given. Three explanations are suggested: a channel, a huge 'pipe' in the Chalk, or a disturbance such as a fault or a landslip; but the author is not satisfied with any of them. Two borings at Lowestoft show that Crag extends to a depth of 240 feet in one case, and over 200 feet in another: confirming estimates of Mr. Harmer and Mr. Clement Reid. In one of these, Chalk was reached at 475 feet. Three other wells in the neighbourhood confirm the great depth of the newer Tertiary strata. Sections are also given from the following places:—Boulge, Hitcham Street, Ipswich (corroborating the evidence for a deep channel filled with Drift given by the section at St. Peter's Quay, New Mill), Shotley, Stansfield, and Brettenham Park. The last shows the greatest thickness of Drift recorded in the county, namely, 312 feet.

2. 'The Cellular Magnesian Limestone of Durham.' By George Abbott, Esq., M.R.C.S., F.G.S.

The Permian Limestone covers about 1¼ square miles near Sunderland; it alternates with beds of marl containing concretionary limestone-balls, and attains a thickness of 65 feet or so. The cellular limestones frequently contain more than 97 per cent. of calcium-carbonate. Magnesium-carbonate occupies the interspaces or 'cells' of this limestone, and also the spaces between the balls. The hundred or more patterns met with in it can be arranged into two chief classes, conveniently termed honeycomb and coralloid, each with two varieties; and each class has four distinct stages, both classes having begun with either parallel or divergent systems of rods. The second stage is the development of nodes at regular distances on neighbouring rods; and these in the third stage, by lateral growth, become bands. Finally, in the fourth stage the interspaces become filled up. The upper beds are usually the most nearly solid. In the coralloid class the nodes and bands are smaller and more numerous than in the honeycomb class. In both classes tubes are frequently formed. The rods have generally grown downwards, but upward and lateral growth is common. A section of Fulwell Quarry is given.

December 17th.—Prof. Charles Lapworth, LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. 'Note on the Magnetite-Mines near Cogne (Graian Alps).' By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S.

These mines have been worked probably since Roman times, but are now almost deserted. They are situated in the Val de Cogne, one of the larger tributaries to the Val d'Aosta from the Graian Alps. The author, in company with the Rev. E. Hill, last summer examined two localities where the ore has been worked. At one, the Filon Licone, the mass of magnetite is probably about 80 or 90 feet thick and some five times as long. At the other place, the Filon Larsine, the mass apparently is not nearly so thick. The ore is a pure magnetite, jointed like a serpentine, a thin steatitic film being often present on the faces. At both localities the magnetite is found to pass rapidly into an ordinary serpentine, the transitional rock being a serpentinized variety of the cumberlandite described by Prof. Wadsworth in his 'Lithological Studies.' The serpentine is intercalated, like a sill, between two thick masses of calc-mica-schists, with which green schists (actinolitic) are as usual associated, no doubt intrusively. All these represent types common in the Alps. The author discusses the relations of the magnetite and serpentine, which, in his opinion, cannot be explained either by mineral change or by differentiation *in situ*, but indicate that a magnetitic must have been separated from a peridotic magma at some considerable depth below the surface, and the former, when nearly or quite solid, must have been brought up, fragment-like, by the latter; as in the case of metallic iron and basalt at Ovifak (Greenland).

2. 'The Elk (*Alces machlis*, Gray) in the Thames Valley.' By Edwin Tulley Newton, Esq., F.R.S., F.G.S.

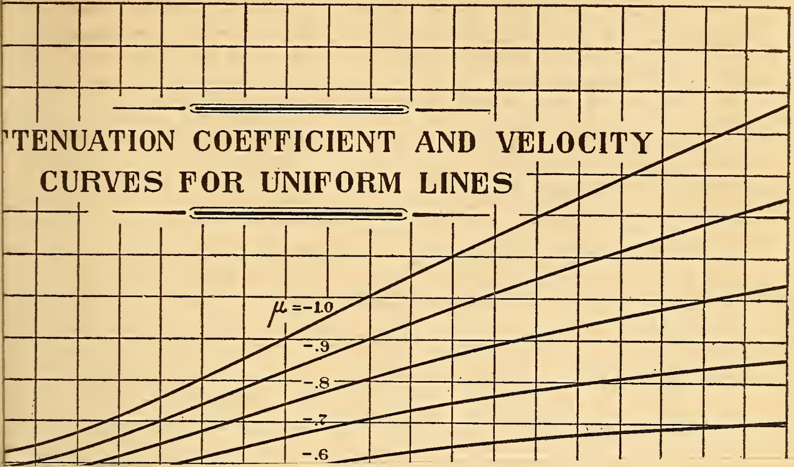
3. 'Observations on the Tiree Marble, with Notes on others from Iona.' By Ananda K. Coomáraswámy, Esq., B.Sc., F.L.S., F.G.S.

The gneiss near Balephetrish has a general south-westerly and north-easterly trend, and the limestone occurs in it as lenticles of various sizes, having a similar foliation. Descriptions of pink, grey, and white varieties of the limestone in this locality are given. The inclusions comprise those of gneiss containing quartz, felspars, hornblende, augite, scapolite, and sphene as characteristic minerals, and mineral-aggregates consisting of sahlite, coccolite, scapolite, sphene, apatite, calcite, and mica. The contact-phenomena are not specially well displayed, but several instances are described; and in these the minerals of the modified gneiss interlock with those of the modified limestone, and there is no actual line of junction seen under the microscope, although an abrupt change is evident. The dynamic phenomena include the rounding of the minerals (frequently, however, an original character) and the formation of 'augen.' The carbonates are present as a fine-grained granular matrix, the result of the breaking-down of larger grains, probably at a temperature not above 300° C., as indicated by the experiments of Adams & Nicolson. Although there are exceptions, gneiss-inclusions and mineral aggregates have usually been protected from the effects of extreme pressure. The description of minerals includes carbonates, pyroxene, amphibole, forsterite, scapolite, sphene, mica, apatite, and spinel. White, greenish, and black marbles are described from Iona, where they are associated with actinolite-felspar schists and others; they are included in the gneiss. Sedimentary rocks suggestive of Torridon Sandstone occur along the eastern shore of Iona.

January 7th, 1903.—Prof. Charles Lapworth, LL.D., F.R.S.,
President, in the Chair.

The following communication was read:—

'On the Discovery of an Ossiferous Cavern of Pliocene Age at Dove Holes, Buxton (Derbyshire).' By William Boyd Dawkins, M.A., D.Sc., F.R.S., F.G.S., Professor of Geology in Owens College, Victoria University (Manchester).


TENUATION COEFFICIENT AND VELOCITY
CURVES FOR UNIFORM LINES
μ = −1.0
−.9
−.8
−.7
−.6

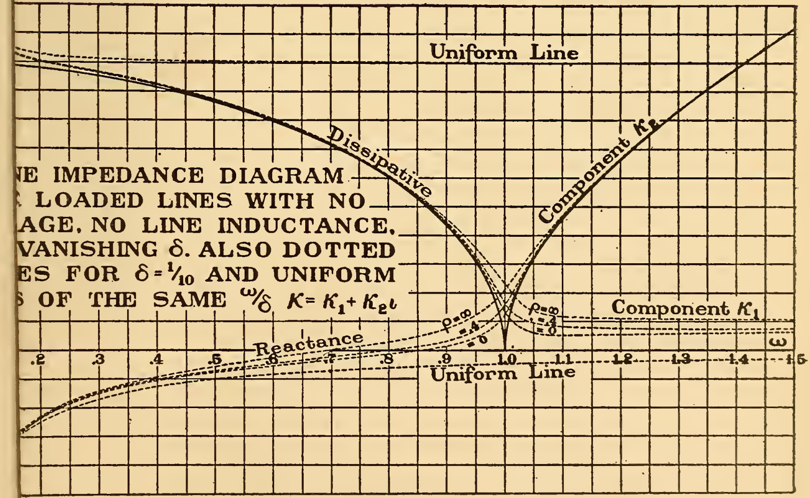

E IMPEDANCE DIAGRAM
LOADED LINES WITH NO
AGE. NO LINE INDUCTANCE.
VANISHING δ. ALSO DOTTED
ES FOR $\delta = 1/10$ AND UNIFORM
OF THE SAME ω/δ $K = K_1 + K_2\iota$
Uniform Line
Dissipative
Component K_2
Component K_1
$\rho = \infty$
= .4
= 0
$\rho = \infty$
= .4
= 0
Reactance
ω
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
1.5
Uniform Line

Diagram VI.

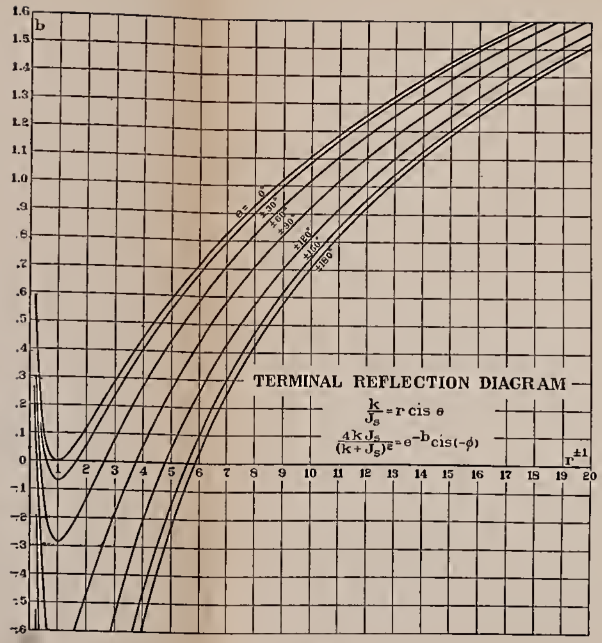


Diagram I

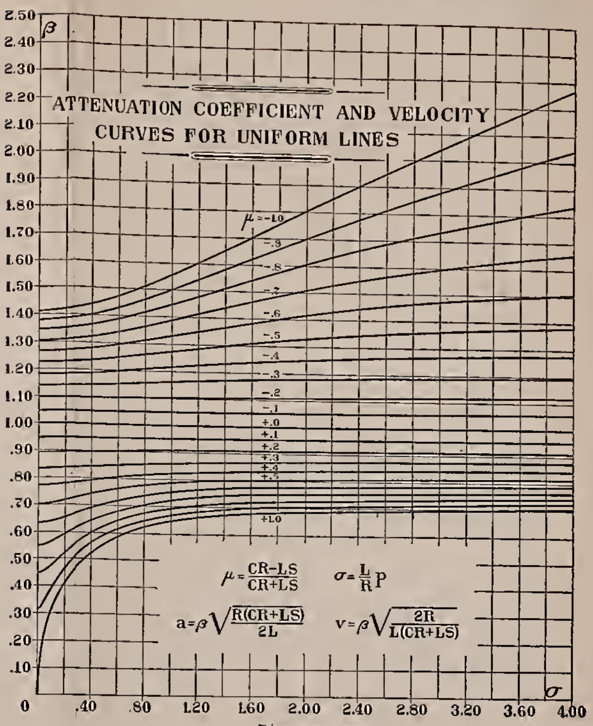


Diagram III

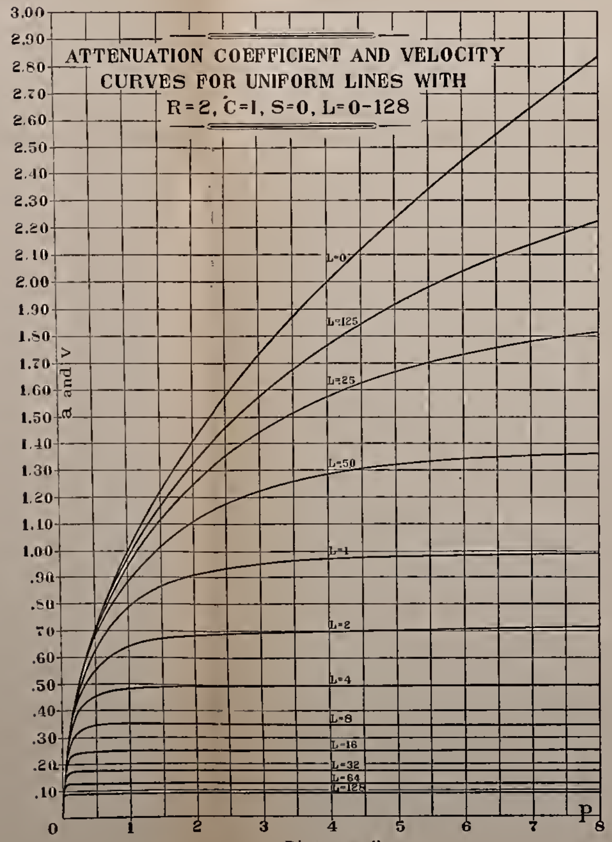


Diagram II.

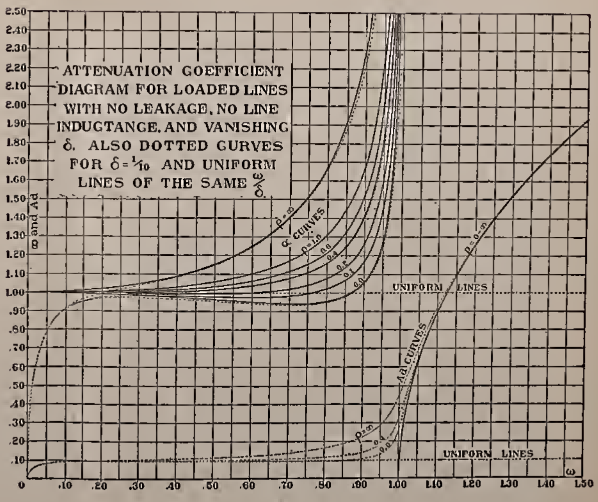


Diagram IV

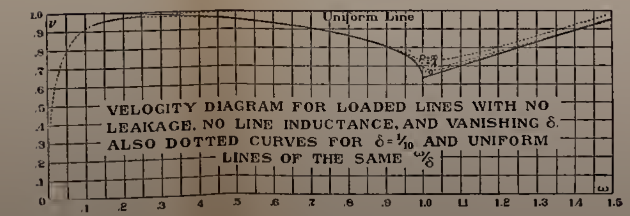


Diagram V.

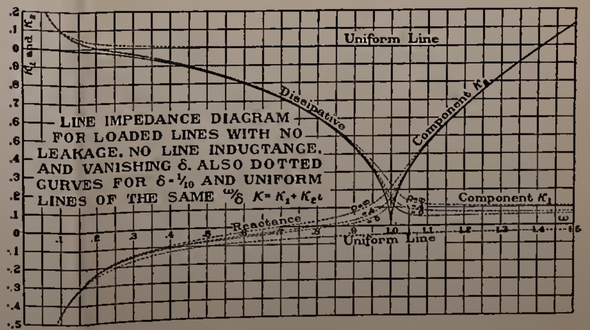


Diagram VI.

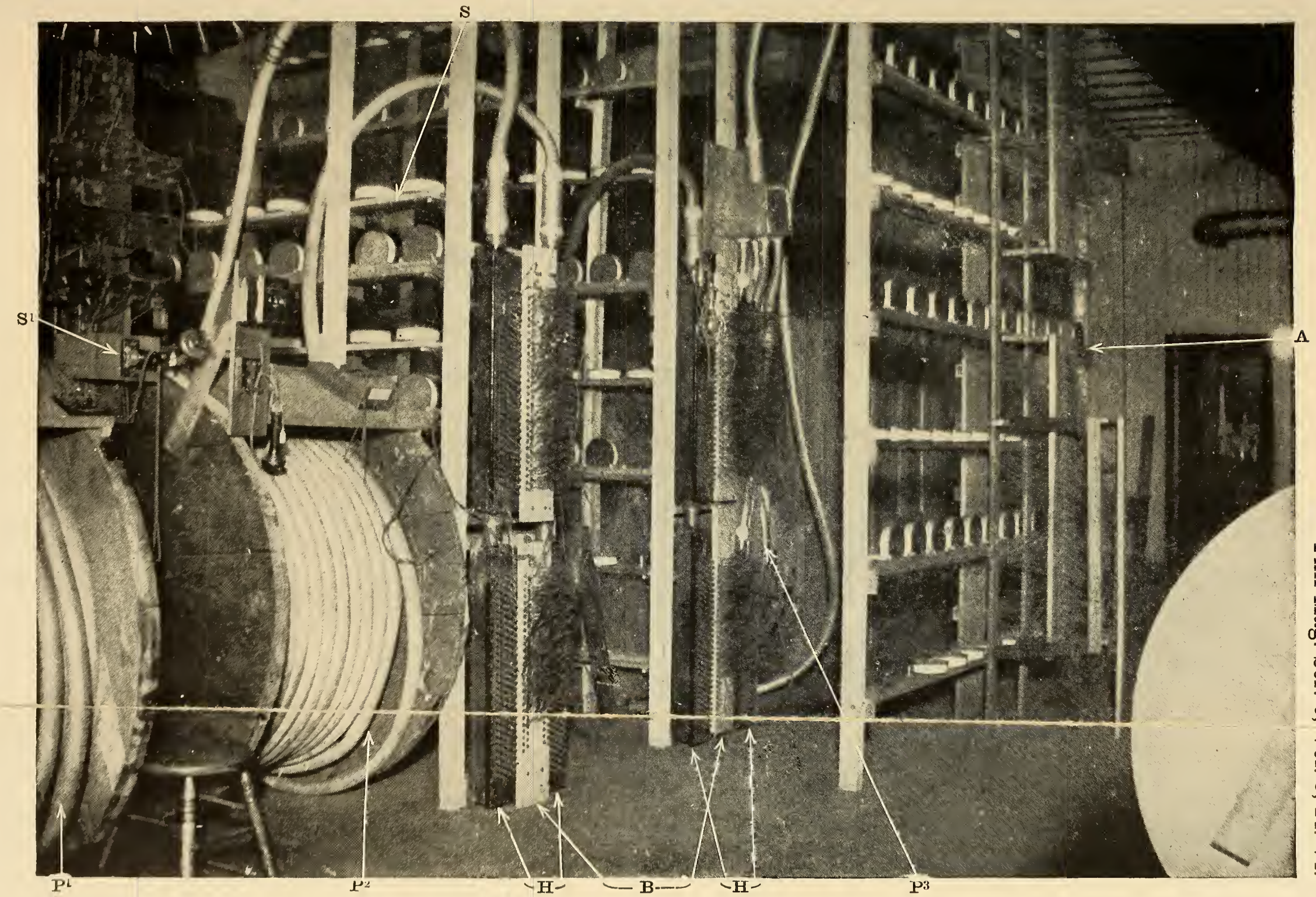

S
S¹
A
P¹
P²
H
B
H
P³

Fig. 11.

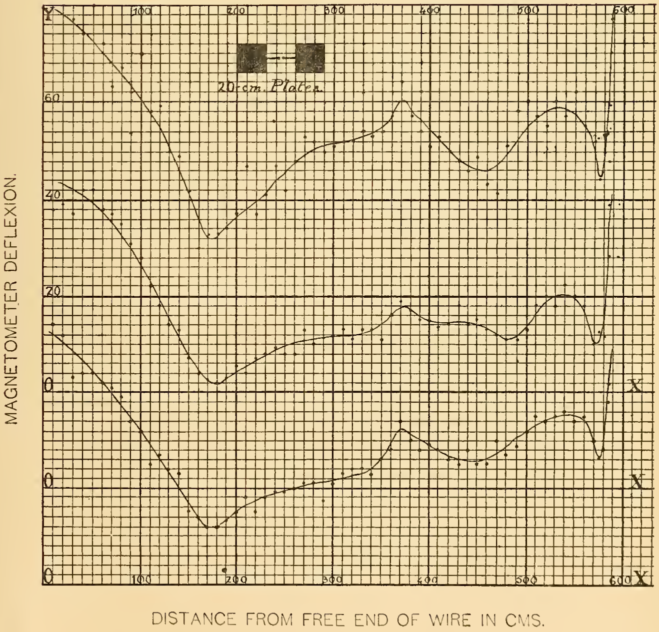

Y
100
200
300
400
500
600
20 cm. Plates.
60
40
20
0
0
0
X
X
X
MAGNETOMETER DEFLEXION.
DISTANCE FROM FREE END OF WIRE IN CMS.

Fig. 7.

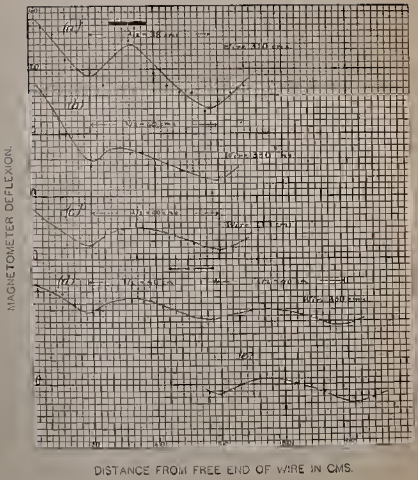


Fig. 8.

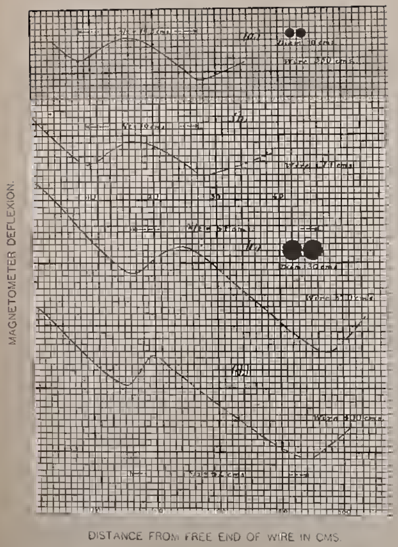


Fig. 9.

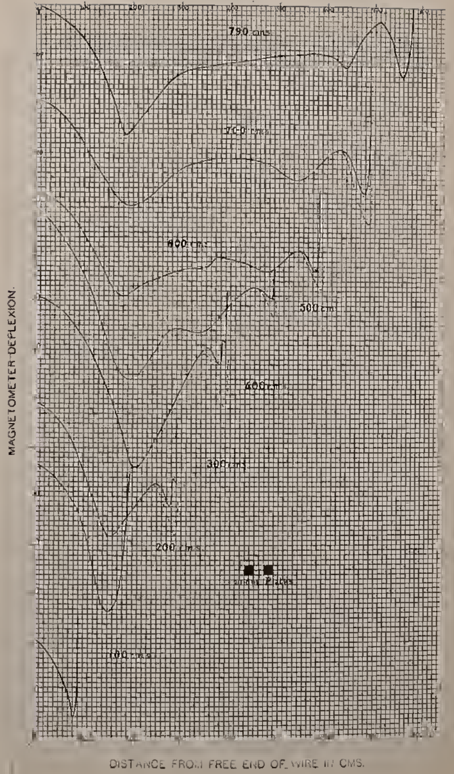


Fig. 10.

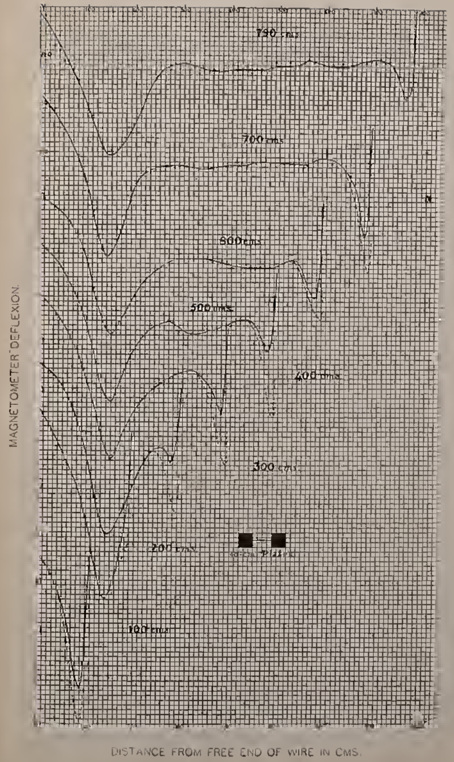
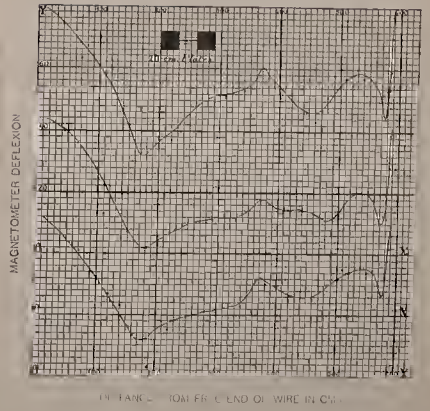


Fig. 11.



Phil. Mag. Ser 6, Vol. 5, Pl. VIII.

Fig. 4

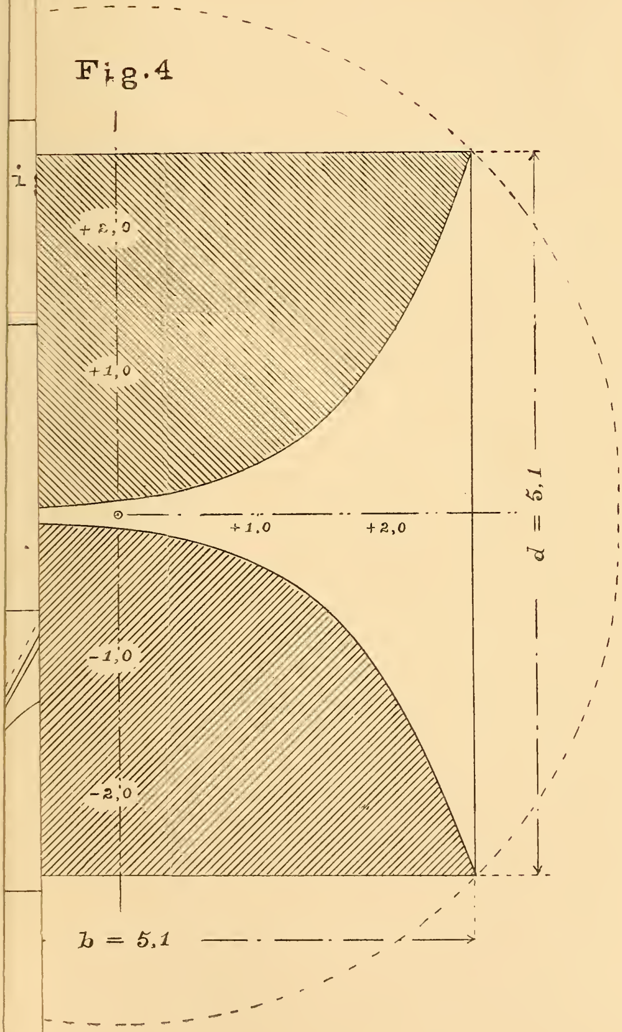


Fig 1.

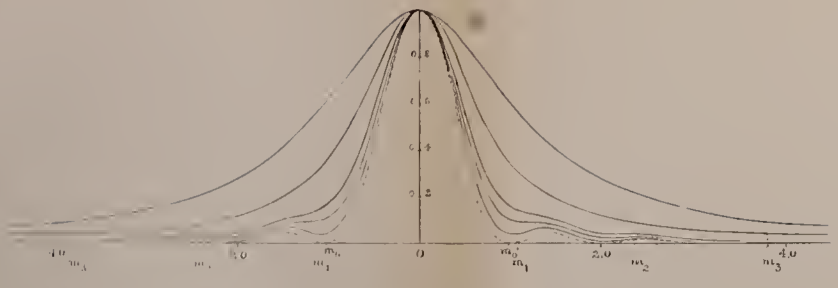


Fig. 2

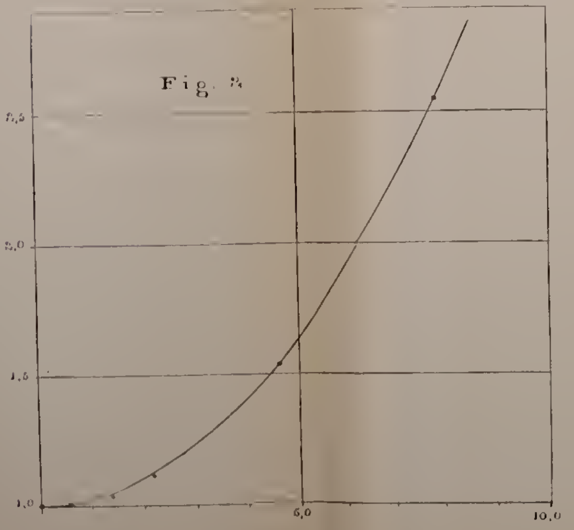


Fig. 3.

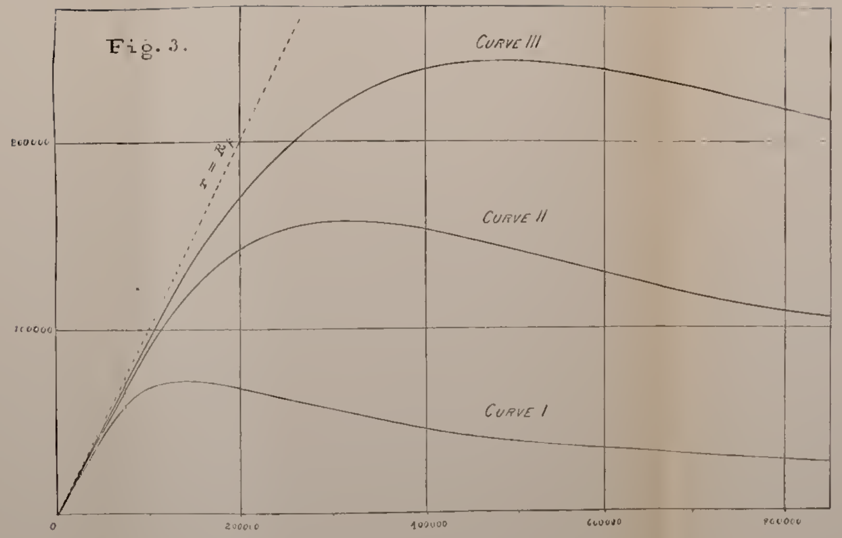
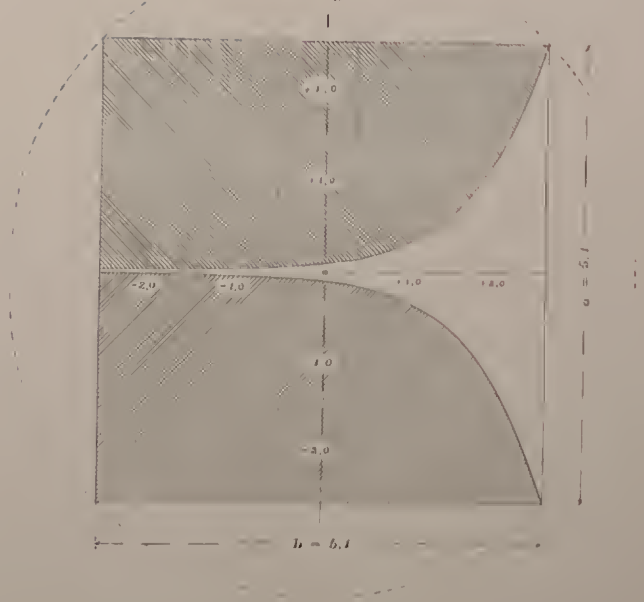


Fig. 4



THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SIXTH SERIES.]

APRIL 1903.

XXXVIII. *The Conductivity produced in Gases by the aid of Ultra-Violet Light.* By JOHN S. TOWNSEND, *M.A., Wykeham Professor of Physics, Oxford*[*].

[Plate IX.]

IN a former paper[†] on this subject, I gave an account of some experiments which were made with a view to finding the nature of the conductivity which is obtained when ultra-violet light falls on the negative electrode in a gas. The results confirmed the theory of the genesis of ions by collision which had been previously deduced[‡] from experiments with Röntgen rays and from Stoletow's experiments. It was also shown that the negative ions thus produced in a gas are identical with the negative ions set free from the electrode by the action of the ultra-violet light. The gases which were examined were air, carbonic acid, and hydrogen.

I propose in this paper to give the results of some experiments which I have made with hydrochloric acid gas and water vapour, and to compare the results with those obtained with the other gases. In all cases the same general theory affords an explanation of the phenomena, and we are led to conclude that negative ions are generated in air, carbonic acid gas, hydrogen, water vapour, or hydrochloric acid gas, which are all identical with the negative ions set free from a zinc plate by the action of the ultra-violet light.

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[*] Communicated by the Author.

[†] Phil. Mag. June 1902.

[‡] Ibid. February 1901.

The experiments with hydrochloric acid gas were conducted in precisely the same manner as has been already described for the first three gases. In order to use water vapour it was necessary to alter the arrangement of the apparatus, since the pressures cannot be found with a McLeod gauge, and it is undesirable to introduce the vapour into the Toepler pump.

Plate IX. fig. 1 shows the apparatus which was used for adjusting and measuring the pressure of the water vapour. The parallel plates for measuring the conductivities were set up in the air-tight vessel A, which was connected with one side of the oil manometer M by the tube T. The bulb B containing water was joined to a side tube provided with a stop-cock S, through which the water vapour was admitted to the apparatus. The other side of the manometer was connected through drying-tubes to the McLeod gauge and the Toepler pump. Sulphuric acid was used in the tube D_1 near the manometer, and phosphorus pentoxide in the second tube D_2.

The oil used in the manometer was that which is supplied for lubricating the Geryk vacuum-pump; it had a specific gravity ·87, and a small vapour-pressure which may be neglected in comparison with the pressure of the water vapour in any of the experiments. The oil floated on a mercury column in the tube U, which was connected by flexible tubing with a mercury reservoir.

In order to remove the air from the apparatus the stop-cock S and the manometer were opened, and the pressure was taken down to a few millimetres of mercury. The stop-cock was then closed and the pressure was further reduced to about a tenth of a millimetre by the Toepler pump. The exact value of the pressure could be found by the McLeod gauge.

In order to reduce the pressure of the air in A and B to about 1/1000 millimetre, the oil was raised in the manometer so as to stop the connexion between the two sides of the apparatus. The stop-cock S was then opened and the vapour from B was allowed to pass into A until the surface of the oil in the tube H_2 was about fifteen centimetres lower than the surface in H_1. After closing the stopcock the mercury reservoir was lowered carefully in order to allow the gas on the left of the manometer to bubble through the oil in the column H_1 until the difference in level on the two sides of the manometer was reduced to about one centimetre. The mercury reservoir was again raised and the process was repeated, until the pressure of the air in A was reduced to the desired amount. The sulphuric acid and phosphorus pentoxide absorbed the water vapour on the right of the manometer, and the air which was also carried through was estimated by the McLeod gauge. The air was pumped out by the Toepler pump when the pressure exceeded about a tenth of a millimetre of mercury. It was found that the air was very rapidly removed from the vessel A by the above process.

The pressure of the vapour in A was adjusted to any required value by closing S, and allowing the excess of vapour to pass through the oil column in H_1. The pressure expressed in millimetres of mercury is $\frac{h}{15\cdot 6}+h'$, where h is the height of the column of oil in H_1 above the column in H_2, and h' the pressure of the air on the right of the manometer as found by the McLeod gauge.

It was easy to measure the height h within half a millimetre, so that the pressure was found to a thirtieth of a millimetre of mercury, which is about the accuracy required when the pressure of the water vapour was not less than one millimetre of mercury.

The experiments were made with the pressure below the maximum pressure at the temperature of the room, so that the water vapour did not condense and injure the ebonite insulation in the electrical part of the apparatus.

The condensation on the surface of the glass vessel A and the tube T gave rise to some inconvenience in adjusting the pressure. Thus the pressure in A does not attain its final value immediately after some vapour is admitted from B, or removed through M. In the former case vapour would condense slowly on the glass, and the pressure would gradually fall a little for some time after the change in pressure had been made. The reverse took place after some vapour had been removed. It was not possible, therefore, to make a large number of experiments at precisely the same pressure.

The conductivities were measured in the manner described in the previous paper, and the values found are given in the following tables. The pressure P is given in millimetres of mercury, and the experiments are numbered according to the pressure at which they were made. The electric force X is given in volts per centimetre. The corresponding conductivities for the different distances between the plates are given in the columns n_1, n_2, n_3, &c., the suffix denoting the distance between the plates in millimetres. The ratios of the conductivities are given in the column R.

TABLE I.—HCl.

	P.	X.	n_1.	n_2.	n_3.	n_4.	n_5.	R.
1 ...	31·5	1750	28·7	42·5	...	...	...	1·48
2 ...	18	1750	56	407	...	...	...	7·28
3 ...	15·2	1050	32·5	56·5	98	...	...	1·74, 1·73
3 ...	15·2	1575	112	902	...	...	...	8·05
4 ...	5·1	350	32	...	48·5	...	74	1·52, 1·53
4 ...	5·1	575	46	...	187	...	735	<4·06, 3·94
4 ...	5·1	706	32·3	101	335	...	...	3·14, 3·31
4 ...	5·1	875	51·5	268	1600	...	...	5·2, 5·95
5 ...	3·02	350	29·2	...	81	...	220	2·76, 2·71
5 ...	3·02	525	46·5	131	361	...	...	2·82, 2·76
5 ...	3·02	700	76·5	361	...	...	...	4·64
6 ...	1·72	350	36	...	153	...	656	4·26, 4·3
6 ...	1·72	525	54	176	590	...	...	3·26, 3·35
6 ...	1·72	700	80	388	...	...	...	4·85
7 ...	·98	350	39	...	182	...	880	4·66, 4·83
7 ...	·98	525	20·5	59	176	531	...	2·9, 3·0, 3·0
7 ...	·98	700	26·6	98	361	1570	...	3·7, 3·7, 4·4
7 ...	·98	1050	39	186	...	...	...	4·76
8 ...	·595	350	29	...	117	...	495	4·04, 4·24
8 ...	·595	525	38	...	217	...	1460	5·7, 6·73
8 ...	·595	700	46·5	122	350	...	...	2·62, 2·86
8 ...	·595	1050	61	180	...	...	...	2·95

TABLE II.—H_2O.

	P.	X.	n_1.	n_2.	n_3.	n_4.	n_5.	R.
1 ...	10·8	350	51	...	...	...	56	1·10
1 ...	10·8	700	88	...	301	...	...	3·42
1 ...	10·8	1050	161	620	...	...	...	3·85
2 ...	6·5	350	53·5	...	79	...	114	1·47, 1·44
2 ...	6·5	700	115	313	870	...	...	2·73, 2·78
2 ...	6·5	875	166	718	...	...	...	4·32
3 ...	3·36	350	59	...	148	...	392	2·51, 2·64
3 ...	3·42	700	123	...	443	...	...	3·66
4 ...	2·14	350	54·5	...	185	...	601	3·39, 3·25
4 ...	2·28	700	99	343	1200	...	...	3·46, 3·50
4 ...	2·34	875	129	552	...	...	...	4·28
4 ...	2·37	525	72	187	494	...	...	2·62, 2·64
5 ...	1·08	350	49·5	...	158	...	512	3·19, 3·24
5 ...	1·13	700	68	172	427	...	...	2·53, 2·49
5 ...	1·17	1050	87	260	...	...	...	3·0

When the increase in conductivity obtained by separating the plates is due to the genesis of new ions by the motion of negative ions through the gas, the theory indicates that the ratios $\frac{n_2}{n_1}$, $\frac{n_3}{n_2}$, &c., should be equal. In most of the cases given in the above tables this condition is satisfied. When the value of the electric force X is sufficiently large, other ionizing actions are called into play as the distance between the plates increases, so that the ratio $\frac{n_{d+1}}{n_d}$ increases as the distance between the plates increases. A few examples of this are given in the table for hydrochloric acid gas. Thus in the experiment $P=5{\cdot}1$, $X=875$ the ratio $\frac{n_3}{n_2}$ exceeds the ratio $\frac{n_2}{n_1}$ by an amount which cannot be attributed to experimental error. Another example is to be found when $P={\cdot}98$ and $X=700$; the ratios $\frac{n_2}{n_1}$ and $\frac{n_3}{n_2}$ are equal to one another, and are both less than the ratio $\frac{n_4}{n_3}$. I am at present engaged in making some further experiments in this direction, which I hope to have ready soon for publication.

When the distance between the plates does not exceed a certain limit, depending on the values of X and P, the ratios of the conductivities $\frac{n_2}{n_1}$, $\frac{n_3}{n_2}$, &c. are equal, and the inequalities $n_1 < n_2 < n_3$ &c. can be accurately explained by attributing the increases in conductivity to the action of the negative ions alone. All the experiments for any gas can then be represented by a single curve. The theory shows that $\frac{\alpha}{p}$ should be a function of $\frac{X}{p}$, α being the number of ions generated by a single negative ion in travelling through one centimetre of a gas at pressure p under the electric force X. The values of α can be found from the experimental results by substituting the numbers found for n in the formula $\frac{n_2}{n_1}=\epsilon^{\alpha\times{\cdot}1}$ or $\frac{n_3}{n_1}=\epsilon^{\alpha\times{\cdot}2}$. The points whose coordinates are $\frac{\alpha}{p}$ and $\frac{X}{p}$ are marked on the accompanying diagrams (figs. 2 & 3, Pl. IX.), and it can be seen that a single curve passes through all the points. This shows that α, X, and p, as determined experimentally, are connected by an equation of the form $\frac{\alpha}{p}=f\left(\frac{X}{p}\right)$ which affords further confirmation of the theory.

It was found necessary to give each curve in two parts since the variables extend over such large ranges.

I have already shown how some physical properties of gases and ions may be deduced from these results, such as the mean free path of an ion, and an approximate value of the size of a molecule. The first of these quantities may be found by finding the number of molecules that a single ion encounters in going through a centimetre of gas at a given pressure; this will be the maximum value to which α approaches as the electric force increases. A simple investigation of the curves obtained for ultra-violet light will be sufficient for this purpose.

Let an ion be travelling in a gas under an electric force X. The velocity with which it encounters a molecule depends on the free path which it traverses previous to the collision. Let it be supposed that two new ions are formed whenever the velocity at collision exceeds a certain value, so that an ion will acquire the requisite velocity under a force X, if it travels along a path x such that $\mathrm{X}x = \text{or} > \mathrm{V}$, where V denotes a constant difference of potential. Let the gas be at a pressure of one millimetre, and let N be the number of encounters that an ion makes with molecules of the gas when it travels through a distance of one centimetre. The mean free path will be $\frac{1}{\mathrm{N}}$, and the number of paths which exceed the distance x will be $\mathrm{N}\epsilon^{-\mathrm{N}x}$. When $\mathrm{X}x = \mathrm{V}$ new ions will be produced, so that the number of ions which a single ion generates in going through one centimetre will be $\mathrm{N}\epsilon^{-\frac{\mathrm{NV}}{\mathrm{X}}}$. This is the value of α corresponding to X when $p=1$. Hence the equations of the curves should be of the form $\alpha = \mathrm{N}\epsilon^{-\frac{\mathrm{NV}}{\mathrm{X}}}$, where N and V are constants to be determined by any two points on the curves. This simple formula gives the values of α fairly accurately for the larger forces, and the following tables show how it may be applied to the gases which have been examined.

Thus for air when $\mathrm{N}=15{\cdot}2$ and $\mathrm{V}=25$ we obtain the following values of α (Table III.). The values of α taken from the curves (in the former paper) are given in the same table, the pressure p being one millimetre.

The values of α corresponding to the larger forces are thus seen to agree with the numbers obtained from the simple formula $\mathrm{N}=\epsilon^{-\frac{\mathrm{NV}}{\mathrm{X}}}$, so that N represents the maximum value of α, or the number of collisions which an ion makes in going through one centimetre at one millimetre pressure.

Since the formula is not in agreement with the experimental results for the smaller forces, it is necessary to modify the original hypothesis in order to obtain an explanation of the results over the whole range of forces.

TABLE III.

Air. N=15·2, V=25·0.

X.	1400.	800.	600.	400.	200.	100.	70.
a obtained from the curve for air......	12	9·4	7·9	5·8	2·5	·73	·25
$a=N\epsilon^{-\frac{NV}{X}}$	11·6	9·4	8	5·8	2·2	·33	·07
a given by 2nd formula	11·5	9·5	8	5·9	2·6	·66	·26

Hydrogen. N=5·5, V=25·1.

X.	1200.	400.	300.	200.	100.	50.	30.
a obtained from the curve for H_2......	5·1	4·1	3·6	2·8	1·37	·36	·08
$a=N\epsilon^{-\frac{NV}{X}}$	5·0	4·0	3·5	2·8	1·37	·35	·05

Carbonic acid gas. N=18·9, V=22·9.

X.	1200.	800.	600.	400.	300.	200.	100.	50.
a obtained from the curve for CO_2 ...	13·8	11	9	6·4	4·8	2·8	·82	·15
$a=N\epsilon^{-\frac{NV}{X}}$	13·2	11	9·2	6·4	4·5	2·18	·25	·003

Hydrochloric acid gas. N=22·2, V=16·5.

X.	1500.	1000.	700.	400.	300.	200.	100.	70.
a obtained from the curve for HCl ...	17·5	15·4	13	8·9	6·8	4·1	1·21	·40
$a=N\epsilon^{-\frac{NV}{X}}$	17·5	15·4	13·2	8·9	6·5	3·5	·57	·12

Water vapour. N=12·7, V=20.

X.	900.	500.	300.	200.	100.	60.
a obtained from the curve for H_2O ...	9·4	7·3	5·1	3·6	1·31	·44
$a=N\epsilon^{-\frac{NV}{X}}$	9·4	7·3	5·1	3·2	·85	·19

It has been assumed that two new ions, one positive and one negative, are produced by a collision on all occasions when the velocity of the negative ion exceeds a certain fixed value. It is probable that there are other circumstances besides the velocity of the negative ion which determine what takes place on collision, so that ions may be produced on some occasions when the negative ion collides with a molecule with a comparatively small velocity. A comparison between the numbers obtained experimentally and those given by the formula $\alpha = N\epsilon^{-\frac{NV}{X}}$ shows that this is the more correct explanation. Thus with air it is only the larger values of α that are accounted for by supposing that the negative ion requires a velocity corresponding to a fall of potential of 25 volts. It is evident, from the values of α obtained experimentally for the smaller forces, that new ions are produced when the velocity is much smaller than this. Taking the value 15·2 already obtained for N, we may arrive at a more correct formula if we include some encounters in which the velocity is as small as that corresponding to a fall of potential of about 10 volts. Let C_1 be the average number of new ions arising from C collisions, in which the velocity is intermediate between the velocities corresponding to 10 and 20 volts. Let C_2 be the number arising from C collisions when the velocities are intermediate between those corresponding to 20 and 30 volts. It may be supposed that for voltages above 30 the velocity acquired will be sufficient to produce new ions at every collision.

The number of collisions, which occur in one centimetre when the velocity is intermediate between those corresponding to 10 and 20 volts, is $N\left(\epsilon^{-\frac{10N}{X}} - \epsilon^{-\frac{20N}{X}}\right)$. On the average the number of ions arising from these collisions will be

$$\frac{C_1}{C} \cdot N\left(\epsilon^{-\frac{10N}{X}} - \epsilon^{-\frac{20N}{X}}\right).$$

Hence α is the sum of three terms

$$\alpha = \frac{C_1}{C} \cdot N\left(\epsilon^{-\frac{10N}{X}} - \epsilon^{-\frac{20N}{X}}\right) + \frac{C_2}{C} N\left(\epsilon^{-\frac{20N}{X}} - \epsilon^{-\frac{30N}{X}}\right) + N\epsilon^{-\frac{30N}{X}}.$$

The number N has been already found, and it only remains to deduce $\frac{C_1}{C}$ and $\frac{C_2}{C}$ from the experiments. It will be found that the formula gives results in good agreement with those found for air when

$$\frac{C_1}{C} = \cdot 118, \quad \frac{C_2}{C} = \cdot 349, \text{ and } N = 15\cdot 2.$$

The numbers corresponding to the various forces are given in the last line of the above table for air.

In the case of hydrogen the experimental results are fairly well explained by supposing that ions are produced on some occasions when the velocity corresponds to about 20 volts. For the other gases it appears that collisions in which the velocities correspond to about 5 or 10 volts give rise to new ions on some occasions.

From this theory it is possible to find only an upper limit for the energy required to ionize a molecule. An accurate value of the latter quantity cannot be found from the experiments. There is only a very small probability of a positive ion producing others by collision when it has the kinetic energy acquired in passing between two points differing in potential by 10 or 20 volts. The positive ions are therefore not so efficient for generating ions as the negative ions, so that it is reasonable to suppose that ions may be produced by other processes, which are more efficient than the negative ions.

Since I first brought forward evidence to show that ions are produced by negative ions when their velocity on collision with a molecule is comparatively small, a number of papers have been published, in which the principle has been applied to the ordinary continuous discharge in a tube containing gas at a low pressure. In one of his papers on this subject J. Stark* refers to my work, and states that the velocities which I gave in my first paper are too small. According to Stark a negative ion must travel between two points differing in potential by 50 volts, in order to acquire sufficient velocity to produce new ions on collision, because there is a fall of potential of 50 volts near the anode when a continuous discharge takes place in air. Even if it be granted that the fall of potential at the electrode is to be explained by this property of a moving negative ion, the phenomenon gives no reason for supposing that new ions are not generated by collision when the velocity of the negative ion is less than that corresponding to 50 volts.

The lengths of the mean free paths, in centimetres, of a negative ion travelling in a gas at one millimetre pressure is given in the following table. The mean free paths are the reciprocal of the above values of N.

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* J. Stark, *Annalen der Physik*, 1902, Band vii. p. 437.

If it be supposed that a collision occurs between a negative ion and a molecule, when the ion approaches within a distance R of the centre of the molecule, then R is determined by the equation $\pi R^2 n = N$, where n is the number of molecules per c.c. of a gas at a millimetre pressure. The following values of $10^8 \times R$ in centimetres were found, taking n equal to $2 \times 10^{19} \div 760$.

The radius S of the sphere of action deduced from experiments on viscosity is given in the third line of the table. The values were obtained from the numbers for $\pi S^2 N_0$ given by Meyer (Meyer, 'Kinetic Theory of Gases,' p. 300), N_0 the number of molecules in a c.c. of gas at 760 mm. pressure being taken equal to 2×10^{19} as in the above calculation for R.

	Air.	H_2.	CO_2.	HCl.	H_2O.
Mean free path $\frac{1}{N}$	·066	·182	·053	·045	·079
$10^8 \times R$	1·36	·82	1·52	1·64	1·24
$10^8 \times S$	1·72	1·26	2·07	2·00	1·99

The quantity 2S is the smallest distance between the centres of two molecules during a collision, and is not the same as 2R. The latter quantity is deduced from the maximum value of α, so that in this case we are considering collisions which would give rise to new ions if the negative ion were travelling with a certain velocity. It appears from the above numbers that a negative ion may pass inside the sphere of action of a molecule with a high velocity without producing new ions.

XXXIX. *A Portable Capillary Electrometer. By* S. W. J. Smith, *M.A., Demonstrator in Physics, Royal College of Science, London**.

[Plate X.]

THIS instrument is a modification of the form of capillary electrometer represented in the first figure, and consisting of two wide tubes joined across by a capillary tube which is cylindrical, and may be horizontal or may slope upwards at any angle from *b* towards *a*. The apparatus contains mercury and sulphuric acid of about maximum conductivity distributed roughly as shown. A spring-key, like that repre-

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* Communicated by the Physical Society: read December 12, 1902.

sented in the figure, is commonly used with the instrument, and keeps the platinum terminals P_1 and P_2 at the same potential unless the lever S is depressed. When the lever

Fig. 1.

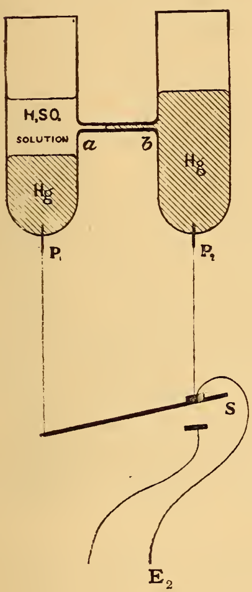
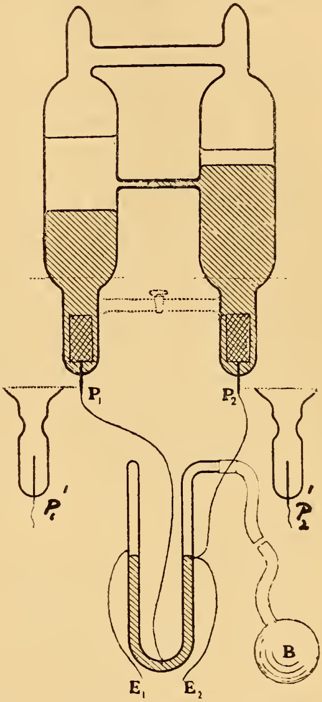


Fig. 2.



is depressed the potentials of the terminals become E_1 and E_2, which may, for example, be the potentials of two points in a potentiometer circuit. It is the function of the instrument to determine whether these potentials are the same or different.

The nature of the modifications made in the present electrometer is shown in the second figure.

To prevent evaporation of the sulphuric acid solution, without preventing free motion of the liquids within the apparatus, the wide tubes are closed at the top; but are joined across by another tube opening into them as shown. With this arrangement the apparatus is made air-tight, and can, if desired, be made air-free by exhaustion of the apparatus before sealing. It is obvious also that the apparatus can be upset without spilling of the liquid. The two limbs are of equal size, and the capillary passes from the middle of one to the middle of the other. The apparatus contains approximately enough mercury to completely fill one limb, and about half as much sulphuric acid solution. By suitably adjusting the distribution of the mercury and the solution in the two limbs, the apparatus can be arranged for use with the capillary tube either horizontal or tilted upwards at a considerable angle. The maximum angle of tilt available is increased by increasing the lengths of the limbs in comparison with the length of the capillary. It is easy to construct an electrometer which can be used with the capillary at almost any inclination between horizontal and vertical.

The distribution of the mercury can be altered most easily by means of a cross-piece provided with a tap, as represented in the figure by dotted lines. When the tap is open there is free communication between the mercury in the two limbs, and the relative amount in each can be altered by tilting the apparatus. When the tap is closed the two quantities of mercury are insulated from each other. The addition of this arrangement tends to complicate the construction of the instrument, and, although it is very convenient in practice, it is not indispensable. Any desired changes in the distribution of the mercury and the solution can usually be effected without much trouble, by means of the capillary and the upper cross-tube.

To prevent the platinum wires forming the electrodes being wetted by the acid solution, if the apparatus should accidentally, or during transit, be laid on its side or turned upside down, the lower ends of the tubes may be drawn out, as shown at P_1' and P_2' in the second figure, and slightly constricted above the ends of the platinum terminals. This precaution may be dispensed with if the electrodes are formed by welding pieces of platinum foil, which are afterwards amalgamated, on to the ends of the wires P_1 and P_2. The apparatus can then be turned upside down and shaken, so that the amalgamated foil becomes wetted by the acid, without any further ill-effect being produced than an occasional slight wandering of the zero of the instrument for a short time after it is righted again.

The usual spring-key has several disadvantages. Thus, if it is made of brass, the contacts frequently become unsatisfactory through surface tarnishing, and if, to avoid this, the bearing surfaces are made of platinum the key sometimes shows pronounced thermoelectric effects. Further—and this is a point of some importance in a portable instrument—the key cannot conveniently be fastened on to the same stand as the rest of the instrument, for, unless the stand and the support on which it rests are very rigid, the pressure necessary to depress the spring produces sufficient movement of the meniscus, by change in the inclination of the capillary tube during the act of depression, to render the detection of minute changes of surface-tension impossible.

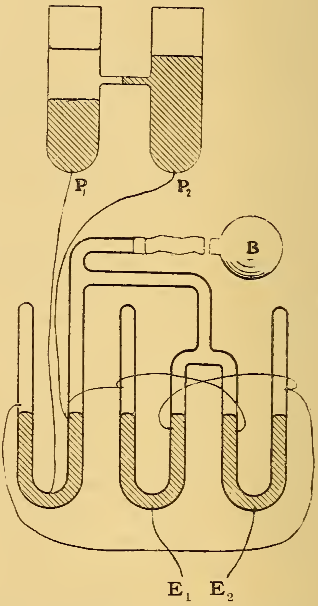
The mercury-key, represented in the second figure, is free from these disadvantages. It consists, as shown, of a **U**-tube closed at one end and communicating at the other with a pneumatic-pressure ball and containing mercury in the bend. Three platinum wires are fused into the tube and connected as shown. It is obvious that the same change of contacts is produced by squeezing the ball B, as by depressing the lever S in the spring-key. The mercury in this key takes the place of the lever in the spring-key, and the two different contacts between it and E_1 and E_2 respectively are here quite definite and practically independent of the amount of pressure exerted upon the ball B. Further, the contacts are not exposed directly to the laboratory atmosphere. The thermoelectric effects are very small since the changing contacts take place between platinum and mercury which are almost identical thermoelectrically. The warmth communicated to the key from the hand of the operator can be neglected, and the heat produced by the compression of the air in the key need only be very small. The key can be fixed to the same stand as the rest of the apparatus, for even if the pressure which changes the contacts is applied as suddenly as possible the maximum vertical pressure upon the stand is only a few grams, whereas in the case of the ordinary spring-key it may be 500 grams or more.

By adjusting the length of the mercury column in the key so that it is only slightly less than the length of the **U**-tube between the two extreme platinum wires, the change of potential at P_1 from E_2 to E_1 and conversely, can be made almost instantaneously. Hence measurements can be made with the instrument even if the zero is altering fairly rapidly. With a key of this kind it is also obvious that the observation of the meniscus through the microscope can receive a very near approach to undivided attention.

Commutators and keys which make a set of connexions in a prescribed order can be constructed on the same principle as the pneumatic key above described. The third figure (p. 402) represents a combined commutator and electrometer key.

The **U**-tube to the left is the key already described, and the double **U**-tube to the right is the commutator. The positions of the different wires are so arranged with respect to the levels of the mercury, that it requires greater pressure to change the contacts in the double U-tube, than in the tube to the left. The first effect of pressure is to throw the electrometer into the potentiometer or other circuit, connecting P_1 with E_1 and P_2 with E_2. On increasing the pressure, the connexions in the double U-tube are reversed and P_1 is connected with E_2 and P_2 with E_1. Hence, when the contacts change in the commutator, we get a motion of the electrometer meniscus corresponding to approximately twice the difference of potential between E_1 and E_2, and so, in this way, the sensitiveness of the instrument is doubled.

Fig. 3.



While it is clear that to get the minimum thermoelectric effect in mercury-platinum keys, it would be necessary to use a method of changing the contacts in which compression of air in the key does not take place, yet the thermoelectric electromotive forces which occur in the pneumatic keys described are much too small to produce an observable effect upon the readings of the most sensitive capillary electrometer*.

The sensitiveness of the electrometer, using the simple key first described, is such that when the diameter of the wide tubes is about 1 cm. and the diameter of the capillary is about 1 mm., a movement of the meniscus perceptible with certainty in a microscope magnifying 100 times is produced by a potential-difference equal to ·0001 volt. The actual extent of the movement is somewhat variable, and amounts usually to about ·01 mm. The following numbers, obtained with apparatus previously described (Phil. Trans. A. 1899, vol. cxciii. p. 63), show the effect of comparatively large

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* Since this paper was read I have found that mercury keys (similar in principle to those referred to above) in which the thermoelectric effects are reduced to a minimum are described by Kamerlingh Onnes, *Leyden Communications*, No. 27, p. 31, 1896.

polarizing electromotive forces upon the surface-tension between mercury and sulphuric acid solution of density 1·17 :—

E.M.F. Volts.	Surface-Tension.
0	γ
0·0202	1·021 γ
0·0404	1·040 γ
0·0605	1·059 γ
0·0807	1·080 γ
0·1009	1·097 γ

γ is the "natural" surface-tension between the mercury and the solution. Its approximate value is 300 ergs per sq. cm. Judging from these numbers, it would seem that the surface-tension is altered by about one part in 10,000 by a polarizing E.M.F. of ·0001 volt. In the case in which the capillary-tube is horizontal and the wide tubes are vertical, the relation between the motion of the meniscus δx and the corresponding change in surface-tension $\delta\gamma$ is expressed approximately by

$$a^2\rho\, g\, \delta x = \mathrm{A}c\, \delta\gamma$$

if we assume that the capillary and wide tubes are of uniform cross-section—a being the area of cross-section of the capillary, c its circumference, A the area of cross-section of the wide tubes, and ρ the sum of the densities of the mercury and the solution. From this formula it would appear possible to produce a much larger movement of the meniscus than ·01 mm. by means of a potential-difference of ·0001 volt by using a very narrow capillary, especially if the cross-section of the capillary were elliptical instead of circular. It is found in practice, however, that the motion of the meniscus under minute polarizing forces is controlled very largely by stickiness and accompanying changes in the angle of contact between the liquids and the glass, and by variation in the cross-section of the tube at the place where the meniscus rests. The sensitiveness of the instrument to small electromotive forces is practically as great when the diameter of the capillary is 1 mm. as when it is very much less. A very narrow capillary is less easy to manipulate than a comparatively wide one (about 1 mm. in diameter) and is only advantageous when it is desirable that the capacity of the instrument should be as small as possible, or that its action should be as rapid as possible. In the latter case the length of the capillary should also be small.

If the capillary-tube, instead of being horizontal, is inclined at an angle θ to the horizontal, the equation given above becomes

$$ag\{(\rho_1+\rho_2)a/\mathrm{A}\,.\cos\theta+(\rho_1-\rho_2)\sin\theta\}\,\delta x = c\,\delta\gamma,$$

in which ρ_1 is the density of the mercury, and ρ_2 that of the solution. From this equation it follows: (1) that if θ is positive (mercury thread sloping upwards towards the meniscus) the sensitiveness is not increased appreciably by making A very large in comparison with a, unless θ is very small; and (2) that if θ is negative (meniscus at lowest part of thread) the mercury becomes unstable when θ is numerically greater than $\tan^{-1}(\rho_1+\rho_2)a/(\rho_1-\rho_2)\mathrm{A}$, *i. e.* when θ is numerically greater than a/A approximately, since in order that the polarization may be practically confined to the capillary electrode, the ratio a/A must be small. It also follows that if it were proposed to design an instrument which should have the utmost sensitiveness possible, attention would have to be paid to the straightness of the capillary as well as to the uniformity of its cross-section. It is not necessary, however, to take the precautions here indicated in order to obtain the sensitiveness already quoted; it may be obtained with almost any capillary-tube chosen at random, and with θ having such a positive value that the restoring force for a small displacement is considerable enough to render the instrument easy to work with.

The sensitiveness of ·0001 volt, which is obtainable without any difficulty if the mercury is clean, is sufficient for a great many measurements in which the electrometer can be employed, and for these the electrometer (which for the purpose in question is really a surface-tension galvanometer) is more convenient than an ordinary galvanometer with a suspended magnetic system. The electrometer is much more easily set up than an ordinary galvanometer. There is no suspension, no lamp and scale, and, practically, no levelling; but it is advisable when working with the instrument that the potential of E_1 should never be more than a few tenths of a volt less, or more than about a volt greater, than the potential of E_2. These conditions of working are, in general, not difficult to satisfy. If the potential-differences applied exceed either of the limits above mentioned, it is sometimes necessary to run some of the mercury through the capillary tube in order to get the instrument again into its best working order. The capillary electrometer is already used almost universally in physico-chemical laboratories, and the modifications herein suggested may, perhaps, have the effect of slightly extending the sphere of its usefulness. The accompanying Plate X., taken from a photograph, represents one form of the instrument described. Its size is about two-fifths of that of the actual instrument. The arrangement of the different parts will be obvious from the description already given. The illumination of the end of the mercury-thread is effected by means of a concave mirror attached to the base of the instrument.

XL. *On the Connexion between Freezing-points, Boiling-points, and Solubilities.* By MEYER WILDERMAN, *Ph.D., B.Sc. (Oxon.)*[*].

A. IN *Comptes Rendus*, lxx. p. 1349 (1890), Guldberg gave the connexion between the lowering of freezing-point and lowering of vapour-pressure of solutions. In a similar manner van't Hoff and Roozeboom connected two vapour-pressure curves meeting at one common point (the point of transition), belonging to two hydrates of the same salt, or to the same substance in two different allotropic states, &c. (see van't Hoff's *Studien zur chemischen Dynamik*, translated by Ernst Cohen, pp. 235, 247, also 226). In this paper the connexion between the freezing-point, boiling-point, and solubility curves will be considered.

Le Chatelier and van't Hoff have deduced the following thermodynamic equations for the *solubility curve*, which are analogous to those of Clausius for the vapour-pressure curve:—

$\frac{d\lg_n p}{dT} = \frac{q}{RT^2}$, where p is the concentration, T the absolute temperature, q the heat of solution (Le Chatelier); $\frac{d\lg_n p}{dT} = \frac{q}{2T^2}$, where p is the osmotic pressure of the solution (van't Hoff). Taking into further account the connexion between the concentration of the solution, C, and its osmotic pressure, p, we get $\frac{d\lg_n C}{dT} = \frac{q}{2T^2}$ for non-electrolytes, and $\frac{d\lg_n C}{dT} = \frac{q}{2iT^2}$ for electrolytes, (A), where q is not independent of temperature; putting $q = q_0 + \alpha T$, the above equations assume the form

$$\frac{d\lg_n C}{d\,T} = \frac{q + \alpha T}{2T^2} \quad \text{and} \quad \frac{d\lg_n C}{dT} = \frac{q + \alpha T}{2iT^2}.$$

The considerations involved in the deduction of the above equations show that they will, as a general rule, apply best to dilute solutions, *i. e.*, of substances of small solubility, and that they will require some modification when we pass to the consideration of substances of greater solubility. Van't Hoff[†], in his illustration of the fact that q calculated and observed gives satisfactory confirmation of his equation, selected for this reason a number of substances of small solubility and temperatures where the solubility was the least. Le Chatelier further showed that from a consideration

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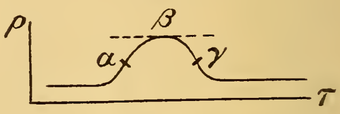
[*] Communicated by the Author.

[†] *Studien zur chemischen Dynamik*, p. 215.

of equation (A) it follows that the solubility curves should be of the form shown in fig. 1; *i. e.*, the curve must first increase, starting at the lower temperature asymptotically to the abscissa of temperatures, then have a point of inflexion (α), reach a maximum (β), then again decrease, having then another point of inflexion (γ), approaching at higher temperatures again asymptotically the abscissa. The solubility curve must thus decrease above and below the temperature belonging to β.

Fig. 1.



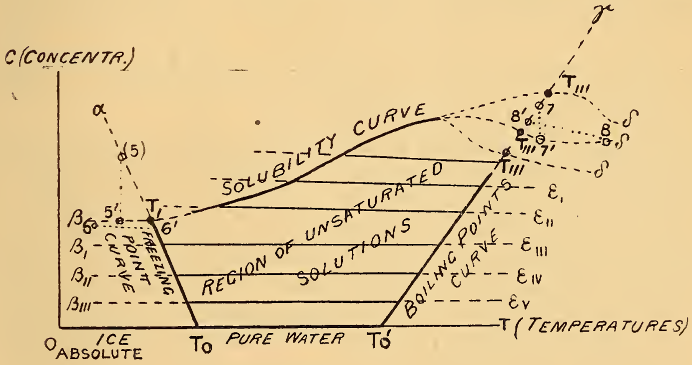
In the next place we have from van't Hoff's thermodynamic deductions the following relations for the *freezing-point curve*, where the solidified solvent and the solutions of different concentrations are in equilibrium, $n=\frac{(T_0-T)N.\lambda}{2T_0^2}$ for non-electrolytes, and $n=\frac{(T_0-T)N.\lambda}{2iT_0^2}$ for electrolytes, where n is the number of molecules dissolved, N the number of molecules of the solvent, λ the latent heat of melting, which is also a function of temperature. T_0 is the freezing-point of the pure solvent, T is the freezing-point of the given solution. This law, which holds good strictly for dilute solutions, becomes for several reasons more complicated in the case of more concentrated solutions. But even in very concentrated solutions, so far as experience goes, the greater the concentration of the solution, the lower is its freezing-temperature.

In the third place we have to consider the *boiling-point curve*, where the solvent or solutions and their vapour are in equilibrium. Attention should again be restricted to solutions of non-volatile substances. Here we have the following thermodynamic relations existing between the concentrations of the solutions, and the rise of boiling-point, analogous to that for freezing-point (Arrhenius) $n=\frac{(T-T_0')N.l}{2T_0'^2}$ for non-electrolytes and $n=\frac{(T-T_0')N.l}{2iT_0'^2}$ for electrolytes, where T_0' is the boiling-point of the pure solvent, l is the latent heat of evaporation, which is also a function of temperature. This equation holds good for dilute solutions, and becomes more complicated for more concentrated solutions. But in case of non-volatile substances in solution, even for the most concentrated solutions, the greater the concentration of the solution the higher is its boiling-point.

Since the solubility (or the concentrations of the dissolved substance) decreases above and below T_β, *at* β, *where* $\frac{dp}{dT}=0$ *on the one hand, and on the other hand on the freezing-point curve the concentrations always increase with the decrease of* T, *and on the boiling-point curve the concentrations always increase with the increase of* T, *we have the general result for all non-volatile substances that the solubility and the freezing-point curves as well as the solubility and the boiling-point curves must always cut each other.*

Fig. 2 gives an illustration of this. At the point $T_{/}$, which is common to the solubility and freezing-point curves, the dissolved substance in its solid state, the solid solvent, the saturated solution (and vapour) are in equilibrium. At the point $T_{///}$, where the solubility and boiling-point curves intersect, the dissolved substance in its solid state, the saturated solution and its vapour are in equilibrium. *Points* $T_{/}$ *and* $T_{///}$ *are the freezing-point and boiling-point of the saturated solution* in the presence of an excess of the dissolved substance in the solid state, and are as characteristic as the freezing-point and boiling-point of the pure solvent. The points $T_{/}$ and $T_{///}$ are the only points where the concentration of the solubility and of the freezing-point curves as well as the concentration of the solubility and of the boiling-point curves are the same.

Fig. 2.



It is evident that, once having the points $T_{/}$ and $T_{///}$, we can connect with each other the concentrations of the solubility, freezing-point and boiling-point curves, the latent heat of melting, latent heat of solution, latent heat of evaporation, &c., and calculate, *e. g.*, solubilities from freezing-points or boiling-points, &c. I shall now proceed to do this in a few cases under the assumption that q, λ, l do not vary with temperature, which, however, is never quite the case. I choose for this purpose boric acid and chlorate of potassium, for which the values of q prove to change little with temperature. It is evident that better results would be obtained if the variation of q, l, λ with temperature were taken into account in the calculation of the same.

From the equation of the solubility curve $\frac{d \lg_n C}{dT} = \frac{q}{2T^2}$ and $\frac{d \lg_n C}{dT} = \frac{q}{2iT^2}$ we get for the temperature $T_{,}$ (where the solubility and freezing-point curves cut each other) and any other temperature T the equation $\lg \frac{C}{C_{,}} = \frac{-q}{2 \times 2{\cdot}3026}\left(\frac{1}{T} - \frac{1}{T_{,}}\right)$ for non-electrolytes (I.) and $\lg \frac{C}{C_{,}} = \frac{-q}{2 \times i \times 2{\cdot}3026}\left(\frac{1}{T} - \frac{1}{T_{,}}\right)$ for electrolytes (I.′) (van't Hoff's law).

In case of electrolytes we shall assume that i remains the same for all concentrations and all temperatures, taking for the same the average of i at $T_{,}$ and T. In reality this is never the case, but as the values of i vary in more concentrated solutions only little, and, as far as experiment goes, also not much with the temperature, we may make here this assumption for the sake of simplifying the calculation.

In Table I. are given the solubilities, freezing-points, and boiling-points observed by Arrhenius, Raoult, Beckmann, Gerlach; van't Hoff's i's, as obtained from freezing-points and electrical conductivity; $T_{,}$ and $T_{,,,}$, the points of intersection of the freezing-point and solubility curve, as well as of the solubility and boiling-point curves, as found by myself or other observers.

In Table II. the values of q are calculated for boric acid (non-electrolyte) and for ClO_3K (electrolyte) through the whole length of the solubility curve under the assumption that q does not change, or only very little, with temperature. This is pretty well the case with boric acid, and is less the case with potassium chlorate; the values of q for ClO_3K continuously diminishing with temperature. The value of q calc. falls for potassium chlorate between 0° and 100° from 10·49 to 9·4, if the total region from 0° to T° is taken. This drop in the values is naturally still greater when small intervals are successively taken. At higher temperatures the drop in the

TABLE I.

Boric Acid, $B(OH)_3$.

Temp. t.	*Solubility.* Grams substance per 100 grams of water.	*Freez.-pt.* Grams substance per 100 grams of water.	i. Freezing-points.	i. Solubility.	$T_{,}$ and $T_{,,,}$.
−0·532°		1·706*	1·02		
−0·318		1·024	1·02		$T_{,}=273$ −0·585
−0·129		0·41	1·02		
0	1·9(5)†				
10	2·9				$T_{,}=273$ −0·585
20	4·0				
30	...				
40	7·0			1 to 1·02	
50	9·8				
60	11·0				
70	...				
80	16·8				$T_{,,,}=273$ +102·3
90	...				
100	34·0				
		Grams substance. Boiling-pt.	i. Boiling-point.		
100·185		2·38‡	1·079		
100·380		4·88	1·077		$T_{,,,}=273$ +102·3
100·589		7·42	1·057		
100 930		12·19	1·043		
101·390		17·27	1·042		

Potassium Chlorate, ClO_3K.

Temp. t.	*Solubility.* Grams substance per 100 grams of water.	*Freez.-pt.* Grams substance per 100 grams of water.	i. Freezing-points.	i. Solubility.	$T_{,}$ and $T_{,,,}$.
−0·408°		1·532	1·465		
−0·2079		0·766	1·798		$T_{,}=273$ −0·797§
−0·1058		0·380	1·831		
−0·05371		0·1915	1·859		
0	3·3†			(1·70)	
10	...			"	$T_{,}=273$ −0·797
20	7·2			(1·66)	
30	...			"	
40	14·4			(1·62)	
50	19·5			(1·62)	
60	...			"	
70	32·0			(1·60)	
80	39·0			(1·59)	$T_{,,,}=273°$ +105°
90	...			"	
100	56·0			(1·54)	
		Grams substance. Boiling pt.	i. Boiling-point.		
100·5		6·5 ‖	1·812		
101·0		13·2	1·786		$T_{,,,}=105°$† +273°
101·5		20·2	1·751		
102·0		27·8	1·696		
102·5		35·8	1·647		
103·0		44·6	1·586		

* Arrhenius. † Gerlach. ‡ E. Beckmann. § My own observations. ‖ Landolt's Tables.

TABLE II.

Boric Acid, $B(OH)_3$:—

Between $\frac{q}{1000}$:

0° and 10°: $q = \frac{2\times273\times283\times2{\cdot}3026}{10}\lg\frac{2{\cdot}9}{1{\cdot}95} = 6{\cdot}1$

0° and 20°: $q = \frac{2\times273\times293\times2{\cdot}3026}{20}\lg\frac{4{\cdot}0}{1{\cdot}95} = 5{\cdot}7$

0° and 40°: $q = \frac{2\times273\times313\times2{\cdot}3026}{40}\lg\frac{7{\cdot}0}{1{\cdot}95} = 5{\cdot}5$

0° and 50°: $q = \frac{2\times273\times323\times2{\cdot}3026}{50}\lg\frac{9{\cdot}8}{1{\cdot}95} = 5{\cdot}7$

0° and 60°: $q = \frac{2\times273\times333\times2{\cdot}3026}{60}\lg\frac{11{\cdot}0}{1{\cdot}95} = 5{\cdot}2$

0° and 80°: $q = \frac{2\times273\times353\times2{\cdot}3026}{80}\lg\frac{16{\cdot}8}{1{\cdot}95} = 5{\cdot}2$

0° and 100°: $q = \frac{2\times273\times373\times2{\cdot}3026}{100}\lg\frac{34{\cdot}0}{1{\cdot}95} = 5{\cdot}8$

$\frac{q}{1000}$: instead of *5·4* obs. (Julius Thomsen).

Potassium Chlorate, ClO_3K :—

Between $\frac{q}{1000}$:

0° and 20°: $q = \frac{2\times1{\cdot}68\times273\times293\times2{\cdot}3026}{20}\lg\frac{7{\cdot}2}{3{\cdot}3} = 10{\cdot}49$

0° and 40°: $q = \frac{2\times1{\cdot}66\times273\times313\times2{\cdot}3026}{40}\lg\frac{14{\cdot}4}{3{\cdot}3} = 10{\cdot}45$

0° and 50°: $q = \frac{2\times1{\cdot}66\times273\times323\times2{\cdot}3026}{50}\lg\frac{19{\cdot}5}{3{\cdot}3} = 10{\cdot}40$

0° and 70°: $q = \frac{2\times1{\cdot}65\times273\times343\times2{\cdot}3026}{70}\lg\frac{32{\cdot}0}{3{\cdot}3} = 10{\cdot}03$

0° and 80°: $q = \frac{2\times1{\cdot}645\times273\times353\times2{\cdot}3026}{80}\lg\frac{39{\cdot}0}{3{\cdot}3} = 9{\cdot}79$

0° and 100°: $q = \frac{2\times1{\cdot}62\times273\times373\times2{\cdot}3026}{100}\lg\frac{56{\cdot}0}{3{\cdot}3} = 9{\cdot}4$

instead of $\frac{q}{1000}$: *10·04* obs. (Julius Thomsen, Thermochemie Untersuchung, vol. iii.)

Van't Hoff's *Equations for Solubility* :—

$$\frac{d\lg C}{dT} = \frac{q}{2T^2}\ \text{(Boric acid).}$$

$$\frac{d\lg C}{dT} = \frac{q}{2iT^2}\ (ClO_3K).$$

values of q seems to be much greater than at lower temperatures. This may be due not so much to the fact that q actually decreases with the rise of temperature to such an extent, as to the difficulty of getting reliable data for the solubility curve, especially at too high temperatures*. Indeed, from the run of the existing solubility and boiling-point curves of ClO_3K it appears that the curves cut each other at $T_{\prime\prime\prime}=103°{\cdot}8$, but in reality much higher concentrations than that belonging to 103°·8 have been observed for the boiling-point curve. When the value of $T_{\prime\prime\prime}$ is found quite independently, namely, by a determination of the point where the saturated solution boils in the presence of an excess of salt, it at once becomes evident that the solubilities as found by the present methods give, especially at higher temperatures, too low values. This point $T_{\prime\prime\prime}$ is found to be for ClO_3K at 105° (Gerlach), not at 103°·8.

Again, from the equation for the freezing-point curve $C'=\frac{(T_0-T)N.\lambda.m}{2T_0^{\,2}}$ (non-electrolytes) and $C'=\frac{(T_0-T)N.l.m}{2iT_0^{\,2}}$ (electrolytes) we get for the temperature $T_{\prime}$ (point of cutting of the solubility and freezing-point curves) and any temperature T'', if we assume that λ remains the same for all temperatures, $\frac{(C)}{C_{\prime}}=\frac{T_0-T''}{T_0-T_{\prime}}$ (for non-electrolytes) (II.) and $\frac{(C)}{C_{\prime}}=\frac{(T_0-T'')i_{\prime}}{(T_0-T_{\prime})(i)}$ (for electrolytes) (II.′).

Connecting (I.) and (II.), and (I′.) and (II.′), we get:—

$$\lg\frac{\text{C sol.}}{\text{(C) fr. p.}}=\frac{-q}{2\times 2{\cdot}3026}\left(\frac{1}{\text{T sol.}}-\frac{1}{T_{\prime}}\right)-\lg\frac{T_0-T''}{T_0-T_{\prime}}$$

(for non-electrolytes) (A), and

$$\lg\frac{\text{C sol.}}{\text{(C) fr. p.}}=\frac{-q}{i\times 2\times 2{\cdot}3026}\left(\frac{1}{\text{T sol.}}-\frac{1}{T_{\prime}}\right)-\lg\frac{(T_0-T'')i_{\prime}}{(T_0-T_{\prime})i_{\prime\prime}}\ \text{(A′)}.$$

Here van't Hoff's $i_{\prime}$ belongs to $T_{\prime}$, i'' to T''. These equations give *the connexion between the concentration of the freezing-point curve, taken at any temperature* T'', *the concentration of the solubility curve at any other temperature* T, *the heat of solution* q, *which we here assume to remain constant, and the temperature* $T_{\prime}$, *which is the point of cutting of the solubility and of the freezing-point curve, the concentration at* $T_{\prime}$ *remaining unknown.* $T_{\prime}$ is found experimentally when we start with an oversaturated solution, cool it in the presence of

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* See my paper "On Real and Apparent Freezing-points, Solubilities, &c.," Phil. Mag. xlv. p. 204 (1898) and August 1902, p. 270.

the dissolved solid, continuously stirring the solution and separating the dissolved substance during this. The cooling and stirring are continued until, in the presence of an ice-crystal, the saturated solution begins to separate ice. The ice is then melted and the experiment repeated more carefully, the point of the first formation of ice being carefully watched.

In the case of electrolytes the value of $i_{/}$ belonging to $T_{/}$ ought to be known, but it can, for our purpose, be assumed to be equal to (i) at any other point on the freezing-point curve not very far removed from $T_{/}$. For non-electrolytes, where the laws of osmotic pressure directly hold good. the molecular freezing-point depression is, for one and the same solvent, the same for all dissolved substances, *i. e.* $\frac{T_0-T''}{(C)}$ or $\frac{(C)}{T_0-T''}$ is constant, and $\frac{(C)}{T_0-T''}=\frac{M}{18\cdot7}$ for water, M being the molecular weight of the dissolved substance, therefore for any lg $(C)-\lg(T_0-T'')$ we may put a constant lg $\frac{M}{18\cdot7}$, and we get instead of (A):

$$\lg C=\frac{-q}{2\times2\cdot3026}\left(\frac{1}{T}-\frac{1}{T_{/}}\right)+\lg(T_0-T_{/})+\lg\frac{M}{18\cdot7}, \quad (A'')$$

for all non-electrolytes in water, &c.

Thus it is enough, in the case of non-electrolytes, to know the temperature ($T_{/}$) *at which the saturated solution of the substance freezes in the presence of an excess of the same, and the heat of solution of the substance in the given solvent* (q), *to be able to calculate its whole solubility curve. In case of electrolytes the additional knowledge of van't Hoff's* i *is necessary.*

In Table III. the solubilities are calculated from freezing-points for boric acid (non-electrolyte) and potassium chlorate (electrolyte). For boric acid the results are also given, when lg $\frac{M}{18\cdot7}$ instead of the observed $\lg(C)-\lg(T_0-T'')$ is taken. Considering that the values of q and λ were assumed to be independent of temperature, and that the solubilities at higher temperatures are for reasons indicated before not very correct, the obtained results are certainly as good as we could possibly expect them to be.

Again, from the equation for the boiling-point curve $C=\frac{(T-T_0')N.l.m}{2T_0'^2}$ for non-electrolytes and $C=(\frac{(T-T_0')N.l.m}{2iT_0'^2}$ for electrolytes, we get for the point of cutting $T_{///}$ and any other temperature T'' between T_0' and $T_{///}$, if we assume that

TABLE III.—*Solubilities calculated from Freezing-points and* q, $T_{,}$, *or from* $q, \frac{M}{1{\cdot}87}, T_{,}$.

Boric Acid, $B(OH)_3$.

(*A*)

$$\lg \frac{(C)\ \text{sol.}}{C\ \text{fr.p.}} = -\frac{q}{2 \times 2{\cdot}3026}\left(\frac{1}{T_s} - \frac{1}{T_{,}}\right) - \lg \frac{T''_{\text{fr.p.}} - T_0}{T_{,} - T_0}$$

$$\lg C_0 = \frac{5400 \times 0{\cdot}585}{2 \times 273 \times 272{\cdot}415 \times 2{\cdot}3026} - \lg \frac{0{\cdot}318}{0{\cdot}585} + \lg 1{\cdot}024$$

Between	*Calc.*		*Obs.*
−0·585 and 0° : C_0	= 1·92	instead of	1·9
,, ,, 10° : C_{10}	= 2·79	,,	2·9
,, ,, 20° : C_{20}	= 3·86	,,	4·0
,, ,, 40° : C_{40}	= 6·95	,,	7·0
,, ,, 50° : C_{50}	= 9·09	,,	9·8
,, ,, 80° : C_{80}	=18·04	,,	16·8
,, ,,100° : C_{100}	=27·8	,,	34!

(*A′*)

$$\lg (C)\ \text{sol.} = -\frac{q}{2 \times 2{\cdot}3026}\left(\frac{1}{T_s} - \frac{1}{T_{,}}\right) + \lg(T_0 - T_{,}) + \lg \frac{M}{1{\cdot}87}$$

$$\lg \frac{M}{18{\cdot}7} = \frac{62}{18{\cdot}7} = \lg 3{\cdot}315$$

	Calculated.		*Observed.*
C_0	= 1·98	instead of	1·9
C_{10}	= 2·81	,,	2·9
C_{20}	= 3·89	,,	4·0
C_{40}	= 7·01	,,	7·0
C_{50}	= 9·16	,,	9·8
C_{80}	=18·63	,,	16·8
C_{100}	=28 03	,,	34·0 !

Potassium Chlorate, ClO_3K.

(*B*)

$$\lg \frac{(C)\ \text{sol.}}{C\ \text{fr.p.}} = -\frac{q}{2 \times i \times 2{\cdot}3026}\left(\frac{1}{T_s} - \frac{1}{T_{,}}\right) - \lg \frac{(T''_{\text{fr.p.}} - T_0)\, i_{,}}{(T_{,} - T_0)(i)}$$

$$\lg C_0 = \frac{10000 \times 0{\cdot}797}{2 \times 1{\cdot}70 \times 272{\cdot}203 \times 273 \times 2{\cdot}3026} - \lg \frac{0{\cdot}408 \times 1{\cdot}70}{0{\cdot}797 \times 1{\cdot}765} + \lg 1{\cdot}532$$

	Calculated.		*Observed.*
Between −0·797 and 0° : C_0	= 3·21	instead of	3·3
,, ,, 20° : C_{20}	= 6·51	,,	7·2
,, ,, 40° : C_{40}	=12·17	,,	14·4
,, ,, 50° : C_{50}	=17·01	,,	19·5
,, ,, 70° : C_{70}	=28·90	,,	32·0
,, ,, 80° : C_{80}	=36·85	,,	39·0
,, ,, 100° : C_{100}	=57·61	,,	56·0

If $i_{,}$ is assumed to remain, as at 0° for solubility, =1·70 for all temperatures.

(*B′*)

	Calculated.		*Observed.*
C_0	= 3·21	instead of	3·3
C_{20}	= 6·63	,,	7·2
C_{40}	= 13·23	,,	14·4
C_{50}	= 18·14	,,	19·5
C_{70}	= 31·84	,,	32·0
C_{80}	= 41·35	,,	39·0
C_{100}	= 69·85	,,	56·0!!

If $i_{,}$ is taken as the average of the $i_{,}$'s belonging to the two limits of temperature (*i.e.* to $T_{,}$ and to 0°, 20°, 40°, 50°, 70°, 80°, 100°). After (C)sol. is calculated by the formula *B*, the (C)sol. are very approximately known, and the $i_{,}$'s belonging to the (C) sol. at the given temperature can be well estimated. when the i's obtained from freezing-points and boiling-points are known. In this way the results obtained for the solubilities become more accurate.

l does not change with temperature, that $\frac{(C'')}{(C_{///})} = \frac{T''-T_0'}{T_{///}-T_0'}$ for non-electrolytes (III.), and $\frac{(C'')}{(C_{///})} = \frac{(T''-T_0')i_{///}}{(T_{///}-T_0')i''}$ for electrolytes (III.′). For the solubility curve we shall have for the same $T_{///}$ and any other temperature between $T_{///}$ and $T_{/}$, $\lg \frac{C}{(C_{///})} = \frac{-q}{2 \times 2{\cdot}3026}\left(\frac{1}{T}-\frac{1}{T_{///}}\right)$ for non-electrolytes (I.) and $\lg \frac{C}{(C_{///})} = \frac{-q}{2.i.2{\cdot}3026}\left(\frac{1}{T}-\frac{1}{T_{///}}\right)$ for electrolytes (I.′). Assuming that i does not change for concentrated or saturated solutions, and that q does not change with temperature, we get

$$\lg \frac{C\,\text{sol.}}{(C'')\,\text{b.p.}} = \frac{-q}{2 \times 2{\cdot}3026}\left(\frac{1}{T}-\frac{1}{T_{///}}\right) - \lg \frac{T''-T_0'}{T_{///}-T_0'}, \quad \text{(B)}$$

for non-electrolytes, and

$$\lg \frac{C\,\text{sol.}}{(C'')\,\text{b.p.}} = \frac{-q}{2 \times 2{\cdot}3026 \times i_{///}}\left(\frac{1}{T}-\frac{1}{T_{///}}\right) - \lg \frac{(T''-T_0')i_{///}}{(T_{///}-T_0')i''}$$

for electrolytes (B′).

This equation gives *the connexion between solubility at any temperature* T, *the boiling-point at any temperature* T'', *the latent heat of solution* q, *and the temperature* $T_{///}$, *which is the point where the solubility and the boiling-point curves cut each other, the concentration at* $T_{///}$ *remaining unknown.*

In the case of non-electrolytes, since the molecular rise of the boiling-point is the same for all substances when the same solvent is used, $\lg (C'') - \lg (T''-T_0') = \lg \frac{M}{5{\cdot}2}$ for water, *i. e.* we are able to calculate the whole solubility curve, if $T_{///}$ and q are known, using the equation

$$\lg C\,\text{sol.} = \frac{-q}{2 \times 2{\cdot}3026}\left(\frac{1}{T}-\frac{1}{T_{///}}\right) + \lg (T_{///}-T_0') + \lg \frac{M}{5{\cdot}2}\ \text{(B}''\text{)}.$$

In case of electrolytes the additional knowledge of van't Hoff's i is necessary.

In Table IV. the solubilities are calculated from boiling-points for boric acid and ClO_3K: in the first case $\lg \frac{M}{5{\cdot}2}$ instead of the observed $\lg (C'') - \lg (T''-T_0')$ is used. Considering that the values of q and l were assumed to be independent of temperature, and that the solubilities at higher temperatures are not very easily correctly determined,

TABLE IV.—*Solubilities calculated from Boiling-points and q, $T_{\prime\prime\prime}$, or from q, $\frac{M}{5\cdot2}$, $T_{\prime\prime\prime}$.*

Boric Acid, $B(OH)_3$.

(*A*)

$$\lg \frac{C_{\text{sol.}}}{(C_{\prime\prime})_{\text{b.p.}}} = \frac{-q}{2\times2\cdot3026}\left(\frac{1}{T_s}-\frac{1}{T_{\prime\prime\prime}}\right)-\lg\frac{T''-T'}{T_{\prime\prime\prime}-T_o'}$$

$$\lg C_{100} = \frac{5400\times2\cdot3}{2\times373\times375\cdot3\times2\cdot3026}-\lg\frac{0\cdot98}{2\cdot3}+\lg 12\cdot19$$

Between	*Calc.*	*Obs.*
102°·3 and 100° :	C_{100}=27·34 instead of	34 !
„ „ 80° :	C_{80} =18·16 „	16·8
„ „ 60° :	C_{60} =11·38 „	11·0
„ „ 50° :	C_{50} = 8·93 „	9·8
„ „ 40° :	C_{40} = 6·84 „	7·0
„ „ 20° :	C_{20} = 3·79 „	4·0
„ „ 10° :	C_{10} = 3·05 „	2·9
„ „ 0° :	C_0 = 1·91 „	1·9

(*A′*)

$$\lg C_{\text{sol.}} = \frac{-q}{2\times2\cdot3026}\left(\frac{1}{T_s}-\frac{1}{T_{\prime\prime\prime}}\right)+\lg(T_{\prime\prime\prime}-T_o')+\lg\frac{M}{5\cdot2}$$

$$\lg\frac{M}{5\cdot2}=\lg\frac{62}{5\cdot2}$$

Calculated.		*Observed.*
C_{100}=26·23	instead of	34 !
C_{80} =17·41	„	16·8
C_{60} =10·90	„	11·0
C_{50} = 8·55	„	9·8
C_{40} = 6·55	„	7·0
B_{20} = 3·64	„	4·0
C_{10} = 2·92	„	2·9
C_0 = 1·83	„	1·9

Potassium Chlorate, ClO_3K.

(*B*)

$$\lg\frac{C_{\text{sol.}}}{(C_{\prime\prime})_{\text{b.p.}}} = \frac{-q}{2\times i_{\prime\prime\prime}\times2\cdot3026}\left(\frac{1}{T_s}-\frac{1}{T_{\prime\prime\prime}}\right)-\lg\frac{(T''-T_0')\,i_{\prime\prime\prime}}{(T_{\prime\prime\prime}-T_0')\,i_{\prime\prime}}$$

$$\lg C_{100}=\frac{-10000\times5\cdot0}{2\times1\cdot53\times373\times378\times2\cdot3026}-\lg\frac{0\cdot5\times1\cdot53}{5\cdot0\times1\cdot812}+\lg 6\cdot5$$

	Calculated.		*Observed.*
Between 105° and 100° :	C_{100}=68·48	instead of	56·0 !
„ 80° :	C_{80} =41·68	„	39·0
„ 70° :	C_{70} =31·82	„	32·0
„ 50° :	C_{50} =17·15	„	19·5
„ 40° :	C_{40} =12·78	„	14·4
„ 20° :	C_{20} = 6·26	„	7·2
„ 0° :	C_0 = 2·77	„	3·3

$(T''-T_0')=0°\cdot5$. $(C_{\prime\prime})$ b.p.$=6°\cdot5$. $i_{\prime\prime}=1\cdot812$.

If i sol.=1·53, *i. e.* taken as a constant for the whole solubility curve and = to $i_{\prime\prime\prime}$ at 105°.

$T_{\prime\prime\prime}=105°+273°$.

(*B′*)

	Calculated.		*Observed.*
C_{100}	= 68·71	instead of	56·0 !
C_{80}	= 43·09	„	39·0
C_{70}	= 33·21	„	32·0
C_{50}	= 18·42	„	19·5
C_{40}	= 13·83	„	14·4
C_{20}	= 7·17	„	7·2
C_0	= 3·48	„	3·3

$(T''-T_0')=0°\cdot5$. $i_{\prime\prime}=1\cdot812$. $(C_{\prime\prime})$ b.p. = 6°·5. $T_{\prime\prime\prime}=105°+273°$. i sol. is taken as the average of $i_{\prime\prime\prime}=1\cdot53$ at 105°, and the i sol. of the other limiting temperature (100°, 80°, 70°, 50°, 40°, 20°, 10°); i=1·54, 1·59, 1·60, 1·62, 1·66, 1·70. This mode of calculation is done after the results have been calculated by means of the formula *B*, *i. e.* the values of C sol, very nearly found.

the obtained results are as good as we could expect them to be.

In equation (A″) $\lg\frac{M}{18\cdot 7}$ is $=\lg\frac{M.\lambda}{0\cdot 02T_0^2}$ (for water), *i. e.* (A) may be written

$$\lg C=\frac{-q}{2\times 2\cdot 3026}\left(\frac{1}{T}-\frac{1}{T'}\right)+\lg(T_0-T_{/})+\lg\frac{M.\lambda}{0\cdot 02T_0^2},$$

which is the connexion between solubility C at any temperature T, q, λ, $T_{/}$, and T_0. In the same way in equation (B″) $\lg\frac{M}{5\cdot 2}=\lg\frac{M.l}{0\cdot 02T_0'^2}$ (for water), and (B″) may be written :

$$\lg[C]=\frac{-q}{2\times 2\cdot 3026}\left(\frac{1}{[T]}-\frac{1}{T_{///}}\right)+\lg(T_{///}-T_0')+\lg\frac{M.l}{0\cdot 02T_0'^2}$$

which is the connexion between solubility [C] at any temperature [T], q, l, $T_{///}$ and T_0'. Taking the same point on the solubility curve, C = [C], T = [T], we get

$$\frac{q}{2\times 2\cdot 3026}\left(\frac{1}{T_{/}}-\frac{1}{T_{///}}\right)=\lg\frac{T_{///}-T_0'}{T_0-T_{/}}+\lg\frac{l.T_0}{T_0'^2.\lambda}, \cdot \quad (C)$$

This equation gives the connexion between all the constants : the heat of solution q, the latent heat of melting λ, *the latent heat of evaporation l, freezing-point and boiling-point of the pure solvent* T_0 *and* T_0', *and the freezing-point and boiling-point of the saturated solution of any given substance in the presence of an excess of the dissolved substance in the solid* (*or liquid*) *state* $T_{/}$ *and* $T_{///}$.

Example : Boric acid in water : $q=5400$ (J. Thomsen), $T_{///}=375°\cdot 3$, $T_{/}=272°\cdot 415$, $T_0=273$, $T_0'=373°$ (at 760 mm.), $l=536\cdot 35$ (Regnault), $\lambda=80$ (down to 79, according to different investigators).

We get for the above equation (C) :

$$1\cdot 18=1\cdot 15 \text{ (when } \lambda=80 \text{ cal.)}$$

$$1\cdot 18=1\cdot 16 \text{ (when } \lambda=79 \text{ cal.).}$$

Calculating any of the above constants, if it be unknown, from the rest, we get

$q=5263$ instead of 5400 obs. (when $\lambda=80$)

$l=574\cdot 9$ instead of $536\cdot 35$ obs. (when $\lambda=80$)

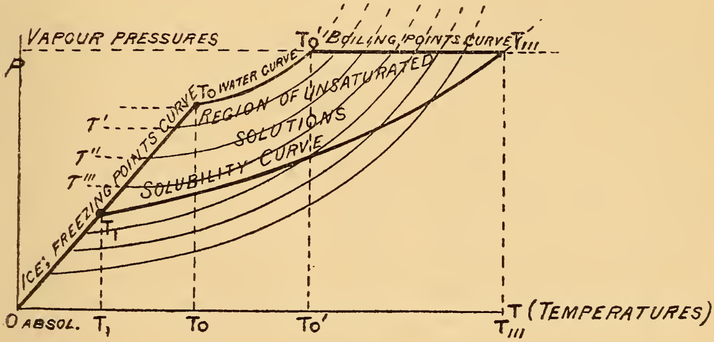
$\lambda=74\cdot 61$ instead of 80 (79) obs., &c.

Thus we can calculate the solubility curve when $T_{/}$ and $T_{///}$ or $T_{/}$ and q, or $T_{///}$ and q are known.

T_0, T_0', λ, l are the same for the same solvent, are different for different solvents, and the freezing-point and boiling-point curves are (for non-electrolytes) in the same solvent independent of the nature of the dissolved substance. On the contrary, q, $T_{/}$, $T_{///}$ are characteristic of both, of the solvent as well as of the dissolved substance. Each substance in solution has in every solvent its own solubility curve.

B. In a similar manner to the above figure 2, the figure 3 may be formed, representing, instead of concentrations, the *vapour-pressures* of three curves at different temperatures.

Fig. 3.



T_0-0 absolute represents the vapour-pressure curve of ice, T_0-T_0' that of pure water, T', T'', T''', T'''', &c. are the vapour-pressure curves of the unsaturated solutions. Since the vapour-pressures of an aqueous solution are known to be smaller than that of pure water, *i.e.* the vapour-pressure curve of a solution runs below that of water, Guldberg drew from this as early as 1870 (C. R. lxx. p. 1349) the conclusion that the freezing-points of the solution must be below that of the pure solvent. It is evident that in the same way we may show that the boiling-point of the solution must be higher than that of the pure solvent. As at the boiling-point the pure solvent and the solution have a vapour-pressure equal to that of the given atmospheric pressure, we have to draw a line $T_0'-T_{///}$ from the ordinate T_0' (say for 760 mm.) parallel to the abscissa; $T_{/}-T_{///}$ is to represent the vapour-pressure curve belonging to the concentrations of the solubility curve, which for different substances will have a different form. As the curve of the saturated solutions meets with the curve of boiling-points the curve $T_{/}$ $T_{///}$ will intersect the whole series of T', T'', T''', T'''', &c., starting for the solution having the concentration $C_{/}$ (belonging to $T_{/}$) and continuing up to the solution having the concentration $C_{///}$ (belonging to $T_{///}$).

C. *Only within* $T_0\ T_{/}\ T_{///}\ T_0'\ T_0$ *and on* T_0 0 *abs., and not beyond the same, is real equilibrium possible*, as may be seen from the above figures (2 and 3). The system which is in equilibrium at $T_{/}$ (fig. 2) cannot be in equilibrium at any point on $\alpha T_{/}$, say (5), since the solution will have to contain more salt than it possibly can below $T_{/}$ (this quantity is given by (5′) on $\beta T_{/}$); it cannot be in equilibrium at any point on $\beta T_{/}$, say on (6), because solutions containing the amount of salt of (6) can only be in equilibrium with ice at a higher temperature, corresponding to (6′) on the freezing-point curve. In the same way the system which is in equilibrium at $T_{///}$ cannot be in equilibrium at any point on $\gamma T_{///}$, say at (7), since for this a concentration higher than that which the system can dissolve at this temperature (given by (7′) on $\delta T_{///}$) will be necessary; it cannot be in equilibrium at any point on $\delta T_{///}$, say at (8), because solutions having the concentration of (8) can be in equilibrium with their vapour at the given atmospheric pressure only at (8′) on $\gamma T_{///}$, *i. e.* at a lower temperature. That systems cannot be in equilibrium beyond the lines $T_0T_{/}$, $T_{/}T_{///}$, $T_{///}T_0'$, $T_0'T_0$, $T_0$0 abs., has been already generally shown in another place*, when the effect of cooling or heating by the surrounding medium was considered. Though it has been shown in the above papers that the equilibrium of the systems represented by the above diagrams are never in reality reached in nature, the above diagrams lose nevertheless nothing of their meaning and theoretical content. The observed equilibria of systems are always more or less removed from the real points of equilibrium, and the apparent points of equilibrium often fall outside the region of $T_0T_{/}T_{///}T_0'T_0$, $T_0$0 abs., but apparent equilibrium is not real equilibrium, but only a state of the system, when a reaction is still going on in the same. At apparent equilibrium one or more parts of the system may even completely disappear and the system may be transformed into another one, quite in conformity with the meaning of Gibbs' "Rule of Phases."

The region included in $T_0T_{/}T_{///}T_0'T_0$ is further most interesting on account of the fact that we can here describe any amount of reversible cycle processes, starting from any point and returning to the same in different ways, *e.g.* starting at $T_{///}$ we can pass along the solubility curve, then along the freezing-point curve, then along the curve of pure water or of an

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* See "On real and apparent Freezing-points, Boiling-points, Solubilities," Phil. Mag. xlv. p. 204 (1898), and August 1902, p. 270.

unsaturated solution, then along the boiling-point curve back to the point $T_{////}$, &c. It is well worth while looking into whether it is not possible, by means of such cycles, to disclose some new thermodynamic connexions between the different phenomena included in the above diagrams.

Davy-Faraday Laboratory of the Royal Institution,
June 1902.

XLI. *Induced Radioactivity Excited in Air at the Foot of Waterfalls.* By J. C. McLennan, *Associate Professor of Physics, University of Toronto*[*].

5

1.—*Introduction.*

THE fine drops of spray into which water is broken on passing over waterfalls was found by Lenard[†] to communicate, on striking the wet rocks at the foot of the fall, a negative charge of electricity to the surrounding air and a positive charge to the water.

From a number of laboratory experiments with jets impinging on metal plates he obtained the same results with pure water, but found that the presence of any impurity greatly lessened the effect. With certain solutions—notably sodium chloride in water—the action weakened with an increase in the strength of the solution, and was finally reversed, a positive charge being communicated to the air and a negative charge to the liquid.

The splashing of rain he found imparted a negative electrification to the surrounding air, while the breaking of waves on the sea-shore electrified it positively.

The experiments of J. J. Thomson[‡] and of Elster and Geitel[§] have confirmed these observations, and, while showing that the sign and the amount of the electrification imparted varied both with the liquid and with the gas in which the splashing occurred, yet the splashing of pure water in air always gave a negative electrification.

A little over a year ago Elster and Geitel[||] found that, if a negatively electrified wire were exposed for some hours in the open air or in a very large room, it became temporarily radioactive. Since then a number of observations have been made upon this effect, and the consensus of opinion appears to be that it is due to the presence in the atmosphere of some

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[*] Communicated by Professor J. J. Thomson.

[†] Lenard, Wied. *Ann.* xlvi. p. 584 (1892).

[‡] J. J. Thomson, 'Discharge of Electricity through Gases,' p. 17.

[§] Elster and Geitel, Wied. *Ann.* xlvii. p. 496 (1892).

[||] Elster and Geitel, *Phys. Zeit.* No. 40. p. 590 (1901).

peculiar constituent similar to the emanation from thorium, which has been shown by Rutherford * to induce radioactivity in any body with which it comes in contact, especially when that body is negatively electrified.

The difficulty of determining and of regulating the atmospheric conditions for observations upon this excited or induced radioactivity suggested the desirability of resorting, for purposes of experiment, to a locality where exceptional electrical conditions were known to exist permanently in the atmosphere. Niagara Falls, according to Lenard's results, is preeminently such a locality, and, through the kindness of the Hon. Thomas Walsh, Superintendent of the Niagara Falls National Park Reservation, the author was enabled in September last to carry out a short series of observations upon excited radioactivity at the foot of the Falls. The general result of the investigation was that during the course of the experiments the amount of radioactivity induced in a wire exposed at the foot of the Falls was found to be very much less than that in a wire exposed in the same manner in Toronto.

2.—*Apparatus.*

In these observations the measurements were made with a quadrant electrometer of the Mascart type as constructed by Carpentier. The silk suspension in the original apparatus was replaced by a phosphor-bronze strip less than 0·025 millimetre in thickness, which was attached at its upper end to an ebonite rod to secure insulation. The needle was kept charged by a battery of small storage-cells similar to those installed in the Reichsanstalt. The deflexions were measured by the movement of the image of an incandescent-lamp filament upon a transparent scale placed at a distance of one metre from the electrometer.

With a potential of 480 volts applied to the needle, the sensibility of the instrument was such as to produce a deflexion of 1000 millims. on the scale for a potential-difference of one volt between the quadrants. In measuring the induced radioactivity, bare copper-wire No. 24 was exposed in the open air by means of specially-constructed insulating supports (fig. 1) attached to a series of bamboo poles erected at convenient distances. The wire was charged by a small Toepler Holtz Electrical Machine driven by a water motor, which maintained a potential of from eight to ten thousand volts.

The insulator shown in fig. 1 consisted of a brass tube

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* Rutherford, Phil. Mag. xlix. p. 1 & p. 161 (1900).

about 20 centimetres long, closed at one end and having a bell-shaped opening at the other. Into this tube an ebonite rod was screwed which could be easily removed when it was necessary to renew its surface. Hooks fastened to the tube and to the ebonite rod provided for the support of the insulator and the suspension of the wire.

Fig. 1.

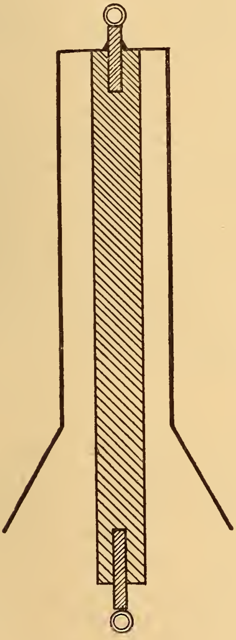
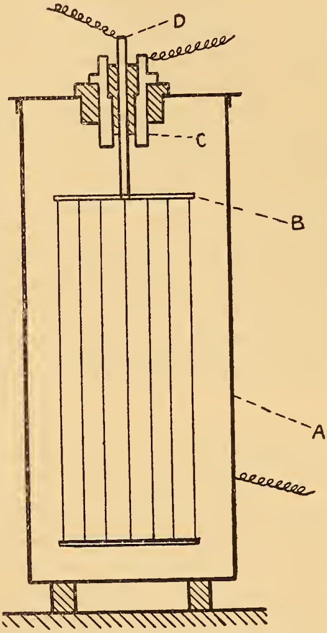


Fig. 2.



In the experiments at the foot of the Falls, it was found that with these insulators a wire could be easily maintained at a potential of 10,000 volts for hours even in a drenching spray.

The exposed wire was tested for induced radioactivity by means of the apparatus shown in fig. 2. A is a galvanized iron cylinder about 30 cms. high and 20 cms. in diameter, resting on an insulated platform and having a movable cover provided with a flanged opening into which was fitted an ebonite plug about five centimetres in diameter. A brass tube C was passed through this plug and into it a second ebonite plug was tightly fitted. This second plug carried a brass rod D from which B a brass reel was suspended, and on this reel the wire to be tested was wound. The brass tube C, which was earthed throughout the measurements, served as a guard-ring and prevented any leak from the vessel A to the rod D across the ebonite plugs.

The saturation current due to spontaneous ionization of the air in the vessel having been first determined by connecting the supporting rod D to the electrometer in the usual way and applying a potential of 100 volts to A, the exposed wire was then wound on the reel, inserted in the vessel, and the saturation current again ascertained. Any increase observed in the ionization current was taken as a measure of the radioactivity induced in the exposed wire.

As it was impossible, in setting up the apparatus in two different localities, to be certain that it was of exactly the same sensibility, a standard of ionization was deemed necessary for purposes of comparison. A radioactive substance which the writer had in his laboratory at the time of making the experiments was chosen, and a small quantity in a glass phial being found to give a constant ionization current when placed in a given position in the chamber A, this current was adopted as a standard and the ionization currents measured in the various tests were expressed in terms of it.

3.—*Experiments.*

Both before proceeding to Niagara, and after returning, a series of exposures was made in the quadrangle of the University at Toronto. Copper wires, approximately 30 metres long, were exposed for periods of two hours at a potential of 8000 to 10,000 volts on a number of days. After a wire had been exposed it was placed in the ionization chamber, the saturation current measured, and its radioactivity, thus ascertained, was expressed in terms of the standard radioactive substance.

The resulting values, taking the standard saturation current as unity, showed considerable variation in the amount of radioactivity excited, the highest value observed being 1·75 and the lowest 0·6. The intermediate values ranged between these limits, but were quite irregular and seemed to depend more upon the existence of wind and its velocity than other changes in the weather. The occurrence of showers did not exert a noticeable effect on the amount of radioactivity excited. It was frequently observed that exposures made in the morning gave greater induced radioactivity than those in the afternoon, but that exposures made after sunset gave values generally equal to, and sometimes greater, than those of the morning.

The following numbers, which represent the observations made upon one day, are typical and show this variation:—

Exposure	9 A.M.—11 A.M.	Excited radioactivity		·8
,,	1 P.M.— 3 P.M.	,,	,,	·6
,,	6 P.M.— 8 P.M.	,,	,,	1·0
,,	9 P.M.—11 P.M.	,,	,,	1·1

The observations were made in Toronto between Sept. 5th and 12th, and between the 19th and 23rd, those made at Niagara occupying the interval. The values in the two series at Toronto exhibited similar variations and were confined in both cases within the limits mentioned. The weather throughout, except for a few showers, was uniformly fine.

In conducting the experiments at Niagara Falls, the electrometer and its attachments were set up in the basement of the landing-station at the foot of the inclined railway. It was a large room having stone walls and a cement floor, and being fairly dry, was well suited for making the tests. The electrical machine which was intended for charging the wire was also located in this room, and the wire to be exposed was led from it out of a window and suspended in three stretches of about 30 metres each, the insulation being secured as already described.

The situation was admirably adapted for making the exposures, as the wire could be led within a metre or two of the vast mass of falling water. The first length of wire was generally enveloped in a very fine spray, that which surrounded the second was heavier, while the downpour upon the third resembled the heaviest rain.

A point of peculiar interest in connexion with the first exposure was that the wire, upon suspension in the spray, immediately became negatively electrified to a potential of about 7500 volts. This voltage was maintained with but little variation both day and night during the period covered by the experiments, and the sign of the electrification was invariably negative.

The results of a number of tests with the different sections of the wire showed, that the removal of the third generally caused a drop in the potential of the remaining sections from 7500 volts to about 5500 volts, while the first section, when exposed alone, gave a potential varying from 3000 to 4000 volts. From this it was evident that the spray was the cause of the electrification, and that the potential of the wire was largely determined by its density.

On account of the permanency of this electrification of the exposed wire, the electrical machine necessary in the Toronto experiments was not employed.

In testing for induced radioactivity, the wire was exposed for periods of about two hours and was removed in sections, each section being replaced by a new length. The same method of testing was used as in Toronto, and the results expressed in terms of the standard radioactive substance.

Exposures were made on four different days with the following results, A, B, and C denoting the sections of the wire of which A was that nearest the observing station, and C that nearest the Falls:—

Date.	Section of wire tested.	Induced Radioactivity. Saturation current of standard substance=1.
Sept. 12th	A.	0·1
	B.	0·31
	C.	None observed.
Sept. 13th	A.	0·16
	B.	None observed.
	C.	Not exposed.
Sept. 16th	A.	0·13
	B.	0·14
	C.	0·11
Sept. 17th	A.	0·15
	B.	0·12
	C.	None observed.

From these numbers it will be seen that but little variation was observed in the radioactivity excited in the sections A and B. In C, however, which was nearest the Falls, measurable radioactivity was present in only one of three exposures.

Ordinarily this section was drenched by masses of falling water in addition to being surrounded by fine spray such as enveloped the rest of the wire. But on Sept. 16th the air currents, during exposure, were such as to drive aside the sheets of water and permit only the fine spray to come in contact with the section.

As already stated the spray enveloping the section B was generally heavier than that in contact with A, but the condition was not permanent as the spray was blown about by gusts of wind whose direction was continually changing in the gorge.

The chief interest attaching to the results was that the radioactivity excited was much less than that in Toronto. It will be noticed that the greatest amount of radioactivity observed at Niagara Falls was 0·3, while the least observed in Toronto during the period covered by the experiments was 0·6. The numbers also show that on the average the radioactivity excited at Toronto was at least from six to seven times greater than that induced at the Falls.

The observations were not made in the two places at the same time, and a direct comparison is therefore impossible, but as there was no break in the weather during the progress of the experiments, and as the values found in Toronto before going to the Falls were almost the same as those obtained on returning, one is warranted in concluding that the air at the foot of the Falls permanently possesses less power to excite radioactivity than the air of localities at some distance.

While the experiments were in progress the spray was frequently examined for radioactivity. This was done by collecting a quantity, evaporating it, and testing the containing vessel. In no case was any trace of radioactivity observed.

Assuming then that excited radioactivity is caused by the presence in the atmosphere of some peculiar constituent, the experiments which have been described would seem to show that this constituent is present to a much less degree in the atmosphere in the neighbourhood of waterfalls than in places remote from them.

That it is possible to reduce the amount of this constituent present in the atmosphere is shown by some experiments recently performed in the Physical Laboratory at Toronto. The windows and doors of a large room, which had been well aired, were closed and, while of course they were not made air-tight, it may be assumed, as they were close-fitting, that the quantity of outside air which they admitted was relatively small. An electrical machine at one end of the room was set in action and a number of zinc disks attached to a wire leading from its negative terminal were suspended for an hour simultaneously at different points in the room. Upon testing these disks for radioactivity by the method employed by C. T. R. Wilson* it was found that radioactivity excited in the disks regularly increased with the distance from the machine.

It was also found, when a series of disks were consecutively exposed for an hour in a fixed position in the room after it had been well-aired and closed, that the radioactivity excited regularly diminished with the time. The admission of a considerable volume of fresh air, as by the opening of a

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* C. T. R. Wilson, Proc. Roy. Soc. vol. lxviii. p. 154.

window, immediately caused an increase in the amount of radioactivity excited in the exposed disks. It was evident, therefore, that the electrical machine in action served as a means of removing from the atmosphere surrounding it the constituent upon whose presence the excited radioactivity depended.

In seeking for an explanation of the diminished radioactivity excited at the Falls, the experiments just described suggest the presence of an agency having an effect similar to that of the electrical machine on the air in the room.

The negative electrification of the wire when in the spray-area pointed to the presence of this agency in the spray itself. The time at the writer's disposal did not permit of a direct investigation into the charge carried by the spray, but the negative electrification of the wire, which it will be remembered was always present and always increased as the wire was extended into the heavier spray, seemed to find its only explanation in a similar electrification of the spray. This being so, it follows at once that the vast quantity of the spray produced by the Falls would act as a huge negatively-charged body in attracting to it from the surrounding atmosphere the constituent responsible for the excitation of induced radioactivity.

In this way a satisfactory explanation is afforded of the relatively small amount of induced radioactivity excited at the foot of the Falls. This explanation requires the spray itself to be radioactive, but when the enormous volume of the spray and the very limited amount of induced radioactivity observed in the locality are taken into account, together with the known decay of induced radioactivity, it would appear reasonable to conclude that experiments conducted with very much larger quantities of spray than those in the writer's tests would be necessary to obtain observable results.

From Lenard's observations one would have expected a positive electrification to be developed on the exposed wire by the splashing of the spray, but the opposite was found. Some experiments on dropping water through ionized gases recently made by Schmauss[*], give some aid in explaining this anomaly. He found that when water was dropped through air ionized by Röntgen rays, it acquired a negative charge from the gas, and he explained this fact by a reference to the experiments of Rutherford[†] and of Zeleny[‡], in which it was shown that

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[*] Schmauss, Wied. *Ann.* [9] i. pp. 224–237 (1902).

[†] Rutherford, Phil. Mag. xliii. p. 241 (1897).

[‡] Zeleny, Phil. Mag. xlvi. p. 120 (1898).

a stream of air, when it was ionized by Röntgen rays and directed against an insulated conductor, imparted to it a negative charge owing to the greater velocity of diffusion of the negative ions. These experiments, in which the gas was in motion and the insulated conductor at rest, Schmauss considered the converse of his own.

Now, in the experiments we are considering, we have water dropping through air which is known to be spontaneously ionized. From the results of Schmauss, we should expect the spray to take up a negative charge from the air. This, if sufficient to overcome the Lenard effect by which a positive charge is developed through the impact of the spray on the wire, should leave the wire negatively charged, and this was the uniform result of the observations.

4.—*Radioactive Rain and Snow.*

In order to ascertain, if possible, the effects of variations in the weather upon the radioactive state of the atmosphere, the writer made a series of daily observations in the month of November. During this period both rain and snow storms occurred. The falling of rain was not found to produce any marked change in the radioactive power of the atmosphere, although, as already shown by C. T. R. Wilson*, the rain itself when tested was active. The falling of snow, however, was accompanied by a very considerable drop in the value of the excited radioactivity. For example, on Nov. 25th the air was dry and cold, and the morning exposure gave a value of 0·92, that for the afternoon exposure being 0·66. The next morning snow began to fall heavily, and an exposure was made in it for two hours. The resulting value for the excited radioactivity was 0·3. The snow-fall continued throughout the day, and the value for the afternoon exposure was again 0·3. This storm was general throughout Ontario, and the snow, which fell to a depth of about three inches, remained for some days on the ground and did not entirely disappear until Nov. 30th. Tests made for radioactivity in the interval showed values ranging from 0·2 to 0·4. On Dec. 1st an exposure made about noon gave a value of 0·9. On this day the weather was again mild and the snow had disappeared. Exposures made in the mornings of Dec. 2nd, 3rd, 4th, and 5th gave the values 0·8, 1·1, 0·9, 0·9 respectively.

The weather continued mild until Dec. 5th, when the temperature dropped below 0° C. On Dec. 6th the cold weather still prevailed and an exposure made from 1 to 3 o'clock in the afternoon gave a value of 0·92. Shortly after 3 o'clock

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* C. T. R. Wilson, Proc. Camb. Phil. Soc. vol. xi. Pt. 6, p. 428.

a light fall of fine snow began, which continued throughout the night. An exposure was made from 3.30 to 5.30 P.M., and also one from 9 to 11 P.M. The resulting value for the former was 0·2, and for the latter 0·32.

As the numbers just given indicate, the falling of snow on both occasions was accompanied by an immediate drop in the excited radioactivity. It will also be noticed that while the ground was covered with snow from the first fall the diminished activity continued. The snow on both occasions was collected as it fell, melted and evaporated, and the residue found to be highly radioactive. Snow which fell in the first storm was tested after it had lain two days on the ground and was found still to possess about 1 per cent. of its original activity.

These results, it will be seen, lend support to the theory that the constituent of the atmosphere to which the excitation of radioactivity is due is an emanation from the earth's surface. It would also seem from the values found for the induced radioactivity that this emanation is cut off to a considerable extent when a wide area of the earth's surface is thickly covered with snow.

The limited number of observations made hardly justifies a definite conclusion as to the manner in which rain and snow become radioactive; but it is possible that water-vapour in moving through the air, whether in the form of clouds or otherwise, gains a negative charge in the same manner as the spray at the Falls, and consequently becomes radioactive. This view is supported by the results of some experiments recently made by the writer. Water-vapour was condensed from the atmosphere upon the surface of a number of cylinders containing a freezing-mixture of ice and salt. The water thus obtained was evaporated in a metallic tray and the residue tested for radioactivity. Such tests were made daily for a period of two weeks. In most of them no radioactivity was observed, but in several slight traces were noticeable, and on four occasions the radioactivity excited was very marked. The experiments were all conducted with equal care, and no cause was apparent for the different results of the observations.

The thanks of the writer are due to Mr. J. S. Plaskett, B.A., for assistance in conducting the experiments, which at Niagara were attended with considerable difficulty, and to Mr. J. C. Rothery, Superintendent of the Niagara Falls' Park and River Railway, for facilities afforded in transporting the apparatus.

Physical Laboratory, University of Toronto,
December 8th, 1902.

XLII. *A Determination of the Charge on the Ions produced in Air by Röntgen Rays.* *By* HAROLD A. WILSON, *Fellow of Trinity College, Cambridge**.

THE experiments described in this paper were undertaken with the object of making a fresh determination of the charge on one ion. This charge will throughout this paper be denoted by e.

Prof. Townsend (Phil. Mag. Feb. 1898), in a paper on the "Electrical Properties of Newly Prepared Gases," has described a determination of the average charge on the droplets composing the cloud formed when newly prepared oxygen is bubbled through water. This charge was found to be about 3×10^{-10} electrostatic units of electricity. There are some reasons for supposing that each droplet contains one ion, and consequently Townsend's result may be regarded as a determination of the charge on one ion. The result which I have obtained is in very good agreement with his.

Prof. J. J. Thomson (Phil. Mag. Dec. 1898 and 1899) has given two estimates of e, the first depending on a determination of the average charge on the droplets of a cloud formed by condensation of water-vapour on the ions produced in air by Röntgen rays, and the second on a similar determination for the ions given off by a zinc plate under the action of ultra-violet light. The mean result of the first research was $e=6\cdot5 \times 10^{-10}$ and of the second $e=6\cdot8 \times 10^{-10}$†.

Since from the value of e the number of molecules in a cubic centimetre of a gas can be immediately deduced, and also since the absolute value of e is of considerable interest in itself, a fresh determination by a different method appeared to be worth making.

The method I have used depends, like Prof. Thomson's, on the fact discovered by C. T. R. Wilson‡, that the ions produced in air by Röntgen rays act as nuclei for the cloudy condensation of water-vapour when supersaturation exceeding a definite amount is produced by a sudden expansion.

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* Communicated by Prof. J. J. Thomson.

† Since this paper was written Prof. Thomson has informed me that he has lately made a fresh determination of e by his original method, but with an improved apparatus, and he has very kindly consented to my mentioning the result he has obtained, here. It is $e=3\cdot8 \times 10^{-10}$, and so agrees very well with the mean result of my experiments, viz. $3\cdot1 \times 10^{-10}$. It appears that in his earlier experiments the cloud was formed mainly on the negative ions and not on both positive and negative ions as was supposed at the time, consequently the result obtained was nearly twice too big.

‡ Phil. Trans. A. 1897, p. 265, and A. 1899, p. 403.

The droplets of the cloud produced presumably each contain one or more ions. Let a droplet containing one ion, and consequently having a charge e, have a mass m which can be determined by observing its rate of fall (v_1 say) in air. If now a vertical electrostatic field of strength X is applied to this droplet, there will be a vertical force on the droplet equal to Xe due to the field, so that the total force on the droplet will be $Xe+mg$, where g is the acceleration due to gravity, and reckoning Xe positive when it is in the same direction as the weight mg. Now the rate of steady motion of a sphere in a viscous fluid is proportional to the force acting on it, so that the rate of fall of the droplet will be altered by the electric field. Let it be now v_2. Then we have

$$\frac{mg}{mg+Xe}=\frac{v_1}{v_2}.$$

The relation between m and v_1 is given by the equation

$$m=3{\cdot}1\times10^{-9}\times v_1^{\frac{3}{2}}\,*$$

so that

$$e=3{\cdot}1\times10^{-9}\frac{g}{X}(v_2-v_1)v_1^{\frac{1}{2}}.$$

Thus if X is known measurements of v_1 and v_2 are sufficient to determine e absolutely. This is the method which I have employed.

It was found that, using strong Röntgen rays, some of the droplets in the cloud had bigger charges than others. In fact there sometimes appeared to be several sets of droplets having charges nearly in the ratios 1 : 2 : 3. It appeared, therefore, that some of the droplets contained one ion, some two ions, and so on. This agrees with Prof. Thomson's observation that when the strength of the Röntgen rays was increased beyond a certain amount, the number of droplets in his clouds did not increase proportionally to the number of ions present at the moment of expansion. Prof. Thomson therefore used weak rays so that in his experiments each droplet probably only contained one ion, which is a necessary condition for the success of the method he employed.

The principal advantages of my method are that it is not necessary to estimate either the number of drops in the cloud, or the number of ions present at the moment of its formation, or to make the assumption that each droplet contains only one ion. Both these estimations involve assumptions which in practice can only be approximately true, and there is

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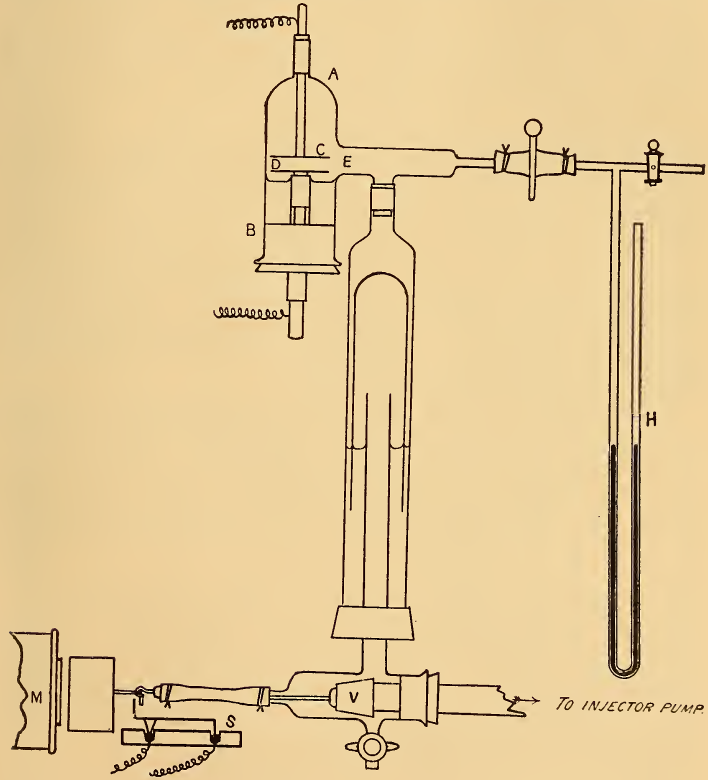
* J. J. Thomson, Phil. Mag. Dec. 1899, p. 561.

always a danger that some of the drops in the cloud contain more than one ion.

The apparatus used is shown in the accompanying diagram. It consisted of a glass tube AB about 4 cms. in diameter and 10 cms. long. Its lower end was closed by an india-rubber stopper and its upper end joined on to a short length of narrow tubing. Two circular brass disks, C and D, each 3·5 cms. in diameter, were supported one above the other in this tube as shown; the cloud on which the observations were made was formed between them, and they could be maintained at any required difference of potential up to 2000 volts by means of a battery of small secondary cells. A glass tube E was sealed on to the side of AB and served to connect the space between the disks with an apparatus for producing a sudden expansion of any desired amount. A small mercury manometer (H) was used to measure the expansion.



The expansion apparatus used was kindly lent to me by Mr. C. T. R. Wilson, and it was similar to those he has described in the papers referred to above. The apparatus was arranged so that the valve V, the opening of which produces the sudden expansion, could be pulled back suddenly by means of an electromagnet (M). This enabled the valve to be pulled away every time in exactly the same way.

The space in the tube AB below the disks was filled with water so that the air between the disks was thoroughly saturated with moisture. This air was rendered "dust free" in the usual way, by repeated expansions with intervals in between to allow the clouds formed to settle. The apparatus was then ready for a measurement of e.

A Röntgen-ray bulb was worked near AB, so that the rays passed between the disks. Then the battery circuit through the magnet was closed and a sudden expansion so produced. A cloud was thus formed between the disks, and the time which its upper surface took in falling from the upper disk to the lower disk was measured. This gave v_1 the rate of fall without an electric field. The experiment was then repeated, but immediately after the expansion the disks were connected to the battery, and so v_2, the rate of fall in an electric field, was obtained.

It was found that if the rays were kept on all the time during an experiment, then very large values for the charge on each droplet were obtained. A field of a few hundred volts per centimetre was then sufficient to cause many of the droplets to rise instead of falling. It soon became clear that the fresh ions formed after the expansion attached themselves to the droplets, so that the longer the rays were kept on after the expansion the bigger the charge on the droplets became. A switch S was therefore put in the primary circuit of the induction-coil used to excite the Röntgen bulb and arranged so that the armature of the magnet turned the switch, broke the circuit, and so stopped the rays a small fraction of a second before the expansion was produced.

The disks C and D were also connected to a commutator which first connected them together, and then on being turned connected them to the large battery used to charge them up.

A narrow beam of light was passed between the disks C and D to illuminate the cloud and enable its upper surface to be observed. The falling of the cloud was watched through a small hole on a level with the disks, and about twenty centimetres away from them in a direction nearly perpendicular to the beam of light. A second screen was put up close to the apparatus having a vertical slit in it through which only the central portion of the illuminated part of the cloud could be seen. This slit and the beam of light were each about half a centimetre wide, so that the portion of the cloud which was observed was that occupying a vertical prism half a centimetre square at the axis of the tube AB between the disks.

The disks were never more than one centimetre apart, and consequently very little circulation of the air could take place between them. When a cloud is formed by expansion in a large vessel, the walls of the vessel heat up the air near them which produces a circulation of the air upwards near the walls and downwards in the middle. If this sort of thing happened in these experiments, v_1 and v_2 would both be obtained too high; but it was found that when the disks were not more than a centimetre apart the circulation which occurred near the glass walls of the tube did not extend to the centre, and the surface of the cloud between the disks remained plane as the cloud fell.

The disks were always connected together until the expansion had taken place, when, if it was desired to determine v_2, they were immediately connected to the battery by turning the commutator lever. If they were connected to the battery before the expansion took place no cloud was obtained because the field removed the ions as fast as they were formed.

In making a measurement of e the time of fall from the upper disk to the lower one was measured with a stop-watch, alternately with and without the electric field. v_1 and v_2 were then calculated from the mean results for the times of fall.

C. T. R. Wilson (Phil. Trans. A, 1899, p. 440) found that with an expansion of nearly 15 cms. of mercury only the negative ions acted as nuclei, but with greater expansions condensation occurred on both positive and negative ions. These results were easily verified with my apparatus. With an expansion of 15 cms. charging the upper disk negatively caused the whole cloud to fall more quickly than it fell when the disks were uncharged, while charging the upper disk positively reduced the rate of fall of the cloud. It was clear, therefore, that the droplets were negatively charged.

Also with considerably larger expansions than 15 cms. some of the droplets fell more slowly and some more quickly when the disks were charged than when they were not charged, showing that both positively and negatively charged droplets were present. However, there always seemed to be more negatively charged droplets present than positively charged ones, and unless the expansion used was nearly enough to produce a fog even in the absence of any ions, the positively charged droplets were not very easy to observe. There seemed, in fact, to be a large excess of negative ions present between the disks and not equal numbers of positive and negative ions. The explanation of this is, no doubt, to be found in the secondary radiation emitted by brass under the action of Röntgen rays. This secondary radiation has been proved to consist of negatively charged corpuscles, so that an excess of negative ions in the air near the disks might have been expected. The excess would, however, not have been expected to be as great as appeared to be the case. It is perhaps possible that when both positive and negative ions are present together, condensation takes place mainly on the negative ions, although when either kind are present alone, there is very little difference between the supersaturations required to produce condensation on the positive or negative ions.

An expansion of from 16 to 17 cms. of mercury was always used in the experiments described below, and all the results are for the charge on the negative ions.

All the droplets did not always fall at the same rate when the electric field was applied. This appeared to be nearly always the case, but was especially so when strong rays were used. There appeared to be several sets of droplets, each set falling all at the same rate. The rate of fall of the most numerous set indicated that the droplets in it had the smallest charges. The observations given below refer to this set only, the other sets will be considered later.

Since the cloud begins to evaporate soon after it is formed, it is very important to get the measurement of its rate of fall over as quickly as possible. I therefore generally only allowed it to fall about half a centimetre, and applied the electric field in the direction which increased the rate of fall. Another reason why a very small distance between the disks had to be used, was that the available P.D. was only 2000 volts, so that unless the disks were near together, the electric field between them was not strong enough to appreciably alter their rate of fall. For these various reasons nearly all the observations were made with the disks as near together as possible, because it was clear that reliable results could not otherwise be obtained. For the same reason the maximum P.D. available was used in nearly every case. It would of course have been more satisfactory if observations could have been made with a greater variety of distances between the plates, and through a larger range of P.D., but to accomplish this with the battery available was not possible.

The following table contains the results of a set of observations:—

Distance between the disks $d=0\cdot45$ cm.
Potential-difference used 1800 volts.

Time of Fall without P.D. $X=0$.	Ditto with P.D. $X=13\cdot3$ E.S. units.
secs.	secs.
(1) 23·6	(2) 17·8
(3) 23·3	(4) 16·9
(5) 23·9	(6) 17·0
(7) 23·8	(8) 17·2
Mean...23·65	Mean...17·22

The numbers in brackets refer to the order in which the observations were made. The above results give

$$v_1=\frac{0\cdot45}{23\cdot65}=0\cdot0190\,\frac{\text{cm.}}{\text{sec.}}$$

$$v_2=\frac{0\cdot45}{17\cdot22}=0\cdot0262\,\frac{\text{cm.}}{\text{sec.}}$$

Consequently, since

$$e=3\cdot1\times10^{-9}\frac{g}{X}(v_2-v_1)v_1^{\frac{1}{2}},$$

we have

$$e=\frac{3\cdot1\times10^{-9}\times981\times0\cdot0072\times(0\cdot019)^{\frac{1}{2}}}{13\cdot3}$$

$$=2\cdot3\times10^{-10}\text{ E.S. units.}$$

Also

$$m=3\cdot1\times10^{-9}\times v_1^{\frac{3}{2}}=8\cdot1\times10^{-12}\text{ gram.}$$

The method of experimenting can be varied by measuring the velocity of fall first with the field in one direction and then with the field in the opposite direction. If v_2 and v_3 are the velocities, then

$$\frac{mg+Xe}{mg-Xe}=\frac{v_2}{v_3},$$

taking v_2 to be the velocity when Xe acts in the downward direction. The mean of v_2 and v_3 gives the velocity when $X=0$.

In an experiment made in this way the following numbers were obtained:—

Distance between the disks 1·0 cm.
P.D. = 2000 volts.

Time of Fall.

X = +6·7.	X = −6·7.
secs.	secs.
(1) 18·4	(2) 21·6
(3) 25·7	(4) 27·1
(5) 19·4	(6) 22·4
(7) 24·2	(8) 27·8
(9) 27·0	(10) 32·6
Mean...22·94	Mean...26·3

These numbers give

$$v_2 = 0·0436 \frac{\text{cm.}}{\text{sec.}}$$

$$v_3 = 0·0380 \frac{\text{cm.}}{\text{sec.}}$$

Also

$$e = \frac{3·1 \times 10^{-9}}{2^{\frac{3}{2}}} \frac{g}{\mathrm{X}} (v_2 - v_3)\ (v_2 + v_3)^{\frac{1}{2}},$$

so that

$$e = 2·6 \times 10^{-10} \text{ E.S. units.}$$

and

$$m = 3·1 \times 10^{-9} \times \left(\frac{v_2 + v_3}{2}\right)^{\frac{3}{2}} = 2·5 \times 10^{-11} \text{ gram.}$$

As already mentioned the cloud soon begins to evaporate after it is formed, so it is important to get the measurement of its rate of fall over as quickly as possible. It was, therefore, found most satisfactory to use the rates of fall with X = 0 and with X positive, making the rate of fall greater than when X = 0.

In making a series of measurements an observation with X positive was always made as quickly as possible after one with X = 0, in order that the strength of the rays and other conditions should be as nearly as possible the same in both cases. Although the individual observations in a series, say with X = 0, often vary a good deal, yet there is usually a corresponding variation in the observations with X positive, so that the value of *e* obtained from the mean results for the series is not necessarily affected by any error due to these variations.

The following tables contain all the other results obtained except a few done at an early stage, before the apparatus had been got to work satisfactorily, none of which are included.

$d=0{\cdot}50$ cm.
P.D. $=2000$ volts.

t_1. (X=0.) secs.	t_2. (X=+13·3.) secs.
12·2	9·6
11·1	9·3
11·4	9·3
12·0	9·2
10·6	9·6
Mean 11·4	Mean 9·4

$v_1=0{\cdot}0439$ $v_2=0{\cdot}0530$
$m=2{\cdot}86\times10^{-11}$
$e=4{\cdot}37\times10^{-10}$.

$d=0{\cdot}50$ cm.
P.D. $=2000$ volts.

t_1. (X=0.) secs.	t_2. (X=+13·3.) secs.
18·3	10·8
20·3	15·6
18·2	17·6
18·0	13·8
18·4	15·4
Mean 18·64	Mean 14·64

$v_1=0{\cdot}0268$ $v_2=0{\cdot}0341$
$m=1{\cdot}36\times10^{-11}$
$e=2{\cdot}73\times10^{-10}$

$d=0{\cdot}5$ cm.
P.D. $=2000$ volts.

t_1. (X=0.) secs.	t_2. (X=+13·3.) secs.
14·9	13·2
15·0	11·4
14·9	12·2
14·0	10·7
Mean 14·7	Mean 11·87

$v_1=0{\cdot}034$ $v_2=0{\cdot}042$
$m=1{\cdot}95\times10^{-11}$
$e=3{\cdot}4\times10^{-10}$.

$d=0{\cdot}55$ cm.
P.D. $=2000$ volts.

t_1. (X=0.) secs.	t_2. (X=+12·1.) secs.
15·6	13·0
17·2	12·8
16·0	12·4
17·0	13·8
17·4	14·1
18·4	15·0
17·2	14·1
16·0	12·8
16·9	13·1
16·7	12·6
Mean 16·84	Mean 13·37

$v_1=0{\cdot}0327$ $v_2=0{\cdot}0411$
$m=1{\cdot}83\times10^{-11}$
$e=3{\cdot}81\times10^{-10}$.

$d=0{\cdot}4$ cm.
P.D. = 2000 volts.

t_1. (X=0.) secs.	t_2. (X=+16·7.) secs.
21·5	10·1
21·9	13·0
20·9	12·0
21·0	12·0
19·4	12·0
21·6	11·6
Mean 21·05	Mean 11·80

$v_1=0{\cdot}0190$ $v_2=0{\cdot}0340$
$m=8{\cdot}1\times10^{-12}$
$e=3{\cdot}8\times10^{-10}$.

$d=0{\cdot}4$ cm.
P.D. = 2000 volts.

t_1. (X=0.) secs.	t_2. (X=+16·7.) secs.
20·0	12·0
20·4	12·0
Mean 20·2	Mean 12·0

$v_1=0{\cdot}0198$ $v_2=0{\cdot}0334$
$m=8{\cdot}64\times10^{-12}$
$e=3{\cdot}5\times10^{-10}$.

$d=0{\cdot}40$ cm.
P.D. = 2000 volts.

t_1. (X=0.) secs.	t_2. (X=+16·7.) secs.
21·0	12·4
20·4	13·2
20·6	13·0
Mean 20·7	Mean 12·9

$v_1=0{\cdot}0193$ $v_2=0{\cdot}0310$
$m=8{\cdot}3\times10^{-12}$
$e=3{\cdot}0\times10^{-10}$.

$d=+0{\cdot}40$ cm.
P.D. = +1500 volts.

t . (X=0.) secs.	t_2. (X=+12·5.) secs.
33·6	20·0
33·0	20·0
30·5	20·0
31·6	20·4
29·4	19·6
Mean 31·6	Mean 20·0

$v_1=0{\cdot}0126$ $v_2=0{\cdot}0200$
$m=4{\cdot}4\times10^{-12}$
$e=2{\cdot}04\times10^{-10}$.

$d=0{\cdot}44$ cm. P.D. = 2000 volts.

t_1. (X=0.) secs.	t_2. (X=+15·2.) secs.
21·8	15·4
22·6	18·2
23·4	16·7
23·6	17·2
	17·6
	16·4
	14·6
	14·4
	14·9
Mean...22·85	Mean...16·10

$v_1=0{\cdot}0193$ $v_2=0{\cdot}0272$ $m=8{\cdot}3\times10^{-12}$ $e=2{\cdot}3\times10^{-10}$.

The following table contains a summary of the above results:—

d.	X.	v_1.	v_2.	*m.*	*e.*
0·45	13·3	$1·9\times10^{-2}$	$2·62\times10^{-2}$	$8·1\times10^{-12}$	$2·3\times10^{-10}$
1·00	±6·7	……	4·36 ,,	25 ,,	2·6 ,,
0·50	13·3	4·39 ,,	5·3 ,,	28·6 ,,	4·4 ,,
0·50	13·3	2·68 ,,	3·41 ,,	13·6 ,,	2·7 ,,
0·50	13·3	3·4 ,,	4·2 ,,	19·5 ,,	3·4 ,,
0·55	12·1	3·27 ,,	4·11 ,,	18·3 ,,	3·8 ,,
0·40	16·7	1·9 ,,	3·4 ,,	8·1 ,,	3·8 ,,
0·40	16·7	1·93 ,,	3·1 ,,	8·3 ,,	3·0 ,,
0·40	16·7	1·98 ,,	3·34 ,,	8·6 ,,	3·5 ,,
0·40	12·5	1·26 ,,	2·00 ,,	4·4 ,,	2·0 ,,
0·44	15·2	1·93 ,,	2·72 ,,	8·3 ,,	2·3 ,,
				Mean ……	$3·1+10^{-10}$

It will now be convenient to consider the less numerous sets of droplets which fell quicker than the principal set on which the above observations were made.

When no field was applied the whole cloud fell at the same rate and its upper surface was sharp. No sign of any separation into sets could be detected. When the field was applied the cloud fell quicker than before, but otherwise its appearance was at first the same. After a few seconds, however, the surface of the cloud began to separate into two; apparently some of the cloud falling quicker than the rest. The line of separation between the two sets was fairly sharp. Sometimes three such sets were observed.

The following numbers were obtained in one series of experiments with the disks 0·4 cm. apart:—

X=0.	X=+12·5. Principal set.	X=+12·5. Second set.	X=+12·5. First set.
secs.	secs.	secs.	secs.
33·6	20·0	15·4	11·0
33·0	20·0	15·0	10·6
30·5	20·0	14·0	10·0
31·6	20·4	…	10·8
29·4	…	…	10·4
Mean 31·62	Mean 20·1	Mean 14·8	Mean 10·56
$v_1=0·0126$	$v_2=0·020$	$v_3=0·027$	$v_4=0·038$

We might suppose that the subsidiary sets are produced by two droplets coalescing under the influence of the field, but it is easy to show by calculation, that a droplet with twice the mass and twice the charge of the others ought to have fallen in about 6 secs. in the above experiment. If we suppose that two droplets, one with a positive charge and the other with a negative charge, coalesced, which of course is a probable thing to happen, the resulting droplet with twice the mass and no charge ought to have fallen in 11·2 secs., which is very nearly the mean time (10·6 secs.) taken by the quickest set to fall. However, it is not easy to see how droplets coalescing could produce a set of drops having a sharp upper limit, for we should expect coalescence to occur from time to time during the existence of the cloud. The existence of a sharp upper surface to the set seems to show that all the droplets forming it were formed at the moment of the expansion.

Another possible explanation of these sets seems to be that when the cloud is formed some of the droplets contain more than one ion. If two ions were very near together during the expansion they might easily give rise to only one droplet. An objection to this view is that such a droplet ought to be larger than one containing a single ion. This objection, however, falls to the ground when the magnitude of the effect of the charge on the equilibrium size of the droplets is remembered, for it is known to be very small.

If we suppose that the droplets in the three sets are all of the same size, but have different charges, then it is easy to calculate these charges. The results of this calculation for the observations given above are

Principal set, charge per droplet		$2·04 \times 10^{-10}$
Second set,	,,	3·94 ,,
First set,	,,	6·94 ,,

If, then, the principal set has one ion per droplet, the second has two, and the first about three.

It has been shown by Townsend (Phil. Trans. A. 1899, p. 129) that the charge on an ion produced in air by Röntgen rays or by other forms of radiation is equal to the charge on the hydrogen ion or atom in solutions. According to the result of the present experiments it consequently follows that the charge on one hydrogen atom is $3·1 \times 10^{-10}$ E.S. unit or 10^{-20} of an electromagnetic unit. One E.M. unit of electricity deposits from a solution 0·01118 gram of silver in electrolysis, and consequently $\frac{0·01118}{107·11} = 1·043 \times 10^{-4}$ gram of hydrogen. It follows that the mass of an atom of hydrogen is approximately $10^{-4} \times 10^{-20} = 10^{-24}$ of a gram. The mass of a molecule of hydrogen is therefore 2×10^{-24} of a gram, so that since the mass of one cubic centimetre of hydrogen at 0° C. and 760 mms. of mercury pressure is 9×10^{-5} gram, the number of molecules (N) in one cubic centimetre of hydrogen is $\frac{9\times10^{-5}}{2\times10^{-24}}$ or approximately $N=4\times10^{19}$.

The mean result of the present experiments, viz. $e=3{\cdot}1\times10^{-10}$ of an electrostatic unit, cannot be very far from the truth. I think that it may be considered established by these experiments that e lies between 2×10^{-10} and 4×10^{-10} E.S. unit.

The values of N which have been obtained from the kinetic theory of gases vary between rather wide limits. The value obtained depending usually on the radius assigned to a molecule of the gas under consideration. O. E. Meyer (‘Kinetic Theory of Gases,’ p. 333) gives the value $N=6{\cdot}1\times10^{19}$, which is based on the assumption that the average radius of a molecule of air is 10^{-8} cm. If $N=4\times10^{19}$ then the average radius of a molecule of air must be $1{\cdot}2\times10^{-8}$ cm.

A great many different lines of argument (see Meyer's ‘Kinetic Theory of Gases’) lead to values for the radius of a molecule or sphere of molecular action near to 10^{-8} cm., but the magnitude of this quantity certainly cannot be considered to be established except within limits not very near together. The agreement between the value of N obtained from the present experiments, and the values deduced from the kinetic theory of gases, may consequently be considered as good as could have been expected.

In conclusion I wish to say that my best thanks are due to Prof. J. J. Thomson for much valuable advice during the carrying out of these experiments in the Cavendish Laboratory.

XLIII. *The Radioactivity of Uranium.* *By* E. Rutherford, *M.A., D.Sc., Macdonald Professor of Physics, McGill University, and* F. Soddy, *M.A.* (*Oxon.*)*.

THE radioactivity of the element uranium has been examined in the light of the theory put forward by the the authors to explain the radioactivity of thorium. The constant radiating power of that element was shown to be caused by an equilibrium process, in which the decay of activity with time was balanced by the continuous production of fresh active matter at a constant rate. This explanation embraces equally well the radioactivity of uranium, although the changes that occur differ widely in degree and complexity from those that maintain the radioactivity of thorium.

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* Communicated by the Authors.

The case of uranium presents some very interesting features for, unlike thorium, this substance produces neither an emanation nor excited activity, and the experimental analysis of the processes that occur is in consequence extremely simple. It will be recalled that the main difficulty in the case of thorium was to separate and distinguish between the various changes that are occurring simultaneously, and to eliminate the effects of the production of the emanation and excited activity from the effects of the primary change which gives rise to the production of Thorium X. These difficulties are absent in the case of uranium.

It was shown in 1900 by Sir William Crookes (Proc. Roy. Soc., 1900, vol. lxvi. p. 409) that the activity of uranium to a photographic plate is caused by the presence of a minute amount of a foreign substance to which he gave the name Uranium X. This substance, like uranium, is precipitated from its aqueous solution by means of ammonium carbonate, but, unlike uranium, is not redissolved by an excess of the same reagent, being left behind with the iron and similar impurities present as a minute insoluble precipitate. The uranium obtained from the solution is completely inactive to the photographic plate. The uranium X left behind in the precipitate is intensively active, and may be obtained, weight for weight, many hundred times as active as the original uranium. It, in fact, possesses in concentrated form all the activity that the uranium has lost.

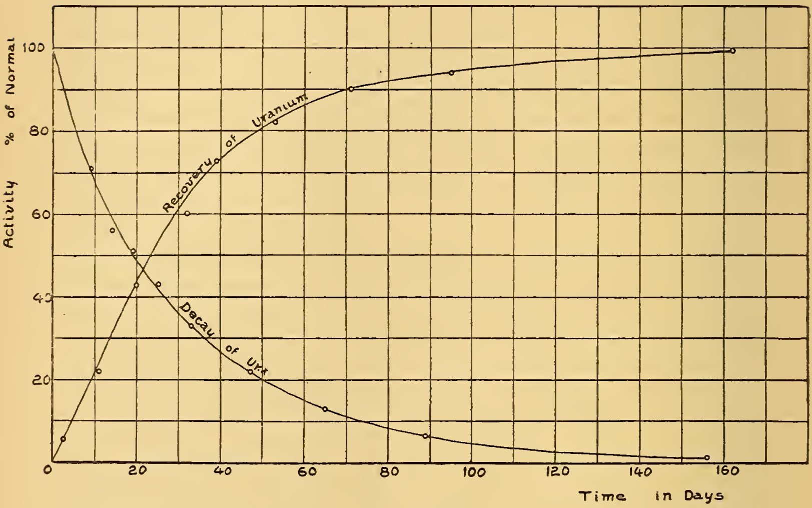
Becquerel, independently (*Comptes Rendus*, 1900, vol. cxxxi. p. 137) reduced the activity of uranium by successive precipitations in its solution of small quantities of barium sulphate. After several precipitations the activity of the uranium was found to be much enfeebled, whereas the first barium sulphate precipitates were more active weight for weight than the original uranium.

It has been shown by one of us (Soddy, Journ. Chem. Soc. Trans. 1902, p. 860) that in the interpretation of these results it of great importance to distinguish between the photographic and electrical effects. For the uranium radiation consists of two types:—(1) the α or easily absorbed rays; (2) the β or penetrating rays which are readily deviable in a magnetic field. The former contribute by far the greater part of the electrical effect, the latter practically all the photographic effect. Uranium freed from uranium X by the methods of Crookes and Becquerel, although inactive to the photographic plate, possesses a nearly normal activity when examined by the electrical method. The uranium X, on the other hand, although intensely active photographically, possesses comparatively little activity when tested in the ordinary way by the electrical method. But its radiation, when tested in a magnetic field, is found to consist almost entirely of deviable rays, whereas the uranium from which it has been separated gives no deviable rays at all (Rutherford and Grier, Phil. Mag. 1902, iv. p. 323). The conclusion was drawn that the chemical separation had effected the separation of the matter causing the photographically active or β rays from the uranium, but had not all affected the easily-absorbed or α rays of the latter. All attempts to alter the amount of α rays from uranium resulted in failure, and this radiation appears to be derived from a specific and non-separable activity of the element uranium itself. The magnetically deviable and penetrating β ray, on the other hand, which causes the photographic effect, is entirely produced by a non-uranium type of matter, uranium X.

Becquerel (*Comptes Rendus*, 1901, vol. cxxxiii. p. 977) has shown that uranium rendered photographically inactive in the manner described recovers its activity with time, and after the lapse of a year is again as active as at first. The barium sulphate, on the other hand, which had been rendered active by precipitation with uranium, completely lost its activity after a year. As this behaviour is exhibited by thorium and thorium X respectively, it seemed likely that the phenomena would prove susceptible to the same explanation in the two cases. Experiments were therefore undertaken to examine the rate of loss of the activity of uranium X with time, and the rate of recovery of the activity of uranium freed from uranium X. The problem resolves itself into a measurement of the amount of penetrating rays given out in the two cases after regular intervals. The electrical method was employed, a very sensitive electrometer being necessary for the measurement of the somewhat small effects involved, and the observations were continued over a period of 160 days.

At the beginning of the period the uranium that had been freed from uranium X by the various methods gave practically no β rays, although less than one per cent. of the normal amount could have been detected. The activity of the uranium X, on the other hand, steadily diminished, until at the end of the period it possessed less than one per cent. of its original activity. The result is shown graphically in the figure. The initial value of the activity of the uranium X is taken as 100, and the final value attained by the uranium is also made equal to 100. It will be seen that the activity of the uranium X decays very approximately in a G. P. with the time, and is, on an average, reduced to half value in about

22 days. The uranium recovers its power of giving β rays just as fast as the uranium X loses its power, and for equal times the proportion of the total activity recovered by the uranium is equal to the proportion of the total activity lost by the uranium X. The laws of decay and recovery are represented therefore, as in the case of thorium, by the two equations



$$\frac{I_t}{I_0}=e^{-\lambda t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I.)$$

$$\frac{I}{I_0}=1-e^{-\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II.)$$

I_0 in each case representing the maximum activity (this being in the first equation the initial, and in the second the final activity), and I_t the activity after time t, λ being the same constant in each case. When t is expressed in days the numerical value of λ is approximately 0·031. In the case of thorium the half value is reached after 4 days, and the value of λ is about 0·173.

As in the case of thorium, uranium that has partially recovered its activity gives on repeating the separation a new quantity of uranium X proportional to the amount of activity recovered. The constant activity of the β rays of uranium is therefore maintained by the continuous production of uranium X at a constant rate, and represents the equilibrium point where the decay of the activity of the uranium X present is balanced by the steady production of fresh uranium X.

The case of uranium is especially interesting on account of two points. The existence of non-separable activity consisting entirely of α rays, as in the case of thorium. The non-existence of α rays in the radiation of uranium X. This is probably an example of a general law that each type of radioactive matter when got by itself, free from the matter which produced it on the one hand and the products of its further change on the other, gives rise to homogeneous rays, and that in all cases the α ray is the first to be produced, the β ray only resulting in the final stages of the disintegration. Uranium gives more definite evidence on this point than thorium, because the period of the change is long enough and the experimental analysis simple enough to enable the chemical separation of the different types of matter involved to be fairly complete. The suggestion was put forward in the first paper on thorium (Phil. Mag. 1902, iv. p. 392) that the non-separable activities of thorium and uranium respectively might possibly be caused by the simultaneous production of a second type of matter in the changes in which thorium X and uranium X are produced. Later (*ibid.* p. 584) it was shown that this explanation is not necessary when radioactivity is considered as an *accompaniment* of the change occurring. This explanation has now been adopted, but a fuller discussion of the nature of radioactive change is reserved until after the case of radium has been dealt with.

McGill University, Montreal, Feb. 20, 1903.

XLIV. *A Comparative Study of the Radioactivity of Radium and Thorium.* *By* E. Rutherford, *M.A., D.Sc., Macdonald Professor of Physics, McGill University, and* F. Soddy, *M.A.* (*Oxon.*)*.

§ 1. THE elements thorium and radium are very closely allied in radioactive properties, notwithstanding the enormous difference that exists in their relative activity. Both produce radioactive emanations, and both emanations in turn excite activity on surrounding objects, which in an electric field is mainly concentrated on the negative electrode. In the details of their properties, however, they differ very widely; so that the behaviour of a radium compound, compared with that of thorium under similar circumstances, often exhibits very striking peculiarities. The explanation already advanced for the case of thorium elucidates satisfactorily everything that has so far been observed for radium; and,

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* Communicated by the Authors.

knowing the time constants of the processes involved, it is possible to predict from general principles the whole course of any series of changes of the radioactivity of radium under any given conditions. The main point of distinction is in the rate at which the emanations in the two cases lose their activity. The intensity of the radiation from the thorium emanation falls to half value in one minute, while that of the radium emanation falls to half value in about four days. In one case, therefore, the change occurs about 6000 times faster than in the other.

On the other hand, the excited activity from radium decays much faster than that produced from thorium. The former is almost inappreciable a few hours after the removal of the exciting cause, whereas the latter continues for several days. In the case of radium the emanation and the excited activity produced by it contribute the major proportion of the total activity, while in the case of thorium these effects are, for various reasons, not so marked.

The experimental analysis of the processes that give rise to the radioactivity of radium have so far not given any evidence of the existence of a stage corresponding to that of thorium X in the case of thorium. It will be recalled that the first stage in the disintegration of thorium is not directly into the emanation, but into an intermediate system named Thorium X, which then gives rise to the emanation by further change. In the case of radium it has not yet been found possible to separate any system intermediate between the radium and the radium emanation. From analogy to thorium one would expect that a Radium X or RaX, analogous to ThX, existed; but the quantity of radium at our disposal has been too small to enable us to obtain a definite answer to this question.

After the removal of the emanation and excited activity radium retains about 25 per cent. of its normal activity, which is not affected by chemical processes, and constitutes a "non-separable" activity, analogous to that possessed by thorium and uranium. But whether this is in reality the *non-separated* activity of "Radium X" superimposed on the true non-separable activity has not yet been determined.

In the present paper the radioactivity has been examined in detail, and the results are in accordance with the view that the radium is changing spontaneously at a constant rate into the radium emanation, whose further changes give rise to the phenomenon of excited activity. In addition, the comparative study of the two emanations has settled some points left over in the discussion (Phil. Mag. 1902, iv. p. 582) of the nature of the emanating-power of thorium (see § 3).

§ 2. *Rate of Decay of the Activity of the Radium Emanation.*

It has long been known that the activity of the radium emanation decays very slowly, and special methods were found necessary for its determination. The emanation mixed with air was obtained from a solution of radium chloride kept in a closed bottle, and was stored over mercury in an ordinary gas-holder. From time to time equal quantities were measured off by a gas pipette and delivered into the testing-vessel. The latter consisted of an air-tight brass cylinder carrying a central electrode insulated by an ebonite stopper provided with a guard-ring connected to the earth. A sufficient voltage to obtain the saturation-current was applied to the outside of the cylinder, and the inner electrode was connected with the electrometer, with a suitable capacity in parallel. The contents of the gas-holder were thoroughly mixed by shaking, and a definite volume measured off by the pipette and blown into the cylinder which was then closed air-tight. The ionization-current *immediately* after the introduction of the emanation furnished the measure of the activity of the latter. The measurements were repeated at suitable intervals over a period of 33 days before the effect became too small to be accurately determined.

The following table expresses the results:—

Time in Hours.	Relative Activity.
0	100
20·8	85·7
187·6	24·0
354·9	6·9
521·9	1·5
786·9	0·19

It will be seen that the activity falls in a geometrical progression with the time and decays to half value in 3·71 days.

If I_0 is the original activity and I_t the activity after time t,

$$\frac{I_t}{I_0}=e^{-\lambda t}.$$

Taking as the value of λ the mean value deduced from the last four observations of the above table, we find

$$\lambda=2{\cdot}16\,.\,10^{-6}=\frac{1}{463{,}000},$$

when t is expressed in seconds.

In these measurements the effect of excited activity was eliminated by taking the current immediately after the introduction of the emanation into the cylinder. In a closed space the ionization-current steadily increases after the introduction of the emanation, very rapidly at first and then more gradually until it attains a maximum after 5 or 6 hours nearly twice as great as at first, and then decreases according to the above law of the decay of the emanation. If when the maximum is attained the emanation is blown out of the testing-vessel the excited activity remains, representing about one-half of the total activity, concentrated on the negative electrode. In the actual measurements it was usual to take a series of readings at regular short intervals after the introduction of the emanation. The proportion of the current due to the emanation could be easily deduced from these readings, for the proportionate increase due to excited activity is for any given interval independent of the quantity and "age" of the emanation, and is the same throughout the whole series of measurements.

During the progress of the work a very similar result to the one above given for the rate of decay of the radium emanation has been published by P. Curie (*Comptes Rendus*, 1902, cxxxv. p. 857) under the title "On the Time-Constant characteristic of the Disappearance of *Radioactivity induced by Radium in a Closed Space*." It is an interesting example of how a measurement of the rate of decay of the excited (or induced) activity in a closed space *containing the radium emanation* gives in reality the rate of decay of the latter, and not of the excited activity at all. The latter decays at the same rate in the free air as when sealed up in glass.

M. Curie measured the penetrating radiation emitted from a sealed glass tube containing the radium emanation; and since the latter gives no penetrating rays (compare § 5), the effect measured was solely due to the excited activity on the walls produced by the emanation. As we have seen, after an initial period of some hours this effect attains a maximum, and then represents the equilibrium-point when the decay of excited activity is balanced by the continuous production of fresh active matter from the emanation. As the activity of the emanation decays, so also does its power of exciting activity decrease in like ratio. Hence the excited activity in a closed tube containing the radium emanation furnishes a measure of the activity of the emanation itself. After the initial period of a few hours has elapsed, its constant of decay is the same as that of the emanation. If at any time the emanation is blown out of the tube, the rate of decay changes at once to the time-rate of decay of the excited activity, as M. Curie's experiments themselves show.

M. Curie performed his experiments under the most varied conditions and the rate of decay of the activity was unaffected in all cases, as we have already shown for the thorium emanation. M. Curie, however, apparently overlooked the initial period of increase, and states that the rate of decay is uninfluenced by an alteration of the time of "activization" (or exposure to the original radium) from 15 minutes to one month. As we have seen, for any period under 5 or 6 hours the excited activity will increase at first instead of decaying, and for a period as short as 15 minutes this effect would be very marked. This increase of activity, due to the steady production of excited activity when the emanation is transposed from one vessel to another, is of course only one example of many similar ones that have now been accumulated. But it would be difficult to get in any single experiment a better illustration of the real nature of the phenomena occurring in radioactivity. A quantity of the emanation is removed from the radium that produced it, and, mixed with air, is stored like an ordinary gas over mercury in a gas-holder. Several weeks after, it may be, a portion is removed to a new vessel, when its activity is found to rise steadily to double its original value in the course of a few hours, showing that all the time it has been manufacturing out of itself the fresh active matter which causes the excited activity. When the maximum is reached, it is not because the process of manufacture has stopped, but because an equilibrium has been reached between the rate of supply of new active matter and the rate of decay of that already deposited.

§ 3. *The Occlusion of the Emanations.*

In the solid state radium compounds give out so small an amount of emanation that special methods must be employed to detect it. As in the case of thorium compounds, heat or moisture, but especially solution in water, increases the emanating-power of radium; but these effects are far more marked in the latter case. The same considerations apply equally to the power of radium to excite or induce activity on bodies in its neighbourhood; for the activity excited under any conditions is proportional only to the amount of emanation present. These variations in the power of exciting activity in radium compounds were observed by Dorn and by M. and Mme. Curie.

Radium compounds can be de-emanated by ignition, and the de-emanated compounds recover their power as soon as they are brought into solution, exactly in the same manner as we have shown for thorium compounds (M. and Mme. Curie, *Comp. Rend.* cxxxiv. p. 85, 1902). It may be stated generally that the emanating-powers of both radium and thorium are at a practical maximum in solution.

The question arises as to what the variations in emanating-power (*i. e.* the amount of emanation produced per gramme per second) are due. It was pointed out in the case of thorium that they can be interpreted in two ways. Either an alteration in the velocity of the reaction producing the emanation occurs, or the same amount is produced in all cases but the time taken for the emanation to escape from the compound is different under different circumstances. This question, which is of comparatively secondary importance in the case of thorium, becomes of paramount importance in the case of radium. For since the radium emanation loses its activity only after a period of several weeks, the view that the emanation is being continually produced at a constant rate necessitates the conclusion that there must exist in a solid non-emanating radium compound a large amount of emanation stored up or "occluded" in the compound. This will be given up when the substance is dissolved, so that there should occur a sudden "rush" of emanation from the solution very much greater than the amount subsequently produced. Assuming that in a solid radium salt no emanation escapes, and that in the same salt when dissolved the emanation escapes as fast as it is formed, it is easy to calculate the ratio of the amount given off on the solution in the first "rush" to the amount given off in any subsequent period.

Let q_0 = the number of particles of emanation produced per second by a given amount of radium.

N_0 = the number of particles stored up in the same quantity in the solid state.

N_0 represents the equilibrium state when the rate of production of fresh particles of emanation is balanced by the rate of change of those already present. If the process of production were stopped, the number N_t left after the time t would be given by

$$N_t = N_0 e^{-\lambda t},$$

where λ is the constant of decay of the activity of the emanation. The rate of change

$$\frac{dN_t}{dt} = -\lambda N_t.$$

At the equilibrium point therefore

$$q_0 = \lambda N_0,$$

$$\frac{N_0}{q_0} = \frac{1}{\lambda} = 463{,}000,$$

substituting the value of λ found in § 2.

The amount of emanation stored up in a non-emanating radium compound should therefore be nearly 500,000 times the amount produced per second. This result was tested in the following way. ·03 gr. of solid radium chloride, of activity 1000 times that of uranium, was placed in a Drechsel bottle, and sufficient water drawn in to dissolve it. The released emanation was swept out by a current of air into a small gas-holder and thence into a large testing cylinder. The maximum ionization current observed immediately after the introduction of the emanation is proportional to N_0.

A rapid current of air was then drawn through the radium solution for a few minutes, and the Drechsel bottle was then closed air-tight for a definite time, viz. 105 minutes. At the end of this period the accumulated emanation was again swept out as before and transferred to the testing vessel. The new ionization current represents N_t the amount of emanation produced in the time t.

N_0, the amount occluded, gave 4·46 divisions of the electrometer per second with a capacity ·494 microfarad in parallel.

N_t, the amount produced in 105 minutes, gave 5·48 divs. with a capacity ·00526 microfarad.

Thus
$$\frac{N_t}{N_0} = \cdot 0131.$$

Assuming there is no decay during the interval,
$$N_t = 105 \times 60 q_0.$$

Thus
$$\frac{N_0}{q_0} = 480{,}000,$$

Making the small correction for the decay during the interval t
$$\frac{N_0}{q_0} = 477{,}000.$$

We have previously shown that from theory
$$\frac{N_0}{q_0} = \frac{1}{\lambda} = 463{,}000.$$

The agreement between theory and experiment is thus as close as could be expected, and is an interesting example of the way the processes occuring in radioactive bodies may be brought to the test of quantitative experiment.

This experiment proves conclusively that the production of emanation occurs at the same rate in a solid non-emanating radium compound as in the solution. In the former case it is occluded, in the latter it escapes as fast as it is produced.

An experiment gave as the value of the emanating-power of solid radium chloride in a dry atmosphere less than half per cent. of the emanating-power of the solution; or to express the result in another way, the amount that escapes per second is less than 10^{-8} of that occluded in the compound. Moisture, however, increases it many times.

Exactly the same consideration applies to the case of thorium. If the manufacture of the thorium emanation proceeds under all circumstances at the same rate, the solution of a solid non-emanating thorium compound should also be accompanied by a "rush" of emanation at first greater than the amount obtained subsequently. But here the very rapid rate of decay of the emanation will make the effect less marked. For the case of the thorium emanation

$$\frac{N_0}{q_0}=\frac{1}{\lambda}=87.$$

It has been shown that thorium nitrate in the solid state only possesses $\frac{1}{200}$ part of the emanating-power of the same compound in solution. A quantity of finely powdered thorium nitrate was dropped into a Drechsel bottle containing hot water and the emanation immediately swept out into the testing vessel by a rapid current of air.

The ionization current in the vessel rose to a maximum, and then fell again immediately to a steady value, showing that the amount of emanation released when the nitrate dissolves is greater than the subsequent amount produced by the solution. The rapid rate of decay renders a quantitative comparison difficult. By slightly altering the arrangement of the experiment, however, a definite proof was obtained that the rate of production of emanation is the same in the solid compound as in the solution. After dropping in the nitrate, a rapid air-stream was blown through the solution for 25 seconds into the testing vessel. The air-stream was stopped and the ionization current in the testing vessel immediately measured. The solution was then allowed to stand for 10 minutes undisturbed, in which time the accumulation of the emanation in the Drechsel bottle again attains a practical maximum and again represents the steady state. The air-stream was then blown through as before for 25 seconds, stopped, and the ionization current again taken. In both cases the electrometer recorded a deflexion of 100 divisions in 6·8 seconds. By blowing the air continuously through the solution the deflexion observed when a steady state was reached was 100 divisions in 12·6 seconds, or about one-half of that observed after the first "rush."

In the case, therefore, of both thorium and radium the manufacture of emanation takes place at the same rate in non-emanating as in highly emanating compounds.

The effect of heating solid non-emanating radium compounds is precisely analogous to the effect of dissolving them. It has long been known that the emanating-power of solid radium preparations is increased to the order of a hundred thousand times by heat. As in the case of solution, the occluded emanation is liberated; and when this has passed off the effect again falls to a value approximating the true emanating-power, *i. e.* the amount of emanation produced per second.

A compound like thorium oxide, possessing in the solid state one-third to one-fourth of the emanating-power of the amount of thorium in solution, has its emanating-power increased 3 or 4 times at a dull red heat. A compound like the hydroxide or carbonate, on the other hand, which possesses as much emanating-power in the solid state as when dissolved, does not suffer much increase of emanating-power with rise of temperature.

The changes of emanating-power that are produced in thorium and radium compounds by ignition, moisture, solution, &c., are therefore to be ascribed solely to changes in the rate of escape of the gaseous emanation into the surrounding medium from the substance producing it. This result is of great importance in the general theory of radioactivity, for it brings into conformity what might otherwise have been regarded as an exception to the view that the processes which maintain radioactivity lie outside of the sphere of known molecular forces.

Attention may here be drawn to the fact that the general phenomenon of occlusion of a gas by a solid is not connected at all with the radioactive properties of the matter in question, although in the present instances radioactivity has furnished a convenient means of accurately studying the problem. The helium is given off from the mineral fergusonite, for example, in part when it is heated, and completely by dissolving the mineral.

It is therefore to be expected that if any of the unknown ultimate products of the changes of a radioactive element are gaseous, they would be found occluded, possibly in considerable quantities, in the natural minerals containing that element. This lends support to the suggestion already put forward (Phil. Mag. 1902, iv. p. 582) that possibly helium is an ultimate product of the disintegration of one of the radioactive elements, since it is only found in radioactive minerals.

§ 4. *The Influence of the Emanation on the Radioactivity of Radium.*

The converse of the changes that occur when a solid radium preparation is dissolved in water has now to be considered. One of the earliest facts observed in connexion with radium was the steady increase of its activity after preparation (Giesel, Wied. *Ann*, vi. *a* p. 91, 1899). Consider the case of a preparation of radium that has been kept for some time in solution in the open air and then evaporated to dryness. The emanation that before escaped is now occluded, and the gradual accumulation of the emanation and of the excited activity it produces causes a gradual increase of the activity of the preparation until a maximum is reached some weeks after. A solid compound of radium, on the other hand, that is dissolved and then immediately evaporated to dryness, loses its occluded emanation, but retains the excited activity that the latter has produced. Hence in this case there will occur a fairly rapid decrease at first as the excited activity decays, followed after a few hours by a slow increase as before, due to the production and occlusion of fresh emanation.

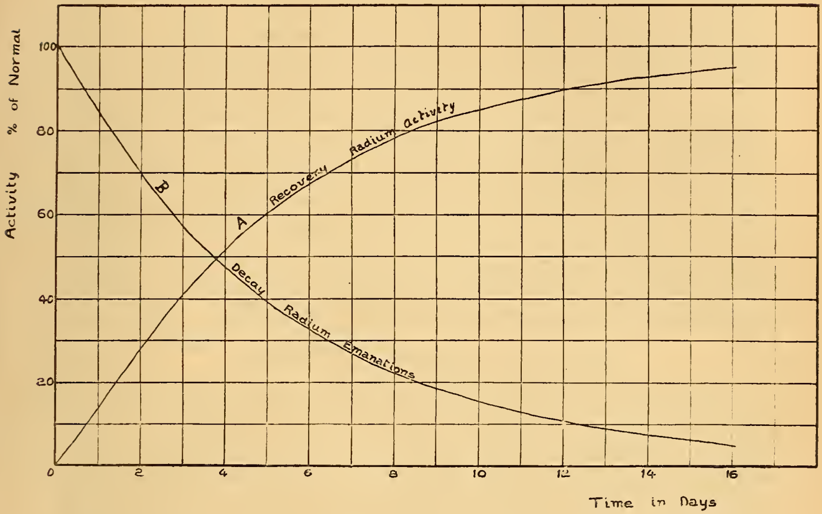
Again, apart from the consideration of the possible existence of RaX analogous to ThX, the general analogy to uranium and thorium would lead us to expect that the removal of the emanation and excited activity will not entirely remove the radioactivity. A certain proportion of the total, constituting a non-separable activity, will remain.

These considerations are borne out by experiment. Radium chloride was dissolved in water and a current of air aspirated through the solution. After a few hours the radioactivity of the salt obtained from the solution was found to have been reduced to a minimum; and longer aspiration over three weeks did not affect it. This is the non-separable activity. The solutions were evaporated to dryness, and the course of the recovery of the activity observed over a period of three weeks, after which the activity remained constant, at about four times the original value.

The following table expresses the results :—

Time in Days.	Activity.	Percentage Activity Recovered.
0	25·0	0
0·70	33·7	11·7
1·77	42·7	23·7
4·75	68·5	58·0
7·83	83·5	78·0
16·0	96·0	95·0
21·0	100·0	100·0

In the second column the final activity is taken as 100. In the third column the proportion of the lost activity regained is tabulated. These results are shown graphically (curve A). The curve B shows the decay of activity of



the emanation drawn from the table in § 2. The two curves are quite analogous to those obtained for the decay and recovery of UrX and ThX respectively. The proportion of the activity regained after an interval t is given by

$$\frac{I_t}{I_0} = 1 - e^{-\lambda t}$$

where λ is the coefficient of decay of activity of the radium emanation. The curve of recovery of the activity of radium can thus be deduced if the rate of decay of the emanation is known. In these experiments the non-separated activity was 25 per cent. of the final activity. The activity of the emanation, together with the excited activity it produced, made up the other 75 per cent.

The above equation is only approximate owing to the existence of a period of retardation of a few hours, due to the time taken for the excited activity to reach a steady value for any given quantity of emanation present. It is, however, too small to affect the results appreciably and may be neglected.

Somewhat similar experiments were performed for thorium. A sample of thorium hydroxide of high emanating-power was ignited over a blast-lamp and converted into the de-emanated oxide. Its radioactivity was found to rise in consequence about 20 per cent. in three days, and remained constant at the higher value.

In the converse experiment the thorium hydroxide was kept for three days in liquid air, *i. e.* under conditions where its emanation is condensed and produces the excited activity in the compound itself. It was spread on a plate and its activity found to *decrease* about 12 per cent. after a few days. These results are to be expected if the rate of production of emanation is constant and independent of chemical or physical conditions. When the emanation is prevented from escaping, its activity, and also the excited activity produced by it, cause an increase in the intensity of the radiations emitted. In the second case, the activity decreased, since some of the emanation escaped from the compound at ordinary temperatures, and, in consequence, some of the excited activity deposited in the compound gradually decayed.

§ 5. *The Radiations of Radium.*

Radium, like thorium and uranium, emits two types of radiation, the α, or easily absorbed rays (deflectible in very intense magnetic fields), and the β, or penetrating rays, readily deviated in a magnetic field. It also emits some very penetrating rays, which, however, have not yet been fully investigated. The non-separable activity of radium, which remains after the emanation and excited activity have been removed, consists only of a rays, the β radiation being less than 1/200 of the amount normally present. In this respect the three radio-elements are analogous.

The radiation from the radium emanation was tested by introducing it in a cylinder made of copper-sheet ·005 cm. thick, which absorbed all the α rays and allowed the β rays to pass through with but little loss. The external radiation from this cylinder was determined at intervals commencing about 2 minutes after the introduction of the emanation. The amount at first observed was extremely small, but increased rapidly and reached a practical maximum in 3 or 4 hours. Thus the radium emanation also only gives α rays, the β rays appearing after the latter has changed into the excited activity. On sweeping out the emanation from the cylinder by a current of air there was no appreciable decrease of the radiation immediately, but the radiation commenced to decay rapidly with the time, falling to half value in about 30 minutes. A similar result has been obtained by P. Curie.

Attention has been called (Rutherford, Phil. Mag. Jan. 1903) to the irregular character of the curves of decay of both thorium- and radium-excited activity, as measured by the α radiation, and the view was put forward that this stage probably represents a double change in the case of thorium, and a treble change in the case of radium. In the latter there is (for a short exposure to the emanation) a very rapid decrease for the first 10 minutes to about 20 per cent. of the original value, then a period of very slow change, and then a more regular decay in which the remaining activity falls to half value in about 30 minutes.

Now the decay curve of the β radiation of the radium-excited activity shows a fairly regular decrease to half value in 30 minutes. Hence there is strong evidence that the β rays are not given out in the first change of the excited activity, but only in the second or third change.

Radium therefore fully supports the view already advanced that the α rays are in all cases the first to be produced, the β rays only resulting in the last stages of the process that can be experimentally traced.

§ 6. *The Chemical Nature of the Radium Emanation.*

The experiments already described on the chemical nature of the thorium emanation were repeated for that of radium. As in the former case all the reagents tried were without effect. The emanation passed unchanged through phosphorus pentoxide, sulphuric, nitric, and hydrochloric acids, and over red-hot lead chromate and metallic magnesium. Water does not dissolve the emanation appreciably, and the activity of the water is solely due to the presence of the excited activity. The emanation in both dry and moist atmospheres is unaffected by passage through a platinum tube electrically heated to the point of incipient fusion. An interesting effect, however, was observed as the temperature approached a white heat in this experiment.

The ionization current due to the emanation decreased with rise of temperature, but returned to its original value when an increased voltage was applied sufficient to give a saturation current through the gas. This effect is due to fine platinum dust given off from the white-hot platinum, and is quite analogous to that of tobacco-smoke observed by Owens (Phil. Mag. 1899, xlviii. p. 377) in this laboratory.

The condensation of the radioactive emanations of thorium and radium at the temperature of liquid air (Proc. Chem. Soc. 1902, p. 219) will be dealt with in detail in a separate communication.

McGill University, Montreal,
Feb. 20, 1903.

XLV. *The Problem of Columbus.* By H. W. Chapman, *B.Sc., University College, London**.

[Plate XI.]

1. IF an ordinary hard-boiled egg be laid on its side on a horizontal plane and be then given a spin round the vertical its axis will rise and at last stand up on its end, still spinning; in this position it will remain until its motion fails and it falls down. This problem I term *Columbus's Problem.* To a first approximation it would appear as if the dynamical problem could be treated as identical with that of a body symmetrical about an axis and with a hemispherical end moving on a perfectly rough horizontal plane.

The only references I have been able to find to the motion of a body of this nature are first, in Jellett's 'Treatise on Friction,' where the case is discussed in which the spin round the long axis of the egg is taken so large that all the other motions are small in comparison with it. A second reference occurs in Routh's 'Advanced Rigid Dynamics,' Article 244, Example 4, where the equation of angular momentum (my Equation 12) is given.

There are several investigations of the more general problem of a solid of any shape moving on a plane. In Poisson's *Traité de Mécanique* the small oscillations of a body on a smooth plane are treated of. In the 5th and 8th vols. of Crelle's *Journal* M. Cournot considers the case of a body on a perfectly rough and also on an imperfectly rough plane, but he confines himself almost wholly (i.) to showing that there are sufficient equations obtainable to determine the coordinates of the body, and (ii.) to the consideration of initial motions.

It therefore appeared of interest to examine whether the problem of the egg could not be completely solved in the most general case. This solution is effected in the following pages.

2. Let O be the point of contact at any time, C the centre of the hemispherical base, and G the centre of gravity of the egg. Let OCZ be the vertical through O, OX the projection of CG, the axis of the body, on the horizontal plane, and OY a perpendicular to OX in this plane. Let $OC=a$, $CG=h$; let the moment of inertia of the body about

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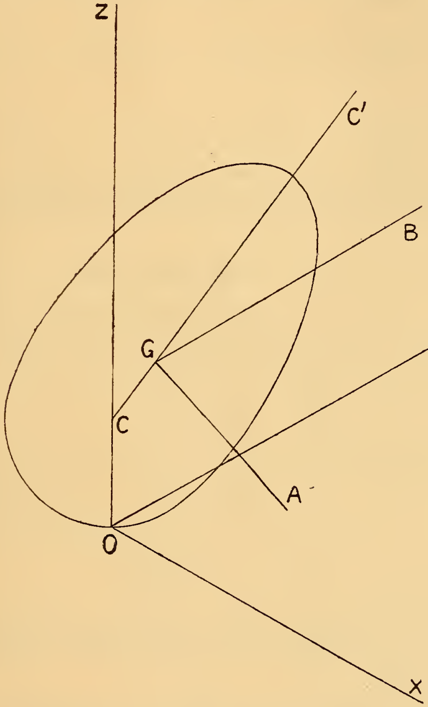
* Communicated by Prof. Karl Pearson, F.R.S.

CG be C, and about any perpendicular to CG through G be A. Let $\angle ZCG = \theta$ and the angular velocity of the plane ZOX about OZ be $\dot{\psi}$. Let R be the normal reaction at O and F_1, F_2 the components of the friction along OX, OY. Take GA the perpendicular to GC in the plane ZCG, GB the perpendicular to this plane, and GC′ the axis of the body as principal axes. They will coincide in direction with OX, OY, OZ when $\theta = 0$. Let the spins of the body round them be ω_1, ω_2, ω_3, and the spins of the axes round their instantaneous positions be θ_1, θ_2, θ_3. Also let the velocities of G parallel to OX, OY, OZ be u, v, w.



3. Then we have clearly

$$\left.\begin{aligned} \omega_1 &= -\dot{\psi}\sin\theta \\ \omega_2 &= \dot{\theta} \\ \theta_1 &= \omega_1 \\ \theta_2 &= \omega_2 \\ \theta_3 &= \dot{\psi}\cos\theta \end{aligned}\right\} \quad \cdots\cdots \quad (1)$$

Also by the modified form of Euler's equations,

$$A\frac{d\omega_1}{dt} - A\theta_3\omega_2 + C\theta_2\omega_3 = \text{moment of external forces about GA},$$

$$A\frac{d\omega_2}{dt} - C\theta_1\omega_3 + A\theta_3\omega_1 = \quad ,, \quad ,, \quad ,, \quad \text{GB},$$

$$C\frac{d\omega_3}{dt} - A\theta_2\omega_1 + A\theta_1\omega_2 = \quad ,, \quad ,, \quad ,, \quad \text{GC}'.$$

These give by (1)

$$-A\ddot{\psi}\sin\theta - 2A\dot{\theta}\dot{\psi}\cos\theta + C\omega_3\,\dot{\theta} = F_2(h + a\cos\theta), \quad . \quad . \quad (2)$$

$$A\ddot{\theta} + C\omega_3\dot{\psi}\sin\theta - A\dot{\psi}^2\sin\theta\cos\theta = Rh\sin\theta - F_1(a + h\cos\theta), \quad . \quad . \quad (3)$$

$$C\omega_3 = F_2 a\sin\dot{\theta}. \quad . \quad . \quad . \quad (4)$$

Next consider the accelerations of G referred to OX, OY, OZ. This system of axes has a spin $\dot{\psi}$ round OZ, so we get

$$\frac{du}{dt} - v\dot{\psi} = \frac{F_1}{M}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{dv}{dt} + u\dot{\psi} = \frac{F_2}{M}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\frac{dw}{dt} = \frac{R}{M} - g. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

We have also the geometrical equations arising from the fact that O has no velocity, since the surface is supposed to be perfectly rough.

Velocity of O along OX = velocity of G parallel to OX
+ velocity of O relative to G parallel to OX
$= u - \omega_2(a + h\cos\theta)$,

$\therefore$ from (1) $u = (a + h\cos\theta)\dot{\theta}$. . . . . . (8)

Velocity of O along OY = velocity of G parallel to OY
+ velocity of O relative to G parallel to OY
$= v + \omega_1(h + a\cos\theta) + \omega_3 a\sin\theta$,

$\therefore$ from (1) $v = \dot{\psi}\sin\theta(h + a\cos\theta) - \omega_3 a\sin\theta$ (9)

and clearly $w = -h\sin\theta\dot{\theta}$. . . . . . . (10)

4. As the plane is perfectly rough we can use the equation of energy. This is

$$\tfrac{1}{2}M(u^2 + v^2 + w^2) + \tfrac{1}{2}(A\omega_1{}^2 + A\omega_2{}^2 + C\omega_3{}^2) + Mgh\cos\theta = \text{constant}.$$

Using (1), (8), (9), (10) this becomes

$$\tfrac{1}{2}\mathrm{M}\left[(a+h\cos\theta)^2\dot{\theta}^2+\{\dot{\psi}\sin\theta(h+a\cos\theta)-\omega_3 a\sin\theta\}^2\right.$$

$$\left.+h^2\sin^2\theta\dot{\theta}^2\right]+\tfrac{1}{2}\mathrm{A}(\dot{\theta}^2+\dot{\psi}^2\sin^2\theta)+\tfrac{1}{2}\mathrm{C}\omega_3{}^2+\mathrm{M}gh\cos\theta=\text{constant}.$$

$$i.\,e.\left\{\frac{\mathrm{A}}{a^2\mathrm{M}}+\left(1+2\frac{h}{a}\cos\theta+\frac{h^2}{a^2}\right)\right\}\dot{\theta}^2+\dot{\psi}^2\sin^2\theta\left\{\left(\frac{h}{a}+\cos\theta\right)^2+\frac{\mathrm{A}}{a^2\mathrm{M}}\right\}$$

$$-2\omega_3\dot{\psi}\sin^2\theta\left(\frac{h}{a}+\cos\theta\right)+\omega_3{}^2\left(\frac{\mathrm{C}}{a^2\mathrm{M}}+\sin^2\theta\right)+\frac{2gh}{a^2}\cos\theta=\mathrm{K}, \quad . \qquad (11)$$

K being the initial value of the left-hand side of the equation.

Multiply (2) by $a\sin\theta$ and (4) by $(h+a\cos\theta)$ and subtract; then

$$\mathrm{C}\dot{\omega}_3(h+a\cos\theta)-\mathrm{C}\omega_3 a\sin\theta\dot{\theta}+a\mathrm{A}\ddot{\psi}\sin^2\theta+2a\mathrm{A}\dot{\theta}\dot{\psi}\sin\theta\cos\theta=0\cdot$$

Integrating and dividing by a

$$\mathrm{C}\omega_3\left(\frac{h}{a}+\cos\theta\right)+\mathrm{A}\dot{\psi}\sin^2\theta=\lambda=\mathrm{C}\bar{\omega}_3\left(\frac{h}{a}+\cos\theta_0\right)+\mathrm{A}m\sin^2\theta_0, \qquad (12)$$

where $\bar{\omega}_3$, m, θ_0 are the initial values of ω_3, $\dot{\psi}$, θ.

This is the equation of angular momentum round the vertical through O.

5. Substituting from (8) and (9) in (6) :

$$\ddot{\psi}\sin\theta(h+a\cos\theta)+\dot{\psi}\dot{\theta}\cos\theta(h+a\cos\theta)-a\dot{\psi}\dot{\theta}\sin^2\theta$$

$$-\dot{\omega}_3 a\sin\theta-a\cos\theta\dot{\theta}\omega_3+(a+h\cos\theta)\dot{\theta}\dot{\psi}=\frac{\mathrm{F}_2}{\mathrm{M}}$$

$$=\frac{\mathrm{C}\omega_3}{a\mathrm{M}\sin\theta}\text{ from (4)},$$

$$\therefore\ \ddot{\psi}\sin^2\theta\left(\frac{h}{a}+\cos\theta\right)+2\dot{\psi}\dot{\theta}\sin\theta\cos\theta\left(\frac{h}{a}+\cos\theta\right)$$

$$=\dot{\omega}_3\left(\frac{\mathrm{C}}{a^2\mathrm{M}}+\sin^2\theta\right)+\omega_3\sin\theta\cos\theta\dot{\theta},$$

$$\therefore\ \omega_3\left(\frac{h}{a}+\cos\theta\right)\frac{d}{dt}(\dot{\psi}\sin^2\theta)=\frac{1}{2}\frac{d}{dt}\left\{\omega_3{}^2\left(\frac{\mathrm{C}}{a^2\mathrm{M}}+\sin^2\theta\right)\right\},$$

$$\therefore\text{ from (12) }\omega_3\left(\frac{h}{a}+\cos\theta\right)\frac{d}{dt}\left[-\frac{\mathrm{C}}{\mathrm{A}}\left\{\omega_3\left(\frac{h}{a}+\cos\theta\right)\right\}\right]$$

$$=\frac{1}{2}\frac{d}{dt}\left\{\omega_3{}^2\left(\frac{\mathrm{C}}{a^2\mathrm{M}}+\sin^2\theta\right)\right\},$$

$$\therefore \text{ integrating, } -\frac{C}{A}\omega_3^2\left(\frac{h}{a}+\cos\theta\right)^2 = \omega_3^2\left(\frac{C}{a^2M}+\sin^2\theta\right)+\text{constant,}$$

$$\therefore \ \omega_3^2\left\{\frac{AC}{a^2M}+A\sin^2\theta+C\left(\frac{h}{a}+\cos\theta\right)^2\right\}=n^2$$

$$=\bar{\omega}_3^2\left\{\frac{AC}{a^2M}+A\sin^2\theta_0+C\left(\frac{h}{a}+\cos\theta_0\right)^2\right\}. \quad (13)$$

We get from this

$$\omega_3 = +\frac{|n|}{\sqrt{\dfrac{AC}{a^2M}+A\sin^2\theta+C\left(\dfrac{h}{a}+\cos\theta\right)^2}}$$

$$\therefore \ \frac{d\,|\omega_3|}{d\theta} = -\frac{|n|\sin\theta\left\{A\cos\theta-C\left(\dfrac{h}{a}+\cos\theta\right)\right\}}{\left\{\dfrac{AC}{a^2M}+A\sin^2\theta+C\left(\dfrac{h}{a}+\cos\theta\right)^2\right\}^{\frac{3}{2}}}$$

$\therefore$ $|\omega_3|$ decreases as θ increases if

$$A\cos\theta > C\left(\frac{h}{a}+\cos\theta\right),$$

$$i.e.\ (A-C)\cos\theta > C\frac{h}{a}.$$

We have then four cases :

(i.) $A > C$ and $h > 0$.

If $(A-C)\cos\theta_0 > C\frac{h}{a}$ we shall have $|\omega_3|$ decreasing as θ increases until $(A-C)\cos\theta = C\frac{h}{a}$, when it will be at a minimum, and then as the top gets further down it will increase again.

If $(A-C)\cos\theta_0 > C\frac{h}{a}$ and the top is rising, $|\omega_3|$ will increase as long as the top rises.

If $(A-C)\cos\theta_0 < C\frac{h}{a}$ and the top is descending, $|\omega_3|$ will increase as long as the top descends.

If $(A-C)\cos\theta_0 < C\frac{h}{a}$ and the top is rising, $|\omega_3|$ will decrease until $(A-C)\cos\theta = C\frac{h}{a}$, and then increase again if $A-C > C\frac{h}{a}$; if $A-C < C\frac{h}{a}$ it will decrease all the way up.

(ii.) $A < C$ and $h > 0$. The condition is never satisfied if $\theta < \frac{\pi}{2}$. If $\theta > \frac{\pi}{2}$ the conditions of the problem are not satisfied unless the body is spherical. In this case the top behaves as in (i.), changing the signs of $(A-C)$ and $\cos\theta$.

(iii.) $A > C$, $h < 0$. The condition is satisfied as long as $0 < \theta < \frac{\pi}{2}$. If $\theta > \frac{\pi}{2}$ it is as in the first case, changing the signs of $\cos\theta$ and h.

(iv.) $A < C$, $h < 0$. This is similar to the first case, if we write $C-A$ for $A-C$ and $|h|$ for h.

In any case the position for which $|\omega_3|$ is a minimum, if a possible one, does not depend on the initial motions. Also ω_3 cannot become zero or change its sign, for the roots of $\frac{AC}{a^2M} + A\sin^2\theta + C\left(\frac{h}{a} + \cos\theta\right)^2 = 0$ are clearly imaginary, the left-hand side being the sum of three positive quantities.

6. Substitute from (12) in (11) for $\dot{\psi}\sin^2\theta$;

$$\frac{\left\{\frac{A}{a^2M} + \left(\frac{h}{a} + \cos\theta\right)^2\right\}\left\{\lambda - C\omega_3\left(\frac{h}{a} + \cos\theta\right)\right\}^2}{A^2\sin^2\theta}$$

$$-2\omega_3\left(\frac{h}{a} + \cos\theta\right)\frac{\lambda - C\omega_3\left(\frac{h}{a} + \cos\theta\right)}{A} + \omega_3^2\left(\frac{C}{a^2M} + \sin^2\theta\right)$$

$$+\dot{\theta}^2\left(\frac{A}{a^2M} + 1 + 2\frac{h}{a}\cos\theta + \frac{h^2}{a^2}\right) = K - \frac{2gh}{a^2}\cos\theta;$$

$$\therefore\ \omega_3^2\left[\frac{C^2\left(\frac{h}{a} + \cos\theta\right)\left\{\frac{A}{a^2M} + \left(\frac{h}{a} + \cos\theta\right)^2\right\}}{A^2\sin^2\theta} + \frac{2C\left(\frac{h}{a} + \cos\theta\right)^2}{A}\right.$$

$$\left. + \left(\frac{C}{a^2M} + \sin^2\theta\right)\right] - \frac{2\lambda\omega_3\left(\frac{h}{a} + \cos\theta\right)}{A}\left[\frac{\frac{AC}{a^2M} + C\left(\frac{h}{a} + \cos\theta\right)^2}{A\sin^2\theta} + 1\right]$$

$$+\dot{\theta}^2\left(\frac{A}{a^2M} + 1 + \frac{h^2}{a^2} + 2\frac{h}{a}\cos\theta\right)$$

$$= K - \frac{2gh}{a^2}\cos\theta - \frac{\lambda^2\left\{\frac{A}{a^2M} + \left(\frac{h}{a} + \cos\theta\right)^2\right\}}{A^2\sin^2\theta};$$

$$\therefore \frac{\omega_3^2\left\{\frac{AC}{a^2M}+A\sin^2\theta+C\left(\frac{h}{a}+\cos\theta\right)^2\right\}\left\{C\left(\frac{h}{a}+\cos\theta\right)^2+A\sin^2\theta\right\}}{A^2\sin^2\theta}$$

$$-\frac{2\lambda\omega_3\left(\frac{h}{a}+\cos\theta\right)\left\{\frac{AC}{a^2M}+A\sin^2\theta+C\left(\frac{h}{a}+\cos\theta\right)^2\right\}}{A^2\sin^2\theta}$$

$$+\dot{\theta}^2\left(\frac{A}{a^2M}+1+\frac{h^2}{a^2}+2\frac{h}{a}\cos\theta\right)$$

$$=K-\frac{2gh}{a^2}\cos\theta-\frac{\lambda^2\left\{\frac{A}{a^2M}+\left(\frac{h}{a}+\cos\theta\right)^2\right\}}{A^2\sin^2\theta};$$

$$\therefore\ A^2\sin^2\theta\,\dot{\theta}^2\left(\frac{A}{a^2M}+1+\frac{h^2}{a^2}+2\frac{h}{a}\cos\theta\right)$$

$$+n^2\left\{C\left(\frac{h}{a}+\cos\theta\right)^2+A^2\sin^2\theta\right\}+\lambda^2\left\{\frac{A}{a^2M}+\left(\frac{h}{a}+\cos\theta\right)^2\right\}$$

$$+A^2\sin^2\theta\left(\frac{2gh}{a^2}\cos\theta-K\right)$$

$$=2\lambda n\left(\frac{h}{a}+\cos\theta\right)\sqrt{\frac{AC}{a^2M}+A\sin^2\theta+C\left(\frac{h}{a}+\cos\theta\right)^2}. \quad (14)$$

The positive value of the root will be the right one if we take n of the same sign as $\bar{\omega}_3$, and therefore as ω_3. This can be done as the sign of n is still at our disposal.

If we put $\cos\theta=\mu$, the equation becomes

$$A^2\left(\frac{A}{a^2M}+1+\frac{h^2}{a^2}+2\frac{h}{a}\mu\right)\dot{\mu}^2+\frac{A\lambda^2}{a^2M}+(\lambda^2+Cn^2)\frac{h^2}{a^2}$$

$$+An^2-A^2K+2\mu\left\{\frac{h}{a}(\lambda^2+Cn^2)+gh\frac{A^2}{a^2}\right\}$$

$$+\mu^2(\lambda^2+Cn^2-An^2+A^2K)-2\frac{ghA^2}{a^2}\mu^3$$

$$=2\lambda n\left(\frac{h}{a}+\mu\right)\sqrt{\frac{AC}{a^2M}+A+C\frac{h^2}{a^2}+2C\frac{h}{a}\mu+(C-A)\mu^2}. \quad (15)$$

The height of the centre of gravity of the egg above the horizontal plane is $a+h\mu$. Hence (15) is the fundamental equation giving the vertical motion of the centre of gravity. This defines the nutation.

7. From (12) $A\dot{\psi}\sin^2\theta = \lambda - C\omega_3\left(\frac{h}{a} + \cos\theta\right)$;

$$\therefore \text{ by (13) } A\dot{\psi}\sin^2\theta = \lambda - \frac{Cn\left(\frac{h}{a} + \cos\theta\right)}{\sqrt{\frac{AC}{a^2M} + A\sin^2\theta + C\left(\frac{h}{a} + \cos\theta\right)^2}}. \quad (16)$$

When $\cos\theta = \mu$ is known in terms of the time, (16) will give $\dot{\psi}$ and therefore ψ in terms of the time. Thus (16) defines the precession.

Now we see from (16) that if θ becomes zero we must either have $\dot{\psi}\sin\theta$ infinite or

$$\lambda - \frac{Cn\left(\frac{h}{a} + 1\right)}{\sqrt{\frac{AC}{a^2M} + C\left(\frac{h}{a} + 1\right)^2}} = 0.$$

But if $\dot{\psi}\sin\theta$ were infinite the kinetic energy would be infinite, as we see from its expression in (11); for the only negative term in that expression is $-2\omega_3\dot{\psi}\sin^2\theta\left(\frac{h}{a} + \cos\theta\right)$, which cannot become infinite, for $\dot{\psi}\sin^2\theta$ is not, neither is ω_3.

$\therefore$ the egg cannot stand up on end unless

$$\lambda\sqrt{\frac{AC}{a^2M} + C\left(\frac{h}{a} + 1\right)^2} = Cn\left(\frac{h}{a} + 1\right).$$

The right-hand side of (16) is an even function of θ, so that if it be expanded in terms of θ we see that the terms containing θ will disappear, and $\dot{\psi}\sin\theta$ will tend to the limit zero, and $\dot{\psi}$ to a finite limit if the above condition be satisfied.

8. The integral of the equation (15) cannot be expressed in known functions, but the following considerations will throw some light on the nature of the motion :—

$$\dot{\mu} = \pm \frac{\left[\begin{array}{l} \frac{2ghA^2}{a^2}\mu^3 - \mu^2(\lambda^2 + Cn^2 - An^2 + A^2K) - 2\mu\left\{\frac{h}{a}(\lambda^2 + Cn^2) + \frac{ghA}{a^2}\right\} \\ \quad - An^2 + A^2K - (\lambda^2 + Cn^2)\frac{h^2}{a^2} - \frac{A\lambda^2}{a^2M} \\ \quad + 2\lambda n\left(\frac{h}{a} + \mu\right)\sqrt{\left(\frac{AC}{a^2M} + A + C\frac{h^2}{a^2} + 2C\frac{h}{a}\mu + (C-A)\mu^2\right)} \end{array}\right]^{\frac{1}{2}}}{A\left\{\frac{A}{a^2M} + 1 + \frac{h^2}{a^2} + \frac{2h}{a}\mu\right\}^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad (17)$$

When $\mu=\mu_0$ this must be satisfied identically, so that the right-hand side must become $\pm(\dot{\mu}_0{}^2)^{\frac{1}{2}}$; thus the positive sign is the proper one if $\dot{\mu}_0$ is positive, and the negative one if $\dot{\mu}_0$ is negative.

If $\dot{\mu}_0=0$, let us differentiate (15) with respect to t and divide by $\dot{\mu}$; this gives :—

$$2\mathrm{A}^2\left(\frac{\mathrm{A}}{a^2\mathrm{M}}+1+\frac{h^2}{a^2}+2\frac{h}{a}\mu\right)\ddot{\mu}+2\frac{h\mathrm{A}^2}{a}\dot{\mu}^2+2\left\{\frac{h}{a}(\lambda^2+\mathrm{C}n^2)+\frac{gh\mathrm{A}^2}{a^2}\right\}$$

$$+2\mu(\lambda^2+\mathrm{C}n^2-\mathrm{A}n^2+\mathrm{A}^2\mathrm{K})-\frac{6gh\mathrm{A}^2}{a^2}\mu^2$$

$$=2\lambda n\sqrt{\frac{\mathrm{AC}}{a^2\mathrm{M}}+\mathrm{A}+\mathrm{C}\frac{h^2}{a^2}+2\mathrm{C}\frac{h}{a}\mu+(\mathrm{C}-\mathrm{A})\mu^2}$$

$$+\frac{2\lambda n\left(\frac{h}{a}+\mu\right)\left\{\mathrm{C}\frac{h}{a}+(\mathrm{C}-\mathrm{A})\mu\right\}}{\sqrt{\frac{\mathrm{AC}}{a^2\mathrm{M}}+\mathrm{A}+\mathrm{C}\frac{h^2}{a^2}+2\mathrm{C}\frac{h}{a}\mu+(\mathrm{C}-\mathrm{A})\mu^2}}. \quad . \quad . \quad . \quad . \quad (18)$$

If we put $\mu=\mu_0$, $\dot{\mu}$ vanishes and we get the initial value of $\ddot{\mu}$. The sign of this is clearly the one to take in (17).

Now the roots of the expression under the radical in the numerator in (17) are clearly irrelevant; this is at once seen from its form in θ.

Also the root of the denominator is irrelevant, being clearly <-1.

From this we see that to every possible value of μ there correspond two and only two values of $\dot{\mu}$, and these are equal and opposite, and we can only pass from one to the other by μ passing through a root of the numerator of (17).

There are three cases to be considered. A root, to be relevant, must <1 in absolute value and be placed so that μ is moving towards it.

(α) The numerator has a real and relevant root, and the first root it reaches is single. Then if this root is α, put $\mu=\alpha+\chi$, χ being small. Then to a first approximation $\dot{\chi}=\beta\chi^{\frac{1}{2}}$, where β is a constant.

This gives $\chi^{\frac{1}{2}}=\frac{1}{2}\beta t$, so that μ reaches the root in a finite time; the motion is then reversed and it goes back again till it reaches another root.

(β) The first root reached is double. Then to a first approximation

$$\dot{\chi}=\beta_1\chi\,;$$

$$\therefore\quad \beta_1 t=\log\chi\,;$$

so that χ can only become zero after an infinite time and the axis of the body approaches asymptotically to a certain cone.

If the root be of higher order still,

$$\dot{\chi}=\beta''\chi^{1+\frac{n}{2}};$$

$$\therefore \quad \beta''t=-\frac{2}{n}\chi^{-\frac{n}{2}};$$

and there is again asymptotic approach to a cone.

(γ) There is no relevant root.

This is impossible, for we have the numerator in (17) positive in every possible position, otherwise $\dot{\mu}$ would become imaginary.

When $\mu=1$ it is

$$-n^2C\left(\frac{h}{a}+1\right)^2-\lambda^2\left\{\frac{A}{a^2M}+\left(\frac{h}{a}+1\right)^2\right\}$$

$$+2\lambda n\left(\frac{h}{a}+1\right)\sqrt{\frac{AC}{a^2M}+C\left(\frac{h}{a}+1\right)^2}$$

$$=-\left\{\lambda\sqrt{\frac{A}{a^2M}+\left(\frac{h}{a}+1\right)^2}-n\left(\frac{h}{a}+1\right)\sqrt{C}\right\}^2.$$

When $\mu=-1$ it is

$$-\left\{\lambda\sqrt{\frac{A}{a^2M}+\left(\frac{h}{a}-1\right)^2}-n\left(\frac{h}{a}-1\right)\sqrt{C}\right\}^2.$$

These are both negative or zero.

So that there is always a relevant root.

We also see that the egg cannot stand up unless

$$\lambda\sqrt{\frac{A}{a^2M}+\left(\frac{h}{a}+1\right)^2}-\sqrt{C}n\left(\frac{h}{a}+1\right)=0.$$

This is the condition found in art. 7, it will be observed that it is independent of the value of $\dot{\mu}_0$.

We see by this that if the top be started with μ between two roots, it will oscillate up and down between the two cones defined by these roots, or else approach one of them asymptotically.

If it be started at a single root we have $\dot{\mu}_0=0$, but $\ddot{\mu}_0$ will clearly not be 0, for this would involve $\left(\frac{dN}{d\mu}\right)_{\mu=\mu_0}=0$, if N is the numerator in (17), and the root would be double.

If it be started at a double root $\dot{\mu}_0=0$ and $\ddot{\mu}_0=0$, so we have a case of steady motion; it is necessary to consider the stability of this.

If the root we start with be α, put $\mu=\alpha+V$ and we have

$$\dot{V}^2=f(\alpha)+Vf'(\alpha)+\frac{V^2}{2\,!}f''(\alpha).$$

$$\therefore\ 2\ddot{V}=f'(\alpha)+Vf''(\alpha).$$

But $\quad f'(\alpha)=0.$

Then, on solving this in the ordinary way, we see that the motion is stable if $f''(\alpha)$ is negative and unstable if $f''(\alpha)$ is positive.

9. The case in which the root considered is $\mu=1$ requires special attention. In this case the vanishing of $\dot{\mu}$ does not imply the vanishing of $\dot{\theta}$, for $\dot{\mu}=-\sin\theta\dot{\theta}$, and thus $\sin\theta=0$, so that $\dot{\mu}=0$ whatever $\dot{\theta}$ may be. Consequently, although the value of μ turns back the body itself need not, but may pass through the vertical position.

We will therefore go back to the equation for θ and make θ small.

It can be written

$\sin^2\theta\dot{\theta}^2=f(\theta)$, where $f(\theta)$ is obtained from (14).

$f(\theta)$ is clearly an even function of θ, so we have, neglecting $\theta^4\dot{\theta}^2$ and θ^6,

$$\theta^2\dot{\theta}^2=f(0)+\frac{\theta^2}{2\,!}f''(0)+\frac{\theta^4}{4\,!}f^{\text{iv}}(0)$$

$$=C_0+C_2\theta^2+C_4\theta^4,\ \text{say}.$$

Put $\quad \theta^2=u.$

Then we have

$$\frac{du}{\sqrt{C_0+C_2u+C_4u^2}}=2dt.$$

$$\therefore\quad 2t+\epsilon=\int\frac{du}{\sqrt{C_0+C_2u+C_4u^2}}$$

$$=\int\frac{du}{\sqrt{C_4\left(u+\frac{C_2}{2C_4}\right)^2-\frac{C_2^2-4C_0C_4}{4C_4}}}$$

This will give

$$u+\frac{C_2}{2C_4}=\sqrt{\frac{C_2^2-4C_0C_4}{4C_4^2}}\cosh\sqrt{C_4}(2t+\epsilon)$$

if C_4 is positive,

and
$$u + \frac{C_2}{2C_4} = \sqrt{\frac{C_2^2-4C_0C_4}{4C_4^2}}\sin\sqrt{-C_4}(2t+\epsilon)$$
if C_4 is negative.

We see that in either case for the approximation ever to be valid we must have $\frac{C_0C_4}{C_2^2}$ small, as is otherwise obvious, for C_0 must be small.

This ensures $\sqrt{\left(\frac{C_2^2-4C_0C_4}{4C_4^2}\right)}$ being positive, which is also seen to be necessary.

In the first case we see that u cannot remain small. This therefore gives the motion near the origin, but need not be further considered.

In the second case we see that for the approximation to hold always, both
$$-\frac{C_2}{2C_4} + \frac{\sqrt{C_2^2-4C_0C_4}}{2C_4}$$
and
$$-\frac{C_2}{2C_4} - \frac{\sqrt{C_2^2-4C_0C_4}}{2C_4} \text{ must be small,}$$
i. e. C_0 and C_2 must both be small.

This is really a case of the last article, the egg oscillating between two cones both near the vertical.

If $C_0=0$ we have
$$u = -\frac{C_2}{2C_4} + \frac{C_2}{2C_4}\sin\sqrt{-C_4}(2t+\epsilon)$$
and C_4 is negative, so
$$u = \frac{C_2}{2(-C_4)}\left\{1-\sin\sqrt{-C_4}(2t+\epsilon)\right\},$$
$$i.\,e.\ \theta^2 = \frac{C_2}{(-C_4)}\sin^2\frac{\sqrt{-C_4}(2t+\epsilon)-\frac{\pi}{2}}{2}$$
$$\therefore\ \theta = \sqrt{\frac{C_2}{-C_4}}\sin\left(\sqrt{-C_4}\,t-\frac{\pi}{4}+\frac{\epsilon\sqrt{-C_4}}{2}\right).$$

This will be always valid near the vertical, and we see that in this case the body oscillates through the vertical inside a cone whose semivertical angle is given by the next root.

If C_2 is small the approximation is always valid. We see by (17) that when $C_0=0$, *i. e.*
$$\lambda\sqrt{\frac{AC}{a^2M}} + C\left(\frac{h}{a}+1\right)^2 = Cn\left(\frac{h}{a}+1\right),$$
$A\dot{\psi}\sin^2\theta$ takes the form $b^2\theta^2+\ldots$

Therefore neglecting θ^4 and substituting in above equation we get

$$\psi=\frac{b_2t}{A}+\text{constant},$$

$$\therefore\ \theta=\sqrt{\frac{C_2}{-C_4}}\sin\left(\frac{A\sqrt{-C_4}}{b_2}\psi+\text{constant}\right).$$

This is a well-known equation, and when $b_2=A\sqrt{-C_4}$ we see that the curve traced out by the axis is a circle on one side of the vertical.

10. There are some cases where the equation (15) can be solved in elliptic functions.

The first is the degenerate case when

$\frac{AC}{a^2M}+A+C\frac{h^2}{a^2}+2C\frac{h}{a}\mu+(C-A)\mu^2$ is a perfect square.

The condition for this is

$$C^2\frac{h^2}{a^2}=\left(\frac{AC}{a^2M}+A+C\frac{h^2}{a^2}\right)(C-A)$$

$$\therefore\ (C-A)\left(\frac{C}{a^2M}+1\right)=C\frac{h^2}{a^2}.$$

This necessitates $C>A$, giving a flattened top, not an egg. The case is real and, it is interesting to note, depends only on the structure of the top, not on the initial conditions.

11. Another case is when a is small so that a^3 can be neglected. In this case we must remember that λ^2, n^2, K have a^2 in their denominators, while the coefficient of $\dot\mu^2$ has no term with a denominator of order higher than a^2.

The only terms with a^4 in the denominator occur in the constant term, and these must disappear since they only occur in terms independent of μ, and must disappear when $\mu=\mu_0$; for the equation (17) is then satisfied identically, so that the right-hand side must reduce to $\dot\mu_0$, and there being no term in $\frac{1}{a^4}$ in the denominator there cannot be in the numerator.

This reasoning will not apply to the terms containing $\frac{1}{a^3}$ for some of them occur in the coefficient of μ.

These are on the left-hand side of (15)

$$2\frac{h}{a}\left\{\frac{C^2\bar{\omega}_3^{\,2}h^2}{a^2}+C\bar{\omega}_3^{\,2}\frac{h^2+\frac{A}{M}}{a^2}\right\}\mu=\frac{2C^2h\bar{\omega}_3^{\,2}\left(2h^2+\frac{A}{M}\right)}{a^3}\mu.$$

And on the right-hand side they are contained in

$$\frac{2}{a}\mathrm{C}\bar{\omega}_3 h\,\frac{\sqrt{\mathrm{C}}\bar{\omega}_3}{a}\sqrt{\frac{\mathrm{A}}{\mathrm{M}}+h^2}\left(\frac{h}{a}+\mu\right)\frac{1}{a}\sqrt{\frac{\mathrm{AC}}{\mathrm{M}}+\mathrm{C}h^2}\left(1+\frac{2\mathrm{C}ha\mu}{\frac{\mathrm{AC}}{\mathrm{M}}+\mathrm{C}h^2}\right)^{\frac{1}{2}}$$

Picking the terms in $\frac{\mu}{a^3}$ out of this we have

$$\frac{2\mathrm{C}^2\bar{\omega}_3{}^2h\left(\frac{\mathrm{A}}{\mathrm{M}}+h^2\right)}{a^3}\left(\frac{h}{a}\times\frac{2\mathrm{C}ha\mu}{\frac{\mathrm{AC}}{\mathrm{M}}+\mathrm{C}h^2}+1\right)\mu=\frac{2\mathrm{C}^2h\bar{\omega}_3{}^2\left(2h^2+\frac{\mathrm{A}}{\mathrm{M}}\right)}{a^3}\mu.$$

Therefore the term in $\frac{\mu}{a^3}$ vanishes.

Thus the term in $\frac{1}{a^3}$ in the absolute term disappears as the one in $\frac{1}{a^4}$ did.

Accordingly if we multiply by a^2 we shall get rid of all terms with a in the denominator.

Now, in expanding the right-hand side, we find that μ is never multipled by a power of a less than its own by more than two, for if we multiply by a^2 we get

$$2\lambda n(h+a\mu)\sqrt{\frac{\mathrm{A}}{\mathrm{M}}+h^2+2a\mathrm{C}h\mu+a^2\{(\mathrm{C}-\mathrm{A})\mu^2+\mathrm{A}\}}$$

and λ and n only contain a once each in their denominators.

Therefore if we expand as far as μ^4 we keep all terms containing a^2; and there is no expansion in terms of μ on the left-hand side, and no power of μ higher than the third.

It follows from this that if we neglect a^3 the equation can be solved in elliptic functions.

This gives a closer approximation to the case of the ordinary top than the usual one where the lower end of the top is taken as a point, i. e. a is neglected altogether.

As such a top is usually spun, $\bar{\omega}_3$ is large and m small, and θ_0 is fairly small. In such a case the condition of art. 8 (γ) is nearly satisfied, so that such a top will stand nearly upright even without slipping.

12. The expressions for the reactions can be obtained from the equations of motion.

From (4)

$$\frac{\mathrm{F}_2}{\mathrm{M}}=\frac{\mathrm{C}\dot{\omega}_3}{a\sin\theta}=-\frac{n\left[\mathrm{A}\cos\theta-\mathrm{C}\left(\frac{h}{a}+\cos\theta\right)\right]\dot{\theta}}{a\left\{\frac{\mathrm{AC}}{a^2\mathrm{M}}+\mathrm{A}\sin^2\theta+\mathrm{C}\left(\frac{h}{a}+\cos\theta\right)^2\right\}^{\frac{3}{2}}}.$$

Clearly this can never become infinite.

From (5)

$$\frac{F_1}{M} = (a + h\cos\theta)\ddot{\theta} - h\sin\theta\dot{\theta}^2 - \dot{\psi}^2\sin\theta(h + a\cos\theta) - \omega_3\dot{\psi}a\sin\theta.$$

This also can never become infinite, as will be seen by considering the expressions for $\dot{\psi}$, $\dot{\theta}$, ω_3.

For the motion to be physically possible, $\dfrac{\sqrt{F_1^2 + F_2^2}}{R}$ must always < some fixed quantity ν, depending on the nature of the egg and plane. We have seen that $\dfrac{\sqrt{F_1^2 + F_2^2}}{R}$ cannot become large by the numerator becoming large; it remains to see whether it can become large by the denominator becoming small.

From (7) we have

$$R = h\ddot{\mu} + g.$$

We must therefore see if $h\ddot{\mu} + g$ can be made to become small without $F_1^2 + F_2^2$ also becoming small.

Equation (18) gives

$$\begin{aligned} A^2\left(\frac{A^2}{a^2M} + 1 + \frac{h^2}{a^2} + 2\frac{h}{a}\mu\right)\ddot{\mu} = &-\frac{h}{a}A^2\dot{\mu}^2 - \left\{\frac{h}{a}(\lambda^2 + Cn^2) + \frac{ghA^2}{a^2}\right\} \\ &-\mu(\lambda^2 + Cn^2 - An^2 + A^2K) \\ &+\frac{3ghA^2}{a^2}\mu^2 + \lambda n\sqrt{\frac{AC}{a^2M} + A + C\frac{h^2}{a^2} + 2C\frac{h}{a}\mu + (C - A)\mu^2} \\ &+\frac{\lambda n\left(\frac{h}{a} + \mu\right)\left\{C\frac{h}{a} + (C - A)\mu\right\}}{\sqrt{\frac{AC}{a^2M} + A + C\frac{h^2}{a^2} + 2C\frac{h}{a}\mu + (C - A)\mu^2}}. \end{aligned}$$

Suppose h positive, and put $\bar{\omega}_3$ negative and m large enough to make λ positive. Take $\mu = 0$.

Then we have

$$\begin{aligned} A^2\left(\frac{A}{a^2M} + 1 + \frac{h^2}{a^2}\right)(h\ddot{\mu} + g) = -\frac{h^2}{a}A^2\dot{\mu}^2 - \frac{h}{a}(\lambda^2 + Cn^2) + A^2g\left(\frac{A^2}{a^2M} + 1\right) \\ + \text{(negative terms).} \end{aligned}$$

We can clearly make this as small as we like by choosing $\bar{\omega}_3$ and m properly.

We have still to see that this is a possible position under the circumstances.

The necessary condition for this is that the numerator of (17) should be positive when $\mu=0$.

The only positive term in this is A^2K, but this contains a term with $\dot{\theta}_0$ in it; we have assumed nothing about $\dot{\theta}_0$, so we can make K as large as we please.

This condition is also sufficient; for having μ_0 at our disposal, we can take it between 0 and the next root.

Also we see that $\dot{\mu}$ need not be small at this point, so that $\dot{\theta}$ need not be; F_2 will thus not become small: so that we can choose our initial conditions so that $\frac{\sqrt{F_1^2+F_2^2}}{R} >$ any number we please. It follows from this that with any material in actual nature, under certain initial conditions, the egg must slip at some time, and accordingly this solution will then fail.

13. To illustrate the motion I took a numerical example. The egg was taken as a hemisphere with half a prolate spheroid with major axis double of its minor, and its minor axis equal to the diameter of the hemisphere, all supposed homogeneous. In this case we have

$$h=\frac{3}{8}a,$$

$$A=M\frac{211}{320}a^2,$$

$$C=M\frac{2}{5}a^2.$$

When we form equation (15) we see that a divides out of every term except those containing g, and there we have $\frac{g}{a}$: for convenience of calculation I took $a=4{\cdot}90\ldots$ cms., so that $\frac{g}{a}=200$, taking one second as the unit of time; I also took $\mu_0=\dot{\mu}_0=0$.

As the top is not a complete sphere, $\ddot{\mu}_0$ must be positive for the solution to apply.

Referring to (18), we see that the condition for this is

$$\lambda n\sqrt{\frac{AC}{a^2M}+A+C\frac{h^2}{a^2}}+\lambda n\frac{C\frac{h^2}{a^2}}{\sqrt{\frac{AC}{a^2M}+A+C\frac{h^2}{a^2}}}-\frac{h}{a}(\lambda^2+Cn^2)-\frac{ghA^2}{a^2}>0.$$

This gives

$$\lambda\bar{\omega}_3\left(\frac{\mathrm{AC}}{a^2\mathrm{M}}+\mathrm{A}+2\mathrm{C}\frac{h^2}{a^2}\right)-\frac{h}{a}(\lambda^2+\mathrm{C}n^2)-\frac{gh\mathrm{A}^2}{a^2}>0\,;$$

i. e.

$$\bar{\omega}_3\left(\mathrm{A}m+\frac{h}{a}\mathrm{C}\bar{\omega}_3\right)\left(\frac{\mathrm{AC}}{a^2\mathrm{M}}+\mathrm{A}+2\mathrm{C}\frac{h^2}{a^2}\right)-\frac{h}{a}\left\{\mathrm{A}^2m^2+2\mathrm{AC}\frac{h}{a}m\bar{\omega}_3\right.$$

$$\left.+\mathrm{C}^2\frac{h^2}{a^2}\bar{\omega}_3{}^2+\mathrm{C}\bar{\omega}_3{}^2\left(\frac{\mathrm{AC}}{a^2\mathrm{M}}+\mathrm{A}+\mathrm{C}\frac{h^2}{a^2}\right)\right\}>\frac{gh\mathrm{A}^2}{a^2}.$$

We see from this that if μ_0 and $\dot{\mu}_0=0$, the top must fall if $\bar{\omega}_3=0$ and h be positive. It is therefore necessary to give the body an initial roll as well as an initial spin. The condition becomes, supposing $\bar{\omega}_3$ not zero,

$$-\frac{h}{a}\mathrm{A}^2m^2+\mathrm{A}^2m\bar{\omega}_3\left(\frac{\mathrm{C}}{a^2\mathrm{M}}+1\right)>\frac{gh\mathrm{A}^2}{a^2}\,;$$

i. e.

$$m\bar{\omega}_3\left(\frac{\mathrm{C}}{a^2\mathrm{M}}+1\right)-\frac{h}{a}m^2>\frac{gh}{a^2}.$$

Putting in the values for h, a, C above we get

$$1{\cdot}4\,m\bar{\omega}_3-{\cdot}375\,m^2>75.$$

This shows that to represent a real case we must have m and $\bar{\omega}_3$ rather large as the spins of tops usually go. Take

$$m=10,\quad \bar{\omega}_3=10 \text{ radians per second.}$$

These give

$$\lambda=8{\cdot}094,\quad \mathrm{K}=145,\quad n^2=97{\cdot}94.$$

And equation (16) gives

$$\dot{\mu}^2=\frac{65{\cdot}21\mu^3-103{\cdot}15\mu^2-143{\cdot}73\mu-59{\cdot}46+8{\cdot}956({\cdot}375+\mu)\times\sqrt{313{\cdot}4+96\mu-83\mu^2}}{{\cdot}7826+{\cdot}3261\mu}.$$

This of course has a root $\mu=0$, and the next root is $\mu={\cdot}328,\ldots$ which corresponds to a rise of the axis through about 19° 9′.

On tracing the curve and integrating it by graphical methods we get fig. 1 (Pl. XI.) which gives the period of the nutation. The integration was done by two methods, shown in fig. 1; firstly, by inverse summation, *i. e.* the curve was divided up by ordinates and the height of the mid-ordinates set off along a vertical as MΠ=NP, a polar distance MO was taken and pp' drawn between the extreme ordinates perpendicular to OΠ. It can be seen that the curve thus obtained is such that the ordinate is proportional to t. The other method was Pröll's method ; in this ordinates are taken as before and from the top of the mid-ordinate a constant length QG is set off to the base-line; qq' is then drawn between the extreme ordinates perpendicular to QG. The time in this case is proportional to the arc of the curve. These two methods both give about ·685 second as the complete period of nutation; the resulting curves are shown in Pl. XI. fig. 1. In fig. 2 the precession is dealt with, $\dot{\psi}$ is found in terms of μ, the equation being

$$\cdot 6594\dot{\psi}(1-\mu^2)=8\cdot 094-\frac{\cdot 3959(\cdot 375+\mu)}{\sqrt{\cdot 9794+\cdot 3\mu-\cdot 259\mu^2}};$$

μ is found in terms of t from fig. 1, and thus a $\dot{\psi}$ and t curve is constructed. This is integrated by the ordinary sum-curve method, and the amount of precession during a period of the nutation found.

Fig. 3 is a polar diagram in which the ray is taken proportional to $\sin\theta$ and the angle to ψ. It starts on the outer circle at C_1, touches the inner at C_2, and meets the outer again at C', the period of nutation being a little more than that of the precession. It is the projection on a horizontal plane of the motion of the centre of gravity relative to the centre of the hemisphere.

The coefficient of friction necessary that the egg may begin without slipping is easily found. Initially we have $\theta=0$, $\dot{\theta}=0$; so we have

$$F_2=0,$$

$$\frac{F_1}{M}=a\ddot{\theta}_0-m^2h-m\bar{\omega}_3a$$

$$=-a\ddot{\mu}_0-m^2h-m\bar{\omega}_3a,$$

$$\frac{R}{M}=h\ddot{\mu}_0+g.$$

Working out $\ddot{\mu}$ from (18), we get $\frac{F}{R}=\cdot 728$.

This shows that slipping would take place as a rule, but that it is perfectly possible to get surfaces rough enough to prevent it. We find $\ddot{\mu}_0=11\cdot 47$; thus the $\ddot{\mu}_0$ terms are much less important than the others, so that slipping would be less likely if m and $\bar{\omega}_3$ were smaller ; but this would involve a larger radius for the hemisphere.

14. The results obtained in this paper show :—(i.) That the axis of an egg-shaped body would certainly not rise towards the vertical unless, when its axis is horizontal, it receives not only

a spin about the vertical, but also a rolling motion round its axis. (ii.) That even when so spun it is very improbable that its axis would rise to the vertical.

It is found, however, that eggs with their axes horizontal generally do rise to the vertical without any delicate adjustment of their initial spins. We are therefore forced to conclude that this rising is in some way connected with the phenomenon of limiting friction. To test this, an egg was cast in rough cement and spun on a rough stone. It was found that while the smooth wooden eggs rose with great ease, this cement egg only rose with difficulty, and usually remained oscillating between two cones as required by the theory for a "perfectly rough" egg. I hope to deal later with the *Problem of Columbus*, supposing the egg to be only imperfectly rough; but the analysis promises to be of a much more complex kind.

I have to thank Professor K. Pearson, who first suggested the problem to me, for a great deal of kind assistance and advice during the course of the investigation. I must also thank Mr. W. Arnold Ogden, Demonstrator in the Department of Applied Mathematics, University College, for the trouble and care he took in plotting the curves for the numerical example and in graphically integrating them.

XLVI. *The Position of Radium in the Periodic System according to its Spectrum.* *By* C. Runge *and* J. Precht[*].

THE spark-spectrum of radium may be splendidly observed by using the bromide recently prepared by Herr Giesel. A few milligrammes, which Herr Giesel was good enough to place at our disposal for this purpose, enabled us, when using a small amount of dispersion, to produce a decidedly more perfect spectrum than any hitherto observed; and with greater dispersion, to investigate the lines which are capable of being easily photographed, with respect to their behaviour in a magnetic field. As a result we found that the strongest lines of radium are exactly analogous to the strongest lines of barium and the corresponding lines of the related elements Mg, Ca, Sr. As shown by Runge and Paschen[†], these lines may be grouped into three pairs, called by them, on account

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[*] Translated from the *Physikalische Zeitschrift*, 4 Jahrgang, no. 10, pp. 285–287.

[†] Runge and Paschen, *Ber. d. Berl. Akademie*, June 26, 1902.

of certain analogies with the spectra of the alkalies, the line-pair of the primary series, the line-pair of the first and that of the secondary series. In the line-pair of the first secondary series there occurs by the side of the line of greater wave-length a feebler line on the side of greater wave-lengths, which Runge and Paschen term a satellite. Measured on the scale of frequency, the two lines of each of the three pairs are the same distance apart for any one element, provided that in the case of the pair of the first secondary series the satellite be taken instead of one of the lines. This distance varies, on the other hand, from one element to another, increasing in a perfectly regular manner with the atomic weight, as will be seen below. In a magnetic field these lines, as has been shown by Runge and Paschen, split up in various ways into components, but in such a manner that, referred to the scale of frequency, the resolution of each line of any one element is precisely the same as that of the corresponding line of each of the other elements.

Now we have found that this also holds for radium, so that Ra is to be classed along with Mg, Ca, Sr, and Ba in a group of chemically allied elements—a conclusion which is supported by the chemical behaviour of radium, in so far as this is known.

The following table exhibits the correspondence between the lines:—

	Mg.	Ca.	Sr.	Ba.	Ra.
Primary Series......	2803	3969	4216	4934	4682
	2796	3934	4078	4554	3815
1st secondary Series	—	3181	3475	4166	4436
	2798	3179	3465	4131	4341
	2791	3159	3381	3892	3650
2nd ” ”	2937	3737	4306	4900	5814
	2929	3706	4162	4525	4533

The resolution of the radium lines in a magnetic field is easily observable with the strongest lines. It is only the resolution of the satellite and of the yellow line 5814 that we have as yet been unable to effect.

For any one element the distances apart of the two lines of each pair are, as already remarked above, equal if measured on the scale of frequency. The same holds good for radium, as shown by the following table:—

	λ.	$10^8/\lambda$.	Difference.
Primary Series......	4682·35 3814·59	21356·8 26215·1	4858·3
1st secondary Series	4436·45 3649·77	22540·5 27399·0	4858·5
2nd " "	5813·9 4533·33	17200·2 22058·8	4858·6

The variations in the numbers corresponding to the distances are sufficiently explained by experimental errors. They correspond to very small errors in the wave-length determinations.

From one element to another the distance apart of the lines increases with the atomic weight in the cases of Mg, Ca, Sr, Ba:—

	Atomic weight.	Distance.
Mg ...	24·36	91·7
Ca ...	40·1	223
Sr ...	87·6	801
Ba ...	137·4	1691

It is suggested to regard the atomic weight as a function of the distance between the lines, and to extrapolate this function for radium. It has already been pointed out by Rydberg, Kayser and Runge, in their investigations on the spectra of the elements, that within a group of chemically related elements the distance apart of the lines of a pair increases regularly with the atomic weight. They state that in the case of alkali metals the atomic weight is very nearly proportional to the square root of this distance. We wish to draw attention to the fact that for the other groups in which line-pairs have been observed, the relation between the width of the line-pairs and the atomic weight is capable of being expressed by a simple formula:—

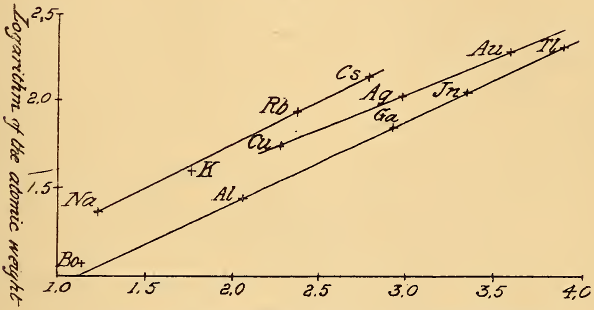
In each group of chemically related elements the atomic weight varies as some power of the distance apart of the two lines of a pair.

The exponent is a proper fraction. This result may otherwise be expressed thus:—

The logarithms of the atomic weights and those of the distances when plotted as coordinates lie on a straight line for a chemically related group of elements.

The following two figures illustrate this law.

Fig. 1.



Logarithm of the line-distance (·01 scale-division =2·3 per cent. of the value).

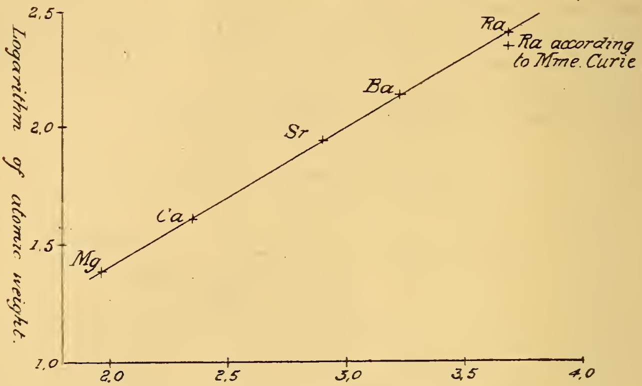
In fig. 1 it will be seen that among the alkalies potassium alone falls slightly below the line passing through the remaining points. We do not mean thereby to suggest that the directly determined atomic weight of potassium is incorrect; but it appears to us interesting that the straight-line law is appreciably departed from precisely in the case of the element whose atomic weight in the periodic system points to an unknown disturbing cause, which produces the inversion of the positions of argon and potassium.

As regards boron, gallium, and indium, the radiation of these elements in a magnetic field has not been investigated. On the other hand, there is no room for doubt as regards the line-pairs corresponding to aluminium and thallium. The same applies to the alkali group, where only the two yellow sodium lines have been investigated in a magnetic field.

In fig. 2 is represented the same relation for Mg, Ca, Sr, Ba, and Ra. The extrapolation gives for the atomic weight of radium the value 258. Of course, the straight line may be to some extent rotated and displaced without any great departure from the points; but the figure shows clearly that the value 225 as determined by Madame Curie is considerably removed from the straight line.

In the following table the straight line is represented by a formula, and the extrapolated value obtained by calculation.

Fig. 2.



Logarithm of line-distance (·01 scale-division =2·3 per cent.).

If x stands for the width of the line-pair, measured on the scale of frequency $10^8/\lambda$, then we have :—

	Calculated atomic weight=antilog. (·2005+·5997 log x).	Observed atomic weight.
Mg ...	23·84	24·36
Ca ...	40·6	40·1
Sr ...	87·5	87·6
Ba ...	136·9	137·4

The extrapolation for radium gives for its calculated atomic weight the value 257·8.

We do not venture to suppose that our value deserves more confidence than that determined by Mme. Curie. It must, however, be remarked that in view of the close relationship of barium and radium, and the small quantities with which the chemist is forced to work, the complete separation of these two bodies is very difficult, and that if the separation had been incomplete Mme. Curie would have found too small a value for the atomic weight. According to the crystallographic observations of F. Rinne, to be published shortly, radium bromide and barium bromide are isomorphic, so that a joint crystallization of both substances (an isomorphic mixture) is, from *à priori* considerations, highly probable—on the assumption of similar solubility relations. From this will be understood the great difficulty of separating these substances by crystallization, so that even after frequently repeated re-crystallizations the corresponding radium compound may contain more or less barium. The same holds for the relation of radium to calcium as well as to strontium and magnesium.

The number 225 is in better correspondence with the periodic system, in so far as it fits the gap between bismuth and thorium in the proper column. According to the value 258, radium would have to be moved two rows further down in the column Mg, Ca, Sr, Ba, and a number of new unoccupied places would be created in the periodic system.

On the other hand, Rutherford's remark may be adduced in support of the higher value of the atomic weight. The higher atomic weight is indicative of a more complicated atomic structure, and therefore of an easier splitting up into electrons. The element which gives off electrons most freely should therefore also have the highest atomic weight.

The radium line 4826·14, which is the most prominent of all in a Bunsen-flame, is also after resolution in a magnetic field found to be analogous to the strongest Bunsen-flame lines Ba 5535, Sr 4607, Ca 4226. All these lines become resolved into triplets, which in the case of the elements considered consist of equidistant lines, the frequency scale being used.

Hanover, Physical Institute of the Technical High School.
January 1903.

XLVII. *Some Remarks on Radioactivity.*

To the Editors of the Philosophical Magazine.

Gentlemen,

In a recent number of the *Comptes Rendus*, Jan. 26, 1903, there appeared a paper by M. Henri Becquerel, entitled 'Sur la déviabilité magnétique et la nature des certains rayons émis par le radium et le polonium," and also one by M. P. Curie " Sur la radioactivité induite et sur l'émanation du radium," in the former of which certain criticisms of my experimental methods, and in the latter of my theoretical views were made.

I am very pleased that M. Becquerel, with the very active material at his disposal, has confirmed in such a direct manner by the photographic method the results which I had previously obtained by the electric method *, showing

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* *Phys. Zeit.* No. 8, p. 235, Jan. 15 (1903); Phil. Mag. Feb. 1903.

that the α or easily absorbed rays of radium are deviated by an intense magnetic field. In the course of his paper M. Becquerel states, "M. E. Rutherford, avec une grande habileté, et par une méthode électrique relativement grossière, a reconnu un phénomène d'une extrême délicatesse. Cependant la méthode employée laisserait prise à diverses objections et à un doute sur l'existence du phénomème en question si l'on n'en apportait pas d'autre preuve. L'une des objections résulte de la disposition expérimentale qui fait traverser des espaces laminaires par un rayonnement dont la partie cathodique est rejetée sur les parois, et les rayons secondaires qui en résultent peuvent donner lieu à des effets dans le sens observé par M. Rutherford. Je me suis alors proposé de mettre en évidence le phénomène par une expérience plus simple et plus sûre. J'ai eu recours à l'une des dispositions photographiques que j'emploie depuis longtemps et qui permettent certaines distinctions qui n'apparaissent pas toujours quand on emploie exclusivement la méthode électrique."

I fully recognize the great simplicity and utility of the photographic method, so ably developed by M. Becquerel himself, for determining the magnetic deviation of rays and determining accurately the curvature of their path, *provided that the rays emitted are sufficiently intense to affect a photographic plate without too long an exposure.*

The difficulty of obtaining satisfactory photographs in cases of less active material is clearly shown by M. Becquerel's own experiments on the rays of polonium described in the same paper. I have unfortunately not had at my disposal very active preparations of radium, and in consequence have had to adapt my methods to obtain effects from such active matter as I possessed. It was for this reason that I employed the electric method, which is capable of extreme refinement, and can be used to compare rapidly the intensities of radiations which would require very long exposures to act appreciably on the photographic plate. As an example of the comparative sensitiveness of the two methods I may recall some of M. Becquerel's own experiments (*Comp. Rend.* p. 209, 1902) in which he was unable to detect photographically any action of the α rays from uranium, or any evidence of the existence of very penetrating rays from it, although the times of exposure in two experiments were as long as 20 and 42 days.

By the electric method the α rays from 1 milligramme of uranium can be quickly measured; and I have recently found that, using 100 grs. of uranium oxide, the existence of very penetrating rays can be detected in a few minutes, through 1 cm. of lead, by the increased rate at which the leaves of an electroscope fall together.

The objection raised by M. Becquerel that the effects observed may have been due to secondary rays set up by the β or "cathode" rays striking the metal boundaries is in direct opposition to the data given in my paper. I have there shown that 89 per cent. of the discharge in the electroscope was due to α rays, since the discharge was diminished by that amount by placing a thin layer of mica ·01 cm. thick over the active material. It is well known that such a thickness of mica completely cuts off the α rays, but allows the passage of the β rays through it with but little absorption. The effect in the electroscope, due to the β rays and the secondary rays set up by them, was thus only slightly altered by the addition of the mica plate, and therefore could not have been initially much more than 11 per cent. of the total. As a matter of fact, I showed that the 11 per cent. was hardly affected by an intense magnetic field, and was due chiefly to the very penetrating rays from radium. With the uncovered active specimen the rate of discharge in very intense fields was reduced by 89 per cent. of the original, showing that all the α rays were deviated in passing through the narrow slits.

It has been shown in previous papers that, with a thin layer of active material, the ionization due to the β rays (including that due to the secondary rays produced by them) is very small compared with that due to the α rays under ordinary experimental conditions. On the other hand, the β rays are photographically very active compared with the α rays; and M. Becquerel, in several of his papers, has drawn attention to the marked photographic action of the secondary radiation set up by them. This may have led him to believe that their electrical effect would be equally marked, but such is not the case.

M. P. Curie in his paper, after giving some experimental results showing that the decay of activity of the radium emanation is unaltered by variations in temperature between 450° C. and −180° C., proceeds as follows:—

"Pour expliquer les phénomènes de là radioactivité induite et la transmission de l'activité par les courants des gaz, M. Rutherford a admis que le théorium et le radium émettent une *émanation radioactive* qui provoque la radioactivité des corps sur lesquels elle vient se fixer. C'est cette émanation qui entretient l'activité induite dans une enceinte fermée activée. M. Rutherford semble croire à la nature matérielle de l'émanation et, dans l'un de ses Mémoires les plus récents*, il considère comme vraisemblable qu'il s'agit d'un gaz de la nature de ceux du groupe de l'argon.

" Je pense qu'il n'y a pas actuellement de raisons suffisantes pour admettre l'existence d'une émanation de matière sous sa forme atomique ordinaire. Nous avons antérieurement, M. Debierne et moi, vainement cherché des raies nouvelles dans les gaz radioactifs extraits du radium. Enfin l'émanation disparait spontanément en tube scellé. Je considère aussi comme peu vraisemblable que les effets qui accompagnent l'existence de l'émanation aient leur origine dans une transformation chimique. On ne connaît en effet aucune réaction chimique pour laquelle la vitesse de réaction soit indépendante de la température entre −180° et +450°."

Since the discovery of the thorium emanation, I have always taken the view that the emanation consists of matter in the radioactive state present in minute quantity in the surrounding gas. The experiments of Miss Brooks and myself ('Nature,' p. 157, 1901) showed that the radium emanation mixed with air diffused very slowly. By comparing the rate of interdiffusion of the emanation into air with that of known gases, it was deduced that the emanation particles behaved like heavy gas molecules of molecular weight probably lying between 40 and 100. I have long recognized that the electrical and other effects produced by the emanations can be manifested by an extremely minute quantity of radioactive matter in the gaseous state. For this reason I am not surprised that MM. Curie and Debierne have failed to obtain evidence by the spectroscope or balance of the existence of the emanation. At the same time I do not doubt that with sufficient quantity of active material the presence of the emanation will ultimately be detected by these means. I do not consider that the emanations remain permanently in the gaseous state, for it seems probable that the emanations gradually change into the matter responsible for excited activity, which is deposited on the walls of the containing vessel. Recent experiments by Mr. Soddy and myself show that the thorium emanation behaves chemically as an inert gas, and in this respect resembles the gases of the argon family. M. Curie has, apparently, not observed a recent paper by us (Proc. Chem. Soc. p. 219, 1902) in which it is shown that if the emanations of thorium or radium mixed with air, oxygen, or hydrogen are passed slowly through a spiral tube immersed in liquid air, the emanations are condensed in the tube, and the issuing gas is completely free

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* Rutherford and Soddy, Phil. Mag. Nov. 1902.

from activity. On removing the spiral from the liquid air, the whole of the condensed emanation (allowing for the decay of activity in the interval) is released at a fairly definite temperature and appears again in the stream of gas. A more detailed account of these investigations will shortly appear in this journal.

These results, in my opinion, conclusively show that the emanations are gaseous in character, for it is very difficult to explain such phenomena except on a material hypothesis.

In addition, I have recently shown that it is extremely probable that the greater proportion of the radiation from the emanation is material in nature, and consists of heavy charged bodies projected with great velocity, whose mass is of the same order as that of the hydrogen atom. In view of these results, which so strongly confirm the theory of the material nature of the emanation, the alternative theory proposed by M. P. Curie that the emanation consists of "centres de condensation d'énergie situés entre les molécules du gaz et qui peuvent être entraînés avec lui," appears to me unnecessary.

The interesting result, obtained by M. Curie, of the exponential law of decay of the radium emanation under all conditions, is only one of many others that have now been accumulated. I quite agree with M. Curie that such results cannot be satisfactorily explained on the laws of *ordinary* chemical change, but the difficulty disappears on the view already put forward by Mr. Soddy and myself (Phil. Mag. Sept. and Nov. 1902) that the radioactivity of the elements is a manifestation of *sub-atomic chemical change*, and that the radiations accompany the change.

There is no *à priori* reason to suppose that temperature would affect the rate of atomic disintegration ; in fact the general experience of chemistry in failing to transform the elements is distinctly opposed to such a view. It is therefore not surprising that, if radioactivity is an accompaniment of sub-atomic change, the process should be independent of the ordinary chemical and physical agents at our disposal. These points, and many others bearing on the same question, are discussed in more detail in a joint paper with Mr. Soddy now in the course of publication.

I am, Gentlemen,
Yours very truly,
E. Rutherford.

McGill University,
Montreal, Feb. 28, 1903.

XLVIII. *New Magneto-Optic Phenomena exhibited by Magnetic Solutions.* *By* Dr. QUIRINO MAJORANA*.

1. GUIDED by the analogy between magnetic and electric phenomena, I wished to determine whether a magnetic field was capable of rendering a magnetic substance doubly refracting, as an electrostatic field is capable of doing in the case of a dielectric (Kerr's phenomenon). I was thus led to the discovery of the following three effects:—

(1) *Magnetic Double Refraction.*

(2) *Magnetic Dichroism.*

(3) Certain rotations of the plane of polarization of light, which I have called *Bimagnetic Rotation.*

2. *Magnetic Double Refraction.*—Experiments on highly magnetic substances, such *e. g.* as thin transparent sheets of iron, or solutions of *ferric chloride*, did not yield any appreciable results. But solutions of *ferrous chloride* were rendered feebly doubly-refracting when placed in a very intense magnetic field. The experiment was conducted in the following manner. The liquid having been placed in a magnetic field, a ray of light was allowed to pass through it in a direction normal to the lines of force. The liquid was placed between two crossed nicols whose principal sections made angles of 45° with the lines of force. On exciting the field, the light re-appeared. With a field intensity of 18,000 C.G.S. units, if the liquid was placed in a tube 7 cms. long, the double refraction represented at most 2 to 3 hundredths of the wave-length of yellow light. On the other hand, dialysed iron or colloidal solution of ferric oxide was frequently strongly active. The degree of activity varied according as the substance was more or less freshly prepared. Thus freshly prepared dialysed iron is entirely inactive, while if it is kept for a long time (ten years or more), the double refraction, under the experimental conditions indicated above in connexion with ferrous chloride, reaches a value of 12 wave-lengths of green light. Dialysed iron thus aged was obtained from old bottles of *fer Bravais* in a druggist's shop.

The magnetic double refraction exhibited by dialysed iron presents numerous peculiarities. It may be either *positive* or *negative*; but if the specimen of the liquid is very old, the

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* Communicated by the Author. This note forms a brief *résumé* of some researches of mine described more in detail in the *Rendiconti della Accademia dei Lincei.* at the meetings of May 31, June 15, August 3 and 17, 1902. I think that some observations contained in a short notice of Dr. J. Kerr (Report Brit. Assoc. 1901, p. 868), with which I became acquainted after the publication of my researches, must be referred to the phenomena there described.

double refraction is positive in a weak field, decreases gradually, and ultimately becomes negative under the action of a strong field. It therefore has a *point of inversion,* corresponding to a field of given intensity, for which the double refraction becomes equal to zero. If the point of inversion is very low, *i. e.* occurs at a weak field intensity, then the following laws hold with a considerable degree of approximation. The magnetic double refraction is :—

(1) Directly proportional to the concentration of the liquid.

(2) Directly proportional to the thickness of liquid traversed in a direction normal to the lines of force.

(3) Directly proportional to the square of the field intensity.

(4) Inversely proportional to the square of the wavelength of the light experimented with.

3. *Magnetic Dichroism.*—Dialysed iron strongly absorbs light. It is therefore easy to foresee that by reason of the phenomenon of double refraction described above, the absorption of a polarized wave will undergo different modifications according to the azimuth of the plane of polarization, when the magnetic field is excited. It is thus that I was able to establish the existence of a series of phenomena to which I propose, with good reason, to apply the term *Magnetic Dichroism.* These phenomena are entirely analogous to those presented by dichroic crystals (*e. g.* tourmaline), with the sole difference that they are only observed when the circuit of the exciting current is closed. The more important results are:—

In the case of the magnetic dichroism exhibited by dialysed iron, it always happens that when one wave is propagated through the interior of the liquid with a velocity less than that of another wave (on account of different azimuths of the plane of polarization, or different directions of propagation), it also suffers less absorption. Photometric measurements have shown that the absorption suffered by vibrations propagated in a direction parallel to the lines of force is the same as that suffered by vibrations propagated normally, the plane of polarization being parallel to the field.

4. *Bimagnetic Rotations.*—This phenomenon is exhibited by solutions of ferric chloride prepared from certain hydrated oxides of iron.

With the arrangement described in connexion with double refraction, the solution of ferric chloride replacing the dialysed iron, it is observed that when the field is excited between the two crossed nicols at 45° to the field, the light reappears; and that it again disappears when the analyser is rotated through a small angle. In another experiment with the polarizer turned through 90° from its original position, the phenomenon is still exhibited, but the rotation (whose absolute value is the same) is in the opposite direction. If the plane of polarization is parallel or normal to the field, no effect is obtained. I have called this rotation of the plane of polarization *bimagnetic*, in order to distinguish it from the *magnetic rotation* of Faraday, the term being intended to emphasize the fact that the first phenomenon is different from the second, and depends on the magnetic property of the liquid used as well as on the magnetic field. The bimagnetic rotation may be *positive* or *negative*, according as the plane of polarization is rotated so as to recede from or to approach the lines of force.

I must refer to my original publication for the method of preparing the *active liquid.* Here it must suffice to mention that in general this may be prepared by oxidizing, in the wet way, small pieces of iron, and then acting on them with a dilute solution of ferric chloride. According to the nature of the iron oxide employed, the rotation is positive or negative.

The maximum rotation observed by me was at most 4° 30′. The following is a theory of this effect which has been suggested to me by Prof. Voigt. The incident vibrations which are propagated at an angle of 45° to the field may be resolved into two components, one normal and the other parallel to the field. It seems that the magnetic action results in producing a different absorption of these two components, which on leaving the liquid give rise to a resultant vibration in a plane different from the original one.

The following are a few details regarding this phenomenon:—

(*a*) The bimagnetic rotatory power is different for different colours, according to a law which I have not succeeded in formulating, and which varies from one liquid to another.

(*b*) The rotation is proportional to the thickness of the liquid traversed, provided the rotation be not excessive.

(*c*) It increases with increase of field intensity, rapidly at first, but beyond a certain not very intense field strength becomes almost constant.

(*d*) All the specimens of liquids endowed with the power of bimagnetic rotation lose this property to some extent.

5. I have finally tried to determine whether magnetic double refraction is an instantaneous or a gradual phenomenon. I believe I may conclude that it is really instantaneous, since samples of dialysed iron became double refracting in a field generated by the discharge of a leyden-jar.

XLIX. *Note on an Elementary Treatment of Conducting Networks.* *By* L. R. Wilberforce, *M.A., Professor of Physics at University College, Liverpool*[*].

It may be worth while to point out that the well known reciprocal relations between the parts of a conducting network can be readily established without an appeal to the properties of determinants.

Let A, B, C, D, . . ., be a number of points connected by conductors AB, AC, AD, . . ., BC, BD, . . ., CD, . . ., of resistances R_{AB}, . . ., and suppose that currents Q_A, . . ., are led into the network at the points A, . . ., from without, subject to the condition $Q_A+Q_B+\ldots=0$, and that internal electromotive forces, E_{AB}, ... act in the conductors in the directions AB, ... Let the currents in the conductors be C_{AB}, . . ., and let the potentials at A, . . ., be V_A, ... The fact that there is no continuous accumulation of electricity at any point gives us a series of equations whose type is :—

$$Q_A=C_{AB}+C_{AC}+\ldots \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

and the application of Ohm's law gives us a series whose type is

$$R_{AB}\,C_{AB}=V_A-V_B+E_{AB}. \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Suppose now that a different system of external currents, Q'_A, . . ., and internal electromotive forces, E'_{AB}, . . ., are applied to the same network, and let the consequent currents and potentials be denoted by accented letters. Equations similar to (1) and (2) will, of course, hold for these quantities.

Multiplying each equation of series (2) by the corresponding current in the second system and adding, we obtain :—

$$\Sigma R_{AB}\,C_{AB}\,C'_{AB}=\Sigma C'_{AB}\,(V_A-V_B)+\Sigma E_{AB}\,C'_{AB}.$$

Now, remembering that $C'_{NM}=-C'_{MN}$, the coefficient of any potential V_M on the right-hand side of this equation is easily seen to be $C'_{MA}+C'_{MB}+\ldots$, and thus is Q'_M. The equation thus becomes :—

$$\Sigma R_{AB}\,C_{AB}\,C'_{AB}=\Sigma V_A\,Q'_A+\Sigma E_{AB}\,C'_{AB}.$$

By a similar process we obtain

$$\Sigma R_{AB}\,C_{AB}\,C'_{AB}=\Sigma V'_A\,Q_A+\Sigma E'_{AB}\,C_{AB}.$$

[If the accented system is made to coincide with the unaccented system, we obtain $\Sigma R_{AB}\,C^2_{AB}=\Sigma V_A\,Q_A+\Sigma E_{AB}\,C_{AB}$, the equation of activity.]

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[*] Communicated by the Physical Society: read Jan. 23, 1903.

From the general equation :

$$\Sigma V_A Q'_A + \Sigma E_{AB} C'_{AB} = \Sigma V'_A Q_A + \Sigma E'_{AB} C_{AB}$$

the required reciprocal relations follow at once.

(i.) Let every Q and Q′ be zero, and every E except E_{AB}, and every E′ except E'_{CD}.

Then : $E_{AB} C'_{AB} = E'_{CD} C_{CD}$, and if $E_{AB} = \pm E'_{CD}$ then $C_{CD} = \pm C'_{AB}$, or, in words, if an E.M.F. in one branch produces a certain current in a second branch, then an equal E.M.F in the second branch will produce an equal current in the first ; and, according as the direction of the latter E.M.F. is the same as or opposite to that of the former current, the direction of the latter current will be the same as or opposite to that of the former E.M.F. Again, if C_{CD} is zero, C'_{AB} will be zero, which leads to the definition of conjugate conductors.

(ii.) Let every E and E′ be zero, and every Q except Q_A and Q_B (which will be $-Q_A$), and every Q′ except Q'_C and Q'_D (which will be $-Q'_C$).

Then : $(V_C - V_D)\ Q'_C = (V'_A - V'_B)\ Q_A$, and if $Q_A = Q'_C$, $V_C - V_D = V'_A - V'_B$; that is, if a certain current led in at A and out at B produces a certain excess of potential of C over D, an equal current led in at C and out at D will produce an equal excess of potential of A over B.

L. *Notices respecting New Books.*

Report on the Total Solar Eclipse of January 21–22, 1898, *as observed at Jeur in Western India. By* Kavasji Dadabhai Naegamvala, *M.A., F.R.A.S., Director of the Observatory.* Bombay : Printed at the Government Central Press.

THIS Report was published at Poona in November 1901. Prof. Naegamvala thinks it necessary to account for the delay in its appearance, which was due to his desire to compare the spectrum of the "flash," which was for the first time adequately obtained at the Indian Eclipse of 1898, with stellar spectra and other related types. He has since been engaged in laborious efforts to secure these for purposes of comparison with the eclipse; but finding that his progress was much hampered by certain mechanical defects in the prismatic camera, he finally decided to publish an account of his observations at Jeur without further delay. As is well known, he is Director of the Maharaja Taktasingji Observatory at Poona, and feeling the importance of taking part in the observations of the eclipse in question, he memorialized the Government of Bombay on the subject as early as February 1896. To prepare himself for efficient participation, he accompanied the expedition sent to Norway to observe the total eclipse of August 9 in that year ;

and though the weather effectually prevented any results being secured on that occasion, Prof. Naegamvala obtained the valuable opportunity of examining the numerous instruments brought together by five different parties of European astronomers. This, of course, was of the greatest service to him in forming his plan of observation and selecting his instruments for the Indian eclipse, but unfortunately some improvements which were considered desirable in his equipment were completed only just in time, which is to be regretted because longer preparation in the matter of adjustments would have secured greater precision when the eventful moment arrived. Nevertheless, results of great value were obtained, the details of which are given in this volume, together with the illustrations requisite to enable readers to follow a scheme carried out with great skill. All the parties in India were favoured with most propitious weather, and the eclipse was well seen and observed, as was cabled to England immediately. (The present writer had the satisfaction of announcing this at a lecture delivered at South Norwood on the evening of the same day.) Jeur (the site selected) is near the very centre of the line of totality, and is a station on the Great Indian Peninsula Railway, nearly east of Poona. A locality at the Southern Maratha line would have been superior in several respects; but owing to the fact that the plague was raging in that neighbourhood, Jeur was preferred, and near it an observing camp was prepared, about one hundred yards to the west of the spot selected by Prof. W. W. Campbell, of the Lick Observatory. Great care was used in training the assistants who went to take part in the work, and the final result was highly satisfactory. To use the words of the Report of the Council of the Royal Astronomical Society in February 1899, "Prof. Naegamvala of the Poona College, assisted by a number of his students, secured an excellent series of photographs both of the corona and also of the chromosphere spectrum with the prismatic camera." To appreciate these, the reader must refer to the volume itself. W. T. L.

Die Internationalen Absoluten Masze, Insbesondere die Electrischen Masze, für Studirende der Electrotechnik. Von Dr. A. von Waltenhofen. Dritte, zugleich als Einleitung in die Electrotechnik bearbeitete Auflage. Mit 42 eingedruckten Figuren. Braunschweig: F. Vieweg und Sohn. 1902. Pp. xi+306.

This book on units covers a very wide field. It is divided into two parts, Part I. dealing with the subject of units, and Part II. consisting of a series of appendices, devoted mainly to the elucidation of various points connected with magnetic and electric theory. This second part is also intended by the author to form an introduction to electrotechnology. In our opinion, the treatment of the subjects considered in Part II. is much too condensed and scrappy to be suitable for a student, although to one already acquainted with the subject it may prove a useful compendium.

The proofs and explanations given are not always remarkable for elegance of treatment. Thus, in dealing with the formula for the E.M.F. of a dynamo, p. 61, the author establishes it by supposing that the E.M.F. in each conductor follows the sine law, and then calculates the mean value of the E.M.F.! This ponderous and clumsy treatment is not only unnecessary, but is positively misleading; for there is no dynamo in existence in whose conductors the E.M.F.-wave so much as approaches the sine law.

As a book of reference, the work should prove useful, for it contains a large number of important data. In the section dealing with inductance, in particular, we notice some very useful approximate formulæ for the self-inductances of coils.

Cryoscopie. Par F. M. Raoult. Paris: C. Naud. 1901. Pp. xiii +106. (*Scientia* Series, No. 13.)

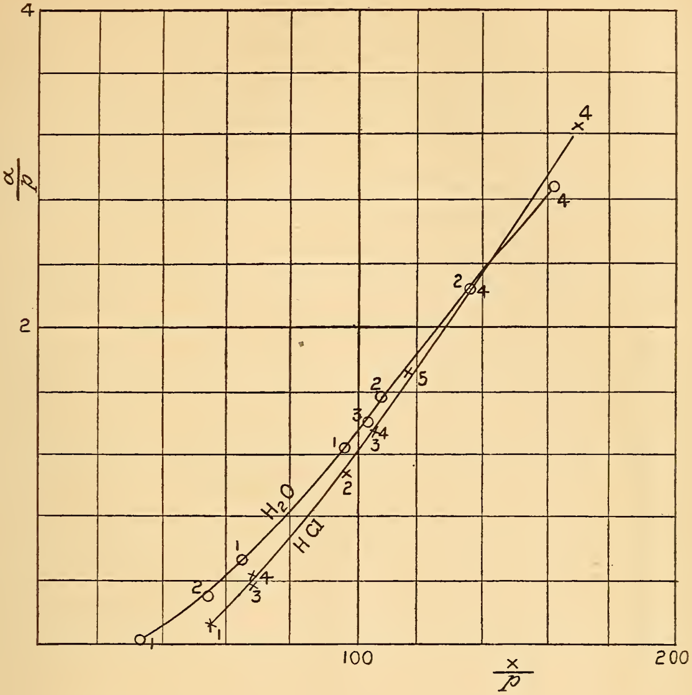
The work of the late F. M. Raoult is of such far-reaching importance that his name is one of the most familiar to students of physical chemistry. Happily for such students, he was enabled, almost immediately before his death, to give the clear and fascinating account of his important researches in the monograph before us. We could wish for no better exposition of the subject. After an account of some general principles in Part I. we are in Part II. introduced to the experimental methods of cryoscopy. Part III. deals with the cryoscopy of organic compounds, and Part IV. with that of electrolytes—a subject which, in the early days of the science, was beset with so many serious difficulties that Raoult's work was accepted with very considerable reserve, if not diffidence, until the daring and brilliant speculations of Arrhenius restored the confidence of the scientific public in the soundness of Raoult's generalizations.

The volume is embellished with a portrait of the author, and an appreciative sketch of his career and work by his friend and pupil, M. R. Lespieau.

Bericht über die Internationale Experten-Conferenz für Weiterschiessen in Graz (XXXIX. Band der Jahrbücher der K. K. Central-Anstalt für Meteorologie und Erdmagnetismus). Wien: Wilhelm Braumüller. 1902. Pp. iv+154.

Anyone interested in either meteorology or folklore will find the present volume interesting reading. Edited by J. M. Pernter, it contains a number of valuable contributions from experts on the various aspects of the modern system of battling with hail-storms, which originated in Graz, and is now extensively practised both there and in Italy. As to whether a hail-storm can or cannot be averted by the firing of specially-constructed cannon is a question still *sub judice*. But it is interesting to learn, from the opening paper of this Report, that the belief in the efficacy of such a method is of comparatively great antiquity.

Fig. 2.



3.

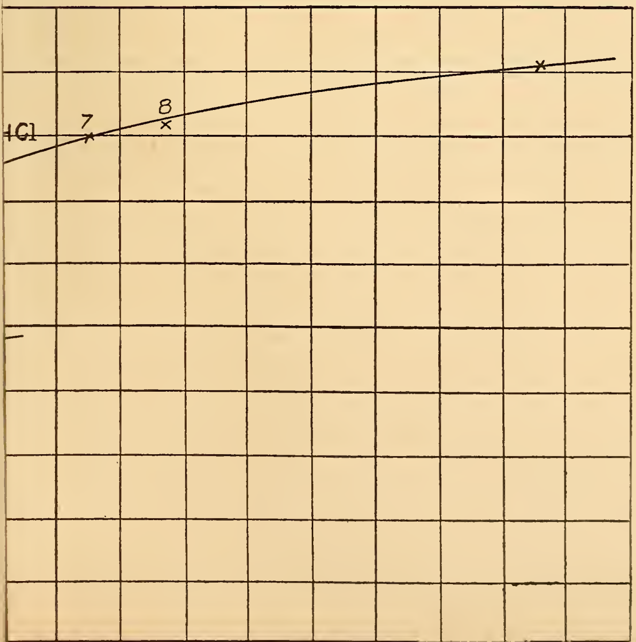


Fig. 1.

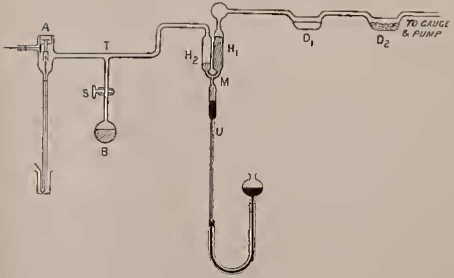


Fig. 2.

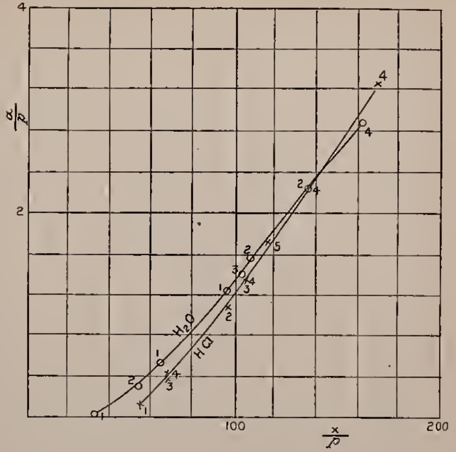
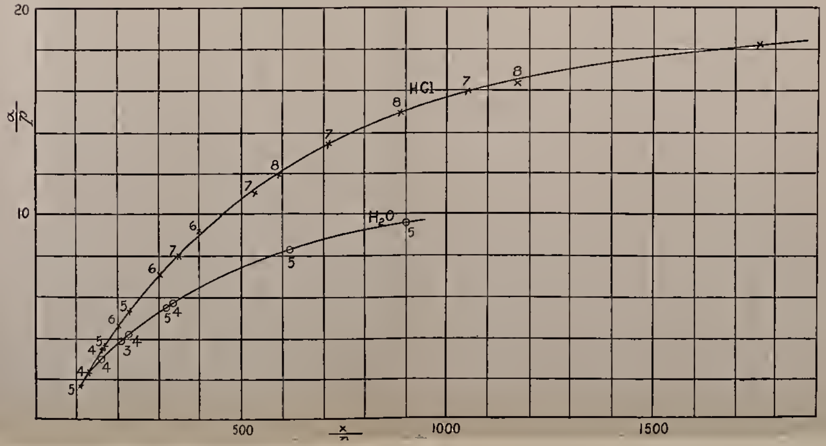
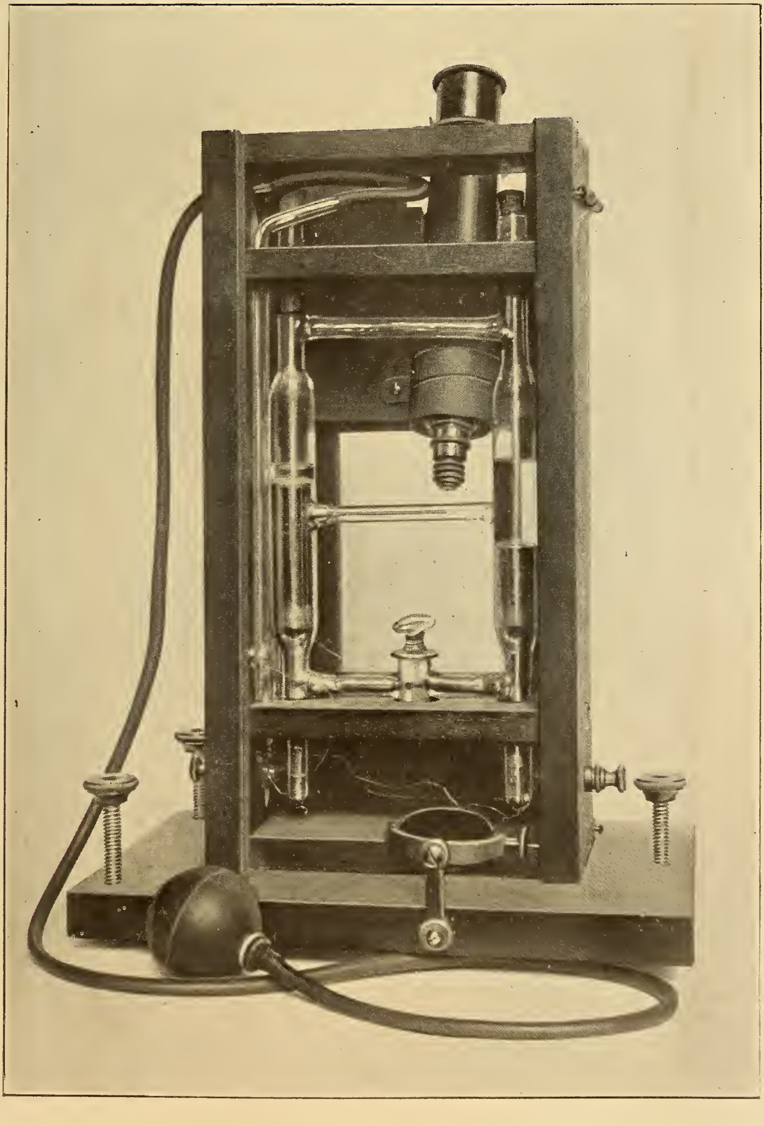


Fig. 3.





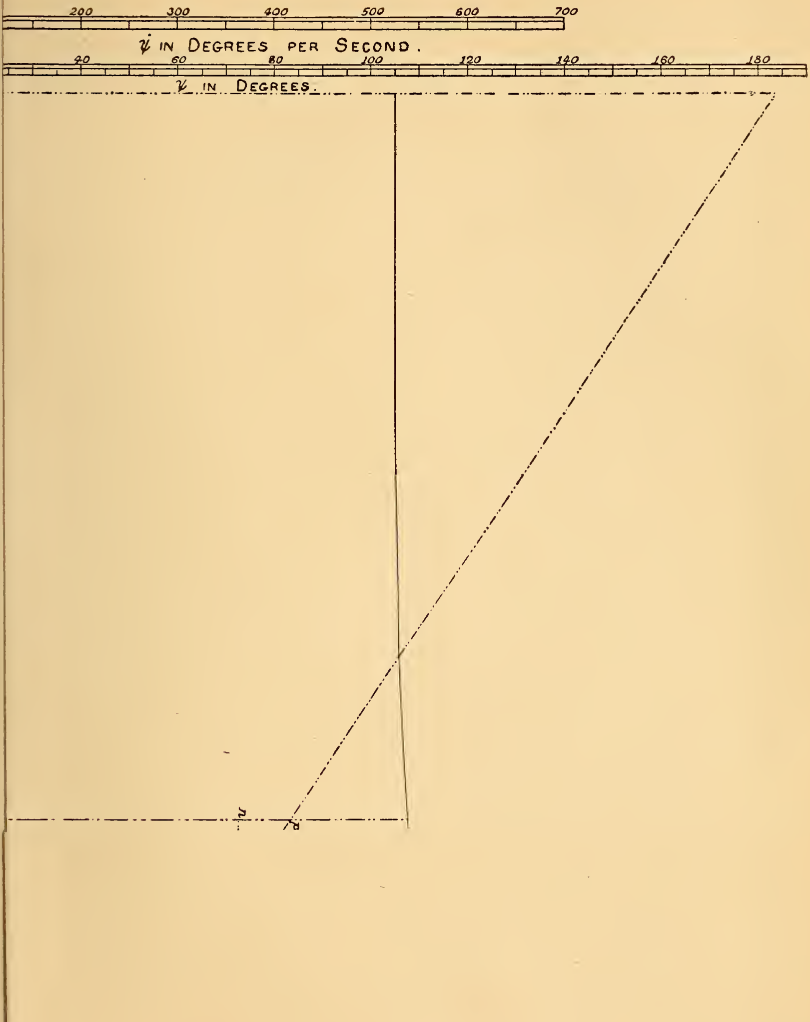
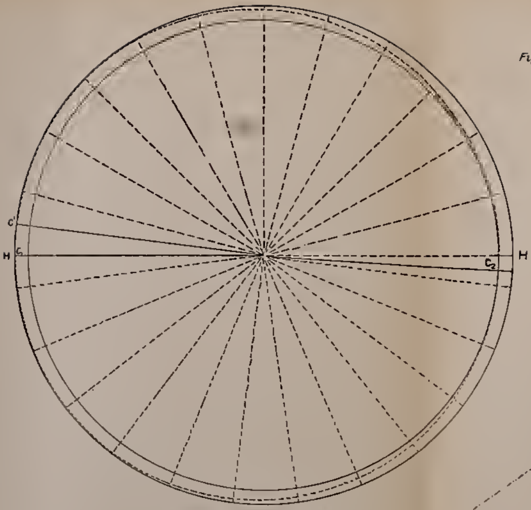
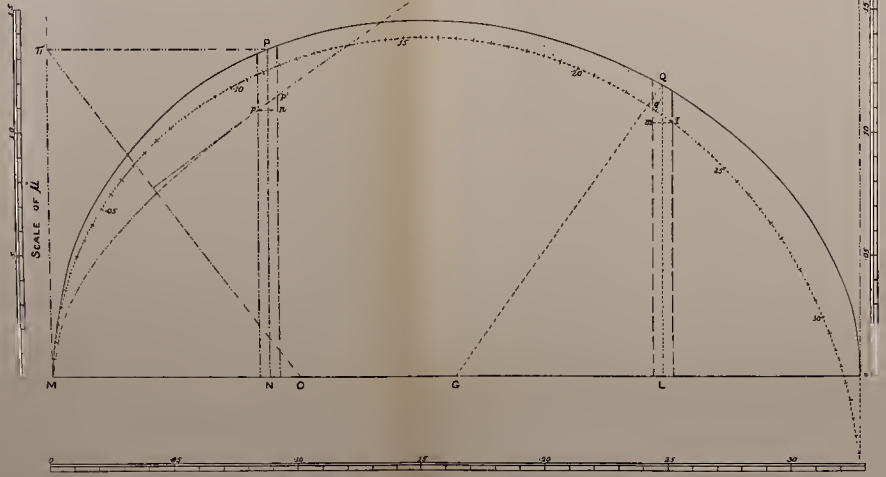

200
300
400
500
600
700
$\dot{\psi}$ IN DEGREES PER SECOND.
40
60
80
100
120
140
160
180
ψ IN DEGREES.

Fig. III



NUTATION DIAGRAM



Scale of μ.

Fig. I.

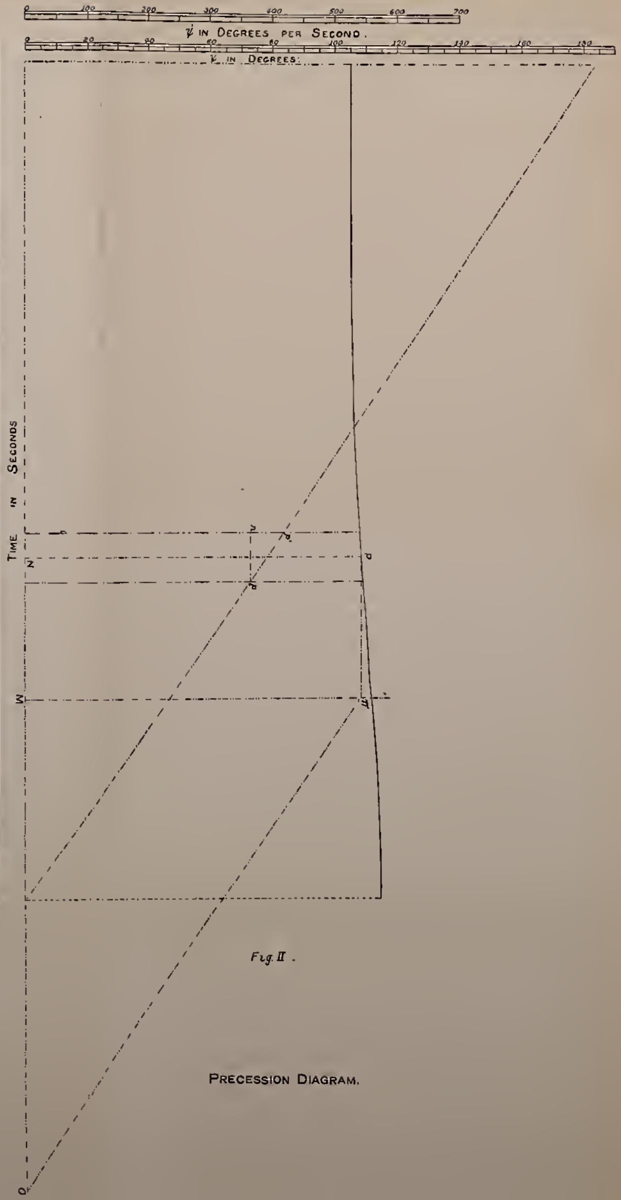


Fig. II.

PRECESSION DIAGRAM.

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AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

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LI. *On the Measurement of Small Capacities and Inductances.*

By J. A. Fleming, *D.Sc., F.R.S., Professor of Electrical Engineering in University College, London,* and W. C. Clinton, *B.Sc., Demonstrator in the Pender Electrical Laboratory, University College, London*[*].

[Plate XII.]

THE measurement of small capacities and inductances has become important in connexion with Hertzian Wave Wireless Telegraphy. The experimental determination of the electrical capacity of telegraph wires and of the overhead wires used for the conveyance of high tension alternating currents, is also called for in connexion with the calculation of sending speeds and of voltage drop in a power line. The advantage of possessing an appliance which will conduct this work quickly and well has led us to design the instrument which is here described.

It is generally admitted that for the measurement of small capacities, when the dielectric is air or some other substance not possessing the quality commonly called absorption, no method is so easy to apply as that depending upon the rapid charge and discharge of a condenser through a galvanometer. This method is almost the only one applicable to the measurement of the small electrical capacities of wires insulated in the air, such as the aerial wires employed in Hertzian Wave Telegraphy, or ordinary telegraph-wires, or small air-condensers, or in fact any form of condenser in which the

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[*] Communicated by the Physical Society: read February 27, 1903.

capacity is independent of the time of charging. This method has been extensively employed, the only difference being in the nature of the commutator for charging and discharging the condenser. Maxwell suggested the use of a tuning-fork as a switch, the vibrating prongs being furnished with a stylus which made and broke contact with a mercury cup, or vibrated to and fro between two fixed contacts. The great objection to this arrangement is the uncertain duration of the contact. Hence other experimentalists have employed an electrically maintained tuning-fork with a vibrating contact used as a means of driving synchronously an electromagnetic contact-breaker, which in turn makes a better and longer contact between two stops alternately. A device of this latter kind was successfully employed by Professor J. J. Thomson *, Dr. Glazebrook †, and Professors Fleming and Dewar ‡ in various experiments connected with the measurement of specific inductive capacity at low temperatures.

We have had considerable experience with all these tuning-fork devices, but we have found them troublesome in practice, especially when a large number of measurements have to be made. In addition there is always an uncertainty as to the actual duration of the contact, which makes it impossible to determine by calculation whether the condenser is being fully discharged at each vibration. After a great many preliminary experiments, we finally devised the following appliance, which when properly made never fails to give satisfaction and renders the measurement of small capacities, even as small as one ten-thousandth of a microfarad, a matter as easy as the measurement of resistance on a Wheatstone bridge.

The instrument as constructed consists of a continuous current electric motor of $\frac{1}{6}$ HP., but for certain purposes, and where very small capacities have to be measured, it is preferable to employ a motor of $\frac{1}{2}$ HP. This motor is bolted down upon a baseboard and has connected with it a starting and regulating resistance. The motor is preferably 100 or 200 volt shunt wound motor. To the shaft of this motor is connected by a flexible coupling the commutating arrangement,

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* See J. J. Thomson, Phil. Trans. Roy. Soc. 1883, p. 718, "On the number of Electrostatic Units in the Electromagnetic Unity of Electricity."

† Also R. T. Glazebrook, Phil. Mag. Aug. 1884, vol. xviii. p. 98, "On a Method of measuring the Capacity of a Condenser"; or Proc. Brit. Assoc. Leeds, 1890.

‡ J. A. Fleming and J. Dewar, Proc. Roy. Soc. London, 1896, vol. lx. p. 368, "On the Dielectric Constant of Liquid Oxygen and Liquid Air."

the function of which is to charge the capacity or condenser to a given voltage and then discharge it through a galvanometer, repeating this process four times in each revolution of the motor. This commutator is fixed on a shaft carried in well lubricated bearings supported on two small A frames (Pl. XII. fig. 1). On this shaft are held, by means of ebonite bushes and washers, three gunmetal disks or wheels, of which the centre one is in shape like an eight-rayed star, whilst the two outer ones are like crown wheels, each having four teeth. The three wheels are so set on the shaft that the teeth or projections of each of the two outer wheels interlock or fall in the space between the teeth of the other, whilst the radial teeth of the intermediate wheel occupy the intervals between the teeth of the two outer wheels. The developed surface of this triple wheel is shown in fig. 2. The whole outer surface is turned true and forms a barrel about four inches in diameter, and two and a half inches wide. On this barrel rest three brass gauze brushes which are carried in well insulated brush holders, and by means of three springs and levers the brushes are firmly pressed against the barrel, the two outer brushes resting on the continuous portions or flanges of the two outer wheels A and B, and the middle brush occupying the centre line and making contact either with the wheel A or wheel B, or with the intermediate wheel I according to their position. It will be seen then that as the commutator runs round, the middle brush is alternately brought into metallic connexion with first one and then the other of the two brushes on either side. The function of the middle wheel (I) is to afford a stepping piece and prevent any shock or jar as the middle brush passes over from one connexion to the other. It also prevents the middle brush from short-circuiting the two outer brushes at any time. If then one terminal of the galvanometer is connected to the brush pressing against the wheel A, and one terminal of a battery is connected to the brush pressing against wheel B, and one terminal of a condenser is connected to the middle brush, the other terminals of the battery, galvanometer, and condenser being connected together, it will easily be seen that as the commutator runs round, the condenser is first charged at the battery, and then discharged through the galvanometer. In the following experiments, speeds of 1200 to 1700 revolutions per minute were used. To count the rotations of the commutator a worm on the shaft drives a wheel of such gear that the latter makes one revolution for every hundred revolutions of the commutator. This wheel carries a pin which at each revolution causes a hammer to strike a gong. Every hundred revolutions, therefore, of the motor or commutator, the gong gives one stroke, and by means of a stop-watch it is easy to take the time of ten strokes of the gong ; in other words, to ascertain the time in seconds of a thousand revolutions of the motor, and therefore of the number of commutations per second. In the case of the motor we have employed, 1000 revolutions take place generally in 40 seconds, which is at the rate of 1500 per minute, and therefore corresponds with 100 commutations of the condenser per second.

We have tried various methods of making the rubbing contacts and found nothing better than brass gauze brushes. Carbon brushes were tried at one time and found to be unsuccessful. It is essential that the commutator surface should be kept bright and clean, and the brass gauze brushes do this themselves when adjusted to the right pressure.

Associated with this commutator we have employed a galvanometer of the movable coil type, either one made by Crompton, or in some cases one made by Pitkin. By the aid of this instrument, given a source of constant voltage by which the motor can be driven steadily, such as a secondary battery, the measurement of small capacities becomes an exceedingly easy matter.

There is, of course, no novelty in the mere use of a rotating commutator for the determination of capacities by the above method. It was employed many years ago by Dr. R. T. Glazebrook for this purpose. See 'The Electrician,' vol. xxv. p. 616, 1890, on "The Air Condensers of the British Association." One of us (Dr. Fleming) had, however, employed the device several years previously for the same purpose. Our only claim to novelty in this matter is that of having worked out a thoroughly satisfactory form of rotating commutator, which is designed more from the point of view of an engineer than an electrical instrument maker.

In the case of the measurement of capacity of insulated wires or aerials, the aerial is connected to the middle brush, one terminal of the galvanometer and battery respectively are connected to the two remaining brushes, and the other terminals of the galvanometer and battery are connected to the earth (see fig. 3). Under these circumstances, when the commutator is in rotation, the galvanometer gives a perfectly steady deflexion due to the passage through it of 100 discharges per second from the condenser. In order to determine the numerical value of the capacity, we have therefore to evaluate the deflexion of the galvanometer and to determine the ampere value of a steady current which will make the same deflexion. This can be accomplished by putting the galvanometer in series with a variable resistance, and placing the two as a shunt on a known small resistance in series with another variable resistance, and then placing on the terminals of this circuit a cell of known electromotive force.

In the case of most movable coil galvanometers, the scale deflexions are by no means proportional to the current, and hence when measuring a series of capacities it is desirable afterwards to plot a calibration curve of the galvanometer scale, from which the condenser currents can be read off directly in microamperes. This, however, is always easily accomplished. In addition, we have to measure the potential of the discharging battery. For most practical purposes this can be done by a Weston voltmeter.

Thus let V represent the voltage of the battery charging the condenser or aerial, C the capacity of the condenser in microfarads, A the current in microamperes through the galvanometer, n the number of charges per second, then

$$A = nCV$$

$$\text{or} \qquad C = A/nV.$$

In order to avoid the necessity for standardizing the galvanometer and measuring the voltage of the charging battery, we have devised a method employing a differential galvanometer which in principle is as follows:—The condenser discharges, as above described, pass through one coil of the differential galvanometer, the other coil being traversed by a current taken from the same battery, and therefore having the same voltage. This second coil is shunted by means of a shunt R and has in series with it a high resistance r. If then these resistances are arranged so that the galvanometer shows no deflexion, we have the following equation for the capacity:—

$$\frac{nVC}{10^6} = \frac{V}{r + \dfrac{GS}{G+S}}$$

$$C = \frac{(G+S)10^6}{nr(G+S) + nGS}.$$

This determines the capacity in terms of a conductance and the reciprocal of a time, thus reducing the number of dimensional quantities to be measured to the minimum.

In carrying out this method, it is perfectly impossible to use any ordinary differential galvanometer, because with an electromotive force of 100 volts or more between the coils the resulting unavoidable leakage entirely vitiates the result. We have therefore devised a differential movable coil galvanometer which has been made for us by Messrs. James Pitkin & Co., and is constructed as follows :—

In this galvanometer there are two sets of fixed field-magnets, and also two movable galvanometer-coils completely insulated from one another, but attached to the same stem, which also carries the mirror. Very fine spiral flexible wires convey the currents into and out of each coil. In order to make the galvanometer differential and therefore show no deflexion when the same current is passed in opposite directions through the coils, it is necessary to be able to adjust exactly the field-strength in the air-gap of the fixed magnets. This we accomplish by means of two curved pieces of soft iron P, which are moved by screws to or from the field-magnets N, S (Pl. XII. fig. 4) so as to shunt more or less of the lines of flux passing between the pole-pieces of the magnet. In this manner we find we can construct a movable coil differential galvanometer which shows no deflexion when the same or equal currents are passed in opposite directions through the two coils, yet each coil is perfectly insulated from the other.

Employing such a differential movable coil galvanometer in connexion with a commutator, we get rid of all necessity for measuring any voltage or electromotive force, and reduce the measurement of capacity simply to a determination of the speed of the commutator (which can be taken with great accuracy by means of a stop-watch) and the known value of the shunt and series resistances in connexion with one coil of the galvanometer. Moreover, we can always tell from the speed of the commutator exactly the time during which the condenser is in connexion with the galvanometer, and hence whether the time of contact is, as it should be, large compared with the time-constant of the discharge circuit.

We have employed one or other of these methods in making a number of measurements of the capacity of aerial wires, such as are used in connexion with Hertzian Wave Telegraphy, and also in the investigation of the laws governing the capacity of such wires when grouped together in certain ways, and we have employed the arrangements for verifying experimentally, as far as possible, the formulæ that have been given for the capacity of insulated wires in various positions in regard to the earth. Taking first the case of single vertical wires insulated in the air, measurements have been made of the capacity of wires suspended vertically in the open air, and also in the interior of a large Laboratory, the dimensions of which are 18 feet high, 32 feet wide, and 44 feet long.

Some preliminary experiments in the open air showed that the capacity of parallel wires suspended in the air, and insulated, is by no means equal to the sum of their separate capacities when in free space, even when the wires are not very near together. A series of experiments was therefore carried out in the Pender Laboratory with flat iron strips, to investigate this fact more carefully. Eleven lengths of iron strip one inch wide, the thickness being 0·05 inch, and 15 feet 4 inches long, were suspended vertically from the ceiling of the Laboratory by silk strings passing over porcelain buttons. To keep the strips straight they were fastened to the floor through pieces of ebonite. Connexion was made at the bottom end of each strip by a terminal to a straight bare copper wire connected to the above described commutator, so that the capacity of any one strip or of any number of strips in parallel could be measured. In the first place, the individual capacity of each strip taken alone and isolated, was measured and found to be nearly the same in each case. Hence in the tabulated results, the absolute values of capacity are not given, but the capacity of each of the above strips by itself in the room, and held vertically, is taken as unity. The voltage of the battery employed in charging the strips was about 148 volts, and the number of revolutions of the commutator 1200 per minute, corresponding to a frequency of 80. One terminal of the insulated battery used for charging was connected to the earth, and also one end of the galvanometer. The other ends of the galvanometer and battery were connected to the outside brushes on the commutator, the middle brush being connected to the insulated strip or strips. A series of capacity measurements was made, taking the strips one at a time, two at a time, three at a time, &c., and at various distances apart, viz.: 12, 6, and 3 inches, and also when close together. The results are tabulated in the following table (p. 500).

The last column in the Table gives the figures showing the sum of the individual capacities of the strips, and it will be seen that the total measured capacity of n strips taken together at a distance d inches apart is always very much less than the sum of the individual capacities of the n strips, that is, much less than n times the capacity of one strip, and the figures show that as the strips are brought nearer together this difference increases. When the strips are about 6 inches apart, that is to say, separated by a distance equal to about 3 per cent. of their length, the capacity of the strips in

Table I.—Measurement of the Capacity of Flat Iron Strips suspended in a large room, taken separately and together, at various distances apart.

Number of strips taken in parallel.	Measured Total Electrical Capacity with distance between strips as below stated.				Sum of the separate individual capacities.
	12-in.	6-in.	3-in.	Close together.	
1	1·00	1·00	1·00	1·00	1·0
2	1·74	1·45	1·34	1·19	2·0
3	2·31	1·80	1·61	1·27	3·0
4	2·79	2·10	1·85	1·44	4·0
5	3·28	2·42	2·03	1·46	5·0
6	3·75	2·70	2·21	1·54	6·0
7	4·18	2·98	2·36	1·59	7·0
8	4·61	3·25	2·52	1·72	8·0
9	5·03	3·51	2·68	1·81	9·0
10	5·46	3·76	2·82	1·96	10·0
11	5·90	4·00	2·97	1·99	11·0

parallel is very nearly proportional to the square root of the number of strips; thus, four strips have only twice the capacity of one strip, and nine strips rather more than three times the capacity of one strip. The same fact has been observed by us in the case of the measurements of the capacity of wires suspended in the open air. Taking for convenience as a unit of small capacity the micro-microfarad (M.M.Fd.), *i. e.*, the millionth part of one microfarad, we have made measurements of the capacity of nearly vertical insulated wires suspended in the air, with their lower ends a few feet from the ground, and have obtained the following results. In these measurements the capacity measured was that of the wire or body under investigation, together with that of a connecting wire, and that of the commutator itself. This latter quantity is about 60 micro-microfarads, and that of the commutator and lead used varied from 80 to 300 M.M.Fd., according to the length of lead. This value is subtracted from the observed total value. The capacity of a wire one-tenth of an inch in diameter and 111 feet long, with the bottom end about 5 feet from the ground, was found to be 205 micro-microfarads. In the next place, 160 wires of the same kind and diameter, but 100 feet long, were arranged in a conical form, so that the common junction of all the wires was about 10 feet from the ground, and the tops of all the wires were distributed around a square of 80 feet side, and at a height of about 112 feet from the ground, the wires being therefore about 2 feet apart at the top, and in nearly close contact at the bottom. Such an arrangement of insulated wires was found to have a capacity of 2685 micro-microfarads; in other words, about thirteen times that of one wire, so that in this case the square-root law also holds very closely. In the same way the capacity of four parallel vertical wires 111 feet long, and one-tenth of an inch in diameter, arranged vertically at the corners of a square of six feet in the side, was measured, and was found to be 583 micro-microfarads; in other words, about two and a half times the capacity of one single wire of the same kind in the same position. Similar measurements have shown that 25 wires 200 feet long, arranged with their bottom ends close together, and about ten feet above the ground, and their top ends about two feet apart, had a capacity not greater than five times that of one single wire of the same kind in the same position. Hence it is clear that in bunching together or placing in contiguity a number of vertical wires in the air so as to form a radiator for use in Hertzian Wave Wireless Telegraphy, account must be taken of this fact, and the assumption must not be made that the capacity of *n* parallel wires placed vertically in the air and insulated, even approaches a value equal to the sum of their individual capacities, unless the distance between the wires is a large percentage of their length.

This effect was further examined in another series of experiments made in the Laboratory. Two of the above-mentioned iron strips, suspended and insulated as before, were placed at different distances apart, and their united capacity measured and compared with the mean value of their separate capacities. Taking this mean value of the capacity of a single strip as unity throughout, the results are as follows:—

TABLE II.

Horizontal distance between strips in inches. Strips 174 inches long.	Horizontal distance between strips as a percentage of their length.	Capacity of the two strips together, that of one strip being unity.
90	49	1·81
57	31	1·85
30	14	1·70
17	9	1·57
13	7	1·60
4	2·1	1·34
$1\frac{3}{4}$	0·9	1·15

The discrepancies between parts of Tables I. and II. are to be accounted for by the adoption of a different arrangement of connecting wires in the two sets of experiments. The way in which allowance should be made for the capacity of the leads, when this is not very small compared with the capacity to be measured, is at present under investigation, and the above Table can only be taken, therefore, as showing that the capacity of two vertical and parallel wires is not twice that of one wire, unless they are at a distance apart of nearly one-third of their length *.

Similar experiments were made with two zinc cylinders, the diameter of each cylinder being 1½ inches, and the length of each cylinder 9 feet 1½ inches, the capacity of each cylinder taken alone in free space is taken as unity. If these two cylinders were suspended one foot apart in the centre of the large Laboratory above described, and hung vertically, their total capacity only amounted to 1·46 times that of either cylinder taken alone. A further experiment was made with these cylinders. One of them was cut longitudinally and rolled out into a flat strip, and suspended in the same position vertically, the capacity of the original cylinder being taken as unity. The capacity of the sheet when rolled out into a strip was found to be 10 per cent. greater than in its original form.

With the same appliances, a series of experiments was made in the Pender Laboratory on the measurement of the capacity of vertical wires of different diameters. Seven wires of different diameters were suspended vertically by means of silk strings from the ceiling of the Laboratory, and the capacity of each wire was measured separately, a correction being made for the capacity of the terminal, and of course also for the fine wire or lead connecting the wire under experiment with the commutator. The lengths of the wires were about 12 feet in all cases. The following Table shows the result of the measurements, the capacity of the wires being given in micro-microfarads (M.M.Fds.), the fourth column showing the capacity as calculated from the formula

$$\text{Capacity (in electrostatic units)} = \frac{1}{2\log_\epsilon l/r}$$

where l is the length of wire and r is the semi-diameter in centimetres.

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* It is clear that the capacity of the object measured, as it would be free in space, is not obtained exactly by deducting that of the leading wire alone from that of the leading wire and object when connected. The assumption that it is so is only a first approximation to the truth.

TABLE III.—Measurement of Capacity of Wires of various diameters suspended vertically in a large room.

Diameter of wire in inches.	Length of wire in feet.	Mean Value of Capacity in M.M.Fds. observed.	Calculated value by the formula above.	Difference in per cent. between the observed and calculated values.
·0047	11·44	18·79	17·62	6·6
·0075	12·23	21·36	19·59	9·0
·0127	12·29	22·56	20·73	8·8
·0182	12·21	23·76	21·38	11·1
·0278	12·04	24·24	22·06	9·9
·0485	12·33	26·51	23·97	10·6
·1381	12·02	32·36	27·00	19·8

The above formula has been deduced on the assumption that the form of a very long thin wire may be considered as a limiting case of a prolate ellipsoid of revolution. It can be shown that the electrical capacity (C) of an ellipsoid of semiaxes a, b, and c in infinite space is given by the expression * :

$$\frac{1}{\mathrm{C}} = \frac{1}{2}\int_0^\infty \frac{du}{\sqrt{(a^2+u)(b^2+u)(c^2+u)}}.$$

If we put $b=c$ in the above formula, it can be shown that

$$\mathrm{C} = \frac{2\sqrt{a^2-b^2}}{\log_\epsilon \dfrac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}}}.$$

Hence the above expression gives us the capacity of the ellipsoid of revolution.

If the ellipsoid is very elongated so that b is very small compared with a, then if e is the eccentricity of the principal elliptical section, e is nearly equal to unity, and $1+e$ is nearly equal to 2.

Hence $\quad (1+e)(1-e)=2(1-e)$ nearly

and $\quad a(1-e^2)=2a(1-e)$ nearly.

Accordingly, since $\sqrt{a^2-b^2}=ae$, we can say that

$$a-\sqrt{a^2-b^2}=b^2/2a \text{ nearly,}$$

and

$$\log_\epsilon \frac{a+\sqrt{a^2-b^2}}{a-\sqrt{a^2-b^2}} = 2\log_\epsilon 2a/b.$$

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* See Article *Electricity* by Prof. Chrystal. 9th Edition of the *Encyclopædia Britannica*, vol. viii. p. 30.

Therefore the capacity of a very elongated ellipsoid of revolution of which a is the major and b the minor semiaxis is given by

$$C = \frac{2a}{2 \log_\epsilon 2a/b}.$$

If therefore we can consider a thin circular-sectioned wire of diameter d and length l as an ellipsoid, we have its capacity in electrostatic units given by the formula

$$C \text{ (in E.S. units)} = \frac{l}{2 \log_\epsilon 2l/d},$$

where l and d are of course measured in centimetres. To reduce a capacity expressed in electrostatic units to microfarads we have to divide by 9×10^5, and therefore to convert capacity expressed in electrostatic units to the same expressed in micro-microfarads, we have to multiply by $1\frac{1}{9}$ or to increase by about 11 per cent.

Hence expressed in micro-microfarads the above capacity is :—

$$C \text{ (in M.M.Fds.)} = \frac{l \times 10^6}{2 \times 2{\cdot}303 \times 9 \times 10^5 \times \log_{10} 2l/d}$$

$$= \frac{l}{4{\cdot}1454 \log_{10} 2l/d}.$$

An approximate formula for the capacity of a telegraph-wire is also easily found. If an infinitely long filamentary wire is uniformly charged with electricity so that it has q electrostatic units of charge per centimetre of length, then from the analogy with the case of an infinitely long straight current, it is easy to show that the force due to the filament at any point distant r centimetres from it. is $2q/r$. Hence if the potential at this point is V we have

$$-\frac{dV}{dr} = \frac{2q}{r}$$

or

$$V = -2q \log r + Ct,$$

where Ct is the constant of integration.

If we have two very long straight circular-sectioned wires suspended in air parallel to one another, at a distance D, the diameter of each wire being $2r$, and r/D being a small quantity, then it is easy to calculate the capacity of the condenser formed of these wires, if we assume them to be so far apart that the electrical charge on each remains uniformly distributed round the surface of each wire. Let one wire be called A, and let it be positively charged, and the other be B, and negatively charged. Let V_A and V_B be the potentials of these wires, and let the charge on each be q electrostatic units per centimetre of length, then their capacity per unit of length (c) is equal to $q/(V_A - V_B)$.

Now from the expression for the potential of the electrified filament we see that

$$V_A = \quad (-2q \log r + Ct) - (-2q \log D + Ct),$$

$$V_B = -(-2q \log r + Ct) + (-2q \log D + Ct),$$

$$V_A - V_B = 4q(\log D - \log r) = 4q \log D/r.$$

The capacity per unit of length is therefore given by

$$c = \frac{1}{4 \log D/r} \text{ (in electrostatic units).}$$

If we employ ordinary logarithms and express the capacity per unit of length in micro-microfarads (c') this becomes

$$c' = \frac{10^6}{4 \times 2{\cdot}303 \times 9 \times 10^5 \log_{10} D/r}$$

$$= \frac{0{\cdot}1208}{\log_{10} 2D/d},$$

where d is the diameter of either wire, and D their distance from centre to centre. The formula for the capacity per unit of length of the single telegraph-wire of diameter d supported at a height h above the earth, is easily deduced from the above. For since the ground-surface must be a zero-potential surface, the capacity c in electrostatic units of the single wire per unit of length under these conditions must be

$$c = \frac{2}{4 \log_\epsilon 2D/d} = \frac{1}{2 \log_\epsilon 4h/d},$$

and the capacity c' per unit of length in micro-microfarads will be

$$c' = \frac{10^6}{2 \times 2{\cdot}303 \times 9 \times 10^5 \log_{10} 4h/d}$$

$$= \frac{0{\cdot}2415}{\log_{10} 4h/d} \text{ (in M.M.Fds.).}$$

Accordingly the capacity C of a telegraph wire l centimetres long and d centimetres in diameter, and at a height h centimetres above earth, is given in micro-microfarads by the formula

$$C = \frac{0{\cdot}2415 l}{\log_{10} 4h/d} \text{(M.M.Fds.)}$$

or very nearly by

$$C = \frac{l}{4 \log_{10} 4h/d} \text{(M.M.Fds.)}.$$

To test this last formula, an experiment was made in the open air with a long wire held parallel to the earth's surface, on insulators at a height of about six feet above the ground. The length of this wire was 500 feet or 15,240 cms. The height of the wire above the ground was 6 feet or 183 cms., and the diameter of the wire was ·0645 inch, or 0·164 cm. The observed value of the capacity of this wire *in situ* was 1081 micro-microfarads. The value of the capacity calculated from the formula

$$C \text{ (in M.M.Fds.)} = \frac{0{\cdot}2415 l}{\log_{10} 4h/d}$$

is nearly 1000 micro-microfarads, the difference between this calculated and the observed value being about 8 per cent.

In the same manner the capacity of a vertical wire was measured in the open air, and compared with the theoretical value as given by calculation. In this case the length of the wire was 111 feet, or 3385 cms., and the diameter of the wire was 0·085 inch, or 0·215 cm. The observed value of this wire when suspended vertically in the air with the bottom end about six feet from the ground, is 205 micro-microfarads. The value calculated by the formula

$$C \text{ (in M.M.Fds.)} = \frac{l}{4{\cdot}1454 \log_{10} 2l/d}$$

is 181 micro-microfarads. The observed value is again greater than the calculated value by about 10 per cent.

It will thus be seen that in all these cases the observed value of the capacity of the wire, whether vertical or horizontal, appears to come out, roughly speaking, about 10 per cent. greater than the calculated value. Approximately, the same difference was found in the case of the capacity of a zinc disk suspended in the Pender Laboratory. The disk was made of sheet zinc circular in form, and 60 inches in diameter. The calculated capacity of this disk in free space is 48·1 electrostatic units, or 53·44 micro-microfarads*.

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* The capacity of a thin circular disk when insulated in infinite space is numerically equal to d/π in electrostatic units, where d is the diameter of the disk in centimetres.

The measured capacity in micro-microfarads was found to be 59·95, the difference being about 12 per cent. In all these cases, except that of the horizontal wire, the differences between the observed and the calculated values appear to depend upon the proximity of neighbouring objects or the ground, and upon the way in which connexion is made to the commutatator. The capacity of a body together with that of the connecting wire is not, strictly speaking, the sum of the separate capacities of the body and the wire measured *in situ.* In an experiment with one of the iron strips, an apparent decrease of 5 per cent. in the capacity was found when the connexion was changed from the bottom to near the middle. The mathematical formula gives us the value of the capacity of the body in infinite space, but its measured capacity is in practice its capacity relatively to earth and depends on two things :—the proximity of neighbouring earth-connected bodies, and the manner of attachment to the measuring device. The first always increases the capacity above the calculated value, while the second decreases it. It appears that the net result in the case of the capacity of a disk of about five feet in diameter, when insulated and hung up in the middle of a room 40 feet long, 18 feet high, and 30 feet wide, with the connexion taken away from the bottom edge, is numerically in excess of its calculated or theoretical capacity in free space by about 10 or 12 per cent.

Another interesting experiment was tried on the relative capacity of two lengths of No. 30 copper wire, each 12 feet long. One of them was preserved straight and suspended vertically in the Laboratory as above described ; the other was bent into a spiral about 2 inches in diameter, and 6 feet in length over all, and then again into a closer spiral $\frac{3}{4}$ inch in diameter, and 18 inches in length over all. Taking the capacity of the straight wire as unity, the capacity of the long coil of large diameter was 0·8, and the capacity of the short coil of small diameter was 0·32, showing how much the capacity of a wire of given length is decreased by coiling it into a spiral.

One of the uses to which the above-described commutator can be put is that of determining the capacity of leyden-jars in absolute measure ; at any rate, the capacity corresponding to frequencies in the neighbourhood of 100. Instrument-makers still retain the absurd custom of speaking of leyden-jars as pint, quart, and gallon sizes, instead of marking on them their capacity in absolute measure. Now that leyden-jars are so much used in wireless telegraphy, the necessity often arises for knowing their approximate absolute capacity, and it is much to be desired that instrument-makers should forsake the custom of denominating their different leyden-jars in the present manner.

Incidentally, the apparatus may be used for more or less accurate determinations of the electromagnetic constant "v". One method by which a small capacity of known value can be made with a fair amount of accuracy is as follows:—Two cylindrical air condensers are constructed, each of which consists of a cylindrical rod or thick-walled tube placed in the interior of another concentric tube. Two condensers of this kind are prepared, one about double the length of the other; one may be, say, a foot long, and the other two feet long. The tubes may be of the quality known as "triblet-drawn" brass tube, one exceeding the other in diameter by about 2 millimetres. These tubes may then be cut up into the requisite lengths. The ellipticity and variation of diameter in length of such tubes are very small indeed.

These pairs of tubes can then be formed into two air condensers by fixing the inner tube concentrically within the outer tube by means of ebonite disks at the end. By the adoption of known mechanical methods, the concentric adjustment of the tubes can be made very accurately, and the radial thickness of the air space determined. In this manner two cylindrical air condensers can be constructed identical in every way, except that they differ in length.

If c is the capacity per unit of length of the middle part of the condenser, where the strain-lines are truly radial, and if L is the length of the condenser, then the capacity C of the condenser is expressed by a function of the form $C=x+cL$, where x is an unknown quantity depending on the distribution of the electric strain at the ends of the tubes. Hence if we measure the capacity of the above two condensers by means of the rotating commutator, and take the difference of these capacities, this is the value of the capacity of a length equal to the difference of the lengths of the condensers, and therefore the capacity per unit of length of one of these condensers is known, disregarding the uncertain distribution of the strain-lines at the ends. If the device of employing a guard-ring or guard-tube is adopted, then the capacity of the inner portion of such a cylindrical guard-tube condenser cannot be determined simply by charging and discharging that inner portion through a galvanometer, without at the same time charging and discharging the guard-tubes through a by-path, or else redistributions of electricity take place at each discharge, which vitiate the result. This source of error was pointed out and guarded against by Prof. J. J. Thomson (1883) and by Prof. J. J. Thomson and Mr. Searle (1890) in making this class of measurement.

Measurement of Inductance.—If two such commutators as we have described were mounted on the same spindle, with the eight radial teeth of each centre wheel (I in fig. 1) insulated from each other, and a second central brush added in the correct relative position to the first, we should obtain an instrument similar in principle to the secohmmeter of Professors Ayrton and Perry; but we have thought it worth while, in order to get a simpler apparatus, to sacrifice reversibility and construct simply a double contact-breaker on the same lines. By making the apparatus substantial and eliminating all insulating material, except air, from the rotating drums, and abolishing all flimsy spring-contacts, we have constructed an instrument which is much more satisfactory to work with than the secohmmeter as made by the ordinary instrument-maker (Pl. XII. fig. 5). This double contact-breaker consists of a steel shaft which carries on it two circuit-interruptors constructed in the following manner:—Each of these consists of two wheels, like crown wheels, having four teeth, and these two wheels are set on insulating bushes with the teeth of one wheel interspaced between those of the other. The shaft carries two such barrels (see fig. 5), and the developed surface of these barrels is shown in fig. 6. The barrels are formed of gun-metal, and against each barrel press two brass gauze brushes carried on insulated brush-holders. One brush bears on the continuous flange of one part of each barrel, and the other brush alternately makes and breaks contact with it by bearing on that part of the barrel occupied by the interlocked teeth. The two barrels can be set relatively to one another in any position on the shaft. These two barrels serve the purpose of making and breaking two separate electric circuits in such fashion that at the moment when one circuit is being broken, the other is complete, and at the moment when the first circuit is being completed, the other is broken. The arrangement is direct-driven through a flexible coupling by a one-sixth H.P. direct-current shunt motor.

In the measurement of inductance this double interruptor is employed like the secohmmeter of Professors Ayrton and Perry. The coil of which the inductance is to be determined is balanced on a Wheatstone-bridge, and the two interruptors of the rotating appliance are inserted respectively in the battery and galvanometer circuits, so that if the apparatus is set rotating after the steady balance of the non-inductive resistance on the bridge has been obtained, it will eliminate every alternate inductive electromotive force due to the inductance of the coil, and cause the galvanometer to give a steady deflexion. To evaluate this inductance in absolute measure, we prefer the method described by Professor A. Anderson*. In this method a variable resistance r is placed in the bridge circuit in series with the galvanometer connected to a Wheatstone-bridge, and a condenser of known capacity C is joined in, as shown in the diagram (see fig. 7), and the double interruptor inserted in the battery and galvanometer circuits. When the steady or ohmic resistance of the inductive coil has been determined in the usual manner, the interruptor is set in rotation, and the value of the resistance r in series with the galvanometer is altered until the galvanometer deflexion vanishes. This last change does not upset the adjustment of the arms of the bridge already made in obtaining the ohmic resistance of the coil. If P, Q, S are the arms of the bridge, and R is the ohmic resistance of the coil under test. of which the inductance is L. then the ohmic resistance R and inductance L of the coil are given by the equation

$$R = PS/Q,$$

$$L = C\{r(R+S) + RQ\}\dagger.$$

Fig. 7 shows the galvanometer and battery connected to a change-over switch $m\,m$ in order that they may be placed relatively to the four arms of the bridge in the position giving the most sensitive arrangement for the resistances employed. We understand that Prof. Stroud has employed one of these arrangements for some time past in the measurement of inductance, but no publication of it appears to have been made prior to that by Prof. Anderson.

This method of measuring inductance by a combination of the double interruptor, with the Anderson method, is one of the most perfectly satisfactory methods that can be employed in the laboratory. It is an absolute method in that it requires no arbitrary standard of inductance, and yet, at the same time, it requires no determination of a speed ; it only assumes the possession of resistance-boxes and a known capacity.

The value of small inductances, such as are best reckoned in millihenrys, can be obtained most accurately by measuring them as the difference of two larger inductances. Thus, for

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* See Phil. Mag. vol. xxxi. p. 329 (1891) ; or 'The Electrician,' vol. xxvii. p. 10.

† For the proof of this formula for the inductance, we refer to the original paper by Professor A. Anderson (*loc. cit.*).

instance, if a coil is given of small inductance, its ohmic resistance is first measured. It is then joined in series with the coil of considerably larger inductance, and the inductance of the two coils together measured as above described. The larger inductance is then determined separately, and the small inductance becomes known by the difference. In this manner it is possible to determine with very fair accuracy the inductance of quite small coils of wire.

In conclusion we have pleasure in mentioning the assistance rendered to us in portions of this work by Dr. G. A. Hemsalech, who devoted a considerable amount of time to the experimental work at one stage of the investigation.

LII. *Note on the Special Epochs in Vibrating Systems.* By JAMES W. PECK, *M.A., Lecturer in Physics in the University of Glasgow**.

IN a vibrating system there are two special states which may occur, viz.:—(1) The system may be at rest in all its parts at the same instant; (2) The system may be in its undisturbed configuration at the same instant in all its parts. If these states occur at all, they will recur periodically. In what follows the conditions under which such special states will occur are found.

Call the time at which the system comes to rest simultaneously in all its parts the *rest epoch*; and the time at which the system is passing through its undisturbed position in all its parts the *undisturbed epoch*, both to be reckoned from the initial time at which the system starts off with arbitrarily given displacements and velocities. It will be shown that in the general case when both the initial displacements and velocities are completely arbitrary (consistent with the conditions of the system) the two special epochs will not occur; but that by relating the system of initial displacements to the system of initial velocities in a certain way the rest epochs may be made to occur; by relating them in another way the undisturbed epochs may be made to occur; and that the condition which makes the one set of epochs possible makes the other impossible, and *vice versa*.

Take any continuous elastic system finite in one dimension (length l) and fixed at both ends. The general equation of its one-dimensional vibrations is

$$\frac{\partial^2 y}{\partial t^2} = V^2 \frac{\partial^2 y}{\partial x^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where y is the displacement coordinate at the time t of the

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* Communicated by Prof. A. Gray.

point whose undisturbed distance from a fixed end is x. V is the velocity of the elastic wave in the system. If the arbitrary set of initial displacements be given by $f(x)$, and of initial velocities by $\phi(x)$, the value of y at time t is

$$\sum_1^\infty \sin\frac{m\pi x}{l}\left[\mathrm{A}_m \cos\frac{m\pi \mathrm{V}t}{l}+\frac{l}{m\pi\mathrm{V}}\mathrm{B}_m \sin\frac{m\pi\mathrm{V}t}{l}\right]; \quad . \quad (2)$$

or more conveniently in terms of the fundamental period T,

$$\sum_1^\infty \sin\frac{m\pi x}{l}\left[\mathrm{A}_m \cos\frac{2m\pi t}{\mathrm{T}}+\frac{\mathrm{T}}{2m\pi}\mathrm{B}_m \sin\frac{2m\pi t}{\mathrm{T}}\right], \quad . \quad (3)$$

where

$$\mathrm{A}_m=\frac{2}{l}\int_0^l f(x)\sin\frac{m\pi x}{l}dx,$$

$$\mathrm{B}_m=\frac{2}{l}\int_0^l \phi(x)\sin\frac{m\pi x}{l}dx.$$

The following deductions from these well-known results are, of course, applicable to a variety of special cases, *e. g.* transverse vibrations in thin strings, longitudinal vibrations in wires, rods, &c., torsional vibrations in rods.

It will be convenient to begin with two special cases:—

I. Suppose the system to start from rest so that $\phi(x)=0$ for all values of x between 0 and l. The rest epochs are given by

$$\sin\frac{2m\pi t}{\mathrm{T}}=0,$$

or

$$t=\frac{k\mathrm{T}}{2m}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where k is any integer. This gives these epochs for any harmonic constituent m; and it is obvious that even in the most general case both the sets of epochs occur always for any harmonic constituent considered separately. But the question is, whether among these epochs for any and every constituent m are to be found those of the fundamental mode. Only when this overlapping happens for every harmonic mode, will the general rest epochs or undisturbed epochs occur. In the present case it is seen from equation (4) above, that k can always be chosen so as to be a multiple of m, whatever constituent is being dealt with, and therefore among the rest epochs of any mode there will always be found those of the fundamental. Hence in this case the general rest epochs occur, and obviously at times T/2, T, 3T/2, &c.

But the general undisturbed epochs will in this case not always occur. The condition is

$$\cos\frac{2m\pi t}{\mathrm{T}}=0,$$

or

$$t=\frac{(2k+1)\mathrm{T}}{4m}, \quad \ldots\ldots\ldots \quad (5)$$

giving the series of times for any harmonic m. But here the cancelling of $2k+1$ by m can only occur when m is an odd number. Hence among the undisturbed epochs of any odd harmonic are always found those of the fundamental; but this coincidence will not occur for the even harmonics. Hence for a system starting from rest, the general undisturbed epochs will only occur if the initial displacements be such that the even harmonics are absent.

II. Suppose the system to start from its undisturbed configuration, i. e. $f(x)=0$ for all values of x between 0 and l. This gives exactly the reverse of the previous case. The rest epochs do not in general occur; but will, if the initial set of velocities be such that the even harmonics are absent; while the undisturbed epochs will always occur. This may be shown by taking the special form of equation (3) for this case and treating it as above.

III. The general case in which both the displacements and velocities are given arbitrarily. Taking equation (3) above, the condition that the rest epoch should occur is

$$\cot\frac{2m\pi t}{\mathrm{T}}=\frac{\mathrm{A}_m}{\mathrm{B}_m}\,\frac{2m\pi}{\mathrm{T}}. \quad \ldots\ldots\ldots \quad (6)$$

Observing that A_m is a distance (or angle) and B_m a velocity (linear or angular), denote $2\pi\mathrm{A}_m/\mathrm{B}_m$ by the time τ_m. Then equation (6) may be written

$$\frac{t}{\mathrm{T}}=\frac{\operatorname{arc}\cot\,(\tau_m/\mathrm{T}_m)+k\pi}{2\pi m}. \quad \ldots\ldots \quad (7)$$

where T_m is the period for the mode m, and k is any integer. This gives the times of recurrence of the rest epochs for any harmonic m; but it is clear that in general the times of the epochs for the fundamental will not be found among those of the constituent harmonics: for τ_m and T_m are quite independent, the first depending upon the initial conditions of displacement and velocity, the other only upon the elasticity (or its equivalent), the inertia, and the extent of the system.

If, however, the initial displacement conditions be related to the initial velocity conditions so that

$$\operatorname{arc\,cot}\frac{\tau_m}{\mathrm{T}_m}=m\operatorname{arc\,cot}\frac{\tau_1}{\mathrm{T}_1}\quad . \quad . \quad . \quad . \quad (8)$$

for every harmonic, then (since the m disappears in equation (7)) the general rest epoch will occur; for evidently among the rest epochs of each harmonic are found all those of the fundamental. The first general rest epoch will occur at time

$$\frac{\operatorname{arc\,cot}(\tau_1/\mathrm{T}_1)}{2\pi}\times\mathrm{T}_1,\quad . \quad . \quad . \quad . \quad . \quad (9)$$

and the subsequent ones at times increasing from this by multiples of T/2.

In the set of conditions

$$\operatorname{arc\,cot}\frac{\tau_1}{\mathrm{T}_1}=\tfrac{1}{2}\operatorname{arc\,cot}\frac{\tau_2}{\mathrm{T}_2}=\tfrac{1}{3}\operatorname{arc\,cot}\frac{\tau_3}{\mathrm{T}_3}=\ldots\quad . \quad (10)$$

it is to be noted that arc cot $\frac{\tau_m}{\mathrm{T}_m}$ is not to be taken as the smallest angle with the given cotangent. Suppose τ_1 is given, then arc cot $\frac{\tau_1}{\mathrm{T}_1}$ is to be chosen as follows:—If A_1 and B_1 are each positive, first quadrant; if each negative, third quadrant; if A_1 positive and B_1 negative, fourth quadrant; if A_1 negative and B_1 positive, second quadrant. If A_m and B_m are such that arc cot $\frac{\tau_m}{\mathrm{T}_m}$ (formed in accordance with the above rule) is m times arc cot $\frac{\tau_1}{\mathrm{T}_1}$ (formed in accordance with the above rule) for every m, then the necessary condition for the rest epochs is satisfied.

For the undisturbed epochs to occur we must have

$$\tan\frac{2m\pi t}{\mathrm{T}}=-\frac{\mathrm{A}_m}{\mathrm{B}_m}\frac{2m\pi}{\mathrm{T}}=-\frac{\tau_m}{\mathrm{T}_m},$$

or

$$\frac{t}{\mathrm{T}}=\frac{\operatorname{arc\,tan}\left(-\frac{\tau_m}{\mathrm{T}_m}\right)+k\pi}{2\pi m}\quad . \quad . \quad . \quad . \quad (11)$$

Hence, as before, these epochs will not occur in general, but will at times be given by

$$t=\frac{\operatorname{arc\,tan}\left(-\frac{\tau_1}{\mathrm{T}_1}\right)+k\pi}{2\pi}\,.\,\mathrm{T}_1,\quad . \quad . \quad . \quad (12)$$

provided

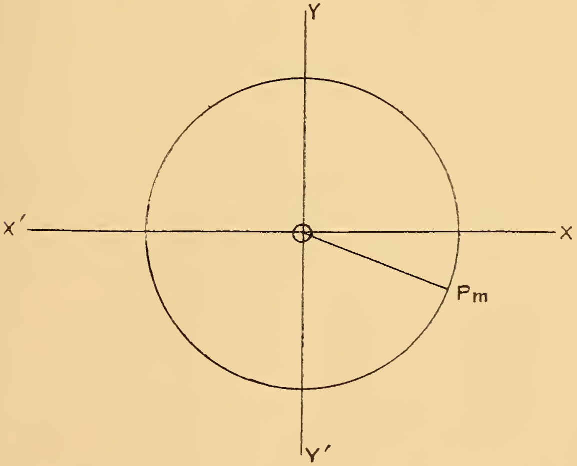
$$\arc\tan\frac{\tau_1}{\mathrm{T}_1}=\tfrac{1}{2}\arc\tan\frac{\tau_2}{\mathrm{T}_2}=\tfrac{1}{3}\arc\tan\frac{\tau_3}{\mathrm{T}_3}=\ldots \quad (13)$$

the angles being taken as before.

The times for the undisturbed epochs of a given harmonic are obviously in quadrature with those for the rest epochs; but the set of conditions (10) which make the general rest epochs possible are incompatible with those which make the general undisturbed epochs possible, and *vice versa*. The conditions (10) and (13) evidently agree with those of the special cases I. and II. above. In I. all the angles of the condition (10) become zero, and of the condition (13) 90° or multiples thereof. The reverse holds in II., and the necessity for the absence of the even harmonics in the cases remarked upon is shown by (10) and (13).

These results are all very clearly illustrated by the usual graphical representation for simple harmonic motion.

Take a line XX′ to represent the rest position, YY′ the undisturbed position. Represent each harmonic by a vector from O rotating in the positive direction with a uniform angular velocity m times that of the fundamental. The general motion will then be represented by the group of vectors (which are infinite in number though in any actual system only the earlier ones in the harmonic series will be appreciable) rotating simultaneously and starting all at once from positions scattered round the circle. These initial positions will be determined by the initial conditions. A general



rest epoch will be indicated by all the vectors being found simultaneously along XX′; and a general undisturbed epoch by their being found along YY′. If OP_m be the position, at the beginning of the motion, of the vector corresponding to the harmonic m, the angle XOP_m is arc cot (τ_m/T_m).

Take, for example, the conditions (10). These indicate that in the diagram the points P_1, P_2, P_3, &c., must have angles (reckoned backwards from OX) which are in the ratio of the natural numbers. Then if all the vectors start off at once with velocities proportional to their places in the harmonic series, all will arrive at OX simultaneously, and half a period (fundamental) later, all the odd ones will lie along OX′ and all the even ones along OX; *i. e.* two rest epochs (of different configuration) have occurred. But all the vectors (starting off in this way) will never be found all in the line YY′ unless in the special case in which the even harmonics are absent.

It is clear that there are three types of possible configuration at the rest epochs, and three types of velocity distribution at the undisturbed epochs. This can be seen most easily from the graphical representation. At a rest epoch, for example, all the vectors may lie along OX, or they may all lie along OX′, or they may lie some along OX and the others along OX′. The first case occurs if condition (10) is satisfied and the configuration recurs at intervals of the fundamental period. The third case also occurs if (10) is satisfied and all the rest configurations of this type are arrived at half a period (fundamental) later than those of the previous type. All the vectors corresponding to the odd harmonics lie along OX′, all those to the even ones along OX. The second case will only occur as a result of (10) if the even harmonics are absent.

Similar results may be arrived at for the times and natures of the undisturbed configurations. If condition (13) is satisfied, the undisturbed epochs occur, and this is indicated by all the vectors being found simultaneously along YY′. The velocity distribution of the system when these epochs occur is of three types, corresponding to all vectors along OY, all along OY′, some in OY and others in OY′. It is also seen from the graphical method that in general conditions (10) and (13) are incompatible. But that if the even harmonics are absent, either condition gives both rest and undisturbed epochs.

Similar results to all these may be worked out for a vibrating system free at both ends instead of fixed, as in this case.

LIII. *On the Thickness of the Liquid Film formed by Condensation at the Surface of a Solid.* *By* Dr. G. J. Parks[*].

It was known more than half a century ago[†] that when a solid is placed in a gas or vapour there is a condensation of the latter on the surface of the solid, and in particular that glass has the power of condensing water-vapour at temperatures above the dew-point.

Arago[‡] proposed to measure the amount of condensation by the optical method of interference, and quite recently Lord Kelvin[§] has suggested a method depending upon electrical conductivity.

In almost every department of physical research glass bulbs or tubes are used, and the presence of moisture on the surface of the glass is a continual source of trouble. Prof. J. Trowbridge[‖] has lately called attention to this matter in connexion with spectrum analysis.

There can be little doubt also that many of the standard results for the specific heats of finely divided or porous solids are incorrect, for if a solid is perfectly dry, heat will be evolved on wetting it[¶] when it is placed in the calorimeter, and if it is not dry then the specific heat obtained is not the true specific heat of the solid; in either case the specific heat obtained will be too high. Thus, from the most recent determination of the specific heat of pure precipitated silica, well dried and sealed in a bulb, the value appears to be ·1808[**], but the values previously obtained for amorphous silica are much higher than this.

The present brief inquiry, which is not intended to be by any means exhaustive of the subject, arose out of another investigation, not yet completed, in which the author has attempted to determine by direct experiment the surface-pressure of water and other liquids in contact with glass.

It was found that everything depended on keeping the surface of the glass perfectly free from moisture until the moment of the experiment; and the author was thus led to consider the quantity of moisture concerned in surface-pressure, in the Pouillet effect, and in surface-action generally.

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[*] Communicated by the Physical Society: read February 27, 1903.

[†] Jamin et Bertrand, Phil. Mag. [4] vi. p. 157 (1853); *Comptes Rendus*, June 1853, p. 994.

[‡] See Phil. Mag. [4] vi. p. 157 (1853).

[§] Lord Kelvin, Phil. Mag. [6] iv. p. 181 (1902).

[‖] Trowbridge, Phil. Mag. [6] iv. p. 156 (1902).

[¶] Parks, Phil. Mag. [6] iv. pp. 240, 251 (1902).

[**] Bellati e Finazzi, *Atti del R. Istituto Veneto*, Tomo lxi. Parte Seconda, p. 507 (1902).

In the first experiment some cotton silicate, similar to that used in the author's previous investigation *, was packed tightly into a test-tube and the mouth of the tube was drawn out to a fine neck, but not sealed.

The weight of the silicate was 3·37 grammes, the average diameter of the cylindrical filaments was ·00175 cm., the sp. gr. was 2·7, and the estimated area of surface was 847 sq. cm. per gm.

Hence the superficial area of the silicate was 3·37 × 847 = 2854 sq. cm., and allowing for the area of surface of the test-tube, the whole area of glass surface amounted to about 2900 sq. cm.

The tube was placed in an open beaker, and this was covered with a large inverted beaker standing over some water in a shallow tray and kept in a closed glass cupboard at nearly constant temperature.

The vapour which filled the chamber slowly diffused into the test-tube through the narrow aperture, and became condensed on the surface of the glass. The experiment continued for 16 days, the tube being weighed at intervals. The outside of the tube was wiped with a clean cloth before each weighing, so that the observed increase of weight was entirely due to condensation by surface-action. The temperature never varied much from 15° C. The following table shows the results of the various weighings and the estimated thickness of the film of moisture. The initial weight of the tube and silicate when dry was 9·3402 grammes.

Time.	Weight of tube and silicate.	Increase of Weight.	Estimated thickness of film (cm.).
12 hours	9·3602	·0200	$6{\cdot}9\times10^{-6}$
1 day	9·3644	·0242	$8{\cdot}3\times10^{-6}$
2 days	9·3672	·0270	$9{\cdot}3\times10^{-6}$
4 ,, ...	9·3710	·0308	$10{\cdot}6\times10^{-6}$
10 ,, ...	9·3774	·0372	$12{\cdot}8\times10^{-6}$
15 ,, ...	9·3790	·0388	$13{\cdot}4\times10^{-6}$
16 ,, ...	9·3790	·0388	$13{\cdot}4\times10^{-6}$

In another experiment the silicate was placed loosely in the tube and the mouth of the tube was allowed to remain at its ordinary width, about 1·5 cm. The experiment was made much more quickly than the first one, but the final result was the same.

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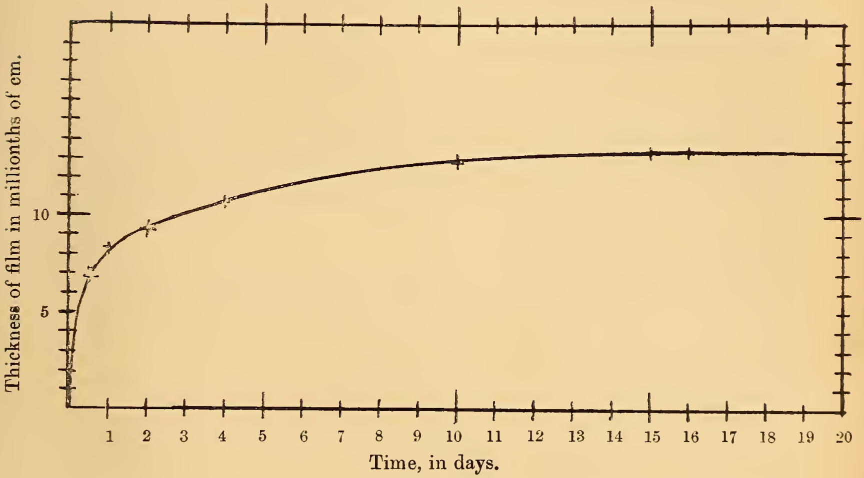
* Phil. Mag. [6] iv. p. 246 (1902).

Temperature during experiment about 12° C.
Weight of silicate 1·10 gm.
Total area of surface of silicate and tube about 1000 sq. cm.
Initial weight of tube and silicate 7·9517 gm.
Weight after 4 days 7·9650 gm.
" 6 " 7·9650 "
Increase of weight ·0133 "
Estimated thickness of film $13{\cdot}3 \times 10^{-6}$ cm.

Fig. 1.



The cotton silicate thus covered with a film of moisture showed no alteration in appearance even when examined under the highest power of the microscope, but when the silicate was placed in water no heat was evolved, though when the same substance was thoroughly dried and placed in water the heat evolved amounted to ·0011 calorie per sq. cm. Hence it may be inferred that the Pouillet effect for water in contact with glass at 12° C. is confined to a film of moisture the thickness of which is about $13{\cdot}3 \times 10^{-6}$ cm.

It will be interesting to compare with this result the results obtained by other experimenters with different substances and under widely different conditions. The earliest measurement of surface condensation of which the author has been able to find an account, is that of Magnus [*]. who, from experiments on the expansion of sulphurous acid gas, found that the amount of gas condensed on the surface of smooth glass

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[*] Magnus, Phil. Mag. [4] vi. p. 336 (1853).

rods was ·0008 cub. mm. per. sq. mm., that is 80×10^{-6} cub. cm. per sq. cm. of surface.

It is not improbable that in these experiments the sulphur dioxide was condensed by chemical combination with a film of water previously existing on the surface of the glass, but it may be noticed that the result obtained is of the same order of magnitude as all the other results quoted in this paper.

Martini * found that some precipitated silica exposed to aqueous vapour increased in weight by 80 per cent. without any alteration in appearance; on putting this moist silica into water no heat was evolved, though the heat evolved on wetting the dry silica amounted to 19 calories per gramme. Martini does not state the area of surface exposed by the powder, but the author has shown † that when dry silica is wetted, the amount of heat evolved is about ·00105 calorie per sq. cm.; and hence we may take the area of surface of the powder used by Martini as about 18,000 sq. cm. per gm., and the extreme thickness of the aqueous film would therefore be $\frac{\cdot 8}{18000} = 44 \times 10^{-6}$ cm.

It should be remarked here that when a powder is exposed for a long time in an open tray it is likely to receive some moisture by the ordinary process of condensation at temperatures below the dew-point, and thus the more exposed portions of the powder may receive excess of moisture.

Bellati and Finazzi ‡ have recently made an excellent series of experiments showing the relation between the amount of moisture absorbed by silica and the heat evolved on putting the powder into water. The area of surface exposed by the silica is not stated, but the authors consider with good reason that if the powder were perfectly dry the heat evolved on wetting it would amount to 26 calories per gm., and hence we may assume the surface exposed by the powder to amount to about 25,000 sq. cm. per. gm.

In the following table the figures of the first two columns have been selected from the original paper referred to, and the other three columns have been introduced by the author for the purposes of the present inquiry. An example will be sufficient to explain the table and the diagram (p. 522). When the dry silica has absorbed, say, 2·38 per cent. of moisture it

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* Martini, *Atti del R. Istituto Veneto*, Tomo lix. Parte Seconda, p. 624 (1900).

† Phil. Mag. [6] iv. p. 247 (1902).

‡ Bellati e Finazzi, *Atti del R. Istituto Veneto*, Tomo lxi. Parte Seconda, p. 514 (1902).

is put into water and the heat evolved is found to be 18·29 calories per gm.

But if the silica had been perfectly dry the heat evolved would have been 26 calories, hence the heat due to 2·38 per cent. of moisture must have been $26-18{\cdot}29=7{\cdot}71$ calories per gm.

The thickness of the film of moisture is about

$$\frac{{\cdot}0238}{25000}={\cdot}95\times10^{-6},$$

and the corresponding amount of heat per sq. cm. is

$$\frac{7{\cdot}71}{25000}=3{\cdot}08\times10^{-4}\text{ calories.}$$

The results show that when the water film is only one millionth of a centimetre in thickness, the heat evolved is about one third of the whole amount, when the thickness of film is two millionths the heat evolved is about one half of the whole, and on further increasing the thickness of the film the amount of heat evolved slowly approaches a maximum which it reaches when the thickness is about $31{\cdot}6\times10^{-6}$, the heat evolved being then ·00105 cal. per sq. cm.

Parts of moisture absorbed by 100 parts of dry silica. (a)	Heat evolved per gramme of silica. (q)	Reduction of the heat evolved by previous absorption of moisture. $(26-q)$	Thickness of water film $\frac{\frac{1}{100}\cdot a}{25000}$.	Heat evolved per sq. cm. by a film of this thickness $\frac{26-q}{25000}$.
2·38	18·29	7·71	$\cdot95\times10^{-6}$	$3\cdot08\times10^{-4}$
5·35	12·23	13·77	$2\cdot14\times10^{-6}$	$5\cdot51\times10^{-4}$
8·59	9·17	16·83	$3\cdot44\times10^{-6}$	$6\cdot73\times10^{-4}$
12·92	7·61	18·39	$5\cdot17\times10^{-6}$	$7\cdot36\times10^{-4}$
18·83	6·50	19·50	$7\cdot53\times10^{-6}$	$7\cdot80\times10^{-4}$
27·36	5·25	20·75	$10\cdot94\times10^{-6}$	$8\cdot30\times10^{-4}$
39·95	3·70	22·30	$15\cdot98\times10^{-6}$	$8\cdot92\times10^{-4}$
46·35	2·94	23·06	$18\cdot54\times10^{-6}$	$9\cdot22\times10^{-4}$
56·48	1·66	24·34	$22\cdot59\times10^{-6}$	$9\cdot74\times10^{-4}$
64·78	·90	25·10	$25\cdot91\times10^{-6}$	$10\cdot04\times10^{-4}$
76·94	·19	25·81	$30\cdot78\times10^{-6}$	$10\cdot32\times10^{-4}$

Dr. C. Barus * gives some valuable data on the size of the water particles produced by condensation on a solid nucleus. In the experiments described it seems that the condensation must in the first place be caused by the surface action of the

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* Barus, Phil. Mag. [6] iv. pp. 24 to 29 and pp. 262 to 269 (1902).

nucleus, though as the exhaustion of the chamber proceeds the average size of the water particles increases by ordinary condensation at temperatures below the dew-point. If we subtract the average diameter of the nuclei from the average diameter of the drops, and halve the remainder, this will give the thickness of the film of water.

Fig. 2.

In the following table the first two columns have been taken from the original paper of Dr. Barus, and the last column has been inserted by the present writer. The results for the first six exhaustions only have been selected.

Dr. Barus remarks that "the use of Kelvin's vapour-tension equation breaks down quantitatively for the present purposes in practice." The reason for this will be clear when it is remembered that Kelvin's vapour-tension equation is only intended to apply to a condition of equilibrium existing between a liquid and its vapour: but in condensation upon solid surfaces another element must be taken account of, viz., a force of the nature of an attraction between the solid and the liquid or vapour, which causes a pressure, Diameter of nucleus 260×10^{-6} cm.

Number of exhaustions.	Diameter of water particle.	Thickness of film.
1 …………	280×10^{-6}	10×10^{-6}
2 …………	310×10^{-6}	25×10^{-6}
3 …………	330×10^{-6}	35×10^{-6}
4 …………	360×10^{-6}	50×10^{-6}
5 …………	390×10^{-6}	65×10^{-6}
6 …………	420×10^{-6}	80×10^{-6}
Diameter of nucleus 360×10^{-6} cm.		
1 …………	370×10^{-6}	5×10^{-6}
2 …………	390×10^{-6}	15×10^{-6}
3 …………	410×10^{-6}	25×10^{-6}
4 …………	420×10^{-6}	30×10^{-6}
5 …………	440×10^{-6}	40×10^{-6}
6 …………	460×10^{-6}	50×10^{-6}

probably a very great pressure, in the liquid at the surface of the solid. The author hopes to be able at some future time to give the numerical values of this surface pressure for various liquids in contact with glass.

In now appears that in all cases where condensation of moisture takes place at a solid surface, and at temperatures not below the dew-point, the thickness of the surface film varies from 10×10^{-6} to 80×10^{-6} cm. according to the substances used and the conditions of temperature and pressure, and for the water film on glass in saturated vapour at 15° C. the thickness is about $13{\cdot}4 \times 10^{-6}$ cm.

According to Prof. J. J. Thomson * the mean radius of the drops formed by condensation in electrified gas is of the same order of magnitude, being 81×10^{-6} cm. for negatively electrified oxygen, and 68×10^{-6} cm. for positively electrified oxygen ; the size of the nucleus is not known, but it is probably very small.

H.M. Dockyard School, Portsmouth.
November 1902.

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* J. J. Thomson, 'The Discharge of Electricity through Gases' (1900).

LIV. *On the Gaseous Constitution of the H and K lines of the Solar Spectrum, together with a Discussion of Reversed Gaseous Lines.* *By* JOHN TROWBRIDGE*.

[Plate XIII.]

I DESCRIBED in the Phil. Mag. July 1902 and Feb. 1903 the discovery of reversed lines in the spectra of gases, when the latter are submitted to powerful disruptive discharges.

In this paper I shall show that the continuous spectrum observed when glass tubes are employed is not due to the incandescence of the walls of the tubes; and also that the lines obtained by me which apparently coincide with calcium lines at wave-lengths 4227 and 3933, 3968 are not due to calcium but are gaseous lines. The group of H and K lines, therefore, of the solar spectrum, although being doubtless a composite spectrum, has a strong basis of gaseous lines. This seems more than reasonable when we consider that the solar protuberances are observed through these lines; and when we also take into account the rarefied nature of the gas and the improbability of a metallic vapour like that of calcium being projected so far from the limb of the sun.

It seemed necessary, in the progress of my work, to determine to what degree metallic electrodes influence the spectra in Geissler tubes of the dimensions I have employed. When long and powerful sparks are produced in air the metallic lines disappear at a distance of less than two inches from the terminals. The photograph, therefore, of the spectrum produced by a spark of three or four feet in length shows nothing but air-lines when the slit of the spectroscope receives the light from the middle of the spark. This is true even when sparks of eight inches are examined. The most effective way, therefore, of sifting out air-lines from metallic spectra is to employ long and powerful sparks. At one time I believed that the oscillatory nature of the discharge influenced the nature of the spectra. I am now of the opinion that self-induction acts merely by diminishing the instantaneous energy of the discharge.

In the present paper I shall confine my attention mainly to the immediate region of the H and K lines of the solar spectrum.

In Geissler tubes, having capillaries not less than two inches in length, the terminals being three and a half or four inches apart, no metallic lines were observed under the conditions of my work. Indeed, to produce metallic spectra at

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* Communicated by the Author.

such distances from the electrodes during the time of duration of the discharges would demand a prodigious velocity of the particles. I have made a careful study of the influence of metallic electrodes in the tubes employed by me and find no spectra due to them.

In order to determine whether the walls of the glass tubes could give lines due to calcium, I first placed aluminium terminals on a sheet of glass of the same kind as that from which the Geissler tubes were made; and having placed the glass against the slit of the spectroscope, I passed powerful discharges of the same nature and energy as were employed in the study of the spectra of gases. The glass was badly corroded along the path of the discharge, showing the same corrosion which was observed in the capillary of the glass Geissler tubes.

No continuous spectrum was observed and no calcium lines. Similar discharges were passed through fifty ohms of No. 36 iron wire; the wire was barely raised to a dull red heat. A photograph was taken of ten centimetres of such wire, illuminated by the discharge from a Geissler tube placed in the same electrical circuit. The photograph showed the wire intact at the moment of the illumination of the tube. It took time to communicate sufficient heat to melt the wire. On the same photograph was shown the subsequent melting of the wire. That is the wire is seen intact, and also the two ends of the wire contorted and burning. If the walls of the capillary of the glass vessels are heated to incandescence the time element must be large, for the gas must first be heated by the discharge and then the walls of the glass by conduction and radiation. Thermodynamic considerations make it impossible that the walls of the glass vessels are heated to incandescence; moreover, Wiedemann* has shown that the heat of electrical discharges in Geissler tubes has been much exaggerated. A photograph was taken of the light from a Geissler tube by means of a rapidly revolving mirror. Beside the tube and in the same circuit was a spark-gap between magnesium terminals. The duration of the light of the Geissler tube was one-fourth of that of the spark between the magnesium terminals in air. There was absolutely no duration of the light of the Geissler tube due to a supposable incandescence of the glass. The light in the Geissler tube arising from powerful disruptive discharges is the strongest and most instantaneous light which has been obtained, and would be useful in the study of rapid motions.

If the glass is not vaporized by the discharges I have

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* Wied. *Ann* vi. (1878).

employed, the spectrum of calcium cannot be produced in the capillary of the glass vessels. A direct test of the question whether the reversed lines observed by me are due to the glass is afforded by the use of quartz vessels, of which the ends were closed by metal plates. There being a complete absence of glass, and previous investigation having shown that the metallic plates or terminals, and the luting employed, gave no metallic spectra. In the case of quartz the powerful disruptive sparks produced absolutely no corrosion of the walls of the quartz capillaries; and the reversed line at approximately wave-length 4227 and wave-lengths 3968, 3963 (H.H.) of the solar spectrum came out with the same intensity as in the case when glass was employed. Moreover, the strong calcium lines towards the ultra-violet, besides those which apparently coincide with the H.H. lines of the solar spectrum, were conspicuously absent.

The reversed lines which I described in my previous article, and which are shown on the plates of that article, are not due to calcium.

These lines may arise from an electrical decomposition of residual air. It seems impossible to fill spectrum-tubes with perfectly dry and pure hydrogen; traces of air must enter from the purifying and drying apparatus, and the impurities may be brought to light by powerful discharges. I have shown in a previous paper that the electrical decompositions in a tube apparently filled with pure hydrogen can produce various spectra, among them that of argon. The most promising method of obtaining pure dry hydrogen appears to be by the use of liquid hydrogen.

In my paper in this Journal, Feb. 1903, I spoke of a remarkable reversal of lines in the ultra-violet which were obtained by the use of quartz tubes. Fig. 4 (Pl. XIII.) shows these lines with a companion spectrum of magnesium.

These reversed lines apparently coincide with spark-lines of silicon in air; and one might conclude that the lines come from a volatilization of the walls of the quartz capillary. There is, however, absolutely no corrosion of the walls of the quartz vessel. The surface of the quartz remains limpid and clear. I have concluded that, just as in the case of the supposed calcium lines discussed above, these reversed lines are also due to a gas. In order to discover whether these lines can be obtained from some gaseous constituent of the air, I have studied the spectra obtained from powerful sparks in air taken from a great variety of metallic terminals. The spectra from terminals of pure platinum, electrolytic silver, and iridium show strong lines which coincide, with the dispersion I have employed, with the great H.H. lines of the solar spectrum, and also with the gaseous lines I have obtained in rarefied hydrogen*. Terminals of aluminium, copper, iron, tin, magnesium, show these lines faintly. The noble metals, which are least affected by the electric discharge and which are therefore used for nonoxidizable contact in electric apparatus, give these lines strongly. Is it not probable that when the electric discharges volatilize to a high degree the metallic terminals, electric discharge prefers a passage through the metallic vapour, and does not sufficiently heat the air to bring out certain air lines? The method of sifting out air lines from metallic spectra by observing the lines which are apparently common to these spectra, and setting down such lines as air lines, is a fallacious method. Silicon is not easily volatilizable, and certain important groups of lines attributed to that metal, obtained by the use of the spark in air, may be atmospheric lines. I have obtained traces of such lines which seem to coincide with the gaseous lines I obtained with rarefied hydrogen in quartz tubes by employing water electrodes. These electrodes were made as follows:—two iridium terminals were placed on pieces of kiln-dried wood four inches apart. The condenser spark could leap only one inch. The wood was wrapped with cotton, inclosing the metallic terminals, around the cotton was wrapped chamois skin; the clear space between the ends of the wood thus protected was half an inch. The terminals thus prepared were soaked in distilled water. A very powerful spark was thus obtained in air which was entirely free from metallic lines. With these terminals it is undoubtedly true that the water-vapour conducted the main body of the discharge, just as the metallic vapour does in dry air. The edges of this spark show a strong red tint, and give the line-spectrum of hydrogen. The centre of the spark is of a brilliant whiteness. Strong bands appear in the position of the reversed lines which I have obtained with rarefied hydrogen in the quartz tubes. I therefore believe that these lines are gaseous lines.

I believe that these lines, and also the great H.H. lines of the solar spectrum, are due to oxygen. At very high temperatures the oxygen atom set free from the salts of calcium and its allied metals is free to vibrate in its own periods. It does not seem improbable that many lines attributed to metals may be oxygen lines; the metal releasing its hold of the oxygen atom at very high temperatures.

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* Compare with paper "On the Constitution of the Electric Spark," Arthur Schuster, F.R.S., and Gustav Hemsalech, Phil. Trans. Roy. Soc. vol. cxciii. series A.

When the liquid terminals described above are saturated with chemically pure chloride of calcium, with nitrate of strontia, with nitric acid, the great H.H. lines and the line at wave-length 4227 are greatly enhanced. This gives strong colour to the above hypothesis. There is evidently an electrochemistry of the air which has been opened by the discovery of argon.

The continuous spectrum observed with disruptive discharges in gases occurs also when electrical discharges are obtained in distilled water, and in certain other liquids. Prof. Wilsing*, Prof. Hale†, and Sir Norman Lockyer‡ have discussed the reversed lines observed under this condition. The phenomenon of continuous spectrum and of reversals is, I believe, of the same nature as the phenomenon observed by me in gases. The continuous spectrum is due to a sudden compression of the medium under the powerful disruptive electrical explosion, and the reversals are due to a polarization and not to a reversing layer. The reversed lines observed by me increase in intensity toward the ultra-violet, and also are strengthened by repeated exposures. This is the case also with the reversed lines observed under water.

The conclusions of my first paper in the Phil. Mag. July 1902 are therefore confirmed by further investigation. At the basis of the great H.H. lines of the solar spectrum, there are strong gaseous lines which I believe to be oxygen lines. The reversed lines are not due to calcium but are due to oxygen.

The accompanying Plate (XIII.) shows the normal spectra which illustrate this article. Fig. 1 represents the gaseous lines which closely correspond with the great H.H. lines of the solar spectrum. Fig. 2 represents the spectrum of calcium in the neighbourhood of the H.H. lines. It is seen that strong lines of calcium are conspicuously absent in fig. 1.

Fig. 3 shows the gaseous lines obtained in a quartz tube filled apparently with pure hydrogen. A strong group of magnesium lines is added for comparison. These magnesium lines are the strongest lines of that metal between wave-length 3000 and 2000.

Fig. 4 gives also the same comparison spectrum of magnesium, and reversed lines of the gas contained in the quartz tube.

In fig. 3 there is no continuous spectrum. The argument of incandescent walls to account for the continuous spectrum in the case of the employment of glass Geissler tubes, would

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* Kayser, 1 C. 1 P. p. 228.

† G. E. Hale, Astrophys. Journ. p. 15 (1902).

‡ N. Lockyer, Proc. Roy. Soc. p. 70 (1902).

require also a heat of at least incandescence to volatilize the silicon in order to produce the bright unreversed lines seen in fig. 3 at wave-length 2882, and wave-lengths from 2542 to 2507.

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LV. *On the Influence of Magnetic Field on Thermal Conductivity.* *By* VINCENT J. BLYTH, *M.A.* (*Glasgow*), 1851 *Exhibition Research Scholar, Emmanuel College, Cambridge*[*].

IN a circuit composed of bismuth and another metal, the thermo-electric E.M.F. is altered if the bismuth be placed in a magnetic field. This alteration was observed by Leduc[†] and by Righi[‡], while using such a circuit as a means of measuring the difference of temperature between two points of a heat-conveying bar of bismuth. Assuming that the change represented a change in the temperature-difference between the junctions, they deduced the result that the thermal conductivity of bismuth was altered by the magnetic field. But von Ettingshausen and Nernst[§] have shown that such a change in the E.M.F. takes place without any alteration of temperature-difference, and that it represents the "longitudinal thermomagnetic effect," which may also be regarded as an alteration of the thermoelectric nature of bismuth by application of magnetic field[¶]. If thermo-electric junctions are to be used for observing temperature-differences with a view to measuring the effect of magnetic field on thermal conductivity, it is necessary that the intrusion of the von Ettingshausen and Nernst effect should be prevented; and this may be done either by keeping the junctions out of electrical contact with the bar under test, or by obtaining the temperature-differences by independent observations of the two temperatures in each case with reference to a standard junction. It is the purpose of this paper to describe a number of experiments made with a view to determining the effect of magnetic field on thermal conductivity.

A cast rod of bismuth (14 cms. long and 1 cm. in diameter) was warmed at one end to 100° C. and kept at zero at the other end; the ends of the rod were soldered into large copper blocks within the heating and cooling chambers, and

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[*] Communicated by Prof. J. J. Thomson, F.R.S.

[†] *Journ. de Phys.* (2) vi. p. 379. [‡] *Compt. Rend.* cv. p. 168 (1887).

[§] Wied. *Ann.* xxxi. p. 760 (1887).

[¶] See Lownds, Phil. Mag. Oct. 1901.

the rod was surrounded by non-conducting material, in order that the flow of heat along it might be uniform and linear. Three thermoelectric junctions of copper and german-silver were attached to the rod—one at the middle point and the other two at a distance of 1 cm. from either end; the junctions were soldered into small radial holes drilled in the rod. The poles of the electromagnet, which were 2 cms. apart, measured 5 cms. × 3 cms., and could be placed so as to embrace either the hotter or the colder half of the rod. After the distribution of temperature in the rod had attained a steady state, the temperatures of the three junctions were individually—and as nearly as possible simultaneously—observed with reference to a standard junction kept immersed in melting ice. Several readings were taken periodically before application of the field, and again several during the interval when the field was applied (usually about 9 minutes); and this process was repeated several times until a large number of readings of temperatures had been obtained. From these the temperature-differences at the ends of that half of the rod subjected to magnetization were derived, and the average of those corresponding to no field compared against the average of those corresponding to the particular field applied. Various field-strengths, from 650 to 3550 C.G.S. lines per sq. cm., were used, but in no case did the temperature-difference with the field on differ from that with the field off by more than a very small amount. Moreover, the want of exact concordance among the values of the temperature-differences obtained showed that these were varying by small amounts throughout the experiments in consequence of accidental causes. Of the apparent changes produced by application of the field the largest was one of 0°·3 C. increase in the temperature-difference at the ends of the magnetized part of the rod. The mean of such changes observed was about 0°·07 C., which would correspond to a diminution of conductivity of about 1/7 per cent. Thus it appears that the effect on the conductivity of bismuth of such fields is exceedingly small, since, had the change amounted to $\frac{1}{2}$ per cent., it could have been easily detected by this method, in spite of the slight fluctuations of temperature which took place during the observations. The E.M.F. in the circuit composed of the copper wires of the thermo-junctions and the bismuth rod between them suffered considerable alteration on the application of the field. Had it been assumed that this was due to a change in temperature-difference, the diminution of conductivity indicated would have been 5·6 per cent. for a field of 3550. This may be compared with the results quoted by van Everdingen[*].

k=conductivity under zero field.
k'= ,, ,, field applied.

	Field 3550.	$\frac{k}{k'}=1{\cdot}058$.
van Everdingen	6000	1·058
Leduc	7800	1·057
von Ettingshausen ...	9000	1·052 to 1·021.

The above experiment was repeated with a bar of bismuth obtained from Messrs. Johnson, Matthey & Co., and in this case the von Ettingshausen and Nernst effect was found to be too small for detection. In the previous case the change in deflexion representing the effect was 10 scale-divisions; but although the conditions were all exactly the same in the trial of the Johnson-Matthey bar no deflexion was observed on applying the field.

In order to measure the temperature-difference between two points directly by a single reading a system of thermo-junctions of german-silver and iron was arranged, the junctions being insulated from the rod. These were thrust into small radial holes in the rod, and kept out of contact by thin slips of mica. No distinct effect of magnetic field on the temperature-difference was detected by this method; moreover, it was found that the temperatures indicated by these insulated junctions differed somewhat considerably from those given by junctions soldered to the rod at the same points. Therefore an arrangement in the form of a thermal Wheatstone's bridge was adopted, whereby it was possible, without admitting the Nernst effect, to have the junctions soldered to the points between which the temperature-difference was to be observed. The two pairs of arms of the bridge (fig. 1) were kept out of electrical contact by means of small strips of insulation inserted between the metal pieces and the walls of the slots in the copper blocks which were soldered to the inside of the heating and cooling chambers. The thermo-junctions of german-silver and iron attached to the points A and B were connected in series through the galvanometer, whose sensitiveness was 11 divisions deflexion per 1° C. difference of temperature. The bars were wrapped up in felt, and the magnet set so as to embrace between its poles one of the arms of the bridge. Various forms of bridge

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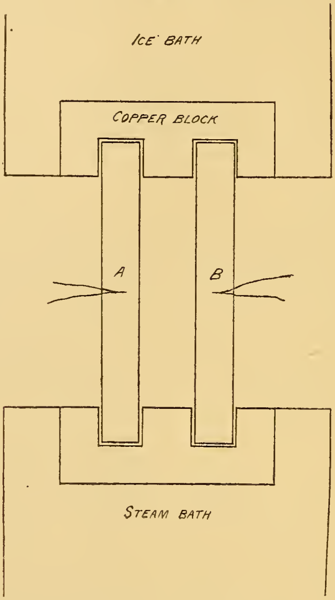
[*] Leiden Communications, 25th March and 22nd April, 1898.

arrangement were experimented with. In one form each pair of arms consisted of a straight bar of the metal let into the blocks in the heating and cooling chambers at its ends, and having a thermo-junction at its middle point. After the flow of heat along the bars had become steady the two junctions were found to be at nearly the same temperature; but when one half of one of the bars was subjected to a transverse magnetic field, this balance was disturbed to a greater or less extent, according to the field applied. With this arrangement soft iron was tested under a transverse field of 2650 c.g.s., and the change of temperature-difference was 0·3 or 0·4 scale-division; for hard steel a similar small change of 0·5 division was obtained by application of a field of 4300. These changes are too small to be regarded as definite. The experiments with mild steel at higher field-strengths are tabulated below.

Fig. 1.



	Field.	Change in Temperature-difference.	Percentage diminution of Conductivity.
Field across hotter half of bar	9400	36 scale-divisions	3·0
	8400	26 ,, ,,	2·1
Field across colder half of bar	9400	13·6 ,, ,,	3·6
	8400	8 ,, ,,	2·1

After the flow of heat had attained a steady state the reading corresponding to the temperature-difference between the middle points of the bars was taken, and also the deflexions representing the actual temperatures of each middle point with reference to a cold junction. The deflexion corresponding to the temperature-difference was initially small, but when the magnet current was switched on, it increased with comparative rapidity for 20 minutes, and thereafter more and more gradually for 10 minutes longer, when it became constant. When the field was removed the difference diminished again, usually requiring from 40 to 45 minutes to regain its steady value. This process was repeated several times and the mean of these rises and falls for each field is represented by each of the numbers given in the table; the first fall and the subsequent rises and falls were less than the first rise, doubtless on account of residual magnetism. By means of the observations of the actual temperatures of the middle points of the bars, it was shown that the changes in temperature-difference were due to a rise in the temperature at the middle point of one of the bars, and an approximately equal lowering of the temperature at the middle point of the other; on the removal of the field the temperatures fell and rose respectively, until the original small difference before the field was applied had been approximately regained. The changes were proved to be not in any degree due to heat transferred from the electromagnet coils. The bar which was not between the poles was in a stray field of about 1900.

By using this bridge method, the alteration in conductivity of bismuth was found to be 0·3 per cent. for a field of 8500; but this result is probably unreliable, since the length of the bismuth bars (8 in.) was afterwards found to be too great to justify neglecting the loss of heat by escape through the felt lagging.

The effect of a longitudinal field was measured in two ways —by the "bridge method," and by the method of observing directly the quantity of heat which flows along a magnetized and an unmagnetized bar in a given time. Preliminary trials showed that a decrease of conductivity would be detectable by the latter method, although they did not provide data for evaluating the change numerically. Two similar bars were set up with their ends in the copper block of the steam-box and insulated from it. One bar passed through a coil which was wound anti-inductively, and arranged so that the two halves could be joined in opposition so as to produce zero field and yet have the same heating effect as when they were put in conjunction to generate a field, which in this case amounted to 41 C.G.S. units. To the top ends of the bars german-silver-iron junctions were soldered. After the distribution of temperature had become steady, the current flowing but generating no field, the junction readings were taken, and then again some time after the field had been excited. The generation of the field produced a rise of temperature at the top of the magnetized bar of 2·2 per cent. in the case of iron and 2·8 per cent. in the case of bismuth. In the actual experiments time readings were taken of the temperature at the top end of a bar whose lower end was fitted hard into the copper block of the steam-chamber, the temperature being initially atmospheric. By drawing curves of these readings the following results were obtained, the material being mild steel and the field 51 c.g.s.:—

Magnet off;	rise of temp. in	20 min.,	144 div.	Percentage decrease of conductivity...... 4·2
,, on;	,, ,,	20 ,,	138 ,,	
,, off;	,, ,,	20 ,,	211 ,,	,, ,, 3·8
,, on;	,, ,,	20 ,,	203 ,,	

By a similar method a rod of soft iron, 6 in. long and 5/8 in. in diameter, was tested both for longitudinal and transverse fields. But in this case thermo-junctions were not used, the temperatures at the top end of the rod being obtained from a mercury thermometer which rested in a glass tube containing mercury attached to the top of the rod; the top of the rod was tinned and amalgamated so as to be in good thermal contact with the mercury. The longitudinal field was supplied by a solenoid which was not anti-inductively wound, but the heating of the thermometer by the

Longitudinal field; giving induction 16,000 c.g.s.

Initial Temperature.	Rise of Temp. in 20 min.		Difference.	Percentage Diminution.
	Magnetism off.	Magnetism on.		
15·3	29°·7 C.	26°·9	2·8	9·4
19·25	28·4	25·0	3·4	12·0
	Rise in	15 min.		
26·6	21·6	19·4	2·2	10·2
	Transverse field; 7850 c.g.s.			
	Rise in 20 min.			
13·2	32·7	32·35	·35	1·07
14·3	32·1	31·6	·5	1·56
15·8	32·0	31·7	·3	·94

coil, which was separated from the rod by Kieselguhr insulation ½ in. thick and a tube of ebonite, was slight; and in all cases a correction was applied for whatever slow change of temperature might exist during each experiment.

On account of the large demagnetizing factor in the case of the transverse magnetization of the rod, the intensity of magnetization would in this case be much smaller than that produced by the longitudinal field. This may account for the comparatively small value of the change produced by transverse field; for Gray and Jones* have found that the change of electrical resistance of iron is dependent on intensity of magnetization rather than directly on magnetic field.

This method was unsatisfactory on account of the difficulty of securing that the initial conditions for the two complementary experiments should be exactly the same as to temperature. It was found better to set up two similar bars of the same material side by side with their ends fixed in the steam-box, and take the two sets of time-readings simultaneously. This modification was applied in the determination of the following result for mild steel bars. The table below contains figures taken from the curves representing the changes of temperature at the ends of the bars.

Time from instant of letting in steam.	Magnet on Left-Hand Bar.			Magnet on Right-Hand Bar.		
	Temp. of R.H.	Temp. of L.H.	Diff.	Temp. of R.H.	Temp. of L.H.	Diff.
0	15·9	15·9	0	16·9	16·9	0
20	26·3	23·95	2·35	26·4	24·9	1·5
40	34·25	30·65	3·6	33·4	31·7	1·7
60	37·85	33·8	4·05	36·9	34·85	2·05
70	39·0	34·6	4·4	37·9	35·8	2·1
80	39·7	35·25	4·45	38·55	36·5	2·05
90	40·15	35·8	4·35	39·0	36·9	2·1
100	40·6	36·2	4·4	39·2	37·1	2·1

It will be seen that after an interval of 80 minutes has elapsed since the steam was blown into the box, the temperature-difference becomes constant. Taking as the mean values of these constant differences 4°·4 and 2°·1 we find the diminution of the rise of either bar, as compared with what the rise would have been had there been no field applied, by

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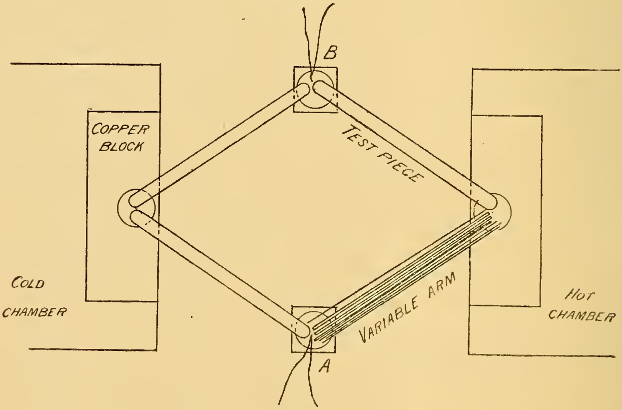
* Proc. Roy. Soc. vol. lxvii. p. 208.

halving the excess of the one difference over the other. Moreover, when a series of readings was taken with neither bar in the field the rise of temperature in 80 min. of the R.H. bar was found to exceed that of the L.H. bar by 3°·25, which is midway between 4·4 and 2·1. Thus the effect of the field was to diminish the rise of temperature by 1°·15, which corresponds to a diminution of the thermal conductivity of 3·1 per cent.; the field in this case was 6500 c.g.s. By repetition of the above experiment this result was fully confirmed.

The application of this method to bars of bismuth 4 in. long, as in the case of the other methods, did not yield any definite results.

For measuring the effect of longitudinal field by the bridge method, a form of bridge was used in which the arms consisted of wires each having a right-angle bend at its ends, so that its ends could dip into mercury-cups; the arrangement of the mercury-cups is shown in fig. 2. One of the arms was composed of a variable number of thin wires, the number of which was adjusted until the temperatures of the cups A and B were equal, as indicated by the sensitive thermo-junctions dipping into them. The wires were all coated with a thin layer of enamel, which broke the electrical circuit through the bridge, thus excluding the Nernst effect when magnetic fields were employed. By use of this arrangement fairly good values were obtained for the conductivity of the specimens tested by comparison with that of a standard copper wire whose conductivity was assumed; and the method proved a very convenient one for this purpose. For the diminution of conductivity of an iron wire under a

Fig. 2.



longitudinal magnetic induction of 17,500 C.G.S. lines per sq. cm., the value 10·2 per cent. was found; and this value is in tolerable agreement with those quoted in an earlier part of the paper as obtained by the direct method.

Summary of Results.

The change in the thermal conductivity of bismuth produced by magnetic field is very small; for a transverse field of 3550 it is considerably less than $\frac{1}{2}$ per cent., and it is scarcely measurable even in higher fields by any of the methods used.

As tested by the bridge method, mild steel suffered a reduction of its conductivity of 3·3 per cent. for an increase of transverse field of 7500, and a reduction of 2·1 per cent. for an increase of 6700. The reduction 3·1 per cent. was observed for the same material by the method of direct measurement on application of a transverse field of 6500.

The effect of a longitudinal field of 51 C.G.S. on the conductivity of mild steel was to diminish it by about 4 per cent.

In the case of soft iron, as tested by direct measurement, a longitudinal field producing a magnetic induction of 16,000 per sq. cm. diminished the conductivity by about 10·5 per cent.; while the effect of transverse field is comparatively small—about 1 per cent. for a field of 7850; by the bridge method the effect of a longitudinal induction of 17,500 was found to be a diminution of conductivity of 10·2 per cent.

I beg to express sincerest thanks to Prof. J. J. Thomson for continual encouragement and assistance.

Cavendish Laboratory, Cambridge.

LVI. *Theoretical Optics since* 1840.—*A Survey.*

By R. T. GLAZEBROOK, *D.Sc.*, *F.R.S.*[*]

SIR GEORGE STOKES took his degree in 1841; the first of the papers contained in his Collected Works was read in 1842: he became Lucasian Professor in 1849.

Speaking as I do so soon after his death, it is, perhaps, not unnatural to look back over the progress of our Science during the sixty years for which he has been one of the most prominent of its exponents.

To attempt such a task in any completeness would need a fuller knowledge and an abler pen than mine; will you, however, bear with me if I take one corner of the field covered by his activities and attempt a brief survey of this.

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[*] Communicated by the Physical Society, being a portion of the Presidential Address delivered on February 13, 1903.

It is, perhaps, the more necessary, for I think it is not always recognized how much of our knowledge of Optical Science is due to Stokes. It was he who first verified with any degree of exactness Huyghens' construction for the refraction of light at a uniaxial crystal; the interpretation of Kirchhoff's discovery of the coincidence between the dark lines of the solar spectrum and the bright lines of certain incandescent solids and gases is due to him, and on this the whole of spectrum analysis rests; he explained the phenomena of fluorescence, and as an old man, some years ago, expounded in his own unrivalled manner the origin of the Röntgen rays and their connexion with the kathode rays. The analysis of a plane wave of light into its constituent parts, and the first dynamical account of diffraction, are due to him; and his experiments, if we accept any modification of the elastic-solid theory of light as true, settled that Fresnel's explanation of the cause of refraction, rather than that of Neumann and MacCullagh, is the right one.

In his brilliant Rede Lecture, Cornu writes:—

"The study of the properties of waves, looked at from every aspect, is then at present the really fruitful path.

"It is that which Stokes, in his double capacity of mathematician and physicist, has followed.... All his beautiful investigations, whether in hydrodynamics or in theoretical or experimental optics, relate to the transformations which waves undergo in the diverse media through which they pass.

"In the varied phenomena which he has discovered or analysed, movement of fluids, diffraction, interference, fluorescence, Röntgen rays, this guiding idea that I have pointed out is ever visible, and it is this which has made the scientific life of Sir George Stokes one harmonious whole."

Let us consider then very briefly the progress of theoretical optics since the days of Stokes' first paper on the subject: "On the Theories of the Internal Friction of Fluids in Motion, and of the Equilibrium and Motion of Elastic Solids"*. The advance in the early part of the century had been most marked. The discovery of the principle of interference by Young, and the brilliant work of Augustin Fresnel, who had covered the ground with giant strides, had placed the undulatory theory on a firm footing, but there was no consistent view of the subject which would account even for the facts then known on a rational basis.

Fresnel's theory of double refraction was not dynamical; he arrived at it in the first place by purely geometrical reasoning, based on Huyghens' construction, and only attempted at

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* Camb. Phil. Trans. viii. (1845).

a later date to give it a mechanical basis. In this attempt he failed. "If we reflect," says Stokes, "on the state of the subject as Fresnel found it and as he left it, the wonder is not that he failed to give a rigorous dynamical theory, but that a single mind was capable of effecting so much."

Between the days of Fresnel and Stokes great men had worked at the subject. Navier, Poisson, and Cauchy in France; Neumann in Germany; MacCullagh in Dublin; and George Green in Cambridge, had all contributed their share, and the results were somewhat confusing.

MacCullagh and Neumann, treating the æther as an elastic solid, had obtained on certain hypotheses Fresnel's laws for reflexion and refraction, and his theory of double refraction. Green, using a somewhat different method, had shown, apparently, that the tangent law was only an approximation to the truth, while the wave-surface could only be deduced from the true equations of an æolotropic elastic solid by some forced and improbable relations between the constants.

According to all the theories, two waves in general can traverse an elastic medium, the one travelling with velocity $\sqrt{A/\rho}$, the other with velocity $\sqrt{B/\rho}$ where A and B are two constants. Of these the first consists of longitudinal, the second of transverse vibrations; and since there is no evidence of the former wave in optics, the constant A must either vanish or be infinite.

Neumann's theory assumed A to vanish; Green had shown that for an elastic solid with free boundaries the condition of stability demanded that $A-4/3\,B$ should be positive, and hence he assumed A to be infinite. On this view of the æther he was clearly right. Such was the position of the problem in 1839, the year in which the papers of Green, MacCullagh, and Cauchy were published. Stokes' earliest paper on the subject, written when he was 26 years old, deals with the properties which we must assign to the æther if we are to explain the facts observed. To propagate transverse waves it must behave to light motions as an elastic solid; the constancy of the length of the year, and other astronomical results, show that it opposes no sensible resistance to the motion of the earth and the planets, for such motions it has the properties of a perfect fluid.

He distinguishes—the fact is well-known now, but it was a great step then—between the two kinds of elasticity, rigidity and resistance to compression. B is a measure of the rigidity, $A-4B/3$ of the resistance to compression. For a fluid, then, which is practically incompressible, the ratio of A to B may be very great, as Green requires it, while in Stokes' view it is still possible that for the tiny motions involved in the propagation of light the fluid may have rigidity.

However, be this satisfactory or not, and the difficulty is one which occurs in every elastic-solid theory of Optics, the result remains that an elastic-solid theory is not consistent with the facts. The phenomena of reflexion and refraction at the bounding surface of two media may be due either to a change in density or to a change in rigidity.

Green's theory of refraction assumes the change to be one of density, the rigidity of the æther in all isotropic media is the same; his theory of double refraction assumes this to arise from a variation of the rigidity in different directions within a crystal.

These difficulties are clearly exposed in Stokes' Report to the British Association in 1862, in which he also shows that MacCullagh and Neumann's theory is impossible so long as the potential energy of the æther when transmitting light is assumed to be that of a strained elastic solid. If we suppose the æther to differ from an ordinary elastic solid but to possess what has been called rotational elasticity, in consequence of which it opposes forces tending to cause molecular twist to an extent proportional to the twist, then MacCullagh's form of the potential energy is obtained and his conclusions hold. From this point of view the matter has been developed of late years by Larmor.

The Report of 1862 deals with another matter, specially interesting to myself, because in later years Stokes encouraged me to pursue it.

Up to that date the experiments to verify Huyghens' construction for a uniaxial crystal had been of the roughest character. Stokes devised a method of testing the construction to a very high degree of accuracy and carried it into effect for Iceland spar. The results are very briefly referred to; they were published later, but hardly in greater detail, at Lord Kelvin's urgent request, in the Proceedings of the Royal Society.

The outcome was that while for a uniaxial crystal at least Huyghens' construction was undoubtedly true, no theoretical basis could be given for it.

It was left to Maxwell to carry the question a stage further. He showed that the laws which regulate the propagation of electric force in a crystal are identical with those of light, while experiment proved that the velocity of light is the same as that of an electric disturbance, and hence we have the electromagnetic theory of light.

It should be noted, however, that this theory, as Maxwell left it, is not mechanical. Electric displacement and magnetic force are vector quantities which accompany each other in a changing electric field. They satisfy certain equations; and it follows from these, and the result is verified by experiment, that they are propagated according to the same laws as light. It is reasonable to suppose that the periodic disturbance which constitutes light is very intimately connected with one or other of these; the supposition that it is identical with Maxwell's electric displacement leads to consequences consistent with fact, and, indeed, in the able hands of those who have developed the theory has been the fruitful means of correlating many varied phenomena; but it does not tell us what electric displacement is, or how it is related to the movements of the æther; neither does it enlighten us as to the structure and mechanical properties of the æther, beyond the simple fact that in the æther transverse waves only are propagated, no forces can be called into play which tend to set up a pressural wave. Maxwell himself attempted to formulate a mechanical model of the æther, and to some extent succeeded. Lord Kelvin, so fertile in his thoughts, has made various suggestions, we will return to one later. To-day the electron theory of electricity, thanks mainly to the brilliant work of Stokes' Cambridge colleague, J. J. Thomson, holds the field; but the relation of the electron to the æther and the mechanism by which electrons produce æther waves have yet to be discovered.

Larmor's suggestion that the flow of æther constitutes magnetic force, while a twist in an æther endowed with rotational elasticity produces electric displacement, forms perhaps the most consistent picture of the process which we possess.

Lord Kelvin, indeed, in 1888 suggested a structure for the æther which allows of a homogeneous mechanical account of optical phenomena being given.

On this view the resistance to compression of the æther is negative, if free it would collapse, but the necessary stability is given by the supposition that it is fixed at the boundaries; it is a structure like a collection of soap-films stretched across a wire framework; if the connexion be broken the whole collapses, so long as it remains the system can propagate transverse waves. With such an æther there is no difficulty in giving a consistent account of Optics, but it is difficult to imagine that the æther has such properties. I believe, however, that Lord Kelvin now thinks that a slight modification of his original hypothesis will lead to the same result so far as optics are concerned, but will enable him to get over the difficulty of postulating fixed boundaries.

On such an hypothesis the molecular velocity of the æther might measure magnetic force, while electric displacement would then be proportional to the curl of the twist, or we might adopt the analogy suggested by Heaviside ('Electrician,' Jan. 23, 1891), and developed, as I have said, by Larmor, according to which the kinetic energy measures the magnetic force and the twist the electric displacement.

The electromagnetic theory, though it does not rest on a mechanical basis, has linked together optical and other phenomena in a striking fashion. The advance from the days of Green has been a great one.

And leaving now the general theory, the development of its details has not been less striking. On all sides there has been advance, and along most of the lines of advance Stokes was a pioneer.

Newton's difficulty in accepting the undulatory theory was really solved when Young enunciated the principle of interference, but it needed Fresnel's experiments to convince men of its truth. It was clear, of course, that the effect at any point due to a wave of light could be calculated by finding the effect due to each element of the wave and summing these; but Stokes, in his papers on diffraction (1851), was the first to establish a correct expression for the effect produced at a distant point by an element of the wave and to show how these effects were to be summed.

The germ of all that has been discovered by means of spectrum analysis is contained in his explanation of Kirchhoff's original experiment, often quoted by Lord Kelvin, and from his paper on "Fluorescence" have sprung the modern theories of dispersion, including anomalous dispersion. On this point the note he has added to this paper in the third volume of his Collected Works has a special interest. Although he did not fathom the connexion between æther and matter, and, on the whole, the criticisms passed by later writers on his theory of aberration are to be accepted as justified, his papers must be studied by any one who is anxious to penetrate the mystery, and did much to put the facts in a clear light.

My survey is, I realize, entirely inadequate; it is but a fraction even of the corner of the field I set out to examine that I have covered, but I must stop. I have said enough, I hope, to show that progress has been continuous and marked, and in no small degree that progress has been due to the work of Sir George Stokes.

I had intended to bring before you some more practical questions connected with the work of my own Laboratory.

These must await a more fitting opportunity; meanwhile let me conclude as I began, by thanking you very heartily for placing me in this position, and assuring you of my desire to forward your best interests.

LVII. *On the Numerics of the Elements.*—Part III.

By Edmund J. Mills, *D.Sc.*, *F.R.S.*[*]

It has been shown in previous parts[†] that the numerics of the elements are of the form

$$y = pn - n\left(\frac{n}{n+1}\right)^x;$$

where p represents the number of the periodic group, $n+1$ the number of periods in the system, and x the integral ordinal within a given group. So far as is known, all the numerics of the existing elementary bodies, excepting that of hydrogen, are included in the above equation when $n=15$; and the range in value is from $y=0$ to $y=240$.

It has been objected[‡] to this method of representation that it includes an infinite number of elements within the range indicated. Ample precedent, however, for this is found in the phenomena of Cumulative Resolution[§]. In the denitration of bismuthic nitrate by water, for instance, there are three distinct continuous stages:—

I. $n\,\mathrm{Bi_2\,O_3\,.\,3N_2\,O_5} - (n-1)\mathrm{N_2\,O_5} = \mathrm{Bi}_{2n}\,\mathrm{O}_{3n}\,.\,\mathrm{N}_{4n+2}\,\mathrm{O}_{10n+5}$,
and at infinity $\mathrm{Bi_2\,O_3\,.\,N_4\,O_{10}}$.

II. $n\,\mathrm{Bi_2\,O_3\,.\,2N_2\,O_5} - (n-1)\mathrm{N_2\,O_5} = \mathrm{Bi}_{2n}\,\mathrm{O}_{3n}\,.\,\mathrm{N}_{2n+2}\,\mathrm{O}_{5n+5}$,
and at infinity $\mathrm{Bi_2\,O_3\,.\,N_2\,O_5}$.

III. $n\,\mathrm{Bi_2\,O_3\,.\,N_2\,O_5} - (n-1)\,\mathrm{N_2\,O_5} = \mathrm{Bi}_{2n}\,\mathrm{O}_{3n}\,.\,\mathrm{N_2\,O_5}$,
and at infinity $\mathrm{Bi_2\,O_3}$.

In the first stage ratios are known for $n = \cdot 1$ and 1; in the second, for $n=2$; in the third, for $n = \frac{6}{5}, \frac{5}{4}, \frac{4}{3}, 1$, and ∞.

Another objection has been raised to the method that it is too easily applicable to any numeric. This objection, however, is not so much a criticism of the mathematical method, as a censure on the weakness of experimental processes. These, in the most favourable cases, cannot be depended upon more nearly than ·02; and the mathematical method can only follow them. So far, increasing experimental accuracy has been attended by a closer coincidence with the theory. The

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[*] Communicated by the Author.

[†] Phil. Mag. 1884, vol. xviii. p. 393; 1886, vol. xxi. p. 151.

[‡] *Ibid.* 1902, vol. iv. p. 103.

[§] *Ibid.* 1877, vol. iii. p. 492.

severest comparison is where the values of x are low: here, if the theory had been inaccurate, gross discrepancies must have been immediately indicated *.

As has been stated in Part II., the form of the periodic function here adopted is based primarily on a law of cooling, followed by polymerization and reversal.

Periodicity itself would appear to necessitate an impulsive origin for the elementary bodies. Liveing, many years ago, attributed this property to chemical change in general.

The object of the present communication is to include the results of the discoveries and discussions of the last sixteen years.

Group I.

$$y=15-15(\cdot 9375)^x.$$

	x.	y.	y calc.
He	5	3·94	4·14
Li	10	7·01	7·13
Be	14	9·09	8·92
Bo	20	10·94	10·87
C	25	11·97	12·01
N	42	14·00	14·00

Group II.

$$y=30-15(\cdot 9375)^x.$$

	x.	y.	y calc.
O	1	[standard] =	15·94
F	5	18·98	19·14
Ne	6	19·86	19·82
Na	12	23·00	23·09
Mg	15	24·28	24·30
Al	25	27·01	27·01
Si	32	28·20	28·10

Group III.

$$y=45-15(\cdot 9375)^x.$$

	x.	y.	y calc.
P . . . . ,	1	30·96	30·94
S	2	31·98	31·82
Cl	7	35·37	35·45
K	14	39·02	38·92
Ar	16	39·76	39·66
Ca	17	39·90	39·99
Sc	42	43·98	44·00

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* Copper, for example, occurs in Group V. It must obviously be entered under $x=3$, 4, or 5; *i. e.* have the numeric 62·64, 63·41, or 64·14. The experimental number having been now practically settled at 63·36, there can be no doubt that $x=4$ is the only correct selection.

Group IV.

$$y=60-15(\cdot 9375)^x.$$

	x.	y.	y calc.
Ti	3	47·99	47·64
V	8	51·26	51·05
Cr	10	52·01	52·13
Mn	17	54·97	54·99
Fe	20	55·81	55·87
Ni	36	58·55	58·53
Co	42	58·83	59·00

Group V.

$$y=75-15(\cdot 9375)^x.$$

	x.	y.	y calc.
Cu	4	63·36	63·41
Zn	6	65·01	64·82
Ga	17	69·90	69·99
Ge	26	72·20	72·20
As	63	74·73	74·74

Group VI.

$$y=90-15(\cdot 9375)^x.$$

	x.	y.	y calc.
Se	5	78·96	79·14
Br	6	79·77	79·82
Kr	9	81·46	81·61
Rb	18	85·25	85·31
Sr	27	87·37	87·37
Yt	36	88·59	88·53

Group VII.

$$y=105-15(\cdot 9375)^x.$$

	x.	y.	y calc.
Zr	1	90·76	90·94
No (Cm)	6	93·68	93·41
Mo	7	95·53	95·45
Ru	22	101·34	101·37
Rh	27	102·32	102·37

Group VIII.

$$y=120-15(\cdot 9375)^x.$$

	x.	y.	y calc.
Pd	1	105·92	105·94
Ag	3	107·68	107·64
Cd	9	111·65	111·61
In	13	113·40	113·52
Vi	25 ?	117 ?	117·01
Sn	36	118·55	118·53
Sb	54	119·55	119·54

Group IX.

$$y=135-15(\cdot9375)^x.$$

	x.	y.	y calc.
I	9	126·56	126·61
Te	10	127·28	127·14
Xn	11	127·52	127·62
Cs	28	132·58	132·54

Group X.

$$y=150-15(\cdot9375)^x.$$

	x.	y.	y calc.
Ba	2	136·76	136·82
La	4	138·40	138·41
Ce	5	139·17	139·14
Prs	6	139·95	139·82
Nd	12	143·05	143·09
Sm	75	149·89	149·89

Group XI.

$$y=165-15(\cdot9375)^x.$$

	x.	y.	y calc.
Gd	8	156·17	156·05
Tb	16	159·40 ?	159·66

Group XII.

$$y=180-15(\cdot9375)^x.$$

	x.	y.	y calc.
Er	1	166 ?	165·94
Thu	7	170·34	170·45
Yb	11	172·48	172·62

Group XIII.

$$y=195-15(\cdot9375)^x.$$

	x.	y.	y calc.
Ta	3	182·40	182·64
W	4	183·61	183·41
Os	17	190·06	189·99
Ir	28	192·65	192·54
Pt	42	194·06	194·00

Group XIV.

$$y=210-15(\cdot9375)^x.$$

	x.	y.	y calc.
Au	2	196·45	196·72
Hg	5	199·28	199·14
Tl	13	203·40	203·52
Pb	22	206·17	206·37
Bi	28	207·52	207·54

Group XV.

$$y = 225 - 15(\cdot9375)^x.$$

	x.	y.	y calc.
Ra	?	225 ± 1	?

Group XVI.

$$y = 240 - 15(\cdot9375)^x.$$

	x.	y.	y calc.
Th	9	231·61	231·66
U	28	237·64	237·54

The Specific Values of some Numerics.

Many of the former values remain practically unchanged. Most of the original memoirs had been consulted, and the necessary calculations made, before the appearance (1903) of the "International Atomic Weights"—the values in which are in several cases nearer than my own to my theoretical figures. Clarke's (1897 and 1902) well-known memoirs * have proved of great service.

Hydrogen and Oxygen.—By a repetition of old methods, several investigators have found that O = 15·88 if H = 1. Keiser (1889), however, was the first to utilize hydro-palladium as a source of pure hydrogen, and in a series of very accordant experiments found O = 15·95; a result not hitherto explained away. Later on (1898), using hydrogen from the same source, in a simpler apparatus, he obtained the number 15·88.

Attention may be directed to some cross ratios to be found in Clarke's (1897) Memoir, but so far not utilized in this connexion:—

p. 108:

$\frac{\mathrm{Au}}{\mathrm{H}_3}\times\frac{3\mathrm{AgCl}}{\mathrm{Au}}\times\frac{\mathrm{O}_3}{3\mathrm{AgCl}}=\frac{196\cdot713}{3}\times\frac{100}{45\cdot824}\times\frac{1}{8\cdot9614}$ †. Hence $\frac{\mathrm{O}}{\mathrm{H}}=15\cdot97.$

p. 310:

$$\frac{\mathrm{O}}{\mathrm{Co}}\times\frac{\mathrm{Co}}{\mathrm{H}}=\frac{21\cdot367}{78\cdot633}\times\frac{58\cdot630}{1}. \quad \text{Hence } \frac{\mathrm{O}}{\mathrm{H}}=\frac{15\cdot90}{1}.$$

pp. 305, 310:

$$\frac{\mathrm{O}}{\mathrm{N}}\times\frac{\mathrm{Ni}}{\mathrm{H}}=\frac{21\cdot430}{78\cdot570}\times\frac{58\cdot456}{1}. \quad \text{Hence } \frac{\mathrm{O}}{\mathrm{H}}=\frac{15\cdot94}{1}.$$

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* Smithsonian Miscellaneous Collections, and Am. Chem. Journ. 1902.

† Stas.

pp. 151, 2 :

$$\frac{O}{Zn} \times \frac{Zn}{H} = \frac{19{\cdot}688}{80{\cdot}312} \times \frac{65{\cdot}079}{1}. \quad \text{Hence } \frac{O}{H} = \frac{15{\cdot}95}{1}.$$

p. 290 :

$$\frac{Fe_2}{H_2} \times \frac{O_3}{Fe_2} = \frac{55{\cdot}608}{1} \times \frac{29{\cdot}992}{70{\cdot}008}. \quad \text{Hence } \frac{O}{H} = \frac{15{\cdot}88}{1}.$$

pp. 179, 180 :

$$\frac{Al_2}{H_2} \times \frac{3H_2O}{Al_2} = \frac{53{\cdot}780}{2} \times \frac{9{\cdot}9818}{10}. \quad \text{Hence } \frac{O}{H} = \frac{15{\cdot}89}{1}.$$

I regard these ratios as very important, because they are now for the first time disclosed, and could not have been obtained intentionally. There is thus a residual uncertainty about O : H.

As regards the methods employed, it is open to question whether a *current* of gas can be dried ; at any rate, I have not succeeded in drying a current of air. Glass globes, and other glass apparatus, must resemble thermometer-bulbs in undergoing progressive contraction. Hydrogen (according to Dittmar and Henderson) decomposes sulphuric acid at the ordinary temperature—presumably in presence of light. Phosphoric anhydride (according to Crookes) is apt, unless previously heated, to give up matter to hydrogen, and, one would suppose, to other gases. Hydrogen made from metals is likely to contain carbonic impurity (Morley). Mercury is a nearly certain impurity in most gases ; its presence reduces the relative gravity of oxygen by about ·02. Böttger's important observation (*Chem. Centr.* 1878, p. 574) that the mixture $H_2 : O$, when exploded, always produces some peroxide, seems to have been almost entirely overlooked : and the same remark applies to Richardson's discovery (Proc. Chem. Soc. 1889, p. 134) that water forms peroxide on exposure to light. A quantity of peroxide amounting to ·05 p. c. of the water would reduce the value $\frac{O}{H}$ by about ·06.

The preparation of hydrogen by electrolysis of baryta-water, and its subsequent occlusion by palladium, is a great step in advance, as enabling hydrogen to be weighed instead of measured. Scott's use of argentic oxide, also, has probably resulted in the production of oxygen of improved quality. But a new source of oxygen, in a substance capable of progressive decomposition, is still to be desired.

It would appear to be in all cases essential to determine the effect of light.

The numeric of oxygen has been at various times taken as 100, 1, 15·96, 15·88, and 16. At present there are two scales in use, viz. O=16, H=1·008; and O=15·88, H=1. When the composition of water is ultimately decided, these ratios may undergo some change. But none of the values proposed has any special physical meaning as a ground for preference in practical use.

The value O=15·94, adopted in this memoir, has the advantage of lying exactly midway between—and so, perhaps, conciliating—the modern hydrogen and oxygen scales. It is calculated from rigorous mathematical conditions, and includes all known elements, excepting hydrogen; it is, consequently, interdependently related to all the elements. There is a reason, therefore, for preferring this value; or, at any rate, some value similarly calculated. It may, indeed, be said that, within the limits of experimental error, the practical value is in fact O=15·94.

Linear periodicity is no longer admissible.

Clarke comments on his own table of numerics (1897) in these terms:—"In most cases even the first decimal is uncertain; and in some instances whole units may be in doubt." The determinations are, in fact, so much affected by constant error, that their probable error is seldom worth calculating. Of all constant errors, the most important would seem due to the fact, now in course of general acceptance, that pure chemical substances do not interact with each other[*].

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[*] Amongst common metals, the numeric of *zinc* is still much too uncertain. For *samarium* I have taken Bettendorff's value; for *zirconium*, Bailey's. The mean of Hardin's, Keiser's, and Joly & Leidié's not too concordant results has been accepted for *palladium*. Other authorities are Meyer and Lenker, *selenium* (mean); Seubert & Kobbe, *rhodium*; Morse & Jones, *cadmium*; Köthner and Pellini, *tellurium* (mean); Jones & Brauner and Pavlíček, *lanthanum* (mean); Jones and Van Schele, *praseodidymium* (mean); Jones, *neodidymium*; Cleve, *ytterbium*; Seubert, *osmium* and *rhodium*; Classen, *bismuth*; Mallet, *gold*. Erbia and terbia remain in considerable doubt. In some cases of modern recalculation confusion has arisen from taking former numbers—at one time announced as "on the hydrogen scale (1·00),"—as being on the *present* hydrogen scale (1·008).

LVIII. *On the Specific Ionization produced by the Corpuscles given out by Radium.* *By* J. J. E. Durack, 1851 *Exhibition Scholar, Trinity College, Cambridge*[*].

In a former paper[†] I have shown that the corpuscles in the Lenard-ray stream make on the average 0·4[‡] positive and negative ions in travelling through one cm. of air at a pressure of one mm. of Hg, or, if we suppose that a corpuscle creates a pair of ions at each collision with the molecules, these corpuscles make 0·4 collision under the conditions of distance and pressure specified above; this number measures what we may call the specific ionization produced by the corpuscles and will be denoted in what follows by the symbol α; it must be noted that we are dealing only with the ionization produced in air, α of course depends on the gas ionized.

Prof. Townsend[§] has shown that for the corpuscles[||] produced in air by Röntgen rays the number of ionizing collisions reaches a constant maximum value (equal to 20[¶]) when the velocity of the corpuscle exceeds a certain amount (about 10^8 cms. per sec.).

I have tried to show[**] that the very large difference in the values of α obtained by Townsend and myself can be accounted for by the difference in the velocities of the corpuscles in the two cases, the velocity of the Lenard rays in my experiments being about 4 10^9 cms. per sec.

If the difference be due to the difference in velocity, then, according to the theory indicated, α must decrease as the speed of the corpuscle increases, provided the corpuscle has sufficient energy to produce ions at all the velocities considered.

Now the velocity of the corpuscles given out by by radium (usually called the deflectable Becquerel rays) has been

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[*] Communicated by Prof. J. J. Thomson, F.R.S.

[†] Phil. Mag. ser. 6, vol. iv.

[‡] Starke & Austin (Drude's *Annalen*, Band ix.) have recently shown that 25 per cent. of the corpuscles in the cathode-rays are reflected on striking the surface of an aluminium plate at perpendicular incidence, this introduces an uncertainty in the value 0·4 given above, as it is not certain what becomes of the corpuscles after reflexion, they being under the influence of an electric field. If, in my former experiments, they return to the plate kept at constant potential without producing further ionization the number 0·4 will have to be reduced in the ratio of 4 to 3, *i. e.* to 0·3; at present 0·4 must be regarded as the probable upper limit of the quantity denoted by a.

[§] Phil. Mag. ser. 6, vol. i.

[||] See a paper by the same author in 'Nature,' vol. lxv. p. 413.

[¶] Further experiments have shown this number to be from 10 to 20 per cent. too large. Townsend, Phil. Mag. ser. 6, vol. iii.

[**] Phil. Mag. *loc. cit.*

measured by Kaufmann with great accuracy[*] and found to have all values between 2·36 10^{10} and 2·83 10^{10}, so that we should expect α for the deflectable Becquerel rays to be less than that for Lenard rays if the explanation offered be correct.

Townsend states in the paper first mentioned that an estimate of α for radium corpuscles was made by him and found to be at least 13[†], a number considerably greater than 0·4.

In the experiments I am about to describe it will be shown that the number 13 obtained by Townsend is about 76 times too large.

The radioactive substance used in my experiments was radium chloride obtained from the Société Centrale de produits chimiques and labelled initial activity 1000.

The radium[‡] was in the first experiments placed inside a closed vessel and covered with an aluminium plate, the leak being measured between this plate and another above it; the space surrounding the radium was in connexion with the space between the plates through a small hole in order to equalize the air-pressure in the two spaces.

With this apparatus the results of the experiments were difficult to interpret owing to apparatus inside becoming radioactive under the action of the "emanation" from the radium.

The radium was then taken outside and placed about 20 cms. away from the leaking system, so that the emanation could not penetrate to the leaking plates, and also it was certain that a magnetic field in the region in which the radium was placed would not appreciably affect the current between the plates directly.

It was found that in this position practically all the leak was due to deflectable Becquerel rays or the corpuscles from radium; the leak due to the corpuscles alone was, however, too small to be measured accurately, and the radium had to be moved closer to the leaking system.

The final arrangement is shown in fig. 1. One gram of radium was strewn uniformly over the bottom of a lead box B, the top of the box was covered with a thin aluminium leaf l 0·0043 mm. thick in two sets of observations, and with an aluminium plate 0·083 mm. thick in a third.

Above the radium a thick lead plate PP had a hole 2·5 cms. in diameter drilled in the centre, this was covered on top

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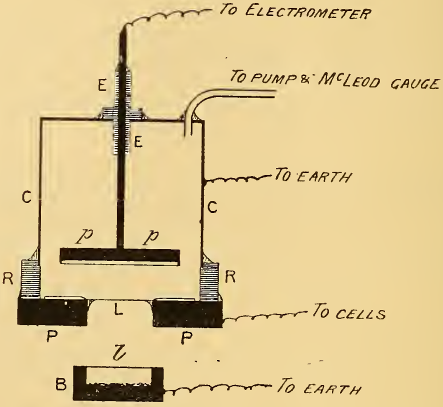
[*] *Nachrichten d. K. Gesell. d. Wissen. Gottingen*, 1901.

[†] In these experiments his electrometer was not sufficiently sensitive to measure the leak due to the corpuscles themselves, so that a lower limit only could be found.

[‡] This substance is generally spoken of as radium, though it is really mostly radium chloride.

with a plate of aluminium L 0·083 mm. thick, and made air-tight by screwing down a thicker plate of aluminium over it

Fig. 1.



and melting an elastic glue into the crevices. A ring of ebonite RR separated the brass box CC from the lead plate. Above the plate L and 13·5 mm. from it was placed another plate *pp*; the back of this plate was of lead, which was turned so as to form a thin rim of lead on the side nearer L; an aluminium plate similar to L was then placed over the rim and fastened to it so that there was an air-space between the aluminium and the lead ; *pp* was connected to a quadrant electrometer with a rod passing through the ebonite plug E and shielded from electrostatic effects.

The space inside CC was in communication with a pump and McLeod gauge.

All joints between metal and ebonite and between metal and glass were made air-tight with sealing-wax.

The plate PP was 8 cms. diameter, and the apparatus is drawn to scale in fig. 1.

During the time the observations were being made CC and B were kept connected to earth, and PP to one pole of a battery of storage-cells, the other pole being to earth. By keeping B connected to earth while P is charged to a high potential the ions formed in the air between B and P are destroyed, and consequently prevented from diffusing out and, may be, finding their way to the electrometer.

It is known from the experiments of Rutherford* that an aluminium plate 0·08 mm. thick is sufficient to absorb all the

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* See Rutherford and Miss Brooks, Phil. Mag. ser. 6, vol. iv. p. 5.

so-called "α" or non-deflectable rays, and hence the conductivity produced in the gas between PP and *pp* was due to the deflectable rays; this was verified by preliminary experiments on the action of a magnetic field on the rate of leak.

It has been shown by many experimenters that a metal plate struck by Röntgen or cathode-rays gives out negatively charged ions; moreover, that the rate at which these ions are given out is greater for the heavy metals than for the light ones, this effect is very small when Röntgen rays fall on an aluminium plate.

For this reason the plate *pp* has been made as described above; there will be very little absorption of the Becquerel rays by the aluminium plate on the face of *pp*, and consequently very little tendency to give out negative ions, practically all the absorption takes place in the lead, but this will not cause any error in the measured leak due to the corpuscles themselves unless these ions are given out with sufficient velocity to carry them back through the aluminium plate; from the experiments of Sagnac on the secondary ionization produced at the surface of a metal by Röntgen rays it is probable that they would not have sufficient velocity to do this.

The opposite surfaces of PP and *pp* being both of the same metal, there should be no error due to a contact P.D. effect.

The electrometer used in these experiments was of the Dolezalek type, the insulation of the quadrants being greatly improved and a gilt mica needle used instead of the paper needle of Dolezalek. The needle was kept charged to a constant potential by dipping the suspending quartz fibre into a solution of $CaCl_2$ and connecting the needle through the fibre to a battery [*].

The ordinary formula for the sensibility of a quadrant electrometer, *the needle being kept at constant potential* V_3, is

$$\theta = \frac{1}{\tau}\frac{dq_{11}}{d\theta}(V_1 - V_2)(V_3 - \tfrac{1}{2}\overline{V_1 + V_2})$$

where θ is the deflexion produced by a P.D. $(V_1 - V_2)$ between the two pairs of quadrants, τ is the torsion of the suspending fibre per unit angular displacement, and q_{11} is the coefficient of capacity of a pair of quadrants, all other conductors in the neighbourhood being kept at zero potential.

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[*] Dolezalek, *Zeits. für Instrument.* Dec. 1901.

If V_2 be kept constantly $=0$, and V_1 be small in comparison with V_3, this formula takes the usual form

$$\theta=\frac{1}{\tau}\frac{dq_{11}}{d\theta}V_1V_3.$$

Now it has been shown by Hopkinson* that the apparent capacity of a pair of quadrants (say the pair 1) when the needle is charged to a potential V_3 is equal to

$$q_{11}+\left.\overline{\frac{dq_{11}}{d\theta}}\right|^2\frac{1}{\tau}V_3^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(A)}$$

Suppose a quantity of electricity Q_1 given to the pair of quadrants 1, the potential V_1 will be

$$V_1=Q_1/q_{11}+\left(\frac{dq_{11}}{d\theta}\right)^2\frac{1}{\tau}V_3^2,$$

and for the formula A we may write

$$\theta/Q_1=\frac{1}{\tau}\frac{dq_{11}}{d\theta}V_3/q_{11}+\left(\frac{dq_{11}}{d\theta}\right)^2\frac{1}{\tau}V_3^2.$$

Hence θ/Q_1 (which is the sensibility for current) has a maximum value for a certain value of V_3, viz. :—

$$V_3=\sqrt{q_{11}\tau}\left(\frac{dq_{11}}{d\theta}\right).$$

When high sensibility for leaks is an important factor the needle should be charged to this potential, and even when high sensibility is not required it is advisable to work with the electrometer at its maximum sensibility, for then small changes in V_3 make no change in θ/Q_1.

The value of V_3 for which θ/Q_1 is a maximum is easily found by measuring the capacity of a pair of quadrants and finding for what value of V_3 this capacity is equal to $2q_{11}$, *i. e.*, twice the capacity when $V_3=0$. With my electrometer this was the case when V_3 was equal to 60 volts. The observations from which α was to be deduced were made as follows :—The plate PP was connected to one pole of a battery of cells (say the positive pole), the other pole being to earth, a small P.D. was set up initially between the two pairs of quadrants, the insulated pair being initially negative with respect to the earthed pair if the leak to be measured was positive, and positive if the leak was negative; thus the needle travelled through its zero position in taking a reading, which was done by finding the time required for the light-spot to pass over a certain number of divisions on the scale, these divisions being half on one side and half on the other side of the zero.

By reading in this way the effect of changes in capacity

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* Phil. Mag. ser. 5, vol. xix.

for different deflexions (which are, however, usually very small) is eliminated, and leaks due to faulty insulation are minimized, these leaks helping the leak to be measured for half the time and opposing it for the other half.

It is of great importance that the P.D. between PP and *pp* should be sufficient to saturate the gas, *i. e.*, to remove the ions as fast as they are formed.

In the first two series of observations the current was measured for several different P.D.'s, and in the third a P.D. was always applied which was known from the previous observations to be sufficient to produce saturation. The nature of the current-E.M.F. curves may be seen from the results given in Table I. and plotted in fig. 2.

Fig. 2.

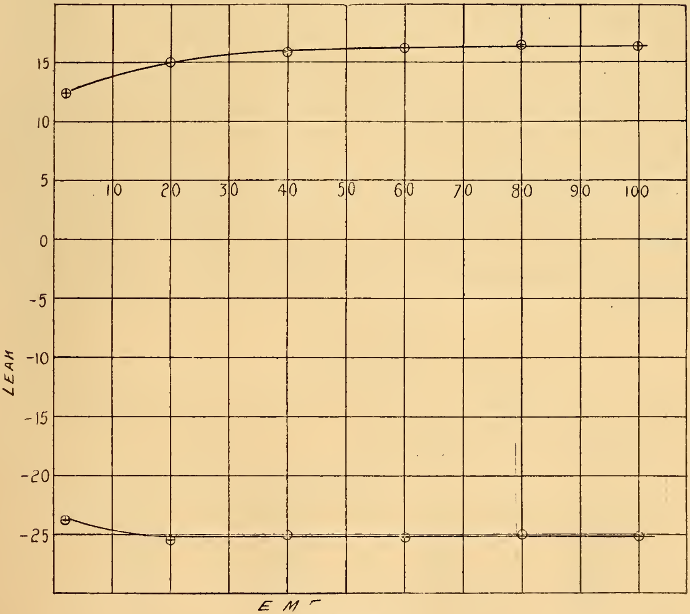

TABLE I.

Pressure.	P. D.	Current.	
		Lower Plate +.	Lower Plate −.
19·0	2	+12·4	−23·8
	20	+15·0	−25·5
	40	+15·8	−25·0
	60	+16·1	−25·2
	80	+16·4	−25·0
	100	+16·3	−25·1

The first column gives the pressure in mm., the second column the average P.D. during the leak between PP and *pp* in volts, the third column the current when PP was connected to the positive pole of the battery, and the fourth the current when the field was reversed.

The positive current is taken in the direction PP to *pp*, so that *pp* receives a positive charge, the unit of current here, as in all the tables and curves, is 10^{-14} amp.

It will be seen from fig. 2 that at a pressure of 19 mm. the gas is practically saturated with a P.D. of 40 volts.

Care must be taken, not only that the E.M.F. is sufficient to saturate the gas, but also that it is not too great, otherwise the negative ions generated by the Becquerel rays may, as has been shown by Townsend (*loc. cit.* Phil. Mag. vol. i.), themselves generate other ions; calculation from Townsend's numbers shows that the effect would begin to be evident in my experiments when $V=45\,p$, where V is the P.D. in volts and p is the pressure in mm. In all the tables V is less than $45\,p$.

As all the observations could not be carried out in a single day, and the radium had to be kept dry to prevent it from deteriorating in strength, the box B was removed at the end of each day and kept in a drying-apparatus, stops were made for B to fit into so that it could be replaced in the same position on the following day, to make sure that this was so the last readings of the previous day were repeated each morning.

Table II.

Pressure.	P. D.	Current.	
		Lower Plate +.	Lower Plate −.
20·5	60 to 100	+18·4	−28·8
15·7	100	+12·9	−23·0
12·0	,,	+ 8·6	−18·3
9·3	60 to 100	+ 6·0	−14·7
7·3	20 to 100	+ 3·5	−12·7

The first series of observations for the determination of α is given in Table II. and plotted in fig. 3; when these five points were determined the box B was accidentally knocked, and the exposed surface of the radium thereby considerably altered, as was seen afterwards on removing the thin aluminium leaf which covered B when the observations given in Tables II. and III. were taken.

Fig. 3.

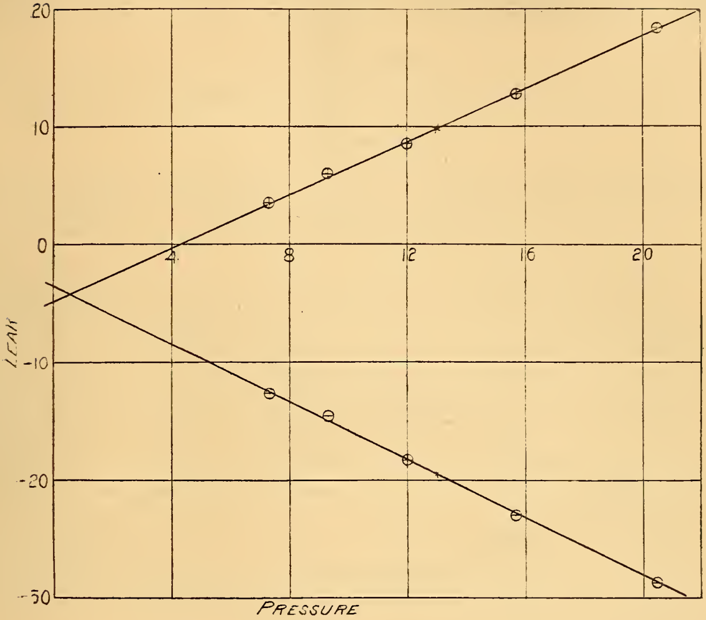

TABLE III.

Pressure.	P. D.	Current.	
		Lower Plate +.	Lower Plate —.
0·68	2 to 20	−2·82	− 4·20
2·52	20 to 40	−1·34	− 5·90
5·26	”	+1·20	− 8·34
7·9	”	+3·36	−10·8
10·7	20 to 100	+5·60	−13·5

The numbers given in Table IV. and plotted in fig. 5. were found with an aluminium plate 0·083 mm. thick on the top of B.

The lines in figs. 3, 4, and 5 have all been drawn through the centroid of the points* which is marked with a cross, the

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* See Pearson "On the Lines and Planes of Closest Fit," Phil. Mag. ser. 6, vol. ii.

centroid of n points, whose coordinates are x_1, x_2, &c., y_1, y_2, &c., being defined by the coordinates

$$\bar{x} = \frac{\Sigma x}{n},$$

$$\bar{y} = \frac{\Sigma y}{n}.$$

Fig. 4.

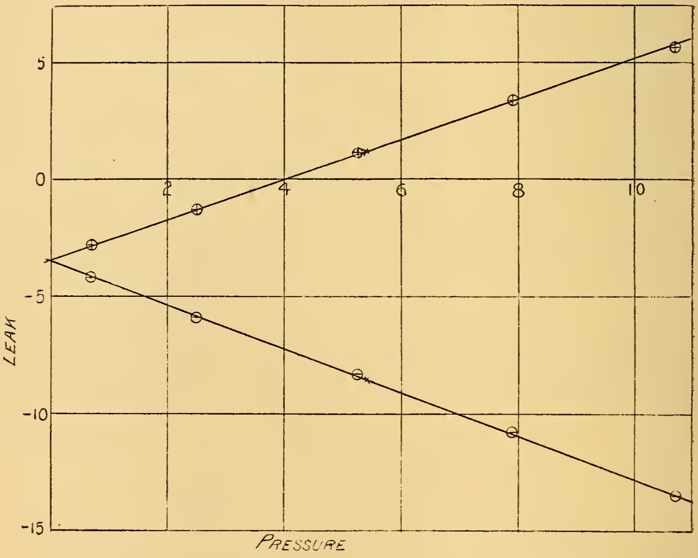


TABLE IV.

Pressure.	P. D.	Current.	
		Lower Plate +.	Lower Plate −.
10·7	60	+5·40	−13·2
7·8	,,	+3·03	−10·3
5·6	,,	+1·36	− 8·4
4·04	,,	+0·09	− 7·2
2·92	20 to 60	−1·15	− 6·0
2·13	,,	−1·60	− 5·44
1·51	,,	−2·24	− 4·86
1·08	,,	−2·80	− 4·58
0·50	2	−3·56	− 4·36
0·015	0	−3·90	− 3·90

Figs. 3, 4, and 5 show that the relation between current and pressure is of the form

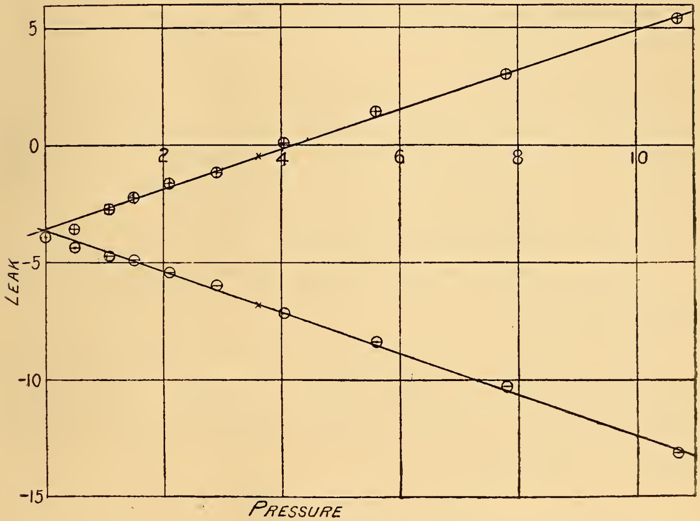
$$\gamma_1 = -c + mp$$

when the lower plate is charged positively, and

$$\gamma_2 = -c - mp$$

when charged negatively, γ_1 and γ_2 denoting the currents, p the pressure, and m and c positive constants.

Fig. 5.



The interpretation of this result is very simple: we have negatively charged corpuscles constituting the deflectable Becquerel rays travelling from PP to *pp* at a rate independent of the pressure, on their way they produce equal numbers of positive and negative ions in the gas, the rate of production being proportional to the pressure.

Let N_0 be the number of corpuscles passing per second through L and e the charge carried by a single corpuscle, then the current due to the corpuscles alone is $-N_0 e$.

Suppose that each corpuscle makes α collisions in traversing one cm. of the gas at a pressure of one mm., let p be the pressure, d the average distance travelled by the corpuscles in going from PP to *pp*, and e' the charge carried by the ions generated in the gas.

When the lower plate is charged positively *pp* will collect positive ions from the gas, and the total current will be

$$\gamma_1 = -N_0 e + N_0 e' \alpha p d.$$

When the field is reversed *pp* will collect negative ions from the gas, and the current will be

$$\gamma_2 = -N_0 e - N_0 e' \alpha p d.$$

It has been shown by many experimenters that e/m, the ratio of the charge to the mass, is approximately the same for cathode-rays, Becquerel rays, the ions producing the Zeeman effect, and the ions given off by Zn under the action of ultra-violet light, and 1000 times greater than that for the H ion in electrolysis. It has also been shown by J. J. Thomson * (by direct measurement of both) that the charge carried by the ions given out by Zn is the same as the charge on the ions produced in air by Röntgen rays. Townsend † has proved, by direct comparison, that the charges on the ions produced in air by Röntgen rays, Becquerel rays, and point discharges, and on the ions given off by Zn are all equal to the charge carried by the H ion in electrolysis.

The same experimenter has shown ('Nature,' *loc. cit.*) that the ions produced in air are identical as regards mass and charge with the ions given off by Zn under the action of ultra-violet light.

From these facts Prof. Thomson has concluded that in all these cases the charges carried by the negative ions are all equal, and the mass of the carrier about 1000 times smaller than the H atom. Hence in the equations 1 and 2 we may put $e = e'$ and we have

$$\gamma_1 = -N_0 e(1 - \alpha p d) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\gamma_2 = -N_0 e(1 + \alpha p d) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From which we obtain

$$-N_0 e = \tfrac{1}{2}(\gamma_1 + \gamma_2)$$

and

$$\alpha = \frac{1}{pd}\left(\frac{\gamma_2 - \gamma_1}{\gamma_1 + \gamma_2}\right).$$

To find the average distance travelled by the corpuscles between PP and *pp* we know from Becquerel's experiments on the velocity of the deflectable Becquerel rays, that the corpuscles are projected in all directions from the surface of the radium, hence in these experiments d will lie between 13·5 mm. (the perpendicular distance between the plates) and 14·3 mm. and cannot be far from 14 mm.

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* Phil. Mag. Dec. 1899.

† Phil. Trans. 1899, 1900.

The average values of N_0e and of α for all the observations in any series of experiments are found directly from figs. 3, 4, and 5, being the values deduced from the position of the centroid in the three cases.

The centroids are given by

III.	IV.	V.
$\overline{p} = 13{\cdot}0$	$\overline{p} = 5{\cdot}42$	$\overline{p} = 3{\cdot}63$
$\overline{\gamma_1} = +\ 9{\cdot}88$	$\overline{\gamma_1} = +1{\cdot}2$	$\overline{\gamma_1} = -0{\cdot}54$
$\overline{\gamma_2} = -19{\cdot}5$	$\overline{\gamma_2} = -8{\cdot}55$	$\overline{\gamma_2} = -6{\cdot}8$

Hence we find

$N_0e = 4{\cdot}8$ III. and $\alpha = {\cdot}168$ III.
$= 3{\cdot}7$ IV. $= {\cdot}175$ IV.
$= 3{\cdot}7$ V. $= {\cdot}168$ V.

The values of N_0e obtained show that the effect of putting an aluminium plate over B (and practically doubling the distance travelled by the corpuscles before they reach the place where the ionization was measured) was to reduce the Becquerel ray current in the ratio of 4·8 to 3·7.

The tilting of the radium also reduced this current as we should expect, for the surface exposed was thereby decreased. This accounts for N_0e being less in fig. 4 than in fig. 3.

The effect on α is hardly appreciable, for the difference only amounts to about 4 per cent. which is inside the limit of possible error.

From the values of α given above it may been that the mean free path of the Becquerel ray corpuscles in air at 1 mm. is about 6 cms. This very large value for the mean free path accounts for the very small absorption of the deflectable Becquerel rays.

In conclusion, my thanks are due to Prof. J. J. Thomson for many suggestions given during the progress of the work.

Cavendish Laboratory, Cambridge.

LIX. *Condensation of the Radioactive Emanations.* By E. Rutherford, *M.A.*, *D.Sc.*, *Macdonald Professor of Physics, McGill University, Montreal, and* F. Soddy, *M.A. (Oxon.)*.

[Plate XIV.]

IN a previous paper (Phil. Mag. 1902, iv. p. 581) we have shown that the radioactive emanation from thorium passes in unchanged amount through a white-hot platinum tube and through a tube cooled to the temperature of solid carbon

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* Communicated by the Authors.

dioxide. The acquisition of a liquid-air machine by the laboratory has enabled us to investigate the effect of lower temperature on the emanations from both thorium and radium. The result has been to show that both emanations condense at the temperature of liquid air, and possess sharply defined points of volatilization and condensation.

If either emanation is conveyed by a slow stream of hydrogen, oxygen, or air through a metal spiral immersed in liquid air, no trace of emanation escapes in the issuing gas. When the liquid air is removed and the spiral plunged into cotton-wool, several minutes elapse before any deflexion of the electrometer-needle is observed, and then the condensed emanation volatilizes as a whole, and the movement of the electrometer-needle is very sudden, especially in the case of radium. With a fairly large amount of radium emanation under the conditions mentioned, a very few seconds elapse after the first sign of movement before the electrometer-needle indicates a deflexion of several hundred divisions of the scale per second. It is not necessary in either case that the emanating compound itself should be retained in the gas-stream. After the emanation is condensed in the spiral the thorium or radium compound may be removed and the gas-stream sent directly into the spiral. But in the case of thorium under these conditions the effects observed are naturally small, owing to the very rapid loss of activity of the emanation with time, which experiment showed occurs at the same rate at the temperature of liquid air as at ordinary temperatures. As a matter of fact, in the case of radium the salt itself was seldom used. It was convenient to obtain the emanation from the solution and store it mixed with air in small gas-holders, the loss of activity during the course of a day's experiments being only a small part of the whole.

If the radium emanation is condensed in a glass U-tube, the progress of the condensation can be followed by the eye by means of the fluorescence which the radiations excite in the glass. With a sufficiently slow gas-stream the fluorescence is confined to the limb where the gas enters. If the ends of the tube are sealed and the temperature allowed to rise, the glow diffuses throughout the tube, and can be again concentrated at any point to some extent by application of a pad of cotton-wool soaked in liquid air. The U-tube can be made to impress its own image on a photographic plate through aluminium-foil, and the impression is uniformly dense throughout the length of the tube. It retains its luminosity to a feeble extent after several days.

The suddenness of the volatilization-point of the condensed emanation is very remarkable considering the minuteness of the actual amount of matter that must be involved. Arrangements were made to investigate the phenomena in an accurate quantitative manner. The method adopted was to condense the emanations in a spiral copper tube and to employ the latter as its own thermometer by determining its electrical resistance. For this purpose a constant current was maintained through the spiral, and the fall of potential between two fixed points on the spiral was determined by means of a Weston millivoltmeter. This method proved very reliable and convenient. A great number of preliminary experiments showed that to obtain accurate results two requirements must be satisfied. In the first place, since the temperature measured is the average temperature of the whole spiral, the latter must be completely immersed in a bath of liquid kept well stirred. In the second place, in order to be sure that the spiral was not heated locally by the entering gas-stream, it was necessary to subject the latter to a preliminary cooling to the desired temperature. This was accomplished by the apparatus represented in fig. 1 (Pl. XIV.). The spiral and connecting tubes were made out of a continuous copper tube of length 310 cms., internal diameter 2 mm., and thickness of wall ·32 mm. This was first wound into an inner spiral of 16 turns of mean diameter 1·80 cm., which was soldered together into a compact cylinder. This effected the preliminary cooling of the gas-stream. The tube was then wound back over the inner spiral into an outer spiral of 14 turns of mean diameter 2·90 cms. The turns of the outer spiral were separated from each other and from the inner spiral by air-spaces. The outer spiral constituted the thermometer, and the potential-leads were soldered on to the top and bottom and inclosed in glass tubes. The system was supported inside a glass cylinder closed at the bottom, of height 41 cms. and diameter 3·5 cms., by means of an air-tight rubber cork fitting the open end, through which the ends of the spiral and the leads passed. A small stirrer at the bottom of the tube was driven by a central rod passing through a suitable bearing supported by the inner spiral, and through a glass tube in the centre of the cork. This rod was operated by an electric motor supported above the cork. The spiral was kept from actual contact with the glass by a sheet of mica perforated into holes, and was given sufficient rigidity by means of an ebonite ring fitting tightly into the space between the upper part of the inside and outside spiral. A current was sent (fig. 2, Pl. XIV.) through the spiral by means of leads soldered above the cork from a storage-battery, passing through a Weston ammeter and sliding-resistance. By means of the latter the current was kept always constant at 0·900 amp. The potential-leads were connected with a Weston millivoltmeter which registered at ordinary temperature a deflexion of about 6 millivolts, or 60 divisions on the scale, at the temperature of liquid air rather less than 2 millivolts. This corresponds to a resistance at ordinary temperature of about ·01 ohm., and it can readily be shown that the heating effect of the current in the spiral is negligible. No substance seems to be known which is liquid at the ordinary temperature and remains liquid at the temperature of condensation of the radium emanation (about −150°). Ethyl chloride most nearly fulfils this condition, but solidifies in the neighbourhood of −140° C. A bath of this substance, however, proved useful in one series of measurements with the thorium emanation. The rest of the determinations were carried out in a bath of liquefied ethylene. This boils at −103°·5 and freezes at −169°, and gave just the range of temperature desired in these experiments. About 70 litres of the gas, purified by fractional distillation, was ordinarily used. This was sent into the apparatus by the tube A, Pl. XIV. fig. 1, escaping by the tube carrying the stirring-rod. The liquefied ethylene always covered the top of the spiral to the depth of several centimetres. The apparatus was surrounded by a tall copper cylinder well covered with lagging which contained the liquid air. Copper was preferable to glass for the purpose, for it ensured in the actual determinations a more uniform supply of heat to the apparatus.

Calibration of the Copper Thermometer.

The readings of the voltmeter described were determined at the following temperatures: 100°, 0°, the boiling-point of ethylene −103°·5, the freezing-point −169°, and the temperature of liquid air. The ethylene employed was carefully fractionated for this purpose. 120 litres were condensed and the first and last 20 litres rejected, the determinations being made with the middle fraction. The temperature of liquid air is a variable, depending on the composition of the liquid, but if the latter is known the temperature can be fixed with great accuracy from the tables given by Baly. A sample was therefore drawn off into a gas-holder from beneath the surface of the liquid, at the time the temperature was read, and its composition determined by analysis. These constants were frequently redetermined throughout the course of the experiments and found to remain unaltered.

The following table represents the results :—

Temperature.	Resistance (ohms).	Ratio.
100° C.	·00947	135·1
0°	·00701	100
−103°·5	·00437	62·3
−169°	·00262	37·4
−192°·2	·00202	28·8

In the last column the ratio of the resistance is given, the value at 0° being taken as 100. In Pl. XIV. fig. 3 the results are plotted with the resistance as ordinates and the temperature as abscissæ. It will be observed that the curve is very nearly a straight line cutting the axis, if produced, at very nearly the absolute zero. For the particular thermometer used, therefore, the readings of the millivoltmeter may be taken without appreciable error to be proportional to the absolute temperature. The instruments employed were accurately calibrated. The accuracy of the temperature determination by this method depends only on the sensitiveness of the millivoltmeter. At the temperature at which most of the observations were made, one division of the scale corresponded to about 4° C., and the readings could be made to 1/10 of a division. The determinations were therefore accurate to within 0°·5, which was sufficient for the purpose. The great advantage of the method is the ease and certainty with which a continually changing temperature can be followed.

Experiments for the Radium Emanation with a steady current of Gas.

Experiments with the radium emanation are much simpler than for that of thorium, since the activity does not decay appreciably over the time required for a complete series of observations, and much larger effects can be obtained. Pl. XIV. fig. 2 represents the general arrangement of the apparatus for the determination of the volatilization temperature of the radium emanation in a steady current of gas. The latter (either hydrogen or oxygen) was conveniently obtained from a set of eight voltameters, arranged in series across the 110 volt circuit and capable of taking a current up to 3 amperes. The latter, measured by a Weston ammeter, furnished a measure of the number of c. c. of gas passing per second. This enters the apparatus at A. The radium emanation mixed with air is stored in the gas-holder B. The exit of the copper spiral is connected with a testing-cylinder T of the kind previously described, in which the ionization current through the gas, due to the rays from the emanation, is measured by the electrometer E. D is a drying-tube.

The ethylene bath was cooled by liquid air slightly below the temperature of condensation, and a definite volume of the emanation was sent into the apparatus from B, and conveyed by a very slow gas-stream for 10 minutes into the spiral so that it was condensed near the beginning of the spiral. The current of gas to be employed is then adjusted and the temperature of the bath allowed to rise slowly. One observer took the determinations of the temperature and the lapse of time, the other the readings of the electrometer. The temperature at which the electrometer-needle commenced to move was recorded, and the rate of movement at succeeding temperatures. In most of the experiments the temperature rose at a rate of about 1°·6 to 2° per minute.

The following table gives an illustration of the results obtained:—

Temperature.	Divisions per second of the electrometer.
−160°	0
−156°	0
−154°·3	1
−153°·8	21
−152°·5	24

The observed temperature of the first appearance of the emanation is subject to a correction for the time taken for the emanation to be swept into the testing-vessel after volatilization. This depends on the volume of the spiral and its temperature, and on the current of gas, and can be approximately calculated for each experiment. Knowing the rate of rise of temperature in the experiment the actual temperature at which volatilization commenced could be deduced. In the table given above for a gas-stream of 1·38 cms. per second the application of this correction lowers the temperature of volatilization about 0°·8 C. The following table includes some of the corrected results for the radium emanation. Under the column T_1 the temperatures at which the emanation began to volatilize are given, under T_2 the temperatures at which one half of the total amount had been given off.

Gas.	c. c. per second.	T_1.	T_2.
Hydrogen. . .	·25	−151·3	−150
	·32	−153·7	−151
	·33	−153·7	−151
	·92	−152	−151
	1·38	−154	−153
	2·3	−162·5	−162
Oxygen . . .	·34	−152·5	−151·5
	·33	−152·5	−151·5
	·58	−155	−153

With hydrogen streams from ·25 c. c. to 1·38 c. c. per second and for the slow stream of oxygen the results are in good agreement and give a mean value for T_1 of $-153°$, for T_2 $-151°·5$. But a well-marked difference appears when the stream of hydrogen is increased to 2·3 c. c. per second. This corresponds to an initial velocity of 50 cms. a second through the spiral, and 20 cms. per second after the temperature of the bath has been obtained. The result is therefore to be expected, for in such a rapid stream the gas is not cooled down to the temperature of the spiral and the volatilization-point of the emanation is in consequence apparently lower. For the same reason the temperature observed for the oxygen stream of only ·58 c. c. a second is probably too low, for this gas is cooled with more difficulty than hydrogen. Even if the temperature of the spiral is ultimately attained, a rapid current of gas would tend to sweep out the emanation it had volatilized in its passage, without giving it time to be recondensed in the subsequent portions of the spiral. This effect, for reasons to be discussed later, would also be greater in oxygen than in hydrogen. Further determinations for the radium emanation by another distinct method are given later in the paper.

At this stage some experiments may be mentioned that were performed with a much larger quantity of radium emanation to determine the amount that is volatilized at various temperatures. In one experiment at $-154°$, no escape of emanation was observed although less than 1/10000 part could have been detected. At $-152°$ about one half per cent. and at $-150°$ considerably more than half of the total amount had come off. There is no doubt that in a bath, kept constant at the temperature of initial volatilization, all would volatilize if sufficient time were allowed, but it is probable that the time required would be considerable. There is in fact evidence that the condensed radium emanation possesses what corresponds to a vapour-pressure in an ordinary substance.

Experiments for the Thorium Emanation by the same Method.

The rapid loss of the activity of the thorium emanation, which decays to half value in one minute, makes the determination of its volatilization-point a more difficult task. In the first place too slow a gas-stream cannot be employed or the ionization effects are too small. In the second place the thorium compound must be retained all the time in the gas-stream, unless the temperature of the spiral is made to rise so rapidly that its determination becomes impracticable. The results therefore bear a different interpretation from those given for radium, for in this case the point measured is the temperature at which some of the thorium emanation *first escaped condensation*. and not the point at which volatilization begins of that already condensed. In place of the T-tube and gas-holder of fig. 2 (Pl. XIV.) a highly emanating thorium compound was placed in series with the gas-stream, and the temperature T observed at which the emanation first began to make its appearance in the testing-vessel. The following are some of the results obtained :—

Gas.	c. c. per Second.	T.
Hydrogen	·71	−155° C.
	1·38	−159°
Oxygen	·58	−155°·5
	·58	−156°
	·58	−155°·5

If these results are compared with those obtained for the radium emanation it will be seen that the temperatures with an equal gas-stream in the two cases are very nearly the same. Thus, in the determinations in an oxygen stream of ·58 c.c. per second, the radium emanation commenced to volatilize at −155°, and some of the thorium emanation escapes condensation at −155°·5 C. It was at first thought that this result indicated that the condensation-points of the two emanations were identical. It will be recalled that no difference could be detected in the chemical properties of the two emanations, both being quite unaffected by the most powerful chemical reagents. Yet it seemed improbable that the two emanations could be materially identical on account of the completely distinct character of their radioactive properties. Not only are their rates of decay widely different, being 5000 times faster in the one case than the other, but the excited activities they give rise to are also completely different, not only in the rate of decay, but even in the number of changes through which they apparently pass before their activity disappears. In the course of further work a very distinct difference of behaviour in the condensation phenomena in the two cases was brought to light. It was observed that some of the thorium emanation was condensed at temperatures as much as 30° above the point of complete condensation. The curve fig. 5 (Pl. XIV.) is an example of the results obtained. The maximum ordinate taken as 100 represents the amount of emanation entering the testing-vessel at temperatures far above the point at which condensation commences. This amount begins to decrease at about −120°, and becomes less than 1 per cent.

of its original value at −154°. This curve was obtained in a steady stream of oxygen of ·38 c.c. per second. For faster currents the curve is displaced slightly to the right.

When tested under the same conditions, the radium emanation showed no such behaviour. When the solution of radium chloride is retained in the gas-stream, the temperature at which some of the emanation escapes condensation is only slightly above the point before found at which the condensed emanation commences to volatilize. Apart from the question of the actual condensation-points themselves, there is, therefore, a well-marked distinction in the character of the phenomena in the two cases. To investigate this difference, a new method was devised which allowed determinations to be made with the two emanations under comparable conditions.

Experiments by the Static Method.

The use of a steady stream of gas through the spiral in which the emanation is condensed has many disadvantages, some of which have been alluded to. By the use of a mercury-pump, and by working in a partial vacuum, these disadvantages are avoided, and the conditions of experiment made more definite. Pl. XIV. fig. 4 represents the arrangement employed.

The Geissler pump P was connected with the copper spiral S and the thorium compound in the tube A, and possessed a volume large in comparison with the volume of the whole of the rest of the apparatus. The small bulb V was first filled with hydrogen or oxygen entering at C, and the thorium tube-spiral and connecting-tubes exhausted by the pump to a pressure of a few millimetres of mercury. The three-way tap was then reversed, the tap E being open and F closed. In this way a quantity of the emanation was swept out of A into the spiral; E was closed, and the emanation allowed to remain in the spiral a definite time. This period varied in different experiments from 10^s to 90^s. At the expiration of this interval, the pump in which the mercury had been lowered was put into communication with the spiral by the tap F, which was then closed, the mercury raised, and the emanation expelled into H and carried on to the testing-vessel by a steady current of oxygen entering the tube at K, and kept continuously passing throughout the experiment. The pressures employed were deduced from the readings of the height of the mercury in the pump-tube when the mercury was lowered, and the relative volumes of various parts of the apparatus. The various manipulations of the taps and of the mercury-pump were all timed throughout by a stop-watch, and the observations with the electrometer were always taken at the same interval after the commencement of the operations. In this way the decay of activity of the emanation was the same in each experiment, and the results obtained in different experiments comparable with one another. One observer took charge of the manipulation of the apparatus, the other recorded the lapse of time, the temperature of the spiral at the instant the contents were drawn into the pump by opening the tap F, and the readings of the electrometer after the emanation had been sent into the testing-vessel. The latter could be taken within 90 seconds from the time the emanation was removed from the thorium in those cases where it remained in the spiral for a period of 30 seconds. The tap F was a three-way, so that the pump could be cut out of the circuit and experiments in a steady stream of gas carried on without alteration of the apparatus. The amounts of the emanation that remain uncondensed at different temperatures are shown graphically in fig. 6, Pl. XIV. The different curves represent different series of observations with hydrogen and oxygen respectively, in which the time during which the emanation remained in the spiral was in some cases 30 seconds, in others 90 seconds. Curves A and B illustrate the difference in the condensation-curves for hydrogen and oxygen under similar conditions. The pressure in the spiral after the removal of the uncondensed emanation corresponded to 19 mm. of mercury. The curves show that a greater proportion of the emanation is condensed for the same temperature in hydrogen than in oxygen. The curves C and D, which were obtained under different conditions of pressure and amount of emanation from curves A and B, show that a greater proportion is condensed in 90 seconds than in 30 seconds. The proportion condensed in a steady stream is less than in any of the experiments by the static method. In all cases, however, condensation commences at about the same temperature, viz., −120° C., and there is no doubt that this must be taken as the real condensation-point of the thorium emanation, and that the identity in the temperatures observed in the earlier experiments with a steady stream must be regarded as purely accidental.

Experiments with the Radium Emanation.

The apparatus (fig. 4, Pl. XIV.) was slightly altered for the determination of the volatilization-point of the radium emanation. The thorium tube was replaced by a drying-tube of calcium chloride and the bulb V filled with air mixed with the radium emanation which was then allowed into the exhausted spiral kept below the temperature of condensation. The apparatus was then repeatedly exhausted by the pump, and after each exhaustion a bulb-full of oxygen was sent into the spiral, the temperature of the bath being allowed to rise slowly during the exhaustion. The temperature at which the first trace of emanation escaped and the amounts at succeeding temperatures were noted as before. The following table is an example of the results obtained :—

Temperature.	Divisions of Electrometer per second.
−153°	0
−151°	0
−148°·5	·74
−146°·5	5·3
−143°	5·1
−139°	·7
−135°	·08

The mean of several results gave −150° as the point at which the emanation first began to volatilize, and this is in good agreement with the result by the blowing method, that is, −153°. The difference is in the expected direction, for in the static method the mass of the gas employed is much smaller, and any emanation that is volatilized by the rush of heated gas in its passage through the spiral has time to be recondensed. The temperature −150° C. may therefore be taken with considerable confidence as being the true point at which the radium emanation first commences to volatilize. On the other hand, the table shows a somewhat less sudden volatilization than in the case of the blowing method, but this is inherent to the static method employed. The glass spiral connecting-tube between the pump and the copper spiral had a greater volume than the latter itself, and at each exhaustion some of the volatilized emanation is left in this spiral. In the case of the thorium emanation this decays practically to zero before the next observation is taken, but in the case of the radium emanation it does not, and is added to the amount removed at the next exhaustion. The temperature of volatilization found in these experiments has almost exactly the value given by Ramsay and Travers for the boiling-point of nitric oxide under atmospheric pressure 149°·9 C. A bath of liquified nitric oxide was prepared, and used in place of the ethylene in former experiments. Its boiling-point rose steadily until about one-fifth had boiled off. It then became constant at −151° C., as determined by the resistance of the copper spiral, and remained so until the latter began to be no longer completely covered. The nitric oxide was not sufficiently pure to enable much weight to be put on this result as a determination of temperature, for from its behaviour it obviously must have contained a considerable quantity of dissolved nitrogen, but it is of interest as being a completely independent check on the thermometer at almost the exact point of condensation, and shows that the value ascribed to the latter cannot be far from the truth. Such a bath of boiling liquid rising very slowly in temperature over the exact range in which volatilization takes place, afforded a means, however, of examining more exactly the progress of the volatilization after the initial point was reached. The latter occurred in this case at −155° C., a steady current of air being maintained through the spiral. In four minutes the temperature had increased to −153°·5, and the amount volatilized was about four times as great as at −153°. In the next 5½ minutes the temperature had increased to 152°·3, and the whole amount practically had volatilized, which was at least fifty times the amount at the temperature of −153°·5. Such a result would of course be explained by slight local inequalities in the temperature of the spiral, but since the latter was immersed in a rapidly boiling liquid it is difficult to believe that such could have been the case. It seems more reasonable to attribute it to a true vapour-pressure possessed by the condensed emanation, although great refinement in the experimental methods would be necessary before such a conclusion could be considered established.

The Explanation of the Anomalous Behaviour of the Thorium Emanations.

The results obtained are satisfactory in so far as they show that the two emanations do not condense at the same temperature. The anomalous behaviour of the thorium emanation in condensation, which in the first experiments seemed to indicate that the two emanations condensed at the same temperature, has been shown to be due to an effect, not present in the case of the radium emanation, which depends on the nature of the gas, the concentration of the emanation, and the time that the latter has been left to condense. It remains to develop a view which gives a satisfactory explanation of this behaviour. In the first place the actual number of particles of emanation that are present must be almost infinitesimally small compared with the number of particles of the gas with which they are mixed. It is difficult to make an accurate calculation of the number actually present, but an estimate of the order of the number present can be deduced from the following considerations. The radiation from the thorium and radium emanations consists, as far as it is known, entirely of α rays. The view has recently been put forward that these, in the case of radium, consist of projected particles of the same order of mass as the hydrogen atom, carrying a positive charge, and travelling with a velocity about 1/10 the velocity of light. It is extremely likely that the radiations from the two emanations are quite comparable in character, and produce in their passage through the gas a similar number of ions. From results deduced from experiments made in an attempt to measure the charge carried by the α rays there is no doubt that each of these projected particles produces at least 10^4, and possibly 10^6, ions in its path before being absorbed in the gas. For the present purpose, 10^5 ions will be taken as a probable value. The electrometer employed readily measured currents of 10^{-3}E.S. units per second. Taking the charge on an ion as 6×10^{-10} E.S. units, this corresponds to a production of $1{\cdot}7 \times 10^6$ ions per second, which would be produced by 17 expelled "rays" per second. Each radiating particle cannot expel less than one ray, and may expel more, but it is likely that the number of rays expelled by a particle of the thorium emanation is not greatly different from the number expelled by a particle of the radium emanation. The view will be developed more generally in a subsequent paper*, that the decay of activity of a radioactive substance is caused by the number of particles present diminishing owing to their changing into new systems, the change being accompanied by the expulsion of rays. From the law of the rate of decay $I_t = I_0 e^{-\lambda t}$, on this view λN particles change per second when N are present. Therefore to produce 17 rays per second λN cannot be greater than 17. Since in the case of the thorium emanation λ equals 1/87, it follows that N cannot be greater than 1500. The electrometer used therefore detects the presence of about 1500 particles of the thorium emanation, and since, in the static method, the volume of the condensing spiral was about 15 c. c., this corresponds to a concentration of about 100 particles per c. c. An ordinary gas at atmospheric pressure probably contains 10^{20} particles. On this estimate therefore the thorium emanation could have been detected if it possessed a partial pressure in the condensing spiral of 10^{-18} atmosphere. It is thus not surprising that the condensation-point of the thorium emanation is not

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* *Infra*, p. 576.

sharply defined. It is rather a matter of remark that condensation can occur at all with such sparse distribution of emanation particles in the gas, for in order for condensation to take place the particles must first approach within each other's sphere of influence.

Now consider the case of the radium emanation. The rate of decay is about 5000 times slower than that of the thorium emanation, and consequently the actual number that must be present to produce the same number of rays *per second* in the two cases must be of the order of 5000 times greater for the radium than for the thorium emanation. This conclusion involves only the assumptions that the same number of rays are produced by a particle of emanation in each case, and that the rays expelled produce in the passage through the gas the same number of ions. The number of particles that must be present for the electrometer to detect them in this experiment must therefore be about 5000 × 1500, *i. e.* of the order of 10^7. The difference of behaviour in the two cases is well explained in the view that *for equal electrical effects* the number of radium emanation particles must be far larger than the number of thorium emanation particles. It is to be expected that the probability of the particles coming into each other's sphere of influence will increase very rapidly as the concentration of the particles increases, and that in the case of the radium emanation, once the temperature of condensation is attained all but a negligibly small proportion of the total number of particles present will condense in a very short time. In the case of the thorium emanation, however, the temperature might be far below that of condensation, and yet a considerable proportion remain uncondensed for comparatively long intervals. On this view the experimental results obtained are exactly accounted for. A greater proportion condenses the longer the time allowed for condensation under the same conditions. The condensation occurs more rapidly in hydrogen than in oxygen, owing to the diffusion being greater in the former gas. For the same reason the condensation occurs faster the lower the pressure of the gas present. Finally, when the emanation is carried by a steady gas-stream, a less proportion condenses than in the other cases, because the concentration of emanation particles per cubic centimetre of gas is less under these conditions.

Decay of Activity of the Condensed Emanation.

Some experiments were made to test whether the rate of decay of activity of the thorium emanation was altered at the temperature of liquid air. The method employed was to pass a slow steady stream of the thorium emanation, mixed with hydrogen or oxygen, into the copper spiral immersed in liquid air for a space of five minutes. The emanation was thus condensed in the spiral. The current of gas was then stopped, and after definite intervals, extending in successive experiments from one to five minutes, the spiral was rapidly removed from the liquid air, plunged into hot water, and the emanation present swept rapidly with a current of air into a large testing-vessel. The results showed that the emanation lost its activity at the same rate at the temperature of liquid air as at ordinary temperature, *i.e.* its activity fell to half value in about one minute. This is in agreement with results previously noted for other active products, showing that the rate of decay is unaffected by any physical or chemical agency.

Summary of Results.

The results show that the thorium emanation begins to condense at about −120° C. The rapid rate of decay of its activity renders a determination of the point at which the *condensed* emanation commences to volatilize experimentally impracticable. But under all conditions tried some of the emanation escapes condensation at temperatures much below the temperature of initial condensation. In a slow stream of gas the presence of the emanation is first observed at about −155° C. It is probable that −120° represents the true temperature of volatilization and condensation, and that the escape of emanation below this temperature is due to the extremely small number of condensing particles present. The radium emanation commences to volatilize at −153° in in a steady stream of gas, and at −150° in a stationary atmosphere, and this latter value may be accepted with considerable confidence as being the true temperature of initial volatilization. In the case of radium there is no sensible difference between the temperature of volatilization and of condensation, and the whole of the emanation is condensed at temperatures only slightly below the initial point of volatilization. This difference of behaviour of the two emanations is explained on the view that the number of particles of emanation present for equal effects is probably many thousand times greater in the case of radium emanation than in the case of thorium emanation. All the radium emanation is volatilized within a very few degrees of the initial point, the rate of volatilization of course depending on the rate of rise of temperature. But with a very slowly rising temperature, practically all of the emanation comes off very suddenly at a temperature not much more than one degree above that at which only 2 per cent. has volatilized. The general indication of all the experiments, considered together, is to show that the condensed emanation possesses a true vapour-pressure, and that the emanation commences to volatilize slowly two or three degrees below the temperature of rapid volatilization even when the process occurs in a stationary atmosphere. The emanations therefore possess the usual properties possessed by ordinary gaseous matter, in so far as the phenomena of volatilization and condensation are concerned. It was shown in a recent paper that they also possess the property possessed by gases of being occluded by solids under certain conditions. These new properties, taken in conjunction with the earlier discovered diffusion phenomena, characteristic of the radioactive emanations, leave no doubt that the latter must consist of matter in the gaseous state.

McGill University, Montreal,
March 9, 1903.

LX. *Radioactive Change.* *By* E. Rutherford, *M.A.*, *D.Sc.*, *Macdonald Professor of Physics, McGill University, and* F. Soddy, *M.A.* (*Oxon.*).

Contents.

§ 1. *The Products of Radioactive Change and their Specific Material Nature.*

In previous papers it has been shown that the radioactivity of the elements radium, thorium, and uranium is maintained by the continuous production of new kinds of matter which possess temporary activity. In some cases the new product exhibits well-defined chemical differences from the element producing it, and can be separated by chemical processes. Examples of this are to be found in the removal of thorium X from thorium and uranium X from uranium. In other cases the new products are gaseous in character, and

[*] Communicated by the Authors.

so separate themselves by the mere process of diffusion, giving rise to the radioactive emanations which are produced by compounds of thorium and radium. These emanations can be condensed by cold and again volatilized; although they do not appear to possess positive chemical affinities, they are frequently occluded by the substances producing them when in the solid state, and are liberated by solution; they diffuse rapidly into the atmosphere and through porous partitions, and in general exhibit the behaviour of inert gases of fairly high molecular weight. In other cases again the new matter is itself non-volatile, but is produced by the further change of the gaseous emanation; so that the latter acts as the intermediary in the process of its separation from the radioactive element. This is the case with the two different kinds of excited activity produced on objects in the neighbourhood of compounds of thorium and radium respectively, which in turn possess well-defined and characteristic material properties. For example, the thorium excited activity is volatilized at a definite high temperature, and redeposited in the neighbourhood, and can be dissolved in some reagents and not in others.

These various new bodies differ from ordinary matter, therefore, only in one point, namely, that their quantity is far below the limit that can be reached by the ordinary methods of chemical and spectroscopic analysis. As an example that this is no argument against their specific material existence, it may be mentioned that the same is true of radium itself as it occurs in nature. No chemical or spectroscopic test is sufficiently delicate to detect radium in pitchblende, and it is not until the quantity present is increased many times by concentration that the characteristic spectrum begins to make its appearance. Mme. Curie and also Giesel have succeeded in obtaining quite considerable quantities of pure radium compounds by working up many tons of pitchblende, and the results go to show that radium is in reality one of the best defined and most characteristic of the chemical elements. So, also, the various new bodies, whose existence has been discovered by the aid of their radioactivity, would no doubt, like radium, be brought within the range of the older methods of investigation if it were possible to increase the quantity of material employed indefinitely.

§ 2. *The Synchronism between the Change and the Radiation.*

In the present paper the nature of the changes in which these new bodies are produced remains to be considered. The experimental evidence that has been accumulated is now sufficiently complete to enable a general theory of the nature of the process to be established with a considerable degree of certainty and definiteness. It soon became apparent from this evidence that a much more intimate connexion exists between the radioactivity and the changes that maintain it than is expressed in the idea of the production of active matter. It will be recalled that all cases of radioactive change that have been studied can be resolved into the production by one substance of one other (disregarding for the present the expelled rays). When several changes occur together these are not simultaneous but successive. Thus thorium produces thorium X, the thorium X produces the thorium emanation, and the latter produces the excited activity. Now the radioactivity of each of these substances can be shown to be connected, not with the change in which it was itself produced, but with the change in which it in turn produces the next new type. Thus after thorium X has been separated from the thorium producing it, the radiations of the thorium X are proportional to the amount of emanation that it produces, and both the radioactivity and the emanating power of thorium X decay according to the same law *and at the same rate*. In the next stage the emanation goes on to produce the excited activity. The activity of the emanation falls to half-value in one minute, and the amount of excited activity produced by it on the negative electrode in an electric field falls off in like ratio. These results are fully borne out in the case of radium. The activity of the radium emanation decays to half-value in four days, and so also does its power of producing the excited activity.

Hence it is not possible to regard radioactivity as a *consequence* of changes that have already taken place. The rays emitted must be an *accompaniment* of the change of the radiating system into the one next produced.

Non-separable activity.—This point of view at once accounts for the existence of a constant radioactivity, non-separable by chemical processes, in each of the three radio-elements. This non-separable activity consists of the radiations that accompany the primary change of the radio-element itself into the first new product that is produced. Thus in thorium about 25 per cent. of the α radiation accompanies the first change of the thorium into thorium X. In uranium the whole of the α radiation is non-separable and accompanies the change of the uranium into uranium X.

Several important consequences follow from the conclusion that the radiations accompany the change. A body that is radioactive must *ipso facto* be changing, and hence it is not possible that any of the new types of radioactive matter—*e. g.*, uranium X, thorium X, the two emanations, &c.—can be identical with any of the known elements. For they remain in existence only a short time, and the decay of their radioactivity is the expression of their continuously diminishing quantity. On the other hand, since the ultimate products of the changes cannot be radioactive, there must always exist at least one stage in the process beyond the range of the methods of experiment. For this reason the ultimate products that result from the changes remain unknown, the quantities involved being unrecognizable, except by the methods of radioactivity. In the naturally occurring minerals containing the radio-elements these changes must have been proceeding steadily over very long periods, and, unless they succeed in escaping, the ultimate products should have accumulated in sufficient quantity to be detected, and therefore should appear in nature as the invariable companions of the radio-elements. We have already suggested on these and other grounds that possibly helium may be such an ultimate product, although, of course, the suggestion is at present a purely speculative one. But a closer study of the radioactive minerals would in all probability afford further evidence on this important question.

§ 3. *The Material Nature of the Radiations.*

The view that the ray or rays from any system are produced at the moment the system changes has received strong confirmation by the discovery of the electric and magnetic deviability of the α ray. The deviation is in the opposite sense to the β or cathode-ray, and the rays thus consist of positively charged bodies projected with great velocity (Rutherford, Phil. Mag., Feb. 1903). The latter was shown to be of the order of $2 \cdot 5 \ 10^9$ cms. per second. The value of e/m, the ratio of the charge of the carrier to its mass, is of the order $6 \ 10^3$. Now the value of e/m for the cathode-ray is about 10^7. Assuming that the value of the charge is the same in each case, the apparent mass of the positive projected particle is over 1000 times as great as for the cathode-ray. Now $e/m = 10^4$ for the hydrogen atom in the electrolysis of water. The particle that constitutes the α ray thus behaves as if its mass were of the same order as that of the hydrogen atom. The α rays from all the radio-elements, and from the various radioactive bodies which they produce, possess analogous properties, and differ only to a slight extent in penetrating power. There are thus strong reasons for the belief that the α rays generally are projections and that the mass of the particle is of the same order as that of the hydrogen atom, and very large compared with the mass of the projected particle which constitutes the β or easily deviable ray from the same element.

With regard to the part played in radioactivity by the two types of radiation, there can be no doubt that the α rays are by far the more important. In all cases they represent over 99 per cent. of the energy radiated *, and although the β rays on account of their penetrating power and marked photographic action have been more often studied, they are comparatively of much less significance.

It has been shown that the non-separable activity of all three radio-elements, the activity of the two emanations, and the first stage of the excited activity of radium, comprise only α rays. It is not until the processes near completion in so far as their progress can be experimentally traced that the β or cathode-ray makes its appearance †.

In light of this evidence there is every reason to suppose, not merely that the expulsion of a charged particle accompanies the change, but that this expulsion actually *is* the change.

§ 4. *The Law of Radioactive Change.*

The view that the radiation from an active substance accompanies the change gives a very definite physical meaning to the law of decay of radioactivity. In all cases where one of the radioactive products has been separated, and its activity examined independently of the active substance which gives rise to it, or which it in turn produces, it has been found that the activity under all conditions investigated falls off in a geometrical progression with the time. This is expressed by the equation

$$\frac{I_t}{I_o} = \epsilon^{-\lambda t}$$

where I_o is the initial ionization current due to the radiations, I_t that after the time t, and λ is a constant. Each ray or

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* In the paper in which this is deduced (Phil. Mag. Sept. 1902, p. 329) there is an obvious slip of calculation. The number should be 100 instead of 1000.

† In addition to the a and β rays the radio-elements also give out a third type of radiation which is extremely penetrating. Thorium as well as radium (Rutherford, *Phys. Zeit.* 1902) gives out these penetrating rays, and it has since been found that uranium possesses the same property. These rays have not yet been sufficiently examined to make any discussion possible of the part they play in radioactive processes.

projected particle will in general produce a certain definite number of ions in its path, and the ionization current is therefore proportional to the number of such particles projected per second. Thus

$$\frac{n_t}{n_o}=\epsilon^{-\lambda t},$$

where n_t is the number projected in unit of time for the time t and n_o the number initially.

If each changing system gives rise to one ray, the number of systems N_t which remain unchanged at the time t is given by

$$N_t=\int_t^\infty n_t \,.\, dt = \frac{n_o}{\lambda}\epsilon^{-\lambda t}.$$

The number N_o initially present is given by putting $t=0$.

$$N_o=\frac{n_o}{\lambda}$$

and

$$\frac{N_t}{N_o}=\epsilon^{-\lambda t}.$$

The same law holds if each changing system produces two or any definite number of rays.

Differentiating

$$\frac{dN}{dt}=-\lambda N_t,$$

or, the rate of change of the system at any time is always proportional to the amount remaining unchanged.

The law of radioactive change may therefore be expressed in the one statement—the proportional amount of radioactive matter that changes in unit time is a constant. When the total amount does not vary (a condition nearly fulfilled at the equilibrium point where the rate of supply is equal to the rate of change) the proportion of the whole which changes in unit time is represented by the constant λ, which possesses for each type of active matter a fixed and characteristic value. λ may therefore be suitably called the "radioactive constant." The complexity of the phenomena of radioactivity is due to the existence as a general rule of several different types of matter changing at the same time into one another, each type possessing a different radioactive constant.

§ 5. *The Conservation of Radioactivity.*

The law of radioactive change that has been deduced holds for each stage that has been examined, and therefore holds for the phenomenon generally. The radioactive constant λ has been investigated under very widely varied conditions of temperature, and under the influence of the most powerful chemical and physical agencies, and no alteration of its value has been observed. The law forms in fact the mathematical expression of a general principle to which we have been led as the result of our investigations as a whole. Radioactivity, according to present knowledge, must be regarded as the result of a process which lies wholly outside the sphere of known controllable forces, and cannot be created, altered, or destroyed. Like gravitation, it is proportional only to the quantity of matter involved, and in this restricted sense it is therefore true to speak of the principle as the conservation of radioactivity*. Radioactivity differs of course from gravitation in being a special and not necessarily a universal property of matter, which is possessed by different kinds in widely different degree. In the processes of radioactivity these different kinds change into one another and into inactive matter, producing corresponding changes in the radioactivity. Thus the decay of radioactivity is to be ascribed to the disappearance of the active matter, and the recovery of radioactivity to its production. When the two processes balance—a condition very nearly fulfilled in the case of the radio-elements in a closed space—the activity remains constant. But here the apparent constancy is merely the expression of the slow rate of change of the radio-element itself. Over sufficiently long periods its radioactivity must also decay according to the law of radioactive change, for otherwise it would be necessary to look upon radioactive change as involving the creation of matter. In the universe therefore the total radioactivity must, according to our present knowledge, be growing less and tending to disappear.

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* Apart from the considerations that follow, this nomenclature is a convenient expression of the observed facts that the total radioactivity (measured by the radiations peculiar to the radio-elements) is for any given mass of radio-element a constant under all conditions investigated. The radioactive equilibrium may be disturbed and the activity distributed among one or more active products capable of separation from the original element. But the sum total throughout these operations is at all times the same.

For practical purposes the expression "conservation," applied to the radioactivity of the three radio-elements, is justified by the extremely minute proportion that can change in any interval over which it is possible to extend actual observations. But *rigidly* the term "conservation" applies only with reference to the radioactivity of any definite quantity of radioactive matter, whereas in nature this quantity must be changing spontaneously and continually growing less. To avoid possible misunderstanding, therefore, it is necessary to use the expression only in this restricted sense.

Hence the energy liberated in radioactive processes does not disobey the law of the conservation of energy.

It is not implied in this view that radioactivity, considered with reference to the quantity of matter involved, is conserved under all conceivable conditions, or that it will not ultimately be found possible to control the processes that give rise to it. The principle enunciated applies of course only to our present state of experimental knowledge, which is satisfactorily interpreted by its aid.

The general evidence on which the principle is based embraces the whole field of radioactivity. The experiments of Becquerel and Curie have shown that the radiations from uranium and radium respectively remain constant over long intervals of time. Mme. Curie put forward the view that radioactivity was a specific property of the element in question, and the successful separation of the element radium from pitchblende was a direct result of this method of regarding the property. The possibility of separating from a radio-element an intensely active constituent, although at first sight contradictory, has afforded under closer examination nothing but confirmation of this view. In all cases only a part of the activity is removed, and this part is recovered spontaneously by the radio-element in the course of time. Mme. Curie's original position, that radioactivity is a specific property of the element, must be considered to be beyond question. Even if it should ultimately be found that uranium and thorium are admixtures of these elements with a small *constant* proportion of new radio-elements with correspondingly intense activity, the general method of regarding the subject is quite unaffected.

In the next place, throughout the course of our investigations we have not observed a single instance in which radioactivity has been created in an element not radioactive, or destroyed or altered in one that is, and there is no case at present on record in which such a creation or destruction can be considered as established. It will be shown later that radioactive change can only be of the nature of an atomic disintegration, and hence this result is to be expected, from the universal experience of chemistry in failing to transform the elements. For the same reason it is not to be expected that the rate of radioactive change would be affected by known physical or chemical influences. Lastly, the principle of the conservation of radioactivity is in agreement with the energy relations of radioactive change. These will be considered more fully in § 7, where it is shown that the energy changes involved are of a much higher order of magnitude than is the case in molecular change.

It is necessary to consider briefly some of the apparent exceptions to this principle of the conservation of radioactivity. In the first place it will be recalled that the emanating power of the various compounds of thorium and radium respectively differ widely among themselves, and are greatly influenced by alterations of physical state. It was recently proved (Phil. Mag. April 1903, p. 453) that these variations are caused by alterations in the rate at which the emanations escape into the surrounding atmosphere. The emanation is produced at the same rate both in de-emanated and in highly emanating thorium and radium compounds, but is in the former stored up or occluded in the compound. By comparing the amount stored up with the amount produced per second by the same compound dissolved, it was found possible to put the matter to a very sharp experimental test which completely established the law of the conservation of radioactivity in these cases. Another exception is the apparent destruction of the thorium excited activity deposited on a platinum wire by ignition to a white heat. This has recently been examined in this laboratory by Miss Gates, and it was found that the excited activity is not destroyed, but is volatilized at a definite temperature and redeposited in unchanged amount on the neighbouring surfaces.

Radioactive "Induction."—Various workers in this subject have explained the results they have obtained on the idea of radioactive "induction," in which a radioactive substance has been attributed the power of inducing activity in bodies mixed with it, or in its neighbourhood, which are not otherwise radioactive. This theory was put forward by Becquerel to explain the fact that certain precipitates (notably barium sulphate) formed in solutions of radioactive salts are themselves radioactive. The explanation has been of great utility in accounting for the numerous examples of the presence of radioactivity in non-active elements, without the necessity of assuming in each case the existence of a new radio-element therein, but our own results do not allow us to accept it.

In the great majority of instances that have been recorded the results seem to be due simply to the *mixture of active matter with the inactive element.* In some cases the effect is due to the presence of a small quantity of the original radio-element, in which case the "induced" activity is permanent. In other cases, one of the disintegration products, like uranium X or thorium X, has been dragged down by the precipitate, producing temporary, or, as it is sometimes termed, "false" activity. In neither case is the original character of the radiation at all affected. It is probable that a re-examination of some of the effects that have been attributed to radioactive induction would lead to new disintegration products of the known radio-elements being recognized.

Other Results.—A number of cases remain for consideration, where, by working with very large quantities of material, there have been separated from minerals possible new radio-elements, *i. e.* substances possessing apparently permanent radioactivity with chemical properties different from those of the three known radio-elements. In most of these cases, unfortunately, the real criteria that are of value, viz., the nature of the radiations and the presence or absence of distinctive emanations, have not been investigated. The chemical properties are of less service, for even if a new element were present, it is not at all necessary that it should be in sufficient quantity to be detected by chemical or spectroscopic analysis. Thus the radio-lead described by Hoffmann and Strauss and by Giesel cannot be regarded as a new element until it is shown that it has permanent activity of a distinctive character.

In this connexion the question whether polonium (radio-bismuth) is a new element is of great interest. The polonium discovered by Mme. Curie is not a permanent radioactive substance, its activity decaying slowly with the time. On the view put forward in these papers, polonium must be regarded as a disintegration product of one of the radio-elements present in pitchblende. Recently, however, Marckwald (*Ber. der D. Chem. Gesel.* 1902, pp. 2285 & 4239), by the electrolysis of pitchblende solutions, has obtained an intensely radioactive substance very analogous to the polonium of Curie. But he states that the activity of his preparation does not decay with time, and this, if confirmed, is sufficient to warrant the conclusion that he is not dealing with the same substance as Mme. Curie. On the other hand, both preparations give only α rays, and in this they are quite distinct from the other radio-elements. Marckwald has succeeded in separating his substance from bismuth, thus showing it to possess different chemical properties, and in his latest paper states that the bismuth-free product is indistinguishable chemically from tellurium. If the permanence of the radioactivity is established, the existence of a new radio-element must be inferred.

If elements heavier than uranium exist it is probable that they will be radioactive. The extreme delicacy of radioactivity as a means of chemical analysis would enable such elements to be recognized even if present in infinitesimal quantity. It is therefore to be expected that the number of radio-elements will be augmented in the future, and that considerably more than the three at present recognized exist in minute quantity. In the first stage of the search for such elements a purely chemical examination is of little service. The main criteria are the permanence of the radiations, their distinctive character, and the existence or absence of distinctive emanations or other disintegration products.

§ 6. *The Relation of Radioactive Change to Chemical Change.*

The law of radioactive change, that the rate of change is proportional to the quantity of changing substance, is also the law of monomolecular chemical reaction. Radioactive change, therefore, must be of such a kind as to involve one system only, for if it were anything of the nature of a combination, where the mutual action of two systems was involved, the rate of change would be dependent on the concentration, and the law would involve a volume-factor. This is not the case. Since radioactivity is a specific property of the element, the changing system must be the chemical atom, and since only one system is involved in the production of a new system and, in addition, heavy charged particles, in radioactive change the chemical atom must suffer disintegration.

The radio-elements possess of all elements the heaviest atomic weight. This is indeed their sole common chemical characteristic. The disintegration of the atom and the expulsion of heavy charged particles of the same order of mass as the hydrogen atom leaves behind a new system lighter than before, and possessing chemical and physical properties quite different from those of the original element. The disintegration process, once started, proceeds from stage to stage with definite measurable velocities in each case. At each stage one or more α "rays" are projected, until the last stages are reached, when the β "ray" or electron is expelled. It seems advisable to possess a special name for these now numerous atom-fragments, or new atoms, which result from the original atom after the ray has been expelled, and which remain in existence only a limited time, continually undergoing further change. Their instability is their chief characteristic. On the one hand, it prevents the quantity accumulating, and in consequence it is hardly likely that they can ever be investigated by the ordinary methods. On the other, the instability and consequent ray-expulsion furnishes the means whereby they can be investigated. We would therefore suggest the term *metabolon* for this purpose.

Thus in the following table the metabolons at present known to result from the disintegration of the three radio-elements have been arranged in order.

Uranium.	Thorium.	Radium.
↓	↓	↓
Uranium X.	Thorium X.	Radium Emanation.
↓	↓	↓
?	Thorium Emanation.	Radium-Excited Activity I.
	↓	↓
	Thorium-Excited Activity I.	ditto II.
	↓	↓
	ditto II.	ditto III.
	↓	↓
	?	?

The three queries represent the three unknown ultimate products. The atoms of the radio-elements themselves form, so to speak, the common ground between metabolons and atoms, possessing the properties of both. Thus, although they are disintegrating, the rate is so slow that sufficient quantity can be accumulated to be investigated chemically. Since the rate of disintegration is probably a million times faster for radium than it is for thorium or uranium, we have an explanation of the excessively minute proportion of radium in the natural minerals. Indeed, every consideration points to the conclusion that the radium atom is also a metabolon in the full sense of having been formed by disintegration of one of the other elements present in the mineral. For example, an estimation of its "life," goes to show that the latter can hardly be more than a few thousand years (see § 7). The point is under experimental investigation by one of us, and a fuller discussion is reserved until later.

There is at present no evidence that a single atom or metabolon ever produces more than one new kind of metabolon at each change, and there are no means at present of finding, for example, either how many metabolons of thorium X, or how many projected particles, or "rays," are produced from each atom of thorium. The simplest plan therefore, since it involves no possibility of serious error if the nature of the convention is understood, is to assume that each atom or metabolon produces one new metabolon or atom and one "ray."

§ 7. *The Energy of Radioactive Change, and the Internal Energy of the Chemical Atom.*

The position of the chemical atom as a very definite stage in the complexity of matter, although not the lowest of which it is now possible to obtain experimental knowledge, is brought out most clearly by a comparison of the respective energy relations of radioactive and chemical change. It is possible to calculate the order of the quantity of energy radiated from a given quantity of radio-element during its complete change, by several independent methods, the conclusions of which agree very well among themselves. The most direct way is from the energy of the particle projected, and the total number of atoms. For each atom cannot produce less than one "ray" for each change it undergoes, and we therefore arrive in this manner at a minimum estimate of the total energy radiated. On the other hand, one atom of a radio-element, if completely resolved into projected particles, could not produce more than about 200 such particles at most, assuming that the mass of the products is equal to the mass of the atom. This consideration enables us to set a maximum limit to the estimate. The α rays represent so large a proportion of the total energy of radiation that they alone need be considered.

Let m = mass of the projected particle,
v = the velocity,
e = charge.

Now for the α ray of radium

$$v=2{\cdot}5\ 10^9,$$

$$\frac{e}{m}=6\ 10^3.$$

The kinetic energy of each particle

$$\tfrac{1}{2}mv^2=\frac{1}{2}\frac{m}{e}v^2e=5\ 10^{14}e.$$

J. J. Thomson has shown that

$e=6\ 10^{-10}$ E.S. Units $=2\ 10^{-20}$ Electromagnetic Units.

Therefore the kinetic energy of each projected particle $=10^{-5}$ erg. Taking 10^{20} as the probable number of atoms in one gram of radium, the total energy of the rays from the latter $=10^{15}$ ergs $=2{\cdot}4\ 10^7$ gram-calories, on the assumption that each atom projects one ray. Five successive stages in the disintegration are known, and each stage corresponds to the projection of at least one ray. It may therefore be stated that the total energy of radiation during the disintegration of one gram of radium cannot be less than 10^8 gram-calories, and may be between 10^9 and 10^{10} gram-calories. The energy radiated does not necessarily involve the whole of the energy of disintegration and may be only a small part of it. 10^8 gram-calories per gram may therefore be safely accepted as the least possible estimate of the energy of radioactive change in radium. The union of hydrogen and oxygen liberates approximately $4\ 10^3$ gram-calories per gram of water produced, and this reaction sets free more energy for a given weight than any other chemical change known. The energy of radioactive change must therefore be at least twenty-thousand times, and may be a million times, as great as the energy of any molecular change.

The rate at which this store of energy is radiated, and in consequence the life of a radio-element, can now be considered. The order of the total quantity of energy liberated per second in the form of rays from 1 gram of radium may be calculated from the total number of ions produced and the energy required to produce an ion. In the solid salt a great proportion of the radiation is absorbed in the material, but the difficulty may be to a large extent avoided by determining the number of ions produced by the radiation of the emanation, and the proportionate amount of the total radiation of radium due to the emanation. In this case most of the rays are absorbed in producing ions from the air. It was experimentally found that the maximum current due to the emanation from 1 gram of radium, of activity 1000 compared with uranium, in a large cylinder filled with air, was $1{\cdot}65\ 10^{-8}$ electromagnetic units. Taking $e=2\ 10^{-20}$, the number of ions produced per second $=8{\cdot}2\ 10^{11}$. These ions result from the collision of the projected particles with the gas in their path. Townsend (Phil. Mag. 1901, vol. i.), from experiments on the production of ions by collision, has found that the minimum energy required to produce an ion is 10^{-11} ergs. Taking the activity of pure radium as a million times that of uranium, the total energy radiated per second by the emanation from 1 gram of pure radium $=8200$ ergs. In radium compounds in the solid state, this amount is about $\cdot 4$ of the total energy of radiation, which therefore is about

$2\ 10^4$ ergs per second,
$6{\cdot}3\ 10^{11}$ ergs per year,
15,000 gram-calories per year.

This again is an under-estimate, for only the energy employed in producing ions has been considered, and this may be only a small fraction of the total energy of the rays.

Since the α radiation of all the radio-elements is extremely similar in character, it appears reasonable to assume that the feebler radiations of thorium and uranium are due to these elements disintegrating less rapidly than radium. The energy radiated in these cases is about 10^{-6} that from radium, and is therefore about ·015 gram-calorie per year. Dividing this quantity by the total energy of radiation, $2{\cdot}4\ 10^7$ gram-calories, we obtain the number $6\ 10^{-10}$ as a maximum estimate for the proportionate amount of uranium or thorium undergoing change per year. Hence in one gram of these elements less than a milligram would change in a million years. In the case of radium, however, the same amount must be changing per gram *per year.* The "life" of the radium cannot be in consequence more than a few thousand years on this minimum estimate, based on the assumption that each particle produces one ray at each change. If more are produced the life becomes correspondingly longer, but as a maximum the estimate can hardly be increased more than 50 times. So that it appears certain that the radium present in a mineral has not been in existence as long as the mineral itself, but is being continually produced by radioactive change.

Lastly, the number of "rays" produced per second from 1 gram of a radio-element may be estimated. Since the energy of each "ray" $=10^{-5}$ ergs $=2{\cdot}4\ 10^{-13}$ gram-calories, $6\ 10^{10}$ rays are projected every year from 1 gram of uranium. This is approximately 2000 per second. The α radiation of 1 milligram of uranium in one second is probably within the range of detection by the electrical method. The methods of experiment are therefore almost equal to the investigation of a single atom disintegrating, whereas not less than 10^{14} atoms of uranium could be detected by the balance.

It has been pointed out that these estimates are concerned with the energy of radiation, and not with the total energy of radioactive change. The latter, in turn, can only be a portion of the internal energy of the atom, for the internal energy of the resulting products remains unknown. All these considerations point to the conclusion that the energy latent in the atom must be enormous compared with that rendered free in ordinary chemical change. Now the radio-elements differ in no way from the other elements in their chemical and physical behaviour. On the one hand they resemble chemically their inactive prototypes in the periodic system very closely, and on the other they possess no common chemical characteristic which could be associated with their radioactivity. Hence there is no reason to assume that this enormous store of energy is possessed by the radio-elements alone. It seems probable that atomic energy in general is of a similar, high order of magnitude, although the absence of change prevents its existence being manifested. The existence of this energy accounts for the stability of the chemical elements as well as for the conservation of radioactivity under the influence of the most varied conditions. It must be taken into account in cosmical physics. The maintenance of solar energy, for example, no longer presents any fundamental difficulty if the internal energy of the component elements is considered to be available, *i. e.* if processes of sub-atomic change are going on. It is interesting to note that Sir Norman Lockyer has interpreted the results of his spectroscopic researches on the latter view (Inorganic Evolution, 1900) although he regards the temperature as the cause rather than the effect of the process.

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LXI. *Removal of the Voltaic Potential-Difference by Heating in Oil.* *By* J. Brown, *F.R.S.*[*]

IN 1879, at an early stage of my investigations on voltaic action [†], it was suggested that the difference of potential observed near the surfaces of dissimilar bodies in contact is due to chemical action of films condensed on their surfaces from the atmosphere or gas surrounding such bodies.

It was pointed out [‡] that such a condition of things is quite analogous to that of an ordinary voltaic cell divided by a non-conductor through its electrolyte, *e. g.*, copper | electrolyte | air | electrolyte | zinc, the copper and zinc being in contact and the difference of potential being taken between the two air | electrolyte surfaces. The film is therefore probably of an electrolytic nature, thus falling in with Faraday's view [§] that "in considering this oxidation, or other direct action upon the METAL itself as the cause and source of the electric current, it is of the utmost importance to observe that the oxygen or other body must be in a peculiar condition, namely in the state of *combination* and not only so, but limited still further to such a state of combination and in such proportions as will constitute an *electrolyte*." In 1886 I explained [||] the important difference between my view and that of De La Rive, which latter included the formation of non-conducting oxide films on the metal surfaces as necessary to maintain the electrification. I showed [¶] experimentally that if the surfaces of the zinc and copper plates, arranged as in Volta's condenser, be nearly true planes and be brought sufficiently close together to allow their films to come in contact, but not the metals

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[*] Communicated by the Author.

[†] Phil. Mag. vii. p. 111 (1879).

[‡] *Ibid.* p. 110.

[§] Experimental Researches, i. p. 273

[||] Proc. Roy. Soc. lxi. p. 295 (1886).

[¶] *Ibid.* p. 307.

themselves, a voltaic cell is produced of which the films are the electrolyte.

In 1888 I tried the effect of freezing the films on a Volta condenser by subjecting it to a temperature of −21° C. as obtained by a mixture of ice and common salt, with indefinite results, owing perhaps to unsuitable apparatus.

In 1900 Majorana * published experiments showing that on cooling a zinc | gold couple to the temperature of liquid air, the volta effect was reduced from ·88 volt to ·05 volt, and rose again on the return to ordinary temperature to ·75 volt. With couples of other metals similar results were obtained. This effect, in my opinion, corresponds with the cessation of chemical activity at the temperature employed.

To get rid of chemical action at the surfaces of the metals by the removal of the chemically acting substance, many attempts have been made, chiefly by inclosing the couple in a vessel exhausted to a high degree or surrounding it with "pure" inert gases, but without success. Heating the metals has also been frequently tried, but the oxidation or other alteration of their surfaces at higher temperatures intervenes, precluding any true estimation of the effect sought to be investigated.

In order to avoid this source of error in the experiments now to be described, I immersed the couple in a bath of oil of high boiling-point.

The diagram represents in section a zinc-copper Volta condenser with plates C, Z 11·4 centimetres in diameter, screwed on the ends of iron rods A and B of which the lower is fixed and the upper slides in an insulated guide-tube. Means are provided for setting the plates parallel and at a minute distance apart. D represents an enamelled iron dish, a hole in the bottom of which provides for its being fixed between the zinc and the collar *i* on rod B so as to hold the oil.

Heavy petroleum known as Price's gas-engine oil was used. Owing to its viscosity the plates (having nearly true surfaces) could be only slowly separated, although radial grooves were cut in the zinc to permit the more easy penetration of the oil between the plates when these were being pulled apart.

The following is the order of experiment:—The plates, having been well cleaned with fine glass-paper, were set close together and connected one to each pair of quadrants of the electrometer. After momentarily connecting them together by a wire and then separating them in the usual way, in air,

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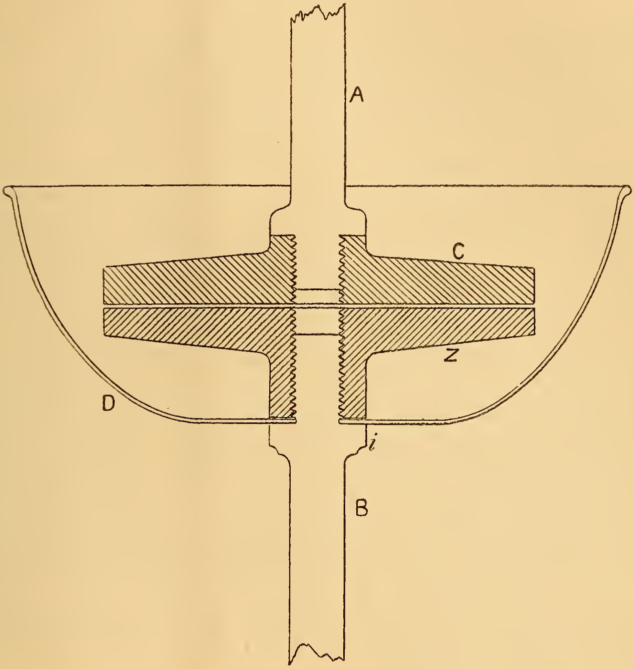
* *Accad. Lincei Atti*, Aug. 19th, Sept. 2nd and 16th (1900).

a deflexion of 140 was observed. Oil sufficient to cover both plates was then poured into the bath; and, on again connecting and separating the plates several times, the deflexion averaged 110 divisions in the same direction as before. The oil bath was then heated to about 145° C., after which the connexion and separation gave no deflexion. The whole was then allowed to cool and again tested, with the same result. The "volta effect" had disappeared. Its disappearance is apparently due to some effect of the heating since the mere immersion in the oil did not cause it, and its absence is not due to temperature merely, since this absence continued after the oil had cooled.



I take it that the volta effect ceased as soon as the condensed films were evaporated. If the disappearance of the volta effect had taken place immediately on immersion in the cold oil, it might have been considered to be caused by some conduction through the oil causing equalization of the potentials observed on air, as happens when plates in air are connected by a drop of water. There is, in fact, some such conduction of a very minute kind, the oil acting as an electrolyte and causing the combination to behave as a voltaic cell of exceedingly high resistance with an electromotive force of about ·7 volt at first, falling after heating to about one-sixth of that amount. It may thus be noted that this electromotive force is greatest at the time when its existence is seen to have little effect on the point in question. In order, however, to finally obviate any conduction effect of this kind, the oil was removed and the plates carefully wiped with cotton-wool till nothing but a mere film of oil remained on their surfaces.

In the first experiment (No. 1) the volta effect was still absent when this had been done, but after one and a half hours, on testing again, I found it had returned and deflexions of about 30 were obtained in the same direction as in air. I concluded that moisture from the atmosphere had found opportunity to reach the zinc surface in some quantity. In a repetition (No. 2) of the whole experiment the same effects were observed up till the removal of the oil, after which in this case, the return of the volta effect did not take place in four days, or if at all present, it was very slightly reversed. In this experiment the oil had been kept at a high temperature for several hours and probably formed a more permanent protective film on the metallic surfaces. In a further experiment (No. 3) in which the high temperature was maintained only for a short period as in No. 1, the results again corroborated No. 1 only that the volta effect appeared still more quickly. In nine days after removal of the oil (except such oil films as adhered to the plates) it had regained almost its pristine value, the average deflexion being then about 130.

At the conclusion of each of the three experiments, the zinc plate, on examination, appeared almost unaltered in appearance—only very slightly tarnished. On the copper there appeared to be a very thin transparent varnish-like film. On re-cleaning the plates with glass-paper the usual volta effect on air was observed.

To sum up, I conclude that all the effects observed fall in satisfactorily with the condensed electrolyte-film theory as described above. On first immersion in cold oil the films continued to act in their usual way, as if in air, though with a somewhat less deflexion, probably owing to a minute conductivity in the oil somewhat reducing the difference of potential during the slow separation of the plates after metallic contact. When heated to above the boiling-point of water, the films evaporated and left nothing to effectively act electrolytically on the plates. After removal of the oil (unless a protective varnish-like film had been formed) the moisture of the air again found access to the surface and a difference of potential was again observed.

LXII. *Notices respecting New Books.*

Electrical Problems for Engineering Students. By WILLIAM L. HOOPER, Ph.D., and ROY T. WELLS, M.S. Boston, U.S.A., and London: Ginn & Company, 1902. Pp. vi + 170.

THIS book of problems should prove very useful to teachers of electrical engineering. Starting with simple problems on the calculation of resistance, the authors go on to the consideration of the magnetic circuit, dynamos, alternating currents and alternators, induction motors, and power transmission. Each chapter of problems is prefaced by suitable notes. In the cases which we have tested, the answers are all correct. In some of the chapters, there is a somewhat wearisome sameness about the examples. We can confidently recommend the book as a very suitable and useful one for a class of engineering students.

LXIII. *Intelligence and Miscellaneous Articles.*

ON THE HEAT EVOLVED WHEN A LIQUID IS BROUGHT IN CONTACT WITH A FINELY-DIVIDED SOLID. BY TITO MARTINI.

A NEW study upon the heat evolved when a liquid is brought into contact with a finely-divided solid recently appeared in this Magazine[*]. Mr. Parks displayed some new calorimetric results obtained by the moistening of silica and sand, which he explains by supposing that the heat evolved is due to the area of surface that is brought into contact with the liquid, and that the heat increases as the surface moistened is enlarged.

In my own experiments regarding the *Pouillet effect*, which the author has clearly recapitulated in his paper, before deciding to advance an explanatory hypothesis, I thought of the possibility of the calorific phenomena being due to the surface area in contact with the liquid; but I observed that an excessively fine powder of quartz produced a result very different from precipitated silica. In fact, while the first only produced very weak thermal effects, the second manifested a considerable rise in temperature, whether in contact with water or with other liquids (alcohol, ether, benzine, &c.). I then thought of measuring the quantity of liquid absorbed by the two powders, with the result that precipitated silica absorbed a much larger quantity of liquid than that absorbed by the powdered quartz.

In consequence of these results, it occurred to me to use another substance that like silica was capable of being finely divided, and make comparisons with this new precipitate and the same substance reduced to powder.

To this end, I used finely-powdered crystallized carbonate of calcium and a precipitate of the same substance. Using the method which I have already described in this Magazine[†], I found that the crystallized carbonate of calcium, moistened with acetic ether, produced a rise of temperature of 0°·26 C., absorbing

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[*] Phil. Mag. August 1902, p. 240.

[†] Phil. Mag. March 1899, p. 329, and December 1900, p. 618.

0·264 c.c. of liquid per gramme of powder. The moistening of the precipitate of carbonate of calcium with the same liquid caused a rise in temperature of 0°·58 C., the powder absorbing 1·563 c.c. of acetic ether per gramme of powder. The precipitated silica, moistened with the same liquid, rose in temperature 31°·40 C., absorbing 1·67 c.c. per gramme. Experimenting with benzine, I found that the precipitate of carbonate of calcium absorbed 1·61 c.c. per gramme of powder, rising in temperature 0°·22 C., while the precipitated silica rose in temperature 11°·21 C., absorbing 1·52 c.c. per gramme. These facts would seem to prove that increase in the area of surface brought in contact with the liquid is not a cause sufficient to explain the marked rise in temperature resulting from the moistening of precipitated silica, animal and vegetable charcoal, and in the case of all those substances which I have denominated as *hygrophiles*; wishing by this appellation to indicate the property that certain powders have of holding tenaciously a portion of the liquid they absorb.

The union of the liquid with hygrophile substances might be, to my mind, a physico-chemical phenomenon analogous to those cited by van Bemmelen in his researches upon hydrates of unstable composition, that are formed by exposing silica to more or less humid air*.

My own recent researches in reference to the phenomena of hygrophile powders placed in contact with alcoholic mixtures and diluted acids† seem to confirm my hypothesis. A non-hygrophile powder, for instance, like quartz or powdered marble, well dried and then placed in contact with an alcoholic mixture (three parts alcohol and one part water), will not alter in any sensible degree the alcoholicity of the mixture; while with silica or animal charcoal, well dried, a part of the water is subtracted from the mixture: and silica, well dried, is capable of subtracting water from a diluted solution of sulphuric acid. From this it can be deduced that the behaviour of hygrophile powders produces results that are due to a more energetic action than a simple mechanical one, which would be sufficient to explain the phenomena manifested in the case of non-hygrophile powders that are moistened with liquids without, however, tenaciously holding any portion of them. For this reason, I hold that the heat evolved from hygrophile powders may be produced from a decrease in the specific heat of that part of the liquid tenaciously held by the powders; because this part of the liquid will have lost its quality as a fluid, and assumed a state of solidity or quasi solidity; for this reason I compare the *Pouillet effect*, in the case of hygrophile powders, to a species of inverted solution.

I may add that if the values found by Parks are inferior to my own and those found by Bellati, this difference is due to a change taking place in the silica at a high temperature, as has been noted by Bellati‡ in reference to the experiments of Linebarger.

Venezia, February 1903.

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* *Archives Néerlandaises de Sciences exactes et naturelles*, t. xv. p. 321. Harlem, 1880.

† *Atti del R. Istituto Veneto*, t. lxi. parte seconda, p. 647, giugno 1902.

‡ *Atti del R. Istituto Veneto*, t. lxi. parte seconda, p. 510.

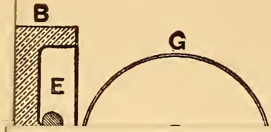
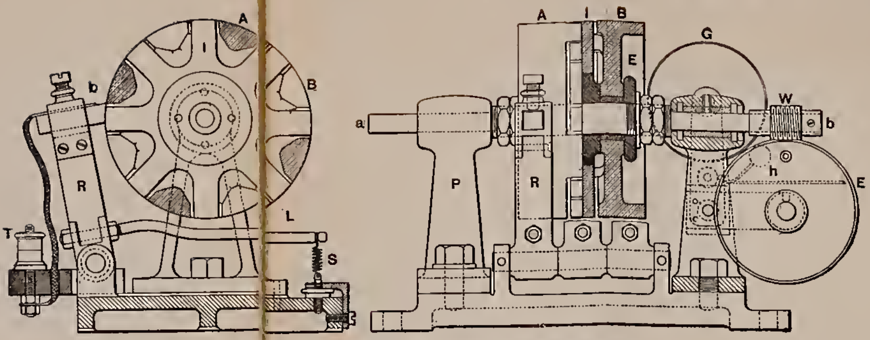

B
E
G

Fig. 1.



Motor-Commutator for Capacity Measurements.

Fig. 2.

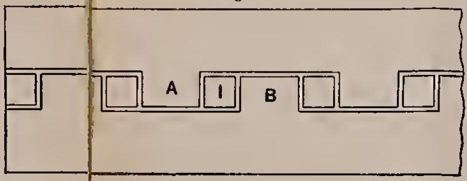


Fig. 3.

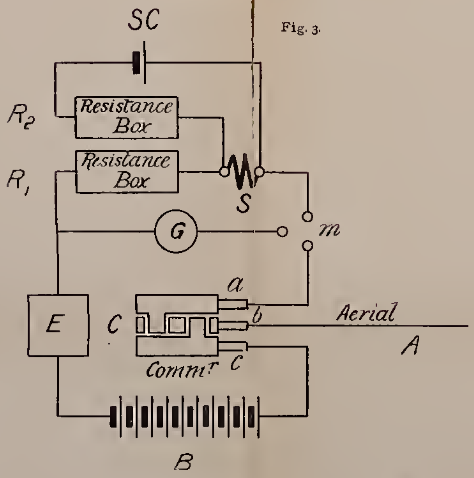


Fig. 4.

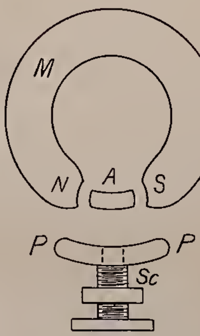
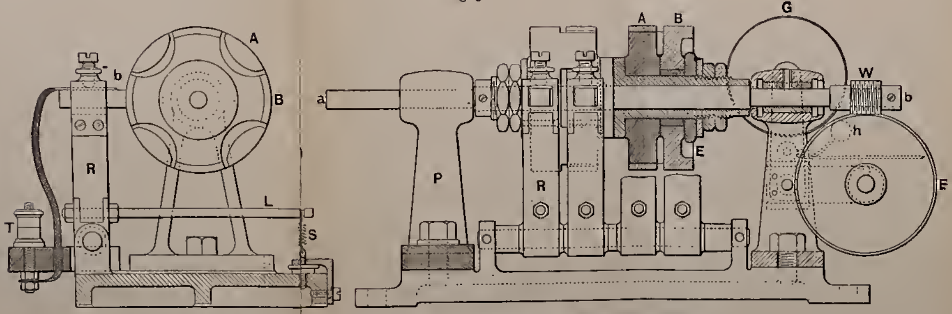


Fig. 5.



Double Circuit Interruptor for Inductance Measurement.

Fig. 6.

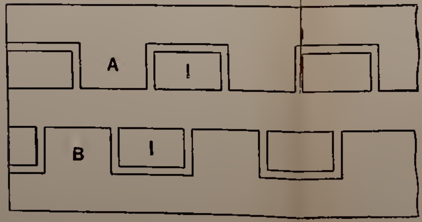


Fig. 7.

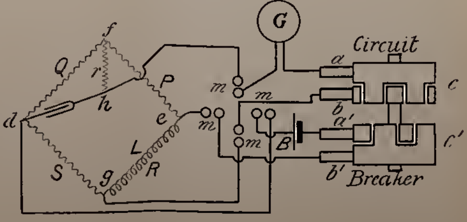


Fig. 1.

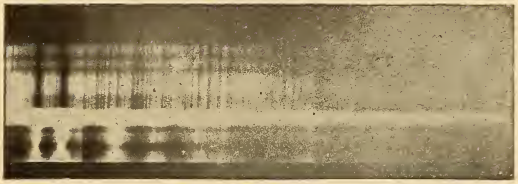


Fig. 2.

Fig. 3.

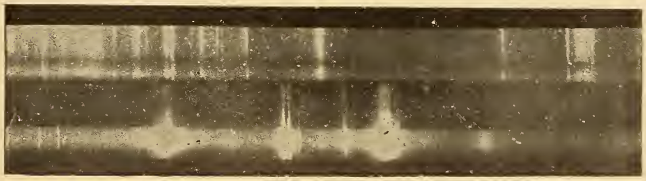
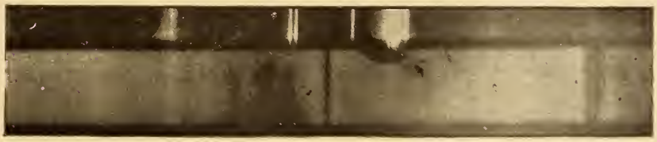
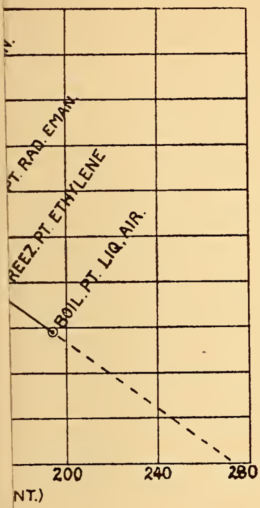
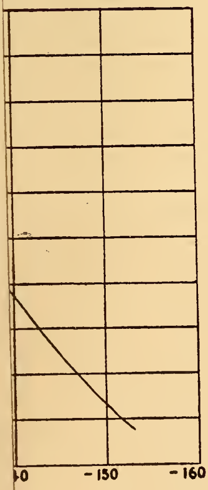


Fig. 4.



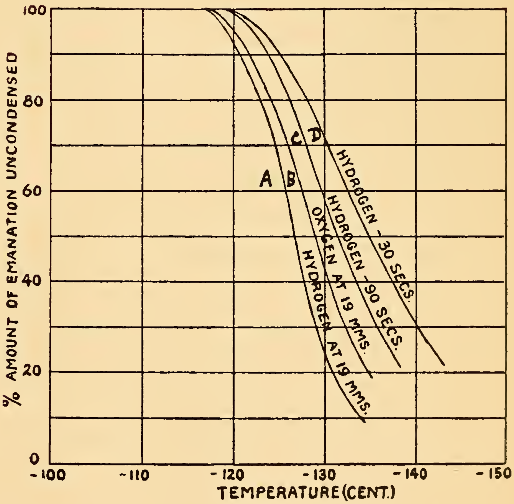


PT. RAD. EMAN.
REEZ. PT. ETHYLENE
BOIL. PT. LIQ. AIR.
200
240
280
NT.)



-150
-160

Fig. 6.



% AMOUNT OF EMANATION UNCONDENSED
100
80
60
40
20
0
-100
-110
-120
-130
-140
-150
TEMPERATURE (CENT.)
A
B
C
D
HYDROGEN - 30 SECS.
HYDROGEN - 90 SECS.
OXYGEN AT 19 MMS.
HYDROGEN AT 19 MMS.

FIG. 1.

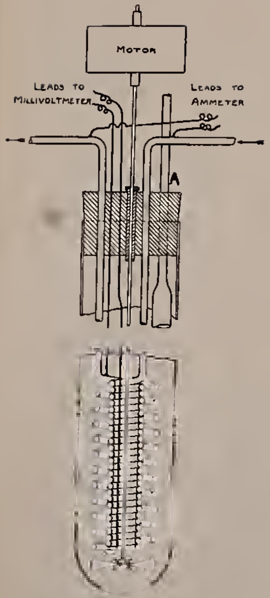


FIG. 2.

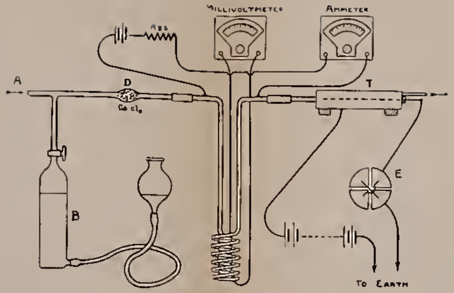


FIG. 3.

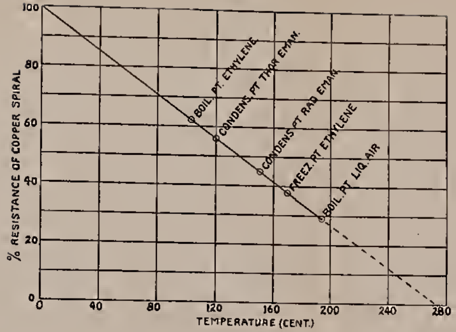


FIG. 4.

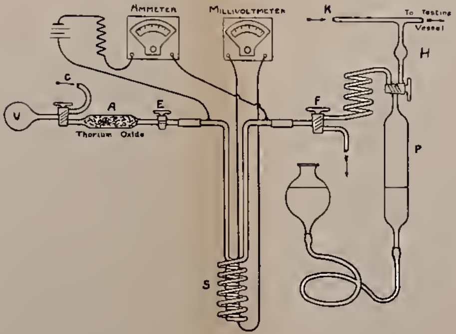


FIG. 5.

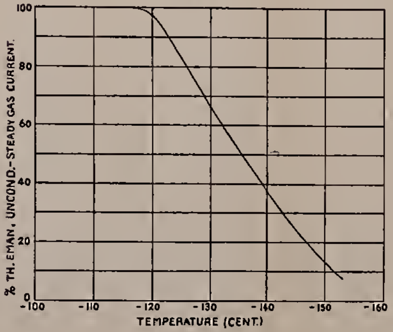
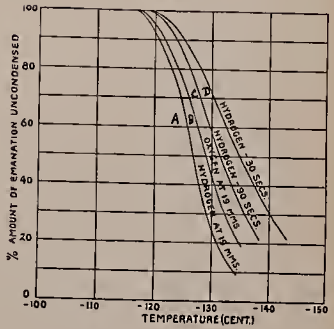


FIG. 6.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JUNE 1903.

LXIV. *The Kinetic Theory of Gases developed from a New Standpoint.* *By* J. H. JEANS, *M.A., Isaac Newton Student and Fellow of Trinity College, Cambridge*[*].

Introduction.

§ 1. THE aim of the present paper is to develop the Kinetic Theory as far as possible from a purely mathematical standpoint, namely that of abstract dynamics, and in this way to remove certain inconsistencies from the theory.

In the orthodox treatment of the subject a gas is regarded as a collection of similar dynamical systems: these systems interact on one another, and the difficulties of the theory centre largely round the question of determining the occurrence of these interactions. The method of the present paper is to regard the whole gas as a single dynamical system. Following this plan we are able to escape all the well-known difficulties—the assumption of a *molekular-ungeordnet* state, the restriction to infinitely small molecules, &c.—and may be able ultimately to arrive at a theory which applies to solids and liquids as well as to gases.

§ 2. The basis upon which the orthodox treatment of the subject rests can be shown to be neither *à priori* logical, nor *à posteriori* justified by success.

The problem of the Kinetic Theory is, virtually, to follow the motion of a dynamical system starting from an unknown

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[*] Communicated by the Author.

configuration. To overcome the difficulty of the initial configuration being unknown we are compelled to regard the whole question as one of probability. Not knowing the positions of individual molecules of the gas, we have to argue: "The probability that there is a molecule of a certain kind within a certain region has such or such a value." The calculation of this value, in the orthodox treatment of the subject, rests upon the "molekular-ungeordnet" assumption of Boltzmann.

The assumption which Boltzmann announces that he is making is that the gas is, and always remains, in a *molekular-ungeordnet* state. It does not appear that any strict definition of a *molekular-ungeordnet* state has ever been attempted. Certainly Boltzmann does not give a definition. Two examples of a *geordnet* state are given in the *Vorlesungen*[*], and these are of such a special nature that the reader feels convinced that it is legitimate to disregard the *geordnet* state altogether. The form in which Boltzmann *uses* the assumption is somewhat different. This has been pointed out by Burbury, who has clearly stated the assumption in its working form, under the designation of "Assumption A"[†].

The effect of this assumption is to enable us to regard certain probabilities at any given instant as independent, and we then assume not only that the probabilities at a later instant are *inter se* independent, but also that they are independent of the events which took place at any earlier instant. This assumption cannot be logically reconciled with the fact that the motion of the system is continuous in time, *i. e.*, that the events which occur at any instant depend on those which occurred at a previous instant.

§ 3. The fundamental assumption, then, cannot be justified *à priori* by its consistency. To show that it is not justified *à posteriori* by its success, it will be necessary to examine some of the consequences of the assumption.

The assumption being granted, it is proved that a certain function H must continually decrease as the time progresses. From this follows the well-known objection of the reversal of velocities[‡]. Let A be a system such that the value of H is H_0, and in the course of a small interval of time let it change to a system B, for which H has the smaller value H_1. Then, if we reverse all the velocities in system B, we get a second system in which the value of H is still H_1. The motion of this system must of necessity be through the various configurations which were passed during the change

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[*] Vol. i. p. 20.

[†] 'Kinetic Theory of Gases,' p. 9.

[‡] Boltzmann, *Vorlesungen*, i. p. 42.

from A to B, and so we arrive at a system which is identical with A except that all the velocities are reversed. For this system the value of H is H_0, and this is greater than H_1. How is this to be reconciled with the theorem that H must always decrease?

Now this theorem of H decreasing must have been implicitly contained in the equations of motion and the fundamental assumption. The H-theorem points to an irreversible process. This irreversibility cannot have been contained in the equations of motion, for these are essentially reversible in time; it must therefore have been introduced in the *molekular-ungeordnet* assumption. The view of the present paper, as will appear later, is that the *molekular-ungeordnet* assumption is not a true assumption at all, but amounts to a licence to misuse the calculus of probabilities. The orthodox view is that the decrease in H is a consequence of supposing the gas to be in a *molekular-ungeordnet* state, and hence that a gas for which H increases must be *geordnet*. By the time this result is reached there seems to be less justification than before for supposing the typical gas to be *ungeordnet*: it will be seen that to every *ungeordnet* state there corresponds a *geordnet* state, so that only one-half at most of all possible arrangements will be *ungeordnet*. Also of the two corresponding states there does not seem to be any reason why one should be labelled *ungeordnet* rather than the other: in other words it would seem to be just as likely that our results when applied to a real gas should be false as that they should be true. For this reason the assumption of a *molekular-ungeordnet* state does not seem to be justified by success.

The present paper contains an outline of a kinetic theory based upon entirely different foundations. This new theory is free from all assumptions, and the arguments are mathematical instead of physical, so that if the reasoning is sound, inconsistencies cannot occur.

The proposed new Basis.

§ 4. A simple illustration will best explain the course of procedure which is to be followed.

Suppose that we are concerned with a series of throws with a die, this die being of the usual type, so that in each throw the chances of each number from one to six being thrown are exactly equal. Suppose that our problem is to find the average value of the throw in an unknown series of throws.

If we consider a series of 10 throws, it can be shown that the "expectation" of the average throw (in other words, the average throw averaged over all possible series of 10 throws) is $3\frac{1}{2}$, but the "expectation" of the difference between this and the average for any single series (in other words, the probable error) is (about) 0·6. If we consider a series of 1000 throws the expectation of the average throw remains the same, but the probable error is only (about) 0·06. If we pass to the limit, and consider a series consisting of an infinite number of throws, the expectation of the average throw remains $3\frac{1}{2}$, but the probable error becomes *nil*.

§ 5. This suggests the definite proposition: "The average value of a throw in an infinite series of throws is $3\frac{1}{2}$." This proposition does not stand on the same level of absolute truth as the proposition "$2\times 2=4$," but its truth is sufficient for all practical purposes, and, moreover, it represents the highest level of truth which is attainable in the absence of a definite knowledge of the values of individual throws. The proposition (understood in its proper sense) is not refuted by pointing out that a series such as

1, 1, 1. . . . *ad inf.* (series A)

is a possible series, and that the average value in this series is not $3\frac{1}{2}$ but unity. The reply to this criticism is that the probability is infinitely against a series of random throws being of the form of series A, or of any other form for which the proposition is not true; for a series of random throws it is infinitely more probable that the proposition will be true than that it will be untrue. We may conveniently indicate that a proposition is of this type, by prefixing the words "It is infinitely probable that . . ."

§ 6. The propositions of the kinetic theory, founded upon the basis which is now proposed, will be of this type; they will state infinite probabilities, and not certainties. The uncertainty as to the positions and velocities of the individual molecules of the gas will correspond to the uncertainty as to the actual values of the throws in the illustrative problem of the dice: the theoretical uncertainty in the final result will replace the uncertainty which enters, in the usual treatment, at the outset by assuming the gas to be *ungeordnet*. The assumption of an *ungeordnet* state, as enunciated by Boltzmann [*], was obviously intended to exclude special cases analogous to the special case of series A. That it does not have this result in the form in which it is used will appear later. But with our present understanding it is quite unnecessary to make any assumption or limitation of this kind, just as in our question of the dice, it was quite unnecessary

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[*] *Vorlesungen*, i. p. 20.

to begin by postulating that there should be no "regularity" in the throw of the dice. A limitation of this kind could not, in any case, add anything to the certainty of the ultimate result. It may be noticed that the difficulty of giving a precise definition of a *molekular-geordnet* state of a gas is exactly paralleled by the difficulty which would be experienced in attempting to define "regularity" in the case of the dice.

Outline of the New Theory.

§ 7. Let us now suppose that we are dealing with a great number N of molecules inclosed in a vessel of volume Ω. We shall consider the simplest case first, and shall accordingly suppose the molecules to be incompressible elastic spheres of the usual type. Each molecule possesses three degrees of freedom, those of molecule A being represented by x_a, y_a, z_a, the coordinates of its centre. The corresponding velocity coordinates will be denoted by u_a, v_a, w_a. The whole gas, regarded as a single dynamical system, will possess 3N degrees of freedom, and its state will be specified by the 6N coordinates

$$u_a, v_a, w_a, x_a, y_a, z_a, \quad u_b, v_b, w_b \dots \quad . \quad . \quad . \quad (1)$$

Let us imagine a generalized space of 6N dimensions. In this space, the system of which the coordinates are given by (1) can be completely and uniquely represented by a single point, namely the point of which the Cartesian coordinates referred to 6N definite rectangular axes are given by (1). If our gas is to be entirely inside a certain containing vessel, we shall only need a certain portion of this space, say that bounded by

$$\left\{\begin{array}{lll} f(x_a, y_a, z_a)=0\,; & f(x_b, y_b, z_b)=0\,; & \dots \\ u_a=\pm\infty\,; & u_b=\pm\infty\,; & \dots \\ v_a=\pm\infty\,; & v_b=\pm\infty & \dots \end{array}\right. \quad . \quad . \quad (2)$$

If the molecules are incompressible spheres of radius R, we shall not need to consider the possibility of a system in which the centres of any two molecules are within a distance smaller than 2R. We may therefore exclude from consideration all those portions of our generalized space which are bounded by

$$(x_a-x_b)^2+(y_a-y_b)^2+(z_a-z_b)^2=4R^2, \quad . \quad . \quad (3)$$

and other similar equations, one for every possible pair of molecules. The simplest case of all is that in which $R=0$; and in this case this last limitation may be disregarded. Taking $R=0$ is the same thing as supposing the diameter to vanish in comparison with the mean free path.

Any point in the space which remains will represent a single possible configuration of the molecules of the gas. This configuration will, in the course of the natural motion of the gas, give place to other configurations, and these will be represented by new points in the generalized space. The natural motion of the gas may accordingly be represented by the motion of a representative point in the generalized space. Any single point will describe a "path" or "trajectory" in this space, and in this way the whole of the generalized space may be mapped out into trajectories. Since the motion of the gas is completely determined when all the coordinates (1) are given, it follows that through any point there is one and only one trajectory: two trajectories can never intersect. Since the motion of the gas is dynamically reversible, it can be seen that there will be a symmetry in the arrangement of these trajectories. Each trajectory will have an "image" which can be obtained from it by changing the signs of the velocity-coordinates u, v, w. So also each point has an image obtained in a similar way. If P is any point and P′ its image, P′ represents the system which is obtained by reversing the motion of the system represented by P*.

§ 8. We are now going to start an infinite number of our dynamical systems, so as to have systems starting from every conceivable configuration, and try what we can discover about their subsequent motion. Or, what comes to the same thing, we are going to imagine the generalized space filled with a continuous fluid, allow this fluid to move along stream-lines which coincide with the trajectories already found, and examine the motion of this fluid.

It is obvious that the initial distribution of density in this fluid may be chosen in a perfectly arbitrary way: all that is necessary is that every point of the generalized space shall be occupied.

We shall find it convenient to choose that the initial distribution of fluid shall be homogeneous. The special advantage

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[*] If we revert to the orthodox standpoint for a moment we see that of all the systems represented in our generalized space, some will be *ungeordnet* and some not. We can imagine our generalized space divided into *ungeordnet* and *geordnet* regions and points. If P is an *ungeordnet* point, its image P′ will, according to Boltzmann (*Vorlesungen*, i. p. 43) be *geordnet*, although the converse is not necessarily true. Thus fully half of our generalized space must be *geordnet*. The conventional treatment of the kinetic theory compels us to *assume*, that if a trajectory starts from an *ungeordnet* point, it must pass only through *ungeordnet* points throughout its whole length. In view of the fact that less than half of the space is *ungeordnet*, this assumption would seem to be anything but axiomatic.

of this choice is that the fluid remains homogeneous throughout the motion. This follows at once from Liouville's theorem*.

Not only does the density at every point of the fluid remain constant, but the velocity at this point, being determined solely by the coordinates of the point, will also remain constant. We have therefore to discuss a case of hydrodynamical "steady motion." There is no flow at infinity across the boundary of the generalized space. For at infinity one or more of the velocity-coordinates must be infinite, so that E the total energy must be infinite; whereas throughout the motion of a point of the fluid E must remain constant.

Comparison with Orthodox Theory.

§ 9. Let us examine the relation between the procedure now suggested and the usual procedure which rests upon the calculus of probabilities. It may, in the first place, be remarked that a problem of probability has only a definite meaning when a certain amount of knowledge is given and a certain amount withheld. For instance, suppose we have an urn containing a number of masses of different weights. If the weights are known, a question such as "What is the probability that a weight selected at random shall weigh less than an ounce?" has a definite meaning and a definite answer: if the weights are not given, the question is meaningless and has no answer. So also in the Kinetic Theory, it is meaningless to talk about the "probability" of a system being in a specified state: the phrase only acquires a meaning when it is understood that the system is selected at random from a given definite series of systems in different specified states. We shall take this given series of systems to be the series represented by a homogeneous fluid filling our generalized space. On this basis questions of probability will have a definite answer. If we had selected a different series of systems—represented, let us say, by a definite heterogeneous fluid—the answer would be different: if we neglect to specify our series of systems the problem is meaningless, and there is no answer at all.

§ 10. Consider, for instance, the question suggested in § 2. "What is the probability, at a single definite instant, that in the element of volume of which the coordinates lie between x and $x+dx$ &c., there shall be found the centre of a molecule of which the velocities shall lie between u and $u+du$ &c.?"

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* "On the Conditions necessary for Equipartition of Energy," Phil. Mag. [6], iv. p. 585, equation (7); or J. W. Gibbs, 'Elementary Principles of Statistical Mechanics,' Ch. I.

With our present conventional basis of probability, we have only to ask "For what proportion of the systems represented in our generalized space is the condition satisfied that there shall be a molecule such that x lies between x and $x+dx\ldots$&c., u lies between u and $u+du$ &c.?" Now for a certain number of systems this condition will be satisfied by molecule A. These systems will be those for which x_a lies between x and $x+dx$; and similar conditions are satisfied by y_a, z_a, u_a, v_a, w_a. These systems together form an element of the generalized space

$$dx\,dy\,dz\,du\,dv\,dw \iiint \ldots dx_b\,dx_c \ldots dy_b\,dy_c, \quad . \quad . \quad (4)$$

the integration being with respect to all the 6N variables except $x_a\,y_a\,z_a\,u_a\,v_a\,w_a$, and extending over all values except such as are excluded by equation (3). Those systems for which the conditions are satisfied by molecule B form an equal and similar element, and so also for every other of the N molecules. The probability which we require is the ratio of the sum of these N elements to the whole volume of the generalized space, and is therefore

$$\mathrm{N}\,dx\,dy\,dz\,du\,dv\,dw\,\frac{\iiint \ldots dx_b\,dx_c \ldots}{\iiint \ldots dx_a\,dx_b\,dx_c \ldots} \quad . \quad . \quad . \quad (5)$$

§ 11. This is the probability when nothing at all is known about the gas. Let us now suppose that the velocities of the individual molecules are known, and calculate the probability in this case. An element such as (4) will not now be contributed by every molecule: there will be an element contributed by each molecule of which the velocities lie within the assigned limits, and the number of these may be taken to be $\mathrm{N}f(u, v, w)\,du\,dv\,dw$. The element of volume is not given by expression (4), but by

$$dx\,dy\,dz \iiint \ldots dx_b\,dx_c \ldots dy_b\,dy_c, \quad . \quad . \quad . \quad (6)$$

the velocity-coordinates not entering into the integration at all. We now find instead of expression (5) a probability

$$\mathrm{N}f(u, v, w)\,dx\,dy\,dz\,du\,dv\,dw\,\frac{\iiint \ldots dx_b\,dx_c}{\iiint \ldots dx_a\,dx_b\,dx_c \ldots}, \quad . \quad (7)$$

§ 12. In the special case of a gas in which the radii of the molecules are very small, the regions which are excluded by equations (3) may be neglected, and we may write

$$\iiint \ldots dx_b\, dx_c \ldots \quad = \prod_{b,c,\ldots} \iiint dx_b\, dy_b\, dz_b = \Omega^{N-1},$$

$$\iiint \ldots dx_a\, dx_b\, dx_c \ldots = \prod_{a,b,c\ldots} \iiint dx_a\, dy_a\, dz_a = \Omega^{N};$$

for we now have $\iiint dx_a\, dy_a\, dz_a = \Omega$, the volume of the containing vessel. Expression (7) now becomes

$$\frac{N}{\Omega} f(u,\, v,\, w)\, dx\, dy\, dz\, du\, dv\, dw. \quad . \quad . \quad . \quad . \qquad (8)$$

The first factor is the *mean* density of molecules in the containing vessel, and the connexion between this result and that usually obtained for a gas, whether homogeneous or not, will be obvious.

§ 13. Let us now revert to the general result of § 11. We found in expression (7) the probability that there should be a molecule (which we may now agree to call A) of which the coordinates should lie between x and $x+dx$, &c. Let us now find the probability that, in addition to this, there shall be a second molecule having its six coordinates lying between x' and $x'+dx'$, &c. The probability that in addition to the original condition satisfied by A, this second condition shall be satisfied by B, can be deduced from expression (7) by limiting the integration in the numerator to values of x_b lying between x' and $x'+dx'$, values of y_b lying between y' and $y'+dy'$, and so on for z_b, u_b, v_b, w_b. The probability of which we are in search will be $Nf(u',\, v',\, w')\, du'\, dv'\, dw'$ times this corrected probability; for this is the number of molecules which can take the part of molecule B. The probability in question is therefore found to be

$$N^2 f(u,v,w) f(u',v',w')\, dx\, dy\, dz\, du\, dv\, dw\, dx'\, dy'\, dz'\, du'\, dv'\, dw'$$

$$\times \frac{\iiint \ldots dx_c\, dx_d \ldots}{\iiint \ldots dx_a\, dx_b\, dx_c\, dx_d \ldots}. \quad . \quad . \quad . \quad . \qquad (9)$$

§ 14. In the special case in which $R=0$ this reduces, by the method of § 12, to

$$\left(\frac{N}{\Omega}\right)^2 f(u,\, v,\, w) f(u',\, v',\, w')\, dx\, dy\, dz\, du\, dv\, dw\, dx'\, dy'\, dz'\, du'\, dv'\, dw'. \quad (10)$$

§ 15. The probability given by expression (10) is exactly that which would be found in a homogeneous gas, with the help of the "molekular-ungeordnet" assumption. The whole supposed point of this assumption is, however, to exclude a certain class of systems, whereas it has just been seen that the result arrived at is only true upon the understanding that all conceivable systems—*geordnet* as well as *ungeordnet*—are included. It would therefore appear that the effect of this assumption is simply to defeat its own ends: it is brought in ostensibly to make a certain calculation of probability legitimate; whereas in point of fact the calculation is illegitimate (or at any rate cannot be shown to be legitimate) if we adhere to the limitations of the "ungeordnet" assumption, and becomes legitimate as soon as these limitations are ignored.

The calculations which have just been given must, in a logically perfect kinetic theory, replace the "molekular-ungeordnet" assumption as the justification for treating the possibilities of two molecules having given coordinates as *independent* events. The fact that the motion of the fluid in our generalized space is steady motion must supply the further justification for supposing these probabilities to remain independent throughout all time. This latter result, it will be noticed, rests on Liouville's theorem, and this in turn rests upon the conservation of energy. There is no justification for supposing probabilities to remain independent when the gas is not a conservative system. It must be noticed that all our results are true only with reference to our arbitrarily chosen basis of probability.

§ 16. We have seen that the "ungeordnet" assumption leads to accurate results as regards frequency of collisions; and hence we infer that all results which depend upon this result and upon the dynamics of collisions will be accurate. The results must, however, be interpreted in a special way. Take, for instance, the H-theorem which deals with a special law of distribution, say f. The theorem must not be taken to prove that $d\mathrm{H}/dt$ is negative for all possible systems corresponding to the given f, but that the expectation of the value of $d\mathrm{H}/dt$ for a system selected at random from all systems having this f is negative, in other words that the value of $d\mathrm{H}/dt$ averaged over *all* systems having this given f is negative. There is no justification for confining the theorem to "ungeordnet" systems, and none for stating the proposition to be true of individual systems: it is, so to speak, only true on the average.

§ 17. We are here confronted with a paradox. For each system for which $d\mathrm{H}/dt$ is negative, there will be a second system—the image of the former (§ 7)—for which $d\mathrm{H}/dt$ will have an equal but positive value. These two systems must of course be equally included in the average, and since the whole number of systems which are included in the average consist of pairs of this kind, it is clear that on the average dH/dt is zero. We are, in fact, integrating dH/dt through the region of our generalized space which is given by a specified f; this region can be divided into two regions such that one is the image of the other, and the values of dH/dt in the two regions are equal in magnitude but opposite in sign. The explanation of the apparent paradox will be found in a later section (§ 32).

The Partition of the Generalized Space.

§ 18. We now discuss a number of questions concerning the distribution of systems of various specified kinds in our generalized space.

§ 19. The first problem which we shall discuss is concerned with the distribution of density of gas inside the containing vessel.

Let us consider a class of system which we shall call class A. To define it, we imagine the vessel which contains the gas divided into a great number n of "cells," each of equal volume ω, so that $n\omega=\Omega$. These cells are to be denoted by the numbers 1, 2, 3, . . . n. Then a system of class A is defined as one such that a_1 molecules have their centres in cell 1, a_2 in cell 2, and in general a_s in cell s, so that of course $\sum\limits_{s=1}^{s=n} a_s=\text{N}$.

Denoting individual molecules, as before, by A, B, C . . ., we see that there will be a certain number of systems represented in our generalized space, such that the molecule A lies in one specified cell, the molecule B in another, and so on for all. It will be easily seen that all systems of this kind occupy a small continuous element, which we may call the element c, and which, since there are N molecules altogether, forms a fraction $(\omega/\Omega)^{\text{N}}$ or $n^{-\text{N}}$ of the whole. This, it must be noticed, is true whether we consider all systems, or only systems in which the molecules have assigned velocities. Obviously also it is true, if we consider systems in which the kinetic energy has a certain assigned value.

Now if the molecules are distributed in the various cells in such a way that there are a_1 in cell 1, a_2 in cell 2, and so on, then all the systems represented by points inside the element c belong to class A. There will be a number of other elements containing only systems of class A; and these will correspond one to each way in which the N molecules can be distributed into the n cells so that there shall be a_1 in the first, a_2 in the second, and so on. The number of ways in which this can be done is

$$\frac{\underline{|N}}{\underline{|a_1}\,\underline{|a_2}\,\underline{|a_3}\ldots\underline{|a_n}}. \qquad (11)$$

The systems of class A are therefore comprised in this number of elements, each element being of the same size as element c. Hence we see that the systems of class A form a fraction θ_a of the whole number of systems, where

$$\theta_a=\frac{\underline{|N}}{n^N\prod\limits_{s=1}^{s=n}\underline{|a_s}}. \qquad (12)$$

This again is true whether we consider all possible systems or only those systems having a given energy.

§ 20. We can evaluate θ_a when N is large compared with n, and there are (in the limit) a very great number of molecules in each of the n cells. We have, when a_s is very great, the approximate formula used by Boltzmann*

$$\underline{|a_s}=\sqrt{2\pi a_s}\left(\frac{a_s}{e}\right)^{a_s}$$

or taking the logarithm of each side

$$\log\underline{|a_s}=\tfrac{1}{2}(\log 2\pi+1)+(a_s+\tfrac{1}{2})(\log a_s-1);$$

and when a_s is very great this assumes the limiting form

$$\log\underline{|a_s}=a_s\log a_s,$$

an equation in which the difference between the two sides is infinite, but is vanishingly small in comparison with either side. Hence from equation (12),

$$\begin{aligned}\log\theta_a&=\log\underline{|N}-N\log n-\Sigma\log\underline{|a_s}\\&=N(\log N-\log n)-\Sigma a_s\log a_s.\end{aligned}$$

Now $N=\Sigma a_s$, and we may write $N/n=a_0$, where a_0 is the *mean* number of molecules in each cell. Making these substitutions, our equation becomes

$$\log\theta_a=\Sigma a_s\log a_0-\Sigma a_s\log a_s=-\Sigma a_s\log\left(\frac{a_s}{a_0}\right).$$

The right-hand member of this equation is, in general, an

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* *Vorlesungen*, i. p. 41.

infinite quantity of the order of N, and is for this reason difficult to manipulate. We accordingly introduce a new quantity K_a defined by

$$K_a = \Sigma \frac{a_s}{N} \log \left(\frac{a_s}{a_0}\right); \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

so that K is, in general, finite; and we have

$$\theta_a = e^{-NK_a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

§ 21. But now the different classes of systems may be represented in a new generalized space—the subsidiary space, as we may call it. This space is to have $n-1$ dimensions, corresponding to n variables $\xi_1\ \xi_2 \ldots \xi_n$ subject to $\Sigma\xi = N$. A system of class A is represented by the point

$$\xi_1 = a_1, \quad \xi_2 = a_2, \ldots \xi_s = a_s. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which we shall call the point A.

The various classes may therefore be represented by the intersections of n systems of parallel lines drawn at unit distance apart. Further, we can represent the different systems which occurred in our original generalized space in the subsidiary space, by placing an imaginary mass θ_a at the point A, θ_b at B, and so on.

We now pass to the limit and take $N = \infty$. The values of $\xi_1, \xi_2 \ldots$ (or what is the same thing $a_1, a_2 \ldots$) will now be infinitely great, and we accordingly take the unit of length in our subsidiary space to be infinitely small.

We can now replace the distribution at points by a continuous volume-distribution. The distribution θ_a at point A is now to be replaced by a density ρ spread through the rectangular unit element of which A is the centre such that the aggregate density in this unit element is θ_a. It is obviously possible (equation 14) to take

$$\rho = e^{-N\overline{K}}$$

as the general continuous distribution, where $\overline{K}$ may be chosen so that it is continuous, and becomes identical with K_a at A, K_b at B, &c. All the systems in our original space may in this way be represented in our subsidiary space.

The number of systems of any specified type in our original generalized space (the total being taken as unity) is therefore equal to the number of the same type in the subsidiary space, and this

$$= \sum_{A, B, \ldots} \theta_a = \iiint \ldots \rho\, d\xi_1\, d\xi_2 \ldots$$

In particular, the number for which K (defined by equation 13) lies between K_1 and K_2 will be

$$\iiint_{\overline{K}=K_1}^{\overline{K}=K_2} \ldots e^{-N\overline{K}}\, d\xi_1\, d\xi_2 \ldots \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where the integration extends through those parts of the subsidiary space for which $\overline{K}$ lies between K_1 and K_2.

§ 22. Now in the subsidiary space $\overline{K}$ will be found to have a minimum value. In equation (13), let us treat $\left(\frac{a_s}{a_0}\right)$ as a continuous variable, and replace it by θ. We then have

$$\overline{K}=K=\sum_s \frac{a_0}{N}\frac{a_s}{a_0}\log\left(\frac{a_s}{a_0}\right)=\frac{1}{n}\sum_s \theta_s \log \theta_s. \quad . \quad . \quad (17)$$

The values of θ are limited by the condition

$$\Sigma \frac{a_s}{a_0}=\frac{N}{a_0}=n,$$

or what is the same thing, by

$$\frac{1}{n}\sum_s \theta_s=1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

For small variations in θ, the condition that $\overline{K}$ shall be a minimum is seen by variation of equations (17) and (18) to be

$$\frac{1}{n}\sum_s \{1+\log \theta_s+\lambda\}\delta\theta_s=0, \quad . \quad . \quad . \quad . \quad (19)$$

where λ is an indeterminate multiplier. We must therefore have

$$1+\log \theta_s+\lambda=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

for all values of s, and hence $\theta_s=$constant. From equation (18) we see that this constant value must be $\theta_s=1$. Thus when we regard a_s/a_0 as a continuous variable the minimum occurs when $a_1=a_2=\ldots=a_s=\ldots=a_0$. When a_s is very great, and only capable of integral values, the minimum still occurs for values such that, except for infinitesimally small quantities,

$$\frac{a_1}{a_0}=\frac{a_2}{a_0}=\ldots=\frac{a_s}{a_0}=\ldots=1. \quad . \quad . \quad . \quad . \quad (21)$$

The minimum value of $\overline{K}$ is found to be $\overline{K}=0$, except for an infinitesimally small quantity: it does not, however, follow that $N\overline{K}=0$. The minimum value of $\overline{K}$ subject to

a_1, a_2, &c., being integral, will, however, be greater than the unrestricted minimum for $\overline{\mathrm{K}}$, so that the infinitesimal value of this former minimum will be positive.

Hence it follows that, except at one point in our subsidiary space and points which are in its immediate neighbourhood, $e^{-\mathrm{N}\overline{\mathrm{K}}}$ is vanishingly small. The density at this point is therefore infinite in comparison with that elsewhere.

§ 23. There now three possibilities between which we have to discriminate. If we draw a small region in our subsidiary space, inclosing the minimum value of K, the density integrated throughout this small region may be either vanishingly small or finite or infinitely great in comparison with the integral density taken throughout the remaining space. It will be found that the last possibility is the true one.

To prove this, we expand $\overline{\mathrm{K}}$ in the neighbourhood of the minimum value $\overline{\mathrm{K}}=0$. We have (equation 17)

$$\overline{\mathrm{K}}=\frac{1}{n}\sum_s\frac{a_s}{a_0}\log\frac{a_s}{a_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

If we put $a_s=a_0+\epsilon_s$, where ϵ_s/a_0 is small, we get

$$\frac{a_s}{a_0}=1+\frac{\epsilon_s}{a_0}$$

$$\log\frac{a_s}{a_0}=\frac{\epsilon_s}{a_0}-\frac{1}{2}\left(\frac{\epsilon_s}{a_0}\right)^2+\ldots,$$

whence, since $\sum\limits_s\epsilon_s=0$,

$$\overline{\mathrm{K}}=\frac{1}{2n}\sum_s\left(\frac{\epsilon_s}{a_0}\right)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

We may now suppose the small region inclosing the minimum value of $\overline{\mathrm{K}}$ to be bounded by $\overline{\mathrm{K}}=\kappa$, where κ is a small positive quantity, and the equation of this boundary in rectangular coordinates will, by equation (23), be

$$\sum_s\left(\frac{\epsilon_s}{a_0}\right)^2=2n\kappa.$$

Hence we see that $\iiint\ldots d\xi_1\,d\xi_2\ldots$ taken inside the region $\mathrm{K}<\kappa$, is proportional to κ^{n-1} so long as κ is small. By differentiation, we find that the value of the integral from $\overline{\mathrm{K}}$ to $\mathrm{K}+d\mathrm{K}$ is proportional to $\mathrm{K}^{n-1}d\mathrm{K}$ so long as $\overline{\mathrm{K}}$ is small. Hence, except for a multiplying factor, the integral (16) may be written in the form

$$\int_{\overline{\mathrm{K}}=\mathrm{K}_1}^{\overline{\mathrm{K}}=\mathrm{K}_2} e^{-\mathrm{N}\overline{\mathrm{K}}}\,\overline{\mathrm{K}}^{n-1}\,d\overline{\mathrm{K}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

so long as K_1, K_2 are both small. We now see that in this case the whole value of the integral arises from the contribution supplied by an infinitesimal range of values of $\overline{K}$ near to and including the lower limit. It is obvious that the proof can be extended so as to include all values of $\overline{K}$ whether great or not.

§ 24. Returning to the original generalized space, the following propositions will now be seen to be true :—

(i.) All except an infinitesimally small fraction of the whole space has a value of K which $<\epsilon$, where ϵ is a small positive quantity, and this is true however small ϵ may be.

(ii.) K is positive at every point—either finite or vanishingly small—and the mean value of K averaged throughout the whole space is vanishingly small.

(iii.) Of that part of the space for which $K>K_0$, where K_0 is some finite positive quantity, all except an infinitesimal fraction of the whole has a value of K which $< K_0+\epsilon$, where ϵ is a small positive quantity, and this is true however small ϵ may be.

§ 25. Let us now suppose that the edges of our cells are so great compared with the average distance between two molecules that we may legitimately regard the number of molecules in each cell as infinitely great, but that at the same time these edges are so small compared with the scale on which the density of the gas varies, that we may regard the density as constant over a large number of adjacent cells. If the cells can be constructed so that these suppositions are simultaneously possible, it will be possible to give a definition of the *density at a point* in the gas which shall be logically sound—we define the density at any point P as the number (or mass) of molecules in the cell which contains P, divided by the volume of this cell.

Let us denote the density at a point by ρ and the mean-density of the gas by ρ_0. By hypothesis, ρ is appreciably constant throughout a cell. An integral such as $\iiint \rho\, dx\, dy\, dz$ taken throughout a cell may accordingly be replaced by $\rho\omega$. The value of ρ/ρ_0 in the sth cell may be replaced by a_s/a_0, when the system is of class A (§ 19).

We now see that instead of defining K by equation (13) we may suppose it defined by

$$K=\frac{1}{n}\Sigma\frac{\rho}{\rho_0}\log\left(\frac{\rho}{\rho_0}\right)$$

where the summation extends throughout all the cells, and if we replace ρ by $\frac{1}{\omega}\iiint\rho\,dx\,dy\,dz$, this becomes

$$K=\frac{1}{\Omega}\iiint\frac{\rho}{\rho_0}\log\left(\frac{\rho}{\rho_0}\right)dx\,dy\,dz. \quad . \quad . \quad . \quad (25)$$

We have now obtained a value of K which is dependent only on the positions of the molecules, being entirely independent of the way in which the gas was divided up into cells. The propositions stated in § 24 are therefore independent of the arrangement of cells.

§ 26. Equation (21) shows that the minimum value of K is given when $\rho=\rho_0$ everywhere; *i. e.*, when the density is constant throughout the gas. Proposition (i.) of § 24 may therefore be taken to state that if a point be selected at random in our generalized space, it is infinitely probable that the corresponding system will be one for which ρ is constant everywhere.

This is not difficult to understand. Selecting a point at random in our generalized space is equivalent to placing N molecules at random at points inside the containing vessel. The fundamental principles of the theory of probability lead us to expect that it will be infinitely probable that the distribution of gas will be uniform.

§ 27. We have discussed the distribution of x, y, z coordinates: the distribution of u, v, w coordinates can be treated in the same way. In this case, however, what is required (for reasons which will appear later) is not a knowledge of the partition of the whole space, but only of that part of it for which the kinetic energy has an assigned value E. This is the part given by the equation

$$\tfrac{1}{2}m\sum_{a,b,\ldots}(u_a^2+v_a^2+w_a^2)=E. \quad . \quad . \quad . \quad (26)$$

Selecting a point at random from this part of our space, is not equivalent to distributing velocities at random to the N molecules, but is equivalent to distributing 3N velocities (u_a, v_a, w_a, u_b, v_b, &c.) about a mean value $2E/3mN$. We shall therefore not expect the resulting distribution to be uniform, but shall expect the velocities to be grouped about this mean value according to the law of trial and error.

We could treat the whole question on the lines on which the former question was treated. We should find that instead of the old function K defined by equation (25), we should have a function H defined by

$$H=\iiint f\log f\,du\,dv\,dw \quad . \quad . \quad . \quad . \quad (27)$$

where f is a function of u, v, w such that the number of molecules of which the velocities lie between u and $u+du$, &c. is $Nf(u, v, w)\, du\, dv\, dw$. We find that H has a minimum value for the region defined by equation (26), and we find that the propositions of § 24 apply equally, *mutatis mutandis*, to this case.

The minimum value of H and the corresponding law of distribution can be found by the variation of equation (27), keeping f subject to

$$\iiint f\, du\, dv\, dw = 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

$$\iiint \tfrac{1}{2} m (u^2+v^2+w^2)\, f\, du\, dv\, dw = \frac{E}{N} \quad . \quad . \quad . \quad (29)$$

The resulting equation is

$$\iiint \left(1+\log f+\lambda+\tfrac{1}{2}\mu m(u^2+v^2+w^2)\right)\delta f\, du\, dv\, dw = 0, \quad . \quad (30)$$

where λ, μ are indeterminate multipliers. The solution is

$$1+\log f+\lambda+\tfrac{1}{2}\mu m(u^2+v^2+w^2) = 0; \quad . \quad . \quad . \quad (31)$$

or, changing λ, μ for new constants,

$$f = Ae^{-hm(u^2+v^2+w^2)}, \quad . \quad . \quad . \quad . \quad . \quad (32)$$

the well-known law of Maxwell and Boltzmann.

§ 28. This law gives $f=0$ when u, v, or w becomes infinite. There is therefore the difficulty that if we divide all possible velocities into "cells" in the manner of § 19, the number of molecules in some of these cells cannot be treated as infinitely great. The difficulty is best met by taking a definite velocity V, such that the molecules of which the velocities do not satisfy

$$u < V, \quad v < V, \quad w < V, \quad . \quad . \quad . \quad . \quad (33)$$

form an infinitesimal fraction of the whole. If the velocities which satisfy (33) can be partitioned into cells in the manner of § 19, so as to satisfy the conditions of § 25, there is no further difficulty, and equation (32) gives the law for velocities which satisfy (33). The law has no meaning for velocities which do not satisfy (33). It is obvious, for instance, that the law given by equation (32) does not impose any upper limit whatever on the possible values of u, v, and w for a single molecule, whereas in point of fact such a limit is definitely imposed by equation (26).

§ 29. We have investigated the law of partition of the coordinates x, y, z and of the coordinates u, v, w separately. They could have been quite easily investigated together as follows :

Assume the number of molecules having coordinates lying between x and $x+dx$, . . . u and $u+du$ . . . &c., to be

$$\mathrm{N}f(x, y, z, u, v, w)\, dx\, dy\, dz\, du\, dv\, dw, \quad . \quad . \quad (34)$$

and introduce a new function H defined by

$$\mathrm{H} = \iiiint\!\!\iint f \log f\, dx\, dy\, dz\, du\, dv\, dw \quad . \quad . \quad . \quad (35)$$

Then it will easily be seen that the propositions of § 24 apply to the region of our generalized space for which the total energy is E, provided we replace K by H, and instead of $\mathrm{K}=0$, write $\mathrm{H}=\mathrm{H}_0$, where H_0 is the minimum value of H defined by equation (35), when f is subject to the conditions

$$\iiiint\!\!\iint f\, dx\, dy\, dz\, du\, dv\, dw = 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

$$\iiiint\!\!\iint \tfrac{1}{2}m(u^2+v^2+w^2) f\, dx\, dy\, dz\, du\, dv\, dw = \mathrm{E}. \quad . \quad (37)$$

The resulting law is found to be

$$f(u, v, w, x, y, z) = \mathrm{A}e^{-hm(u^2+v^2+w^2)}, \quad . \quad . \quad . \quad (38)$$

giving uniformity of density for all values of x, y, z and Maxwell's law of distribution of velocities in a single equation.

The Normal State.

§ 30. When the 6N coordinates of the molecules of a gas are such that H has its minimum value, or a value which differs from this minimum by an infinitesimally small amount, the gas will be said to be in its "normal state." For gases in states other than the normal, the difference between the value of H for the gas and the minimum possible value corresponding to the same energy, may be taken to supply a measure of the divergence of the gas from the normal state.

We now find that proposition (i.) of § 24 may be replaced by

(iv.) All except an infinitesimally small fraction of the whole of the generalized space represents gases which are in their normal states.

§ 31. Let us now examine what becomes of the two remaining propositions.

Suppose that we start the gas from a configuration about which nothing is known except that the total energy is E (speaking physically, we have a gas of which the temperature and pressure are known), then the representative point may be supposed to be selected at random from that part of our generalized space for which the energy is E. Suppose we try to calculate the average value of H throughout the motion of the gas. Since nothing is known about the initial configuration, nothing is known as to which trajectory the representative point is describing. Thus, relatively to the knowledge which we possess, and to our arbitrary basis of probability, the representative point is at any instant equally likely to be at any point of our generalized space for which E has the assigned value. Hence the expectation of the average value of H throughout the motion (lasting through any interval we please) is exactly the same as the average value of H throughout the whole of the region for which E has the assigned value, and therefore is equal to the minimum value of H throughout this region. It follows that all the physical properties of the gas (*i. e.*, properties which depend, firstly, only on the statistical law of distribution, and not on the individual molecules, and, secondly, only on the values integrated through an interval of time, and not on values at any single instant, *e. g.*, the pressure of the gas) may be calculated on the supposition that the gas is in the normal state throughout.

This must be the interpretation of the second theorem of § 24. There is a theoretical possibility of failure, for it is possible (although infinitely improbable) that the value of H may differ from its minimum value by a finite amount through the whole of a stream-line. This question will be continued in a later section (§ 38).

§ 32. We now examine the third proposition of § 24. If we consider all the points on the various stream-lines for a given value of ϵ, which have a value of H, say $\overline{H}'$, different from the minimum, we see (from the proposition analogous to (iii.) of § 24) that only for an infinitesimal fraction of these can H increase *in either direction* to a value of H which is greater by a finite amount than $\overline{H}'$. Thus of the points for which $H=\overline{H}'$, this value of H is a maximum on the particular stream-line to which it belongs, for all except an infinitesimally small proportion of these stream-lines. Hence if we start a gas in any configuration for which H is greater than its minimum value, it is infinitely probable that in the initial motion dH/dt will be zero or negative.

Here we have the solution of the apparent paradox mentioned in § 17. There is no real irreversibility in the motion of the gas on the whole, but there is an apparent irreversibility if we start from a point at which H is different from its minimum value.

Recapitulation and Discussion.

§ 33. The whole of what has been proved amounts to the following: Firstly, a gas not in the normal state tends to approach that state; and, secondly, in examining the physical behaviour of a gas, departures from the normal state are insignificant, and we may legitimately proceed as if the gas were in the normal state throughout.

These results have only been obtained for the simplest type of gas, but it is obvious that they can be extended so as to apply to any kind of gas. The normal state is in each case found by assigning the minimum value to the function analogous to the H-function already discussed—a function which may be conveniently referred to as Boltzmann's minimum-function.

The whole of the physical behaviour and statistical properties of a gas can be deduced from a knowledge of the H-function, just as the behaviour of a dynamical system can be deduced from a knowledge of the energy-function.

Some examples of the use of this function, illustrating some of the peculiarities which may arise, are given in the remaining sections:—

Examples of the Minimum-theorem.

I.—*Field of External Force.*

§ 34. Let us suppose the molecules to move in a field of external force of potential χ, a function of x, y, z. The analysis is exactly similar to that of § 29, except that equation (37) must be replaced by

$$\int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int \{\tfrac{1}{2}m(u^2+v^2+w^2)+\chi\}f\,dx\,dy\,dz\,du\,dv\,dw=\mathrm{E}, \quad (39)$$

and from this we immediately obtain the law

$$f=\mathrm{A}e^{-hm(u^2+v^2+w^2)-2h\chi}. \quad . \quad . \quad . \quad (40)$$

II.—*Mixture of Gases.*

§ 35. Let the N molecules be of different kinds, αN of one kind, βN of another, and so on. The various coordinates can be represented in a generalized space as before. The chance that the whole gas shall be in a specified state is the product of the separate chances that the gas of each kind shall be in the corresponding state, whence we find, as the correct form for H,

$$\mathrm{H}=\sum_{(\alpha)}\alpha\int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int f_\alpha \log f_\alpha\,dx\,dy\,dz\,du\,dv\,dw \quad . \quad . \quad (41)$$

in which f_α is the law of distribution of the molecules of the first kind, and so on. The conditions to which f_α, $f_\beta \ldots$ are subject are, firstly, conditions of the form

$$\iiiint\!\!\iint f_\alpha \, du \, dv \, dw \, dx \, dy \, dz = 1, \quad . \quad . \quad . \quad (42)$$

and similar conditions for f_β, &c., and, secondly, the single energy condition

$$\sum_{(\alpha)} \alpha \iiiint\!\!\iint \tfrac{1}{2} m_\alpha (u^2 + v^2 + w^2) f_\alpha \, du \, dv \, dw \, dx \, dy \, dz = \mathrm{E}. \quad . \quad (43)$$

The equations giving $f_\alpha, f_\beta \ldots$ are found to be

$$1 + \log f_\alpha + \lambda_\alpha + \tfrac{1}{2} \mu m_\alpha (u^2 + v^2 + w^2) = 0,$$

and this gives a solution of the form

$$f_\alpha = \mathrm{A} e^{-hm_\alpha(u^2+v^2+w^2)}.$$

$$f_\beta = \mathrm{B} e^{-hm_\beta(u^2+v^2+w^2)}, \text{ \&c.} \quad . \quad . \quad . \quad (44)$$

The constant h is the same throughout, whence the Boyle-Charles-Avogadro law can be deduced at once.

III.—*Molecules of Finite Size.*

§ 36. The analysis of § 27 applies without alteration to this case, being independent of the size of the molecules. The analysis of §§ 19–26 also applies if a correction is made for the regions of the generalized space which are excluded by equations (3). It will be found that this correction has no effect on the ultimate result.

We also see from § 13 that the "chance of two molecules having assigned positions" is independent of the velocities of these molecules—a result which is in direct opposition to the views put forward by Burbury*.

IV.—*The Law of Equipartition.*

§ 37. The method of the present paper is in no way limited to the simple type of molecule which has been discussed up to the present. If each molecule has m degrees of freedom we must suppose our generalized space to possess $2m\mathrm{N}$ dimensions, and we can proceed exactly as before. If E now denotes the energy of a single molecule, we find that no matter what function of the $2m$ coordinates E may be, the law of distribution is of the form

$$f = \mathrm{A} e^{-2h\mathrm{E}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

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* 'Kinetic Theory of Gases,' chapters v. and vi.

and the law of equipartition can be deduced in the usual way.

This proof of the law of equipartition is independent of the special assumptions both of Maxwell and of Boltzmann. We do not assume (as Maxwell does)

(*a*) That the representative point passes in turn through every point of that part of the generalized space for which the total energy has the assigned value.

(*b*) That the total time during which the point is in any element of this space is proportional to the size of the element.

Neither do we assume (as Boltzmann does)

(*c*) That the gas is, at every instant, "ungeordnet," or, more precisely, that Burbury's "Condition A" is satisfied at every instant.

The precise assumptions upon which our proof rests are:—

(*d*) That at any instant that part of the total energy of the gas which is accounted for by the intermolecular forces forms an infinitesimal fraction of the whole; and

(*e*) That the conservation of energy is maintained throughout the motion of the gas.

V.—*A Gas with a Mass-Velocity.*

§ 38. We have seen (§ 30) that a gas is in a state different from its normal state through only an inappreciable fraction of the whole of the generalized space, but at the same time (§ 31) it is possible that it may be in a state different from normal throughout the whole of a stream-line. For instance, the normal state is such that the mass-velocity of the gas is *nil*, but we know that if the gas starts with a mass-velocity it will retain this velocity throughout its motion, and will therefore never reach a normal state. The stream-lines for which the gas possesses an appreciable mass-velocity form only an inappreciable fraction of the whole, and are not worthy of consideration with reference to our arbitrary standard of probability. With reference to the conditions of nature the case is different, so that we now proceed to consider these particular stream-lines.

Let U, V, W be the components of the mass-velocity of the gas, then the analysis of § 29 will apply, provided we suppose f subject not only to the conditions expressed by equations (36) and (37), but also to

$$\int\cdots\int\int u f\, dx\, dy\, dz\, du\, dv\, dw = \mathrm{U} \quad . \quad . \quad . \quad (46)$$

and two similar equations for V and W. The resulting law is found to be

$$f=Ae^{-hm[(u-U)^2+(v-V)^2+(w-W)^2]}. \quad . \quad . \quad (47)$$

The case of a mass-velocity of rotation may be treated in the same way.

§ 39. We have so far dealt only with the case in which the energy is supposed to remain constant throughout the motion. Besides the energy there are no quantities which are known to remain constant throughout the motion except the six mass-velocities of rotation and translation, and, of course, the total number of molecules in the gas. For the purposes of the Kinetic Theory, we may suppose these mass-velocities to each be zero. The solution is then given by equation (45).

On the other hand, the values obtained for the ratio of the specific heats show that this solution does not accord with the facts of nature. This may be for either of two reasons.

It may be that the number of constant quantities is greater than we have supposed, and that the knowledge of some now unknown constant would alter our result, just as § 38 a knowledge of the mass-velocity altered the result previously obtained. As I have suggested elsewhere, the uniformity of the experimental results obtained from different samples of gas supplies an argument of overwhelming strength against this supposition[*].

Or it may be that the number of constant quantities is less than we have supposed, through the energy of the gas not remaining constant, a possibility which provides an escape from the difficulties in question.

LXV. *On Oscillatory Discharges.*

By A. Battelli *and* L. Magri[†].

[Plate XV.]

Part II.[‡]

The Arrangement and General Course of Experiments.

30. BEFORE reporting the results of experiments, we wish to describe the whole arrangement of the apparatus.

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[*] "The Condition necessary for Equipartition of Energy," Phil. Mag. [6] iv. p. 585, §§ 14–17.

[†] Communicated by the Authors.

[‡] Part I., this volume, *ante*, pp. 1–34.

The electrostatic machine had one electrode put to earth, and the other electrode connected with one of the armatures of a condenser by means of a wooden rod.

The spark- and the metal spiral calorimeters were in series with the circuit traversed by the discharge ; after this had passed, the condenser was put in connexion with a ballistic galvanometer in order to measure the residual charge.

If calorimetric determinations were not to be made, the square or circle forming the metallic circuit was introduced in the place of the metallic calorimeters, the spark passing in the air. If, however, those measurements were also to be made, three or four discharge-photographs were previously taken, the spark-gap being next inserted in the calorimeter, and after having once again produced discharges, simultaneous readings of the metal spiral calorimeter, of the spark-calorimeter, and of the electrometer were taken.

After each series of these readings, the residual charge was measured. The above readings finished, the spark-photographs were often taken again.

PART III.

GENERAL RESULTS OF EXPERIMENTS.

31. From the single elements, as determined by the methods above mentioned, we next calculated the final results of our experiments, as contained in Tables I. to XI.

In the first six tables the results of simultaneous measurements of the period of oscillation, of the amounts of heat evolved in the various parts of the circuit, and of the discharge-potential are recorded.

In Table VII. the periods of oscillation are wanting. Tables VIII. to XI. are exclusively relative to measurements of the periods of oscillation.

In the Tables I. to VII. we have given, in addition to the values of the explosive distance in millimetres and those of the discharge-potential, the mean amount of heat Q_1 evolved with each discharge in the spark, and that Q_2, evolved in the metallic circuit, and the ratio $\frac{Q_1}{Q_2}$ serving to deduce the resistance of the spark from the resistance of the metallic circuit. The last column contains the value of the period, as given by our measurements.

At the beginning of each table the values L_T of the self-induction of the circuit are indicated—including the conductors serving for the connexions—as measured by Nernst's high-frequency current method; the value R'_T of the resistance by the metallic calorimeter, as calculated by Rayleigh's formula, multiplied by the value of the ratio $\frac{\rho}{\rho'}$ of the resistance of unit length of the wire of the spiral to that of an equal length of wire stretched out in a straight line (§ 24, Part I.). The value of the capacity C of the condenser and the theoretical value T of the period, calculated by the formula

$$T = \frac{2\pi}{v} \sqrt{LC},$$

are also given.

The quantities Q_1, Q_2, and $\frac{Q_1}{Q_2}$, likewise given in the tables, will serve for the study of the distribution of energy, to be made in Section V.

The theoretical values of T are, on the other hand, not very sure, owing to the uncertainty attending the value of L corresponding to the spirals, and we are thus not able to ascribe to them more than a relative importance.

32. The results contained in Tables VIII. to XI. are, however, of a much higher importance. They are relative to experiments made with circuits where the self-induction for each period, which period, as derived from the measurements made on the spark-photographs, could be calculated exactly (see §§ 22 and 28, Part I.), and we wish to call attention more especially to these.

On the Plate (Pl. XV.) some of the photographs which served to determine T are reproduced.

Nos. 1, 2, and 4 are reproductions of photographs relative to Tables X., IX. ϵ, and XI. α, respectively. No. 3 is relative to Table IX. δ: this was obtained by producing a discharge between platinum-iridium electrodes, all the remaining being obtained with cadmium electrodes.

Explosive Distance.	Discharge-Potential in E.U. [C.G.S.].	$\frac{1}{2}CV^2$ in Gramme-Calories.	Amount of Heat evolved by each Discharge		Q_1+Q_2.	$\frac{Q_1}{Q_2}$.	Resistance of Spark $r=R'_T\frac{Q_1}{Q_2}$ in Ohms.	Period measured T_s.
			in the Spark Q_1.	in the Met. Circuit Q_2.				
			TABLE I.—Calorimeter No. 2.	Condensers in Parallel.				
	$L_T=74140$.		$R'_T=1·76$ ohms.		C=14175 cm.		$T_c=0·00000679$.	
1	...	...	0·0082	0·0368	0·045	0·223	0·311	0·00000661
1·5	...	...	0·0166	0·0714	0·088	0·232	0·325	0·00000683
2	27·67	0·129	0·0242	0·1013	0·125	0·239	0·323	0·00000677
							MEAN ...	0·00000673
			TABLE II.—Calorimeter No. 1.	Condensers in Parallel.				
	$L_T=29470$.		$R'_T=1·06$ ohms.		C=14175 cm.		$T_c=0·00000428$.	
1	...	...	0·0098	0·0362	0·0460	0·271	0·286	0·00000439
1·5	...	...	0·0203	0·0673	0·0876	0·302	0·319	0·00000428
2	26·95	0·123	0·0289	0·0896	0·1185	0·322	0·341	0·00000431
							MEAN ...	0·00000433
			TABLE III.—Calorimeter No. 1.	Condenser No. 1.				
	$L_T=29470$.		$R'_T=1·38$ ohms.		C=7178 cm.		$T_c=0·00000304$.	
1	...	...	0·0060	0·0161	0·0221	0·3727	0·515	0·00000304
1·5	...	...	0·0123	0·0315	0·0438	0·3905	0·540	0·00000305
2	27·4	0·0642	0·0179	0·0449	0·0628	0·3987	0·551	0·00000302
							MEAN ...	0·00000304

Explosive Distance.	Discharge-Potential in E.U. [c.g.s.].	$\frac{1}{2}CV^2$ in Gramme-Calories.	Amount of Heat evolved by each Discharge		Q_1+Q_2.	$\frac{Q_1}{Q_2}$.	Resistance of Spark $r=R'_T\frac{Q_1}{Q_2}$ in Ohms.	Period measured T_s.
			in the Spark Q_1.	in the Met. Circuit Q_2.				
			TABLE IV.—Calorimeter No. 1. Condensers in Series.					
	$L_T=29470$.		$R'_T=1{\cdot}65$ ohms.		$C=3568$ cm.		$T_c=0{\cdot}00000215$.	
1	...	...	0·0034	0·0098	0·0132	0·3469	0·575	0·00000218
1·5	...	...	0·0063	0·0158	0·0221	0·3987	0·661	0·00000219
2	27·3	0·0317	0·0089	0·0209	0·0298	0·4257	0·723	0·00000217
3	34·8	0·0514	0·0166	0·0342	0·0508	0·4854	0·805	0·00000219
4	38·36	0·0625	0·0215	0·0417	0·0632	0·5156	0·855	0·00000215
5	44·7	0·0848	0·0302	0·0546	0·0848	0·5531	0·918	0 00000214
							MEAN ...	0·00000217
			TABLE V.—Calorimeter No. 3. Condensers in Series.					
	$L_T=17460$.		$R'_T=0{\cdot}827$ ohms.		$C=3568$ cm.		$T_c=0{\cdot}00000165$.	
1	...	...	0·0044	0·0074	0·0118	0·595	0·492	0·00000168
1·5	...	...	0·0079	0·0124	0·0203	0·637	0·527	0·00000170
2	27·01	0·0308	0·0120	0·0176	0·0296	0·682	0·564	0·00000174
3	34	0·0502	0·0207	0·0289	0·0496	0·716	0·593	0·00000168
4	38·87	0·0642	0·0264	0·0349	0·0613	0·756	0·626	0·00000170
5	45	0·0860	0·0372	0·0477	0·0849	0·780	0·845	0·00000169
							MEAN ...	0·00000170

TABLE VI.

Calorimeter No. 4. Condensers in Series.

$L_T=3669$. $R'_T=0·154$ ohms. $C=3568$ cm. $T_c=0·000000758$.

1	...	...	0·0048	0·0041	0·0080	1·171	0·180	0·000000817
1·5	...	...	0·0118	0·0063	0·0181	1·873	0·289	0·000000824
2	25·45	0·0275	0·0166	0·0088	0·0254	1·886	0·290	0·000000824
3	33·04	0·0464	0·0296	0·0148	0·0444	2·000	0·308	0·000000812
4	37·63	0·0602	0·0394	0·0182	0·0576	2·165	0·333	0·000000821
5	44·00	0·0823	0·0518	0·0239	0·0757	2·167	0·334	0·000000828
							MEAN ...	0·000000821

TABLE VII.

Electrodes of Platinum-Iridium.

1	18·38	0·0570	0·0159	0·0402	0·0561	0·396	0·327
1·5	23·37	0·0922	0·0280	0·0640	0·0919	0·437	0·361
2	27·54	0·1304	0·0339	0·0872	0·1211	0·389	0·322

Electrodes of Cadmium.

1	17·30	0·0518	0·0140	0·0365	0·0505	0·384	0·319
1·5	23·54	0·0937	0·0234	0·0640	0·0874	0·366	0·302
2	27·93	0·128	0·0357	0·0897	0·1254	0·398	0·329

TABLE VIII.

Circuit formed by a square of copper wire 0·08 cm. in thickness and 398·6 cm. in side.

α.		β.
Self-induction of the square for T_1=0·00000425 27390 cm. Idem of the connexions 1523 cm. Capacity of Condenser 14175 cm. Capacity of Circuit 97 cm. Value of T=$\frac{2\pi}{v}\sqrt{LC}$=0·000004254. Experimental Value of T.		Self-induction of the square for T_1=0·00000301 27329 cm. Idem of the connexions 1523 cm. Capacity of Condenser 7178 cm. Capacity of Circuit 97 cm. Value of T=$\frac{2\pi}{v}\sqrt{LC}$=0·000003034. Experimental Value of T.
0·000004214	0·000004204	0·000002994
4304	4302	3016
4244	4177	2979
4226	4262	3006
4202	4279	3019
4202	4291	2980
4266	4240	3036
4277	4226	3020
4185	4209	
4210	4213	Mean value T=0·000003006
4196	4252	
Mean value T=0·000004235		

TABLE IX.

Circuit formed by a copper-wire circle 0·452 cm. in thickness, the diameter of the circle being 201 cm.

α.	β.	
Self-induction of the circle for T=0·00000237 7829 cm. Idem of the connexions 1432 cm. Capacity of Condenser C=14175 cm. T=$\frac{2\pi}{v}\sqrt{LC}$=0·00000240. Explosive Distance 2·5 mm. Experimental Value of T.	Self-induction of the circle for T=0·00000167 7824 cm. Idem of the connexions 1432 cm. Capacity of Condenser C=7178 cm. T=$\frac{2\pi}{v}\sqrt{LC}$=0·000001707. Explosive Distance 2·5 mm. Experimental Value of T.	
0·000002334	0·000001655	0·000001665
2348	1693	1658
2389	1660	1654
2358	1648	1693
2370	1685	1689
2371	1692	1668
2378	1679	1671
2408	1677	
2405		
	Mean value T=0·000001672	
Mean value T=0·000002373		

TABLE IX. (*cont.*).

Self-induction of Circle for T=0·00000120 7810 cm.
Self-induction of connexions 1432 cm.
Capacity of Condenser C=3568 cm.

$$T=\frac{2\pi}{v}\sqrt{LC}=0\cdot000001201.$$

γ. Explosive Distance 2·5 mm. Experimental Value of T.		δ. Explosive Distance 5 mm. Experimental Value of T.	
0·000001162	0·000001199	0·000001213	0·000001190
1160	1230	1205	1197
1196	1224	1209	1202
1193	1222	1220	1221
1173	1222	1232	1182
1166	1198	1205	1210
1209	1175	1194	1224
Mean value T=0·000001195		Mean value T=0·000001207	

TABLE IX. (*cont.*).

ε.
Circuit as in Column α.
Electrodes of Platinum-Iridium.
Total Self-induction of Circuit for T=0·00000237 9261 cm.
Capacity of Condenser C=14175 cm.

$$T=\frac{2\pi}{v}\sqrt{LC}=0\cdot00000240.$$

Explosive Distance 2·5 mm.
Experimental Value of T.

0·000002395	0·000002270
2412	2480
2369	2489
2497	2426
2454	2476
2338	2386
2282	2186
Mean value T=0·00000239	

TABLE X.

Circuit formed by small Copper wire 0·452 cm. diameter.
Diameter of Circle 57·2 cm.
Total Self-induction of Circuit for T=0·00000074 2993 cm.
Capacity of Condenser 3568 cm.

$$T=\frac{2\pi}{v}\sqrt{LC}=0\cdot000000684.$$

Explosive Distance 2 mm.
Experimental Value of T.

0·0000007431	0·0000007422
7263	7103
7411	7625
7565	7493
7567	7442
7560	7414
Mean value T=0·000000744	

TABLE XI.

Circuits formed by Copper-Wire Spirals.

α. Self-induction of Large Spiral 4546000 cm. Capacity of Condenser C=14175 cm. $T=\frac{2\pi}{v}\sqrt{LC}=0{\cdot}00005317$. Explosive Distance 2 mm. Experimental Value of T.	β. Self-induction of Small Spiral and Connexions 57797 cm. Capacity of Condenser C=14175 cm. $T=\frac{2\pi}{v}\sqrt{LC}=0{\cdot}000005995$. Explosive Distance 2 mm. Experimental Value of T.
0·00005404	0·000006201
5374	5993
5339	6067
5363	5923
5417	6034
5434	6093
5444	5995
5386	5970
5403	
5303	Mean value T=0·000006034
5347	
5296	
Mean value T=0·00005376	

TABLE XI. (*cont.*)

γ. Self-induction of Small Spiral and Connexions 57797 cm. Capacity of Condenser C=3568 cm. $T=\frac{2\pi}{v}\sqrt{LC}=0{\cdot}000003008$. Explosive Distance 2 mm. Experimental Value of T.	
0·000002986	0·000003034
3037	2981
3011	2904
3173 (?)	3039
3032	3036
3053	3001
3011	3042
3022	3021
Mean value T=0·000003024	

PART IV. DISCUSSION OF RESULTS.

33. In order to have an adequate idea of the importance to be ascribed to the noteworthy agreement observed between the experimental and calculated values of the period T, it will be necessary to give an account of the accuracy attained in the determination of the various elements relative to this measurement.

(a) *Experimental Determination of the Period.*

It will be useful here to consider briefly what results may be derived from the numerous photographs obtained.

First of all there is to be noted that the section of the spark is very large when a considerable amount of electricity is discharged, as in the cases recorded in Tables I., II., VIII. α, IX. α, IX. ϵ, X. α, and X. β.

It next will be worthy of notice that the successive sparks a discharge is made up of do not always pass between the vertices of the spherical calottes forming the electrodes of the spark-gap, but as a rule take various positions on the electrodes, thus lengthening the explosive distance. This phenomenon is clearly seen on many of our photographs, where the aspect of the discharge is that of a strip, whose width, as a rule, increases with time (fig. 2, Plate XV.).

A behaviour more regular in this respect is noted when the sparks are longer, and when a smaller amount of electricity is being discharged. Then the section of the spark is very small, and the variations of length of the photographic images of the various elementary sparks are less.

Now if the spark is produced between rather volatile electrodes—as, for instance, cadmium electrodes—its behaviour is very regular, as may be seen from photograph No. 3 on Plate XV. If the electrodes consist of platinum or platinum-iridium, the spark as a rule shows a very irregular aspect, as that of photograph No. 2 of the above-mentioned Plate, where noticeable displacements between the single partial sparks are to be observed, each of which, so to speak, has to open itself a discharge-way of its own.

On this displacement of the elementary sparks may depend the variability of the period of oscillation from one elementary discharge to another, as observed by Trowbridge and Sabine, as well as the fact noted by Lodge and Glazebrook that the last period of the spark is longer than the rest, this variation being probably due, not to the hysteresis of the air forming the insulator of the condenser, but to the great resistance offered by the spark on its disappearing.

But it is a consequence of Stefan's * theory also, that there should always exist a difference between the initial and final values of the period of the discharge. In fact, according to this theory there is added to the undulatory movement corresponding to Thomson's theory another period capable of modifying materially the period during the first moments of the discharge.

Whatever may be the reason of the above-mentioned displacement of the single-spark components, it is clear that this phenomenon affects to a great extent the accuracy attainable in the experimental determination of the period of oscillation. This accuracy, in fact, depends not only on the constancy of the velocity of rotation of the mirror and of the degree of precision with which this same velocity may be measured at the moment of the photograph being taken ; but it depends equally on the precision with which the distance between the photographic images of two successive elementary sparks may be determined. Now, if these sparks are being displaced on the electrodes, the measured distance does not correspond with the true one.

We, however, eliminated, at least for a great part, this inconvenience of measurements, as, out of the numerous photographs made for each case and for each explosive distance, we used only those on which the images of the sparks were well defined and regularly distributed.

In addition, as already stated, when calculating the mean value of the distances between two successive elementary sparks, the first and last sparks were always left out of the calculation, and the effective period was derived from the mean distance between the remaining small sparks, these latter being always very numerous.

The value given for the experimental period was the mean of those derived from the mean of many photographs for each case and each explosive distance.

The agreement of these values is noteworthy. In order to give an adequate idea of this we record in Tables VIII. to XI. all the values used for determining the experimental value of T for circuits with well-known self-induction.

Measurements of the same value of the period made on different days always gave perfectly concordant figures.

From this fact it may be inferred that, in the values of the period measured by us and recorded in the preceding tables, a notable accuracy has been reached.

* Wied. *Ann.* xli. p. 421 (1890).

(b) *Value adopted for Capacity of Condenser.*

34. The great care bestowed on the absolute measurements of the capacity of the condenser, and the agreement of the value thus obtained with the one resulting from a comparison with the sample kindly forwarded by Prof. Ròiti, entitle us to maintain that the value obtained by us is trustworthy in all respects.

On the other hand, it might be suspected that for large potential-differences between the armatures, as those corresponding with the explosive distances of some millimetres used by us, the charge should extend over the glass edges not covered with tinfoil to a much higher degree than in the case of the very slight charges used with the above-mentioned standardizing, and that hence the true capacity is larger than the one noted. Whether this is really the case, we were not in a position to ascertain; but it is certain that, if for high potentials there occurs a greater diffusion of charge on the glass, this could not augment practically the effective capacity of the condenser, as at the moment of the spark the electricity going on to the glass is not discharged in the same way as that taken by the metallic armatures.

One also might object that the capacity for rapidly oscillating discharges should be different, even for air-condensers, from that given by measurements with slow charges—in fact this objection has been raised against Hertz's experiments.

But applying to our experiments Drude's calculations (*Physik des Æthers*, p. 459), one easily understands that no correction is to be made on this account in the above-mentioned value of the capacity used in our experiments.

Moreover, as the total resistance of the circuit containing the spark will subsequently be shown to be negligible as compared with $\frac{1}{\mathrm{LC}}$—the reduced formula of Thomson thus applying to this case—from the striking agreement which in this case also exists between the calculated and observed periods, it may be inferred that the value adopted for the capacity of our condenser, obtained from determinations made with slow charges and low potentials, is really true also for oscillatory discharges and for the potentials used in our experiments. In addition, this agreement may be regarded as an evidence that the dielectrical hysteresis of the air is really negligible for the periods of the discharges photographed by us.

(c) *Value of Resistance and Self-Induction.*

35. The calorimetric methods used by us afford, in our opinion, the most satisfactory comparison between the resistances offered by two different circuits to oscillatory discharges. We therefore, having by Lord Rayleigh's formula calculated the resistance of some rectilinear conductors, with which we have compared the resistances of our spirals (§ 24 and following), may claim to have succeeded in finding in absolute measure those same resistances with the degree of approximation the calorimetric measurements will allow of.

It might be objected that in fact Lord Rayleigh's formula rigorously applies to perfectly harmonic currents only, and that the effects the damping will produce on the resistance should be taken into account; but one easily understands from Barton's * formulæ that the correction on account of the damping would in our case be less than 1 per cent. Now Barton *, from a calculation recorded in Maxwell's Treatise, recently found (as did Lord Rayleigh) the expression for the resistance and self-induction of a current for damped harmonic currents as well as for those obtained by a condenser-discharge. In Barton's theory the damping of the currents is measured by a certain number k, which, using the notation adopted by us, is given by the equation:

$$k = \frac{R}{2L} \frac{T}{2\pi},$$

and thus in our case is without any doubt always inferior to 0·02. Now, denoting by R″ and R′ the values of the resistances of the same circuit, as calculated by Barton's and Rayleigh's formulæ respectively, their ratio is given by

$$\frac{R''}{R'} = 1 + \frac{k}{2} + \frac{7}{8} k^2 + \dots,$$

a quantity absolutely to be neglected as being inferior to the mean approximation the calorimetric measurements were made with.

Moreover, Cardani's † direct experiments made with condenser-discharges prove experimentally that within the limits of error of those measurements the resistance of a rectilinear wire may for those discharges be regarded as having really the value assigned to it by Lord Rayleigh's formula.

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* Phil. Mag. [5] xlvii. p. 433 (1899).

† *N. Cim.* [4] vii. p. 229 (1898).

36. As regards self-induction, we wish to state that different experimenters, having measured the coefficient of the same coil with direct currents and with alternating currents, have found values differing little from one case to another ; but the reversals used were always of few hundredths per second.

Tallqvist (*l. c.*) more especially dealt with the influence the method of measuring the self-induction of the circuit may possess, comparing the experimental values of the period of oscillation with those deduced from Thomson's formula. From this comparison, he argues that the true values of L for oscillatory discharges are somewhat smaller than those obtained experimentally by the method of direct currents as well as by the telephone method with alternate currents. As a rule, however, the value of L adopted for the spirals in the researches so far carried out in oscillatory discharges has always been either the one calculated by the formulæ true for direct currents, or the one found experimentally with those currents.

On the other hand, our self-inductions have either been calculated directly and with the proper corrections relative to the frequency of the discharges, or have been determined experimentally with high-frequency currents by comparison with already calculated self-inductions. In the case also of the self-induction, the effect of the damping is wholly negligible in our experiments, so that Rayleigh's formulæ may be used instead of those of Barton.

As regards the case of circuits of any form, the method suggested by Stefan * for taking account of the unequal distribution of the current in the section of a wire may not be applied to the small-radius spirals, as for this it would be required that the thickness of the wire be negligible as compared with the radius of curvature of the circuit, and that the current be distributed symmetrically around the axis of the wire. This of course is not true for the ordinary spirals, on account of the dissymmetry of distribution of the currents, dissymmetry due to the action of one winding on another. This perturbing action tends to localize the currents only on some portions of the surface of the conductor ; and that this is really the case is clearly shown by the fact, established by our experiments (see § 24), that in the case of alternating currents a wire bent to a spiral will oppose a much higher resistance than that corresponding to the same wire stretched out in a straight line. As theoretical formulæ able to give us the effective self-induction of

* *Wien. Ber.* xcv. II *a*, p. 917 (1887).

a spiral for high-frequency currents are wanting, we had to apply to the experimental method, which indeed led to satisfactory results.

(d) *Resistance of Spark.*

37. Our experiments gave us also the means of determining the resistance of the spark, which nowadays forms one of the principal problems connected with the electrical discharge. Though it has been the object of some determinations, it can not be said to be known with certainty, and more especially it is not known how it depends on the frequency of the oscillations.

Biernacki* tested the resistance of the spark of a condenser by comparing it with that of an electrolyte inserted between the balls of a resonator identical with the oscillator itself, but this investigation is relative only to the sparks of Hertz's oscillators, viz., to oscillatory discharges of high frequency, where small quantities of electricity only are in question.

Kaufmann †, on the other hand, found that the quantity of heat evolved in the spark by the discharge of a battery of Leyden-jars is connected with the resistance W of the remaining part of the circuit by the formula

$$q = \mathrm{A} + \frac{\mathrm{B}}{\mathrm{W}},$$

A and B being constants. Thus the resistance of the spark is not comparable with a metallic resistance.

Moreover, he found that the heat evolved in the spark increases with the potential-difference more rapidly than the total energy of the discharge; that is to say, he found approximately $\frac{q}{v^3} = \text{const.}$, instead of $\frac{q}{v^2} = \text{const.}$ This latter result is not in accord with those derived from our experiments.

Besides, he found the quantity of heat evolved in the spark to be larger (about double) between two zinc electrodes than between two brass electrodes. We had for cadmium and platino-iridium electrodes about the same values of Q (see Table III.).

More recent and accurate measurements are those of Cardani ‡, who of course determined the *apparent* resistance of the spark by deriving it from the total heat evolved less

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* *Journ. de Phys.* [3] iv. p. 474 (1895).

† Wied. *Ann.* lx. p. 653 (1897).

‡ *N. Cim.* [4] xi. p. 113 (1900).

that evolved in the metallic part of the circuit. According to his experiments—as Orgler* had found by a different method—the resistance R of the spark should be represented, in terms of its length l, by the relation

$$R = Al + B,$$

A and B being constants. But the variations of the resistance with the period of oscillation cannot be deduced from Cardani's experiments. This goes to show that the experiments so far performed, as above stated, fail to give the complete solution of the problem. But, on the other hand, it may be maintained that, in order to take account of the spark, one would have to write the equation for the movement of the electricity under the form

$$\frac{Q}{C}\frac{dQ}{dt}dt + R\left(\frac{dQ}{dt}\right)^2 dt + L\,\frac{dQ}{dt}\,\frac{d^2Q}{dt^2}\,dt + w\,dt = 0, \quad . \ (\alpha)$$

differing from the one applying to the discharge in a wholly metallic circuit by the term $w\,dt$, representing the work accomplished in the production of the spark. If w could be regarded as constant, the action of the spark would be perfectly equivalent to that of a resistance, and w would have to be comprised in the coefficient of $\left(\frac{dQ}{dt}\right)^2 dt$. In that case the solution of (α) would differ from that of Thomson's equation only by the different value of R, which then would represent the combined resistance of the metallic circuit and the spark. But the processes occurring in the spark are very complex, and their nature is not known with certainty.

One might maintain with Heydweiller † that the variation of the resistance of the spark, after being rapid at the beginning of the discharge, would proceed slowly, so that for great resistances of the circuit after a relatively short time a constant "*régime*" would be set up. But if this were true, w would be such a function of t and R that (α) would not be integrable; hence this hypothesis cannot be tested by experiment.

It thus only remained to submit to new measurements the resistance the spark offers under various conditions; these we made with our apparatus, the arrangement of which enabled the total energy spent in the spark to be measured, and to be compared with that spent at the same time in the metallic part, whose resistance R'_T, for oscillations of

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* Drude's *Ann.* i. p. 159 (1900).

† Wied. *Ann.* xliii. p. 310 (1891).

the frequency measured each time, was calculated in the manner mentioned in § 26. In the tables given above the 8th column, containing the values of $R'_T\frac{Q_1}{Q_2}$, where Q_1 is the heat evolved in the spark and Q_2 that evolved in the metallic spiral, serves to give us the mean resistance r of the spark. Though these values of r are perhaps a little smaller than the true ones, on account of the dispersion of heat possibly occurring along the metallic rods of the spark-gap, yet our experiments will allow of the conclusion that the resistance of the spark has been in most cases smaller than that of the metallic part, and without any doubt always inferior to 1 ohm. The measurements completed by us would ascribe to the mean resistance of sparks of from 1 to 5 mm. values ranging from 0·18 to 0·96 ohm, with the reservation above mentioned.

Another important fact may be deduced from our experiments, viz., that the capacity and resistance of the metallic part of the circuit remaining the same, the resistance derived from the ratio $\frac{Q_1}{Q_2}$ increases very slowly as the length of the spark increases (see Tables I. to VII.). This may be explained, either by admitting that the main part of this resistance lies at the passage from the electrode into the air, or that with increase of length the section of the spark increases in proportion.

With the arrangement adopted by us one may besides ascertain how the resistance of the spark depends upon the period of oscillation; and a perusal of the tables above given shows that this resistance—the explosive distance and capacity of condenser being the same—increases with increase of period.

The noteworthy accord between the calculated value of the period of oscillation and the one given by our experiments, is an evidence of the smallness of the value of the effective resistance of the spark; and another evidence of the accuracy of the measurements carried out is afforded by the fairly satisfactory agreement between the disposable energy of the condenser and the sum of the thermic energies evolved in the metallic circuit and in the spark.

It is almost superfluous to state that all we have said regarding the resistance of the spark is relative to the mean values it presents during the whole time it lasts.

PART V. MEASUREMENTS OF ENERGY SPENT IN THE DIFFERENT PARTS OF THE CIRCUIT.

38. The expression

$$W=\frac{1}{2}CV^2,$$

where C is the capacity of the condenser, and V the potential it has been charged to, gives the maximum limit of the energy the condenser is capable of supplying on its being discharged through any circuit.

Now when the discharge occurs, part of the energy the condenser possesses is dissipated in the dielectric; another part is employed to overcome the resistance of the circuit and of the spark; a third part is spent in splitting metallic particles off from the electrodes, and in causing them to glow; and a last part will finally be (radiated) sent off from it, viz., will be spent in the production of the electrostatic and electromagnetic fields. It is evident that these various portions will not all be found again under the form of thermic energy in the discharge-circuit—comprising the spark; and that it will be necessary to account for the means of measuring the single portions themselves.

Direct determinations of the energy dissipated elsewhere than in the metallic part of the circuit and the spark have only been made as far as the amount absorbed by the dielectric of the condenser is concerned; and some are relative to the case of alternating currents supplied by ordinary industrial machines, as those of Rosa and Smith[*], of Lombardi[†], Arnò[‡], and Schaufelberger[§], &c. But in our case the loss of energy in the dielectric of the condenser may be neglected, as we used an air-condenser.

Among the investigations performed in order to determine the heat evolved in the spark and in the metallic part of a discharge-circuit, we wish to mention those of Heydweiller and Cardani, as they were made with a special view to determine quantitatively the phenomenon.

Heydweiller's[||] measurements relate only to continuous discharges, as he inserted in the circuit resistances of several megohms formed by solutions of cadmium iodide in amyl alcohol.

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[*] Phil. Mag. [5] xlvii. p. 19 (1899).

[†] Lombardi, Abstracts from the *Elettricista*, Year 5, No. 10, *Mem. R. Acc. Sc. Torino*, ser. ii. vols. xliv. & xlv.

[‡] *Rend. Acc. Linc.* 1892, 1893, 1894.

[§] 'Inaugural Dissertation' (Faculty of Zurich), 1898.

[||] Wied. *Ann.* xliii. p. 310 (1891).

He determined with a sort of liquid thermo-rheostat the heat evolved in the circuit, and having also measured in the form $\frac{q_0^2 - q_1^2}{2C}$ (where q_0 is the initial quantity of electricity, q_1 the residual electricity, and C the capacity of the condenser) the total work of discharge, he could deduce by difference the work spent in the spark.

The main action of the spark would consist, according to Heydweiller, not in its resistance, but in the work necessary to maintain the discharge-potential.

Cardani *, in investigating the resistance of the spark, dealt indirectly with the distribution of energy in a circuit of constant and small self-induction, where by varying the capacity of the condenser the period of oscillation was also altered between certain limits. Studying next the discharge in rarefied gases, Cardani observed that the part of the energy dissipated in the spark depends on the form of the discharge and on the section of the spark itself, being much larger when the discharge passes in the form of a luminous brush.

But both Heydweiller's and Cardani's measurements fail to afford the complete solution of this part of the problem, as those of Heydweiller apply only to continuous discharges, while those of Cardani are not relative to the energy disposable.

For the solution of the problem it is necessary that the determinations of the thermal energy evolved in the different parts of the circuit should be executed simultaneously; as it is important also that in measurements of this kind the sum of such energies should be compared with the total energy disposable in the discharge.

As, moreover, the arrangement of our experiments for the determination of the period of oscillation and for measuring the various resistances was such as to allow of the necessary measurements being made simultaneously, we also tried to draw some conclusions relative to the energy found in the different parts of the discharge-circuit, as compared with the total disposable energy.

On this account, in addition to the above-described determinations of the capacity and the heat evolved in the metallic parts and in the spark, we had to ascertain the discharge-potential and the value of the residual charge.

Electrometer.

39. In order to obtain the value of the potential at which the discharge began, we availed ourselves of a Righi † idio-

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* *Nuovo Cimento* [3] xxxv. p. 142 (1894); [4] xi. p. 113 (1900).

† *Nuovo Cimento* [2] xvi. p. 89 (1876).

static electrometer, this being very suitable for an accurate determination of high potentials. We, however, added to the needle of this electrometer (made out of a thin aluminium plate) a light electromagnetic damper, formed of a copper-plate frame, moving in a magnetic field, and of a form quite similar to that of a Despretz-D'Arsonval galvanometer.

The needle and the damper were very light, their movement being nearly aperiodic, so as to allow of following the rapid variations of the potential.

As a matter of course, the necessary precautions have been taken in order to protect the damper and the mirror against the electrostatic actions.

Method of securing Constancy of Potential.

40. The electrodes we used for the discharge, after various endeavours, had the form of small cylinders 3 mm. in diameter, terminated by spherical calottes. It proved very difficult, on account of the smallness of the electrodes, to secure a fairly constant potential of discharge for each series of experiments. With aluminium, cadmium, iron, &c. electrodes, the alterations of the surface were so rapid, and the delay of discharge, when the sparks passed in the interior of the calorimeter, was so great and so variable, as to make it impossible to ascribe to the mean deviation a reliable value. In the case where we had to complete calorimetric measurements, we hence found it very convenient to use platinum, and still better platino-iridium electrodes, also in order to avoid oxidation phenomena.

In order to diminish greatly the delay of discharge, we put in the interior of the spark-calorimeter, or at a slight distance from the spark-gap, when the photograph was taken, a small celluloid tube containing a little radioactive substance. The action of this substance was so strong that the successive discharge-potentials were very slightly different from one another, and allowed of obtaining a good average for the value of the discharge-potential, provided the surface of the electrodes was not too much altered.

In any case it was necessary the sparks should occur with sufficient slowness to allow of the needle following the variations of the potential, in order to have reliable calorimeter-readings. On this account, we were not able to make in each case the readings themselves simultaneously with the calorimeter-readings, for which it was necessary that the sparks should follow each other with sufficient rapidity. We therefore made in many cases the determinations of the discharge-potentials immediately before and after each series of calorimetric readings, requiring always a satisfactory accord between the two sets of readings.

We next obtained the absolute value of the discharge-potential by standardizing our electrometer with a good absolute Kelvin balance-electrometer made especially for potentials of the order of magnitude of those used by us.

Acccording to the potential-difference we had to measure, the electrometer was regulated so as to give to its constant the value 1·505 or the value 2·71.

Galvanometer for measuring the Residual Discharge.

41. But in order to know exactly the portion of energy really intervening in the discharge, it was necessary, as above stated, to determine also the value of the residual charge.

For this purpose the condenser was charged by means of a large double Holtz machine, the motion of which was maintained slow and uniform by means of an electromotor. When we wished to determine the residual charge, in order that the condenser might not be charged very quickly, in most cases we approached a pole of the machine itself terminated by a point to a plane electrode connected with one of the armatures of the condenser, instead of establishing a direct connexion with the machine, the other armature being joined to earth.

After ascertaining in the required manner the distance between the electrodes of the spark-gap, the velocity of the motor was modified so as to have sparks passing in the spark-gap at intervals of about one or two minutes. After this we proceeded to measurements; that is, we set free a short pendulum conveniently placed, as soon as the first spark had passed in the spark-gap, so as to establish the connexion between the condenser and one of the terminals of a ballistic galvanometer, the other terminal being joined to earth.

In order to secure a good insulation and a complete protection of the needle from the electrostatic actions, the frame of the galvanometer was formed of only two layers of wire covered with a thick guttapercha coating, and the needle (made up of a small magnetized steel mirror) was inclosed in a cylinder, whose lateral surface was of metallic gauze, the bases being of brass. Readings were effected through a narrow slit made in one of the bases.

In our experiments, where sparks never exceeded 5 mm. in length, and where the resistance of the circuit was excessively small, the residual charge, being due only to the amount of electricity which could not be discharged by the spark itself, was found to be constantly negligible, *i. e.* always inferior to the hundredth part of the initial charge.

Disposable Energy and its Distribution in the Circuit of Discharge.

42. The work done in imparting the potential V to the condenser of capacity C would represent the energy effectively disposable, and should accordingly be found again in the discharge, but for the part dissipated in the dielectric, outside of the metallic circuit and the spark.

This dissipation of energy may reach sensible values in condensers with solid dielectric, and, as a matter of fact, there exists no reliable method of calculating it. In fact the methods used for ordinary alternating currents of industrial machines cannot be applied to the present case, and Wulf's * method, based upon the determination of the damping-coefficient of the amplitude of oscillations, as derived from the residual-charge curves, and of the theoretical decrement, as calculated from the potential-differences corresponding to two successive maxima, does not give results of sufficient accuracy. But with our researches this inconvenience was reduced to a minimum by the use of air-condensers, or at the least was certainly of an order of magnitude inferior to the unavoidable errors of the calorimetrical measurements.

Another portion of energy, not found again in the circuit either, is that radiated by electromagnetic waves.

The theory of oscillatory discharge allows of this part of the energy being calculated, as it affords a means of comparing the intensity i of the current traversing the wires of the discharge-circuit—supposed parallel and at the distance d from one another—with the intensity i' observed in the air-cylinder, having one of the wires as axis and half of the distance d between the two wires as radius of the bases. The ratio between i and i' (see Drude, *Physik d. Aethers*, p. 369) is given by

$$\frac{i'}{i}=\frac{6d^2}{T^2c^2}.$$

These calculations cannot, it is true, be applied to our experimental arrangements; but it may still be observed that they may give account of the order of magnitude of the portion of energy dissipated. If, for instance, it be observed that in the experiments performed by us the value of Tc, that is the wave-length, is always superior to 600 m.; and

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* *Wien. Ber.* cv. II *a*, p. 667 (1896).

that of d, though adopting as maximum distance that between our circuits and the earth, is always smaller than 2 metres, the preceding formula will give

$$\frac{i'}{i} < 6\left(\frac{1}{300}\right)^2, \quad \text{or} \quad \frac{i'}{i} < 0{\cdot}000066.$$

In the case of circuits wound into spirals, the dispersion cannot be much different; hence with our experiments it may always be regarded as negligible.

That the sum of the energies spent outside the metallic circuit is negligible within the limits of accuracy reached with our measurements of the discharge-potential and of the heat evolved in the spark, may also be derived from the experiments themselves. In fact, in the Tables I. to VII. we compared the sum Q_1+Q_2 of the heat evolved in the spark and in the metallic spiral, with the energy corresponding to $\frac{1}{2}CV^2$; and from a perusal of those tables it may be seen that nearly all the energy is found again in the form of heat in those two portions of the circuit. On the other hand, we wish to maintain that the uncertainty as to the true value of V (due to the great variability of the effective length of the spark), and the fact that the spark-calorimeter does not give a very exact measure of all the heat evolved in the spark itself, deprives our comparison of part of its value. In these first researches, however, it was more interesting to study the repartition of the energy between the spark and a metallic part of known resistance, than the absolute value of the total energy; and this repartition we have succeeded in ascertaining with sufficient accuracy.

Conclusions.

43. From a survey of these results the following conclusions may, in our opinion, be drawn:—

1. The period of oscillation agrees, within the limits of experimental errors, with the theoretical value, as given by Thomson's formula. The less satisfactory accordance observed in the case of very short periods (about 7×10^{-7}) is due to the fact that in such cases the self-induction of the circuit cannot be allowed for.

2. The resistance of the spark in the case of little-damped discharges, due to rather large amounts of electricity, as those given by our condensers, and for explosive distances comprised between 1 and 5 mm., is very small and always inferior to 1 ohm. *Ceteris paribus*, this resistance increases considerably less rapidly than the length of the spark. This

would suggest that either the resistance of the spark for the most part is due to the passage from the electrodes into the surrounding gas, or that the section of the spark augments as its length increases.

3. The resistance of a wire bent to a spiral is for oscillatory discharges much higher than that shown by the same wire when stretched out into a straight line.

The difference between the two values augments as the frequency of the discharge increases and the distance between the single spires decreases. Lord Rayleigh's formula thus does not apply to circuits bent into a spiral.

4. The sum of the calorific energies spent by the discharge in the spark and the metallic circuit agrees fairly well with the value of the energy of the condenser.

5. With cadmium electrodes the sparks are much more regular than those corresponding to platinum and platino-iridium electrodes.

6. The values of the spark-resistance and of the energy spent in the spark itself are, in the conditions of our experiments, practically identical for platino-iridium and cadmium electrodes.

LXVI. *On the Connexion between Speed of Propagation and Attenuation of Electric Waves along Parallel Wires. By* W. B. MORTON, *M.A., Professor of Natural Philosophy, Queen's College, Belfast*[*].

WHEN electric oscillations, of frequency $\frac{p}{2\pi}$, are guided by imperfectly conducting leads, the various vectors contain a factor

$$e^{-\kappa z} \sin\left(\frac{2\pi z}{\lambda} - pt + \beta\right)$$

the propagation being along the positive direction of the axis of z. The course of the analysis leads, in general, to an expression for the complex quantity $m = \frac{2\pi}{\lambda} + i\kappa$ as a function of p and of the magnitude $a\sqrt{\frac{\mu p}{\rho}}$, where a is the radius of the wire, μ the permeability, and ρ the resistivity of its material.

In the present paper I start with the approximate formula for m in the case of two parallel wires, as discussed in former

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[*] Communicated by the Author.

papers* in this Journal, and proceed to investigate the relation between the real and imaginary parts for the limiting cases in which $a\sqrt{\frac{\mu p}{\rho}}$ has a very small or very large value. The results are shown graphically, not only for these extreme cases, but also for intermediate values of the quantity $a\sqrt{\frac{\mu p}{\rho}}$. The plotting of the complete curve is rendered possible by the use of Aldis's tables† of the functions $J_0(x\sqrt{i})$ and $J_1(x\sqrt{i})$. In this case

$$x = 2a\sqrt{\frac{\mu p \pi}{\rho}}.$$

The speed of the waves along the wires will be expressed as a fraction of V, the speed of free radiation. For a measure of the attenuation it will be found convenient to take, instead of κ, the quantity $\frac{\kappa V}{p}$ or $\frac{\kappa\lambda_0}{2\pi}$, where λ_0 is the wave-length in free space. For good-conducting wires λ_0 is practically equal to λ, and our measure of attenuation is then the logarithmic decrement of amplitude corresponding to a distance $\frac{\lambda}{2\pi}$ along the wires. For cases of rapid attenuation when λ_0 is no longer nearly equal to λ, we may suppose that the frequency is kept constant, and that the alteration in the state of affairs is brought about by changing the properties of the leads.

For two wires at distance b, we have ‡, if $\frac{a^2}{b^2}$ can be neglected,

$$\frac{p^2}{V^2} - m^2 = \frac{p^2}{V^2} \frac{J_0(x\sqrt{i})}{\log\frac{b}{a} J_1(x\sqrt{i}) \,.\, x\sqrt{i}} \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{V^2 m^2}{p^2} = 1 - \frac{J_0(x\sqrt{i})}{\log\frac{b}{a} J_1(x\sqrt{i}) \,.\, x\sqrt{i}}$$

and

$$\frac{Vm}{p} = \frac{V}{p}\left(\frac{2\pi}{\lambda} + i\kappa\right)$$
$$= \frac{V}{v} + \frac{i\kappa V}{p}$$

where v is the speed of the waves along the wires.

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* Phil. Mag. vol. l. p. 605 (1900); i. p. 563 (1901).

† Aldis, Proc. Roy. Soc. vol. lxvi. pp. 42, 43 (1899).

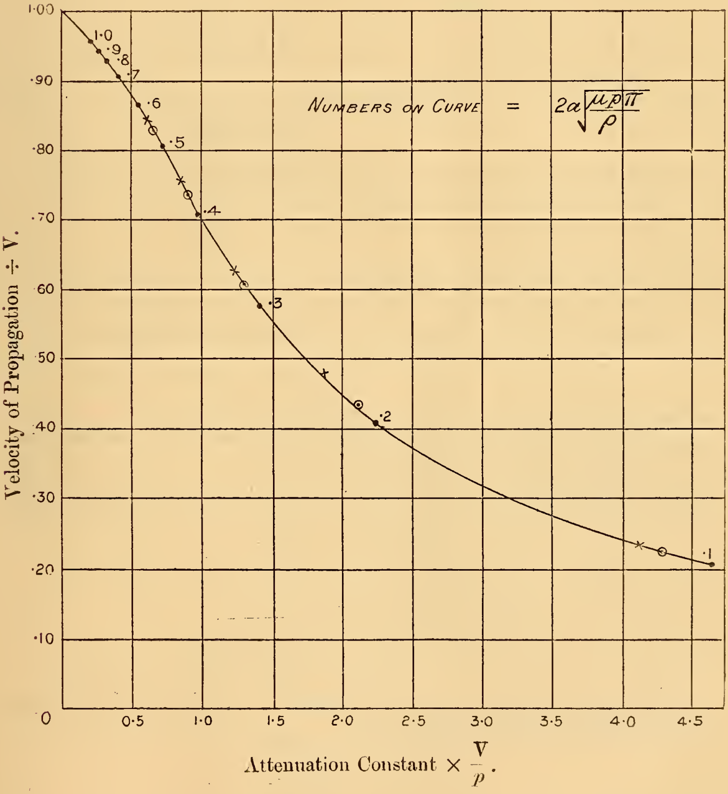
‡ Phil. Mag. vol. l. p. 610, equation (12).

Write

$$\eta=\frac{v}{\mathrm{V}}, \quad \xi=\frac{\kappa \mathrm{V}}{p}=\frac{\kappa\lambda_0}{2\pi},$$

and we have

$$\left(\frac{1}{\eta}+i\xi\right)^2=1-\frac{\mathrm{J}_0(x\sqrt{i})}{\log\frac{b}{a}\mathrm{J}_1(x\sqrt{i})\,.\,x\sqrt{i}} \quad . \quad . \quad . \quad (2)$$



Using the value $\frac{b}{a}=100$, I have plotted the curve showing the connexion between $\xi\eta$ for different values of x, which are specified by the numbers placed beside the marked points.

It is easy to find the shape of the curve at its extremes:

(1) For *very large values of* x, i. e. well-developed "skin-effect."

$$\frac{J_0(x\sqrt{i})}{J_1(x\sqrt{i})}=-i$$

$$\left(\frac{1}{\eta}+i\xi\right)^2=1+\frac{\sqrt{i}}{x\log\frac{b}{a}}$$

$$=1+\frac{(1+i)}{\sqrt{2}\,.\,x\log\frac{b}{a}}$$

$$\frac{1}{\eta}+i\xi=1+\frac{(1+i)}{2\sqrt{2}x\log\frac{b}{a}}\,. \quad . \quad . \quad . \quad . \qquad (3)$$

$$\therefore \qquad \xi=\frac{1}{2\sqrt{2}\,.\,x\,.\log\frac{b}{a}}$$

$$\eta=1-\frac{1}{2\sqrt{2}\,.\,x\,.\log\frac{b}{a}}$$

$$\therefore \qquad \xi+\eta=1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

i. e. a straight line inclined at 45° to the axes.

This part of the curve is compressed into very small scale at the upper part of the diagram.

(2) For *very small values of* x, the current penetrating to the core of the wire.

$$\frac{J_0(x\sqrt{i})}{J_1(x\sqrt{i})}=\frac{2}{x\sqrt{i}}$$

$$\left(\frac{1}{\eta}+i\xi\right)^2=1+\frac{2i}{x^2\log\frac{b}{a}}$$

We may neglect unity in comparison with the large term which follows, and so obtain

$$\frac{1}{\eta}+i\xi=\frac{1+i}{x\sqrt{\log\frac{b}{a}}}\,. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

$$\therefore \qquad \xi=\frac{1}{x\sqrt{\log\frac{b}{a}}}$$

$$\eta=x\sqrt{\log\frac{b}{a}}$$

$$\therefore \qquad \xi\eta=1\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

or the curve at its lower end approximates to the form of a rectangular hyperbola.

It will be seen that in both cases $\log\frac{b}{a}$ disappears from the equation, so that we get the same curve for all distances of the wires apart. In other words we have, in the extreme cases, a definite attenuation (as measured by the quantity ξ) associated with a given speed of propagation. The value of $a\sqrt{\frac{\mu p}{\rho}}$ which gives a particular attenuation and speed is, at the upper, "skin-effect," part of the curve inversely as $\log\frac{b}{a}$. In the opposite extreme region it is inversely as the square root of this logarithm.

I have re-calculated the values of the speed and attenuation for the same values of x (0·1, 0·2, &c.) using $\frac{b}{a}=200$ and $=300$ instead of $=100$. The points so found are marked on the diagram with a circle and a cross respectively. It will be seen that, even in the middle parts, they lie close to the curve drawn for $\frac{b}{a}=100$.

In former papers I have shown that a variety of more complicated cases of propagation along a set of parallel wires may be replaced, as regards attenuation and retardation of the waves, by an equivalent pair of parallel wires. It would seem therefore to be very generally true that—

In systems which cause a given amount of retardation in the speed of the waves, the attenuation-constant, κ, is proportional to the frequency; or, *there is a constant logarithmic decrement in running a distance equal to the wave-length in free space of oscillations of the same frequency.*

We can express in words the relations involved in equations (4) and (6). The former is equivalent to

$$\frac{\kappa\lambda_0}{2\pi}=\frac{V-v}{V}.$$

When the dissipation of energy in the wires is small the logarithmic decrement, on running the fraction $\frac{1}{2\pi}$ of a wave-length, is equal to the fractional decrease of the speed of propagation.

Equation (6) gives

$$\frac{\kappa V}{p} \cdot \frac{v}{V} = 1,$$

$$\kappa = \frac{p}{v} = \frac{2\pi}{\lambda}.$$

When the attenuation is rapid the attenuation-constant approaches the value $\frac{2\pi}{\lambda}$ *where* λ *is the actual wave-length along the wires.*

Queen's College, Belfast,
2nd March, 1903.

LXVII. *On an Oscillating Table for Determining Moments of Inertia. By* W. H. Derriman, *B.Sc., Demonstrator in Physics, University College, Liverpool*[*].

THE following description of an oscillating table for determining moments of inertia is given in the hope that the apparatus may prove useful in the laboratory, both for determining moments of inertia of bodies experimentally, and also for illustrating some of the laws relating to moments of inertia.

With this apparatus the moment of inertia of a body can be determined not only for axes which do, but also for axes which do not pass through the centre of gravity of the body.

If a body of moment of inertia I is suspended by a wire and allowed to make torsional vibrations, the time of vibration, t, is given by the formula

$$t = 2\pi\sqrt{\frac{I}{c}},$$

where c is a constant depending on the dimensions and nature of the material of the wire. This gives the well-known means of determining the moment of inertia of a body about an axis passing through the centre of gravity of the body, the constant c being determined by another experiment with a body of known moment of inertia.

The apparatus which it is the object of this paper to describe consists of a circular wooden table TT supported by brass rods RRR, to which the suspending wire W is

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[*] Communicated by the Physical Society: read January 23, 1903.

attached by a small vice V. In the diagrams shown, fig. 1 represents a side view of the table, and fig. 2 a plan of the top of the table. P is a pointer attached to the centre of the table, and below is a fixed pointer P′ resting on a table beneath. In the top of the table a circular groove (fig. 2) is cut, in which small pieces of lead LLL can slide. These pieces of lead form together half of a circular ring of rectangular cross-section. In setting up the apparatus a plumb-line is first hung from the supporting vice V′ and the pointer P′ placed immediately below. The plumb-line is then removed and the table suspended by the wire W. The body whose moment of inertia we require to determine is placed at the given position on the table and the lead weights LLL moved round in the groove until the centre of gravity of the whole is in the axis V′P′, this being ascertained by the pointer P being exactly above P′. The table therefore always oscillates about the same axis; and since the lead weights are at a fixed distance from this axis, the moment of inertia of the table remains constant. Any alteration of the total moment of inertia is only that due to the body placed on the table.

Fig. 1.

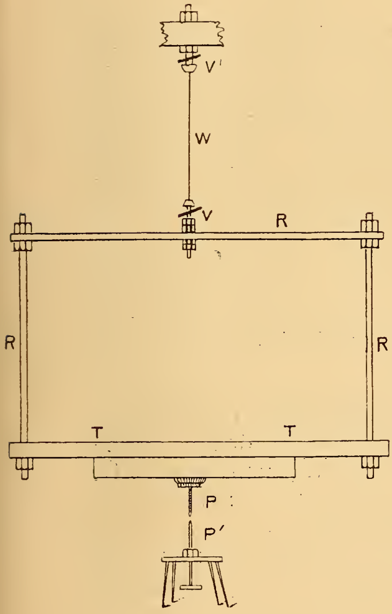
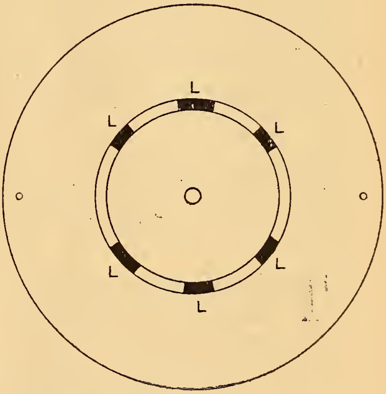


Fig. 2.



If the time of vibration of the table alone is observed and then the time of vibration of the table with a body of known moment of inertia placed on it, the moment of inertia of the table can be calculated. It is only necessary then, in determining the moment of inertia of a body about a given axis, to place it on the table in such a position that the given axis coincides with the fixed axis of vibration, and again determine the time of vibration.

Laws connecting the moments of inertia of a body about different axes can be easily verified with this table, *e. g.*, the law that "the moment of inertia of a body about any axis is equal to its moment of inertia about a parallel axis through its centre of gravity together with the moment of inertia of the whole mass collected at its centre of gravity about the given axis," can be verified by varying the distance of the body from the axis of vibration.

LXVIII. *The Wiedemann Effect in Ferromagnetic Substances.*

By K. HONDA *and* S. SHIMIZU*.

[Plate XVI.]

THE Wiedemann effect in iron and nickel is so well known that it is superfluous to enter into the details of the phenomenon. The experiments by G. Wiedemann†, C. G. Knott‡, Prof. H. Nagaoka and one of us§, show that so long as the longitudinal field is not strong, the direction of twist in iron coincides with that of a circular field, if this direction is right-handedly related to that of the longitudinal field; they also show that in nickel the direction of twist is opposite to that of iron in weak fields. The direction of twist is reversed when either the circular or the longitudinal field changes its direction. The Wiedemann effect in nickel steels of different percentages was recently studied by Prof. Nagaoka and one of us, and it was found that the twist is the same as that of iron. The effect of tension on the Wiedemann effect in iron and nickel was examined by C. G. Knott, who found that tension diminishes the twist in these metals.

The present paper consists of two parts; firstly, we deal with the influence of tension on the Wiedemann effect in nickel steels, and secondly, with the same effect in ferro-

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* Communicated by the Authors.

† G. Wiedemann, Pogg. *Ann.* ciii. p. 571 (1858); cvi. p. 161 (1859); *Electricität,* iii. p. 797.

‡ Knott, Trans. Roy. Soc. Edinb. xxxii. (1), p. 193 (1882–83); xxxv. (2) p. 377 (1889); xxxvi. (2) p. 485 (1891).

§ Nagaoka and Honda, Jour. Coll. Sci. xiii. p. 263 (1900).

magnetic bars and the effect of torque on it. We lately published a paper* relating to the effect of tension on the magnetic change of length; in this we found that the magnetic elongation of nickel steels is largely affected by tension, and that when the tension exceeds a certain value, the contraction is accompanied by magnetization. From Maxwell's explanation as well as that of Kirchhoff for the Wiedemann effect, it seems probable that the direction of twist in nickel steels is reversed when the suspended weight exceeds the said limit. We therefore studied this point particularly and found that the above inference is not correct. So far as we were aware the Wiedemann effect in cobalt had not yet been studied, perhaps because it is difficult to obtain a specimen in the form of a wire on account of its brittleness. It was therefore desirable to have an experiment for the metal. Our apparatus† used in studying the change of rigidity by magnetization was conveniently used for examining the Wiedemann effect in ferromagnetic bars. We had two cobalt bars, one in the cast state and the other in the annealed. The observations showed that the twist in cobalt was just the reverse of that of iron, as was to be expected from its change of length by magnetization.

We tested eight different examples shown in the following table:—

Metal.	Length.	Diameter.
	cms.	cm.
45 per cent. nickel steel ...	20·80	0·0956
” ” ” ...	20·90	0·0516
35 per cent. nickel steel ...	20·92	0·0939
” ” ” ...	20·96	0·0509
Soft iron bar	21·03	1·004
Nickel bar.....................	21·00	1·117
Cast cobalt bar...............	21·00	1·038
Ann. cobalt bar	21·00	1·082

Our arrangement for studying the Wiedemann effect in nickel-steel wires was the same as that used by Prof. Nagaoka and one of us in a former experiment.

To the extremities of a nickel-steel wire 21 cms. long were brazed stout brass wires, and a light mirror was attached to

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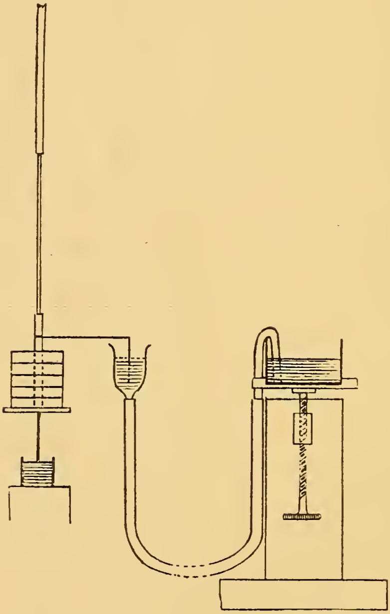
* Phil. Mag. iv. p. 338 (1902).

† Ibid. iv. p. 537 (1902).

the lower brass wire. The upper wire was clamped to a small tripod which rested on the top of a magnetizing coil provided with hole- slot- and plane arrangement. One end of the accumulator was connected with the tripod while the other was led to the mercury pool placed under the suspended wire. The wire hung vertically in the axial line of the coil, which was 30 cms. long, and gave a field of 37·97 c.g.s. units at the centre by passing a current of one ampere. The vertical component of the terrestrial magnetic field was compensated by placing another coil in the interior of the magnetizing coil. The twist was measured by scale and telescope, by which a torsion of 0·2″ per cm. was easily read.



The preliminary experiment showed that the resistance to the twist offered by the mercury in the pool was not negligibly small when the thick brass wire was dipped into the mercury. The resistance was especially noticeable when the brass wire carried a narrow rectangular piece for the purpose of damping. Hence, in order to efface the resistance, a non-magnetic nickel-steel wire 0·5 mm. thick and 5 cms. long was soldered to the lower end of the brass wire and dipped into the mercury pool. By this the damping of the torsional oscillation was rendered very small, especially in the case when a weight was attached. To stop the oscillation a brass wire was fixed horizontally to the vertical wire and bent downward, as shown in the annexed figure. Just below it a small mercury cup was placed; this cup was connected with a large one by a caoutchouc tube. This large cup was placed near the observers and could be raised or lowered by means of a screw adjustment. The motion caused the mercury in the small cup to be raised or lowered, so that the side wire dipped into the mercury or hung free. When we wished to stop the oscillation of the wire, the side wire was dipped into the mercury in the small cup, while the reading was always taken with the wire hanging free of the mercury.

The experiment was conducted in the following manner:—

1. The circularly magnetizing current was kept constant, and the amount of twist due to varying the longitudinally magnetizing current was measured.

2. The wire was then stretched by different loads and the above processes were repeated.

3. The longitudinally magnetizing current was kept constant, and the amount of twist due to varying the circularly magnetizing current was measured.

Before each experiment care was taken to demagnetize the wire completely either longitudinally or circularly by passing an alternate current of gradually diminishing intensity. This was found absolutely necessary to secure correct results.

Twist by varying the longitudinal field.—If the direction of the longitudinal field is right-handedly related to that of the circular field, nickel steel is twisted in the direction of the latter. As shown in Pl. XVI. figs. 1 & 2, under a given circular field, the amount of twist at first increases till it reaches a maximum, after which it gradually diminishes. But the reversal of the twist is never observed, though the field exceeds 1200 C.G.S. units. The position of the maximum twist is slightly displaced in high fields as the longitudinal current increases. The amount of twist is greater in 45 per cent. nickel steel than in 35 per cent. nickel steel.

In the experiment above cited, Prof. Nagaoka and one of us observed in some cases the reversal of the direction of twist in 45 per cent. nickel steel; but in the present experiment we did not notice this reversal of twist.

The effect of tension.—The effect of tension on twist in nickel steels is not so marked as that of tension on the magnetic change of length in the same metal. As seen from figs. 3 & 4, the tension always diminishes the amount of twist; the diminution is large in weak fields, and becomes gradually less as the field is increased. The diminution is approximately proportional to the applied tension.

To test the effect of heavy loading, thin wires about $\frac{1}{2}$ mm. thick were examined. Even by a tension at which contraction occurs by magnetization, the direction of twist in nickel steels is not reversed, though the amount of the maximum twist is reduced to about $\frac{1}{6}$ or $\frac{1}{5}$ its value corresponding to no tension, as seen from figs. 5 & 6.

Whichever theory we adopt, whether Maxwell's or Kirchhoff's, the direction of twist is principally determined by the sign of the quantity $3\lambda-\sigma$, where λ and σ are respectively the length- and the volume-change of the ferromagnetics. When there is no tension acting on the wire, the sign of $3\lambda-\sigma$ must be positive, because the direction of twist in the alloy is the same as that of iron. By applying a heavy load the magnetization is accompanied by contraction, so that λ is negative. Hence, in order that $3\lambda-\sigma$ should be positive, σ must necessarily be negative under a heavy load; that is, the change of volume by magnetization must change its sign from positive to negative as the load is increased.

Twist by varying the circular field.—In figs. 7 & 8 we notice that under a constant longitudinal field the angle of twist at first increases at a constant rate, but later at a gradually diminishing rate. As the longitudinal field is increased the curves approximate to right lines, a result which is to be expected from Kirchhoff's theory of magnetostriction. For, according to the theory, if the circular field is small compared with the longitudinal field, the amount of twist for a given longitudinal field is proportional to the longitudinal current. The amount of twist is greater in 45 per cent. nickel steel than in 35 per cent. nickel steel.

By figs. 7 & 8 we can obtain the twist under a given longitudinal current by gradually increasing the longitudinal field; the result so obtained, if it is compared with figs. 1 & 2, shows that the twist produced by the interaction of the circular and longitudinal fields is independent of the order of applying them.

The apparatus for studying the Wiedemann effect in ferromagnetic bars was that used in the experiment on the change of rigidity by magnetization; the longitudinal current was led to the bar by means of mercury contact without causing sensible resistance. The ferromagnetic bar was soldered at both ends to brass bars of thicker diameter, as in the former experiment just referred to. It was fixed by means of the screw nut at one end of the bar in the axial line of the magnetizing coil, which was placed magnetic east and west. The pivot at the other end of the bar carrying a double wheel was lightly placed in contact with the agate cup fixed to the wooden frame. The twist was measured by means of a rotating cylinder with a reflecting mirror, a vertical scale, and a telescope. Since the Wiedemann effect is an odd function of longitudinal or circular field, it is easily distinguishable from other effects such as the change of the modulus of elasticity, which is an even function of the field. Preliminary experiments showed that the circular field has no effect upon the modulus of elasticity, perhaps because the field is not strong enough to cause such changes. They also showed that the friction at the pivot is not sensible; for the amount of twist when the pivot was left free or when it was supported gave almost coincident values. The direction of currents was also so chosen that the rotation of the mirror causes contraction of the weak spring stretching the thin copper wire. With the arrangement a twist amounting only to $1''{\cdot}83\times10^{-3}$ per cm. of our specimen was easily read.

The measurement was conducted in the same order as in the case of nickel steels. Here we noticed that a slight residual magnetism considerably affected our results; hence, before each deflexion was taken demagnetization was carefully effected.

Twist by varying the longitudinal field.—Fig. 9 represents the curves of twist per cm. in an iron bar plotted against the external longitudinal field. Here c is the longitudinal current per square centimetre. The general course of the curves is similar to that observed in the wire of the same metal. Under a constant circular field, the angle of twist increases at first slowly and then rapidly till it reaches a maximum in a field of about 100 C.G.S. units; it then diminishes and ultimately changes its direction. The field in which the twist reaches a maximum, and also the field of reversal, are markedly larger in the bar than in the wire. Moreover, the diminution of twist in the bar, after reaching a maximum, is comparatively slow. These discrepancies will evidently disappear if we take into account the demagnetizing force acting in a direction opposite to that of the magnetizing force.

The results for nickel are drawn in fig. 10; the general features of the curves are similar to those in the wire of the same metal. The direction of twist is opposite to that of iron in weak fields; but in strong fields the direction does not reverse. Taking into account the demagnetizing force, the discrepancies with regard to the field of the maximum twist and the slow diminution can easily be reconciled.

The direction of twist in cobalt is the same as in nickel. In cast cobalt the amount of twist is rather large, as shown in fig. 11. The twist increases at first slowly and then rapidly, till it reaches a maximum; it then gradually decreases, and ultimately changes its direction as the field is increased. Thus the course of the curves is just the reverse of that in iron. The behaviour of annealed cobalt as regards the Wiedemann effect is remarkably different from that of cast cobalt, as shown in fig. 12. In the first place the amount of twist is much smaller in the annealed than in the cast cobalt. Secondly, the field in which the twist reaches its maximum is rather large in annealed cobalt. Thirdly, the decrease of twist after reaching the maximum is very slow and its direction does not change, though the field is pushed to 1200 C.G.S. units. The results for annealed as well as for cast cobalt are just what is to be expected from the magnetostriction of these specimens. It is also to be observed that these cobalt bars were made of different samples.

Twist by varying the circular field.—Fig. 13 represents the results for soft iron; as the circular field is increased, the twist is increased first slowly and then rapidly. As the longitudinal field is increased the twist reaches a maximum and then gradually diminishes; if the field is strong enough the twist occurs at first in the opposite direction and then in the ordinary. Comparing the above result with those obtained by varying the longitudinal field, we notice one marked difference, that for the same circular and longitudinal fields the amount of twist is largely dependent on the order in which they are applied. The twist obtained by first applying the circular field and then the longitudinal is several times greater than the twist obtained when the order of applying them is reversed.

In nickel the twist is opposite to that of iron; under a given longitudinal field it increases nearly at a constant rate as the longitudinal current is increased, as seen from fig. 14. For a given longitudinal current, the twist reaches a maximum and then gradually decreases as the longitudinal field is increased. Here again we observe that the twist obtained by the application of the circular field, followed by that of the longitudinal one, is far greater than the twist obtained when the order of application is reversed.

The general feature of the twist for cobalt is similar to that in nickel. In cast cobalt (fig. 15) the twist is increased first slowly and then rapidly as the circular field is increased. With the increase of the longitudinal field the twist reaches a maximum and then gradually diminishes. If the field be strong enough the twist occurs at first in the opposite direction and then in the ordinary. In annealed cobalt (fig. 16) the twist is very small and the rate of increase is nearly constant. Here also the twist obtained by first applying the circular field and then the longitudinal is several times greater than the twist when the order of application is reversed.

The effect of torque.—To study the effect of torque, it is convenient to keep the longitudinal field constant and to vary the circular field; for, though the application of the longitudinal field is always accompanied by the twist due to the change of rigidity, the passage of a longitudinal current does not cause any appreciable twist; hence, by varying the circular field, it is not necessary to apply the correction due to the change of rigidity. The torque was given by means of the suspended weight, as in the experiment on the change of rigidity by magnetization. Keeping the longitudinal field constant, we found that in all cases the effect of torque is to diminish the twist by an amount which is nearly proportional to the torque. Figs. 17, 18, 19, & 20 show the general feature of the decrease of twist due to torque. In soft iron and annealed cobalt the effect is very small, but in nickel and cast cobalt it is considerable.

In a paper* on the mutual relation between torsion and magnetism Prof. Nagaoka and one of us have obtained from Kirchhoff's theory the result that for given longitudinal current and field, the amount of twist is inversely proportional to the square of the radius of the ferromagnetic wire. It is interesting to notice that the comparison of the above results in iron and nickel bars 1 cm. thick, obtained by varying the longitudinal field, with the corresponding results in wires of these metals about 1 mm. thick, shows the correctness of the law of the inverse square of the radius.

In conclusion, we wish to express our best thanks to Prof. Nagaoka for useful suggestions in the course of the present experiment.

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* Nagaoka and Honda, Jour. Coll. Sci. xiii. p. 276; Phil. Mag. iv. p. 68 (1902).

LXIX. *On a General Theory of the Method of False Position.*

By KARL PEARSON, *F.R.S.*, *University College, London*[*].

(1) IT is in many cases impossible, in others extremely laborious, to fit a curve or formula to observations by the method of least squares. I have shown in another place[†] that the method of moments provides fits which are sensibly as good as those given by the method of least squares. But while the latter method fails to provide a solution in the great bulk of cases, and while the former is much more frequently successful, there still remains a class of cases in which the unknown constants are involved in the curve or function in such a complex manner that neither method provides the required solution. In such cases the following generalization of the "method of false position" will be found serviceable. Apart from practical value, however, the method is of considerable interest as showing a quite unexpected relationship between trial-and-error methods of fitting and the general theory of multiple correlation.

(2) Let there be a series of observed values $Y', Y'', Y'''\dots$, corresponding to values of another variable $X', X'', X'''\dots$, and suppose we desire to determine the n constants $\alpha, \beta, \gamma\dots\nu$ so that

$$Y=\phi(X, \alpha, \beta, \gamma\dots\nu) \quad . \quad . \quad . \quad . \quad . \quad . \text{(i.)}$$

shall be a curve or formula closely representing the observed facts.

Suppose $(n+1)$ reasonably close trial solutions to be made, i. e. $(n+1)$ false positions given to the curve, and let the corresponding constants be

$$\begin{array}{llllll}
\alpha, & \beta, & \gamma, & . & . & \nu \\
\alpha_1, & \beta_1, & \gamma_1, & . & . & \nu_1 \\
\alpha_2, & \beta_2, & \gamma_2, & . & . & \nu_2 \\
. & . & . & . & . & . \\
\alpha_n, & \beta_n, & \gamma_n, & . & . & \nu_n.
\end{array}$$

Let the corresponding values of y, calculated from these trial solutions, be :

$$\begin{array}{lll}
y', & y''. & y'''\dots \\
y_1', & y_1'', & y_1'''\dots \\
y_2', & y_2'', & y_2'''\dots \\
. & . & . \quad . \quad . \\
y_n', & y_n'', & y_n'''\dots
\end{array}$$

and let there be m such values used,

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[*] Communicated by the Author.

[†] 'On the Systematic Fitting of Curves to Observations and Measurements,' Biometrika, vol. i. pp. 265–304, and vol. ii. pp. 1–23.

For brevity write :

$$\sigma_p^2 = \frac{1}{m} \mathrm{S}(y_p - y)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

where

$$\mathrm{S}(y_p - y)^2 = (y_p' - y')^2 + (y_p'' - y'')^2 + (y_p''' - y''')^2 + \ldots$$

and

$$\sigma_p \times \sigma_{p'} \times r_{pp'} = \frac{1}{m} \mathrm{S}(y_p - y)(y_{p'} - y) \quad . \quad . \quad . \quad \text{(iii.)}$$

where

$$\mathrm{S}(y_p - y)(y_{p'} - y) = (y_p' - y')(y_{p'}' - y') + (y_p'' - y'')(y_{p'}'' - y'') \\ + (y_p''' - y''')(y_{p'}''' - y''') + \ldots$$

Let the actually observed values be, y_0' y_0'', $y_0'''\ldots$, and the best values of the constants for these values :

$$\alpha_0, \quad \beta_0, \quad \gamma_0, \ldots \nu_0.$$

Then, clearly, if p and p' take any values from 1 to n, it is merely straightforward arithmetic to discover the numerical values of any σ_p and $r_{pp'}$. Let

$$\mathrm{Y} = \phi(\mathrm{X}, \quad \alpha_0, \quad \beta_0, \quad \gamma_0, \ldots \nu_0)$$

be the required formula. Then, by the method of least squares, we require to make

$$\mathrm{U} = \mathrm{S}(\mathrm{Y} - y_0)^2$$

a minimum by varying α_0, β_0, $\gamma_0, \ldots \nu_0$.

Now by "reasonably close trial" solutions, I intend to convey that any series of constants α_p, β_p, $\gamma_p, \ldots \nu_p$ differ by fairly small quantities from the "best values." Hence we shall consider the differences $\alpha_p - \alpha_0$, $\beta_p - \beta_0$, $\gamma_p - \gamma_0, \ldots \nu_p - \nu_0$ so small, that to a first approximation their squares may be neglected. The whole process may, however, be repeated when a very close degree of approximation is required, by taking a series of fits with small divergences from the first approximation. We have to our degree of approximation

$$\mathrm{Y} = \phi(\mathrm{X}, \quad \alpha + \overline{\alpha_0 - \alpha}, \quad \beta + \overline{\beta_0 - \beta}; \quad \gamma + \gamma_0 - \gamma, \ldots \quad \nu + \overline{\nu_0 - \nu})$$

or

$$\mathrm{Y} = y + \left(\Delta_0\alpha \frac{d\phi}{d\alpha} + \Delta_0\beta \frac{d\phi}{d\beta} + \Delta_0\gamma \frac{d\phi}{d\gamma} + \ldots + \Delta_0\nu \frac{d\phi}{d\nu} \right.$$

where

$$\Delta_p\alpha = \alpha_p - \alpha, \text{ \&c.}$$

Further let us write

$$d\phi/d\alpha = c_\alpha, \quad \frac{d\phi}{d\beta} = c_\beta, \quad \ldots \frac{d\phi}{d\nu} = c_\nu.$$

Then we have to make

$$\mathrm{U} = \mathrm{S}(y - y_0 + c_\alpha\Delta_0\alpha + c_\beta\Delta_0\beta + \ldots + c_\nu\Delta_0\nu)^2.$$

S denoting a summation of y, y_0 through all the possible

$y', y'', y''', \ldots y_0', y_0'', y_0''' \ldots$ and the corresponding x values in $c_\alpha, c_\beta, \ldots c_\nu$.

This gives us the type equations:

$$S(c_\alpha(y_0-y)) = \Delta_0\alpha S(c^2_\alpha) + \Delta_0\beta S(c_\alpha c_\beta) + \ldots + \Delta_0\nu S(c_\alpha c_\nu),$$

$$S(c_\beta(y_0-y)) = \Delta_0\alpha S(c_\alpha c_\beta) + \Delta_0\beta S(c_\beta^2) + \ldots + \Delta_0\nu S(c_\beta c_\nu),$$

$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot$$

$$S(c_\nu(y_0-y)) = \Delta_0\alpha S(c_\nu c_\alpha) + \Delta_0\beta S(c_\nu c_\beta) + \ldots + \Delta_0\nu S(c_\nu^2). \quad \text{(iv.)}$$

We have thus n equations to find the n unknowns $\Delta_0\alpha$, $\Delta_0\beta, \ldots \Delta_0\nu$, so soon as the summation terms have been found.

But, clearly,

$$y_p - y = \Delta_p\alpha\, c_\alpha + \Delta_p\beta c_\beta + \ldots + \Delta_p\nu\, c_\nu. \quad . \quad . \quad \text{(v.)}$$

Multiply by $y_0 - y$ and sum:

$$m\sigma_p\,\sigma_0\, r_{0p} = \Delta_p\alpha S(c_\alpha(y_0-y)) + \Delta_p\beta S(c_\beta(y_0-y)) + \ldots$$
$$+ \Delta_p\nu S(c_\nu(y_0-y)). \quad . \quad \text{(vi.)}$$

Taking p from $p=1$ to $p=n$, we have n equations to find the unknowns $S(c_\alpha(y_0-y)), S(c_\beta(y_0-y)) \ldots S(c_\nu(y_0-y))$ on the left of equations (iv.) above.

Now let D = the determinant

$$\begin{vmatrix} \Delta_1\alpha, & \Delta_1\beta, \ldots & \Delta_1\nu \\ \Delta_2\alpha, & \Delta_2\beta, \ldots & \Delta_2\nu \\ \cdot\quad\cdot & \cdot\quad\cdot\quad\cdot & \cdot\quad\cdot \\ \Delta_n\alpha, & \Delta_n\beta, \ldots & \Delta_n\nu \end{vmatrix}$$

and suppose d_{pq} to be the minor corresponding to the constituent of this in the pth row and qth column.

Then

$$c_\alpha = \frac{1}{D}\{d_{1\alpha}(y_1-y) + d_{2\alpha}(y_2-y) + d_{3\alpha}(y_3-y) + \ldots + d_{n\alpha}(y_n-y)\}$$

$$c_\beta = \frac{1}{D}\{d_{1\beta}(y_1-y) + d_{2\beta}(y_2-y) + d_{3\beta}(y_3-y) + \ldots + d_{n\beta}(y_n-y). \quad . \quad \text{(vii.)}$$

Hence

$$S(c_\alpha^{\ 2}) = \frac{m}{D^2}\{d_{1\alpha}^{\ 2}\sigma_1^{\ 2} + d_{2\alpha}^{\ 2}\sigma_2^{\ 2} + \ldots + d_{n\alpha}^{\ 2}\sigma_n^{\ 2}$$
$$+ 2d_{1\alpha}d_{2\alpha}\sigma_1\sigma_2 r_{12} + \ldots + 2d_{n-1\alpha}d_{n\alpha}\sigma_{n-1}\sigma_n r_{n-1n}\}$$
$$= \frac{m}{D^2}\left\{\overset{p=n}{\underset{p=1}{S}}(d_{p\alpha}^{\ 2}\sigma_p^{\ 2}) + 2S'(d_{p\alpha}d_{p'\alpha}\sigma_p\sigma_{p'}r_{pp'})\right\}. \quad . \quad . \quad . \quad \text{(viii.)}$$

the second sum S′ embracing all pairs from 1 to n of unequal p and p'.

Multiplying and summing we have

$$\mathrm{S}(c_a c_\beta) = \frac{m}{\mathrm{D}^2}\left\{\mathop{\mathrm{S}}\limits_{p=1}^{p=n}(d_{pa}d_{p\beta}\sigma_p{}^2) + \mathrm{S}'(d_{pa}d_{p'\beta} + d_{p'a}d_{p\beta})\sigma_p\sigma_{p'}r_{pp'}\right\} \quad \text{(ix.)}$$

the symbol S′ being interpreted as before.

Lastly, solving equations (vi.) we have

$$\mathrm{S}\{c_a(y_0 - y)\} = \frac{m\sigma_0}{\mathrm{D}}\left\{\mathop{\mathrm{S}}\limits_{p=1}^{p=n}(d_{p\alpha}\sigma_p r_{0p})\right\}. \quad . \quad . \quad \text{(x.)}$$

If results of which (viii.)-(x.) are the types be substituted in iv. we have n equations to find the unknowns $\Delta_0\alpha, \Delta_0\beta, \dots \Delta_0\nu$.

These equations did not look very hopeful *ab initio*. I solved them, however, by brute force for the first three cases, or for formulæ involving only one, two, and three constants, and to my surprise the results came out with remarkable simplicity of form—namely, the general regression equations discussed in my memoir of 1901 (Phil. Trans. A. vol. 200. p. 9). A little consideration showed that the analytical process was similar to that involved in the discussion of the theory of multiple correlation, but there seemed to be no direct physical reason for applying the results of the correlation theory to the problem of false position. I therefore put equations (iv.) and (viii.)-(x.) before Dr. L. N. G. Filon, who has so often come to my aid in algebraical difficulties, and he has provided me with the following general solution.

We have, using χ_{aa} to denote $\mathrm{S}(c_a{}^2)$, $\chi_{\beta\beta}$ for $\mathrm{S}(c_\beta{}^2)$, $\chi_{a\beta}$ for $\mathrm{S}(c_a c_\beta)$, &c., and ψ_{0a} for $\mathrm{S}(c_a(y_0 - y))$, $\psi_{0\beta}$ for $\mathrm{S}(c_\beta(y_0 - y))$, &c. from (ix.) and (viii.):

$$\chi_{\epsilon a} = \frac{m}{\mathrm{D}^2}\left\{\mathop{\mathrm{S}}\limits_{p=1}^{p=n}(d_{p\epsilon}d_{pa}\sigma_p{}^2) + \mathrm{S}'((d_{p\epsilon}d_{p'a} + d_{p'\epsilon}d_{pa})\sigma_p\sigma_{p'}r_{pp'})\right\}$$

$$\chi_{\epsilon\beta} = \frac{m}{\mathrm{D}^2}\left\{\mathop{\mathrm{S}}\limits_{p=1}^{p=n}(d_{p\epsilon}d_{p\beta}\sigma_p{}^2) + \mathrm{S}'((d_{p\epsilon}d_{p'\beta} + d_{p'\epsilon}d_{p\beta})\sigma_p\sigma_{p'}r_{pp'})\right\}$$

. . . .

$$\chi_{\epsilon\epsilon} = \frac{m}{\mathrm{D}^2}\left\{\mathop{\mathrm{S}}\limits_{p=1}^{p=n}(d_{p\epsilon}{}^2\sigma_p{}^2) + 2\mathrm{S}'((d_{p\epsilon}d_{p'\epsilon})\sigma_p\sigma_{p'}r_{pp'})\right\}$$

. . . .

$$\chi_{\epsilon\nu} = \frac{m}{\mathrm{D}^2}\left\{\mathop{\mathrm{S}}\limits_{p=1}^{p=n}(d_{p\epsilon}d_{p\nu}\sigma_p{}^2) + \mathrm{S}'((d_{p\epsilon}d_{p'\nu} + d_{p'\epsilon}d_{p\nu})\sigma_p\sigma_{p'}r_{pp'})\right\}$$

Multiply by $\Delta_s\alpha, \Delta_s\beta \dots \Delta_s\nu$ respectively and add, remembering that

$\mathop{\mathrm{S}}\limits_{\epsilon=a}^{\epsilon=\nu}(d_{p\epsilon}\Delta_s\epsilon) = 0$, or $= \mathrm{D}$, according as p is not or is equal to s:

$$\mathop{\mathrm{S}}\limits_{\epsilon'=a}^{\epsilon'=\nu}(\chi_{\epsilon\epsilon'}\Delta_s\epsilon') = \frac{m\sigma_s}{\mathrm{D}}\mathop{\mathrm{S}}\limits_{p=1}^{p=n}(d_{p\epsilon}\sigma_p r_{sp}). \quad . \quad . \quad \text{(xi.)}$$

Again from (x.)

$$\psi_{0\alpha} = \frac{m\sigma_0}{D} \mathop{S}_{p=1}^{p=n} (d_{p\alpha}\sigma_p r_{0p})$$

$$\psi_{0\beta} = \frac{m\sigma_0}{D} \mathop{S}_{p=1}^{p=n} (d_{p\beta}\sigma_p r_{0p})$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$\psi_{0\nu} = \frac{m\sigma_0}{D} \mathop{S}_{p=1}^{p=n} (d_{p\nu}\sigma_p r_{0p})$$

Multiply again by $\Delta_s\alpha$, $\Delta_s\beta, \dots \Delta_s\nu$ respectively and add. We find:

$$S\,(\psi_{0\epsilon}\Delta_s\epsilon) = m\sigma_0\sigma_s r_{0s}. \quad . \quad . \quad . \quad . \quad \text{(xii.)}$$

Equations (xi.) and (xii.) are true for every value of s from 1 to n.

Now multiply equations (iv.) by $\Delta_s\alpha$, $\Delta_s\beta \dots$, $\Delta_s\nu$ and add them: we find after dividing by a common factor:

$$\sigma_0 r_{0s} = \Delta_0\alpha\, J_{\alpha s} + \Delta_0\beta\, J_{\beta s} + \Delta_0\gamma\, J_{\gamma s} + \dots + \Delta_0\nu\, J_{\nu s}\,. \quad \text{(xiii.)}$$

where

$$J_{\epsilon s} = \mathop{S}_{p=1}^{p=n} (d_{p\epsilon}\sigma_p r_{sp})/D.$$

There will be n such equations, if we take $s=1$ to $s=n$. Now consider the determinant

$$R = \begin{vmatrix} 1, & r_{01}, & r_{02}, \dots & r_{0n} \\ r_{10}, & 1 & r_{12}, \dots & r_{1n} \\ r_{20}, & r_{21}, & 1, \dots & r_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ r_{n0}, & r_{n1}, & r_{n2}, \dots & 1 \end{vmatrix}$$

where the r's are defined by equations (ii.) and (iii.) above. Let R_{00} be the determinant found by striking out the first row and column, and let $\rho_{tt'}$ be the minor of R_{00} corresponding to the constituent $r_{tt'}$ in R_{00}. Further let R_{0s} be the minor of R corresponding to the constituent r_{0s}, then it may be shown that

$$\mathop{S}_{t=1}^{t=n}(r_{0t}\rho_{tt'}) = -R_{0t'}. \quad . \quad . \quad . \quad . \quad . \quad \text{(xiv.)}$$

Write out the equations like (xiii.) for $s=1$ to $s=n$, multiply them respectively by $\rho_{1t'}$, $\rho_{2t'}, \dots \rho_{nt'}$ and add.

We have by (xiv.):

$$-R_{0t'}\sigma_0 = \frac{\Delta_0\alpha}{D}d_{t'\alpha}\sigma_{t'}R_{00} + \frac{\Delta_0\beta}{D}d_{t'\beta}\sigma_{t'}R_{00} + \ldots + \frac{\Delta_0\nu}{D}d_{t'\nu}\sigma_{t'}R_{00} \quad . \quad \text{(xv.)}$$

since

$$\underset{t=1}{\overset{t=n}{S}}(\rho_{tt'}r_{st}) = 0 \text{ unless } s=t', \text{ and then it } = R_{00}.$$

Rearranging we have:

$$-\frac{R_{0t'}}{R_{00}}\frac{\sigma_0}{\sigma_{\,'}} = \frac{\Delta_0\alpha}{D}d_{t'\alpha} + \frac{\Delta_0\beta}{D}d_{t'\beta} + \ldots + \frac{\Delta_0\nu}{D}d_{t'\nu}. \quad . \quad \text{(xvi.)}$$

Multiply by $\Delta_1\epsilon$, $\Delta_2\epsilon$, ... $\Delta_n\epsilon$ the equations obtained by writing $t'=1$ to n respectively. We find finally:

$$\Delta_0\epsilon = -\left\{\left(\frac{R_{01}}{R_{00}}\frac{\sigma_0}{\sigma_1}\right)\Delta_1\epsilon + \left(\frac{R_{02}}{R_{00}}\frac{\sigma_0}{\sigma_2}\right)\Delta_2\epsilon + \ldots + \left(\frac{R_{0n}\sigma_0}{R_{00}\sigma_n}\right)\Delta_n\epsilon\right\}. \quad \text{(xvii.)}$$

This is the required result, and appears to be a very remarkable one.

(3) We notice that:

(i.) The quantities in round brackets are the well-known partial regression-coefficients of the theory of multiple correlation.

(ii.) The form of the function used is not directly involved in (xvii.), the coefficients being solely functions of the observed and trial solutions.

Hence, if the trial curves be given by the use of a mechanism which involves s degrees of freedom in its placing and setting screws &c., $s+1$ trials will give us by the method of false position the best position and setting of the mechanism to strike the closest curve. In this case the actual mathematical form of the function may be unknown or unknowable *.

(iii.) The multipliers of the constant-differences $\Delta_1\epsilon$, $\Delta_2\epsilon$, &c. are absolutely the same, whatever constant we are seeking. Hence, if they are once determined numerically, however many constants there are in the formula, no additional trouble is involved. For example, in fitting a circle to n arbitrary points, the correction of its radius on the reference-circle

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* For example, it is a common practice with draughtsmen to fill in a curve through a series of plotted points by aid of a spline bent through a series of arbitrary points obtained by the sharp vertical edges of weights placed on the drawing-board. Each such edge has two degrees of freedom. Hence given m such weights and the spline, $2m+1$ trial solutions would by the method of false position give the position for the weights to get the best spline curve through the observations. Of course such a process would be using a steam-hammer to crack nuts, but it will suffice to suggest how perfectly our result is freed of mathematical function or hypothesis.

radius will be given by exactly the same formula as the corrections for the coordinates of its centre.

The various uses of the formula (xvii.) can only be briefly indicated here.

It arose from the consideration of a special physical problem. A somewhat complex formula for astronomical refraction had been obtained which involved for given meteorological conditions one arbitrary constant only. How was the value of this to be determined from the observed values of refraction at different altitudes? The direct application of the method of least squares was idle; the constant was involved in far too transcendental a manner for such a method to be of service. Accordingly two trial solutions were made, and the values of σ_0, σ_1, and r_{01} found; then the correction of the constant, $\epsilon_0 - \epsilon$, is given by

$$\epsilon_0 - \epsilon = r_{01}\frac{\sigma_0}{\sigma_1}(\epsilon_1 - \epsilon) \quad . \quad . \quad . \quad . \quad \text{(xviii.)}$$

where ϵ and ϵ_1 are the two trial values, and ϵ is taken as the reference trial.

This corrected solution has again to be taken as a trial solution with the better of the two trials, and thus a very close value for the constant in question can be determined.

Clearly the only calculation involved in (xviii.) is by (ii.) and (iii.):

$$r_{01}\frac{\sigma_0}{\sigma_1} = \frac{S(y_0 - y)(y_1 - y)}{S(y_1 - y)^2}.$$

Formula (xviii.) immediately led to its generalization for two unknown constants determined by three trials, *i. e.*

$$\epsilon_0 - \epsilon = \frac{r_{01} - r_{02}r_{12}}{1 - r_{12}^2}\frac{\sigma_0}{\sigma_1}(\epsilon_1 - \epsilon) + \frac{r_{02} - r_{01}r_{12}}{1 - r_{12}^2}\frac{\sigma_0}{\sigma_2}(\epsilon_2 - \epsilon) \quad . \quad \text{(xix.)}$$

and this ultimately to the complete generalization given in (xvii.).

If $n+1$ trials are used to determine *one* constant, then it is easy to see that the best result will be obtained by using (xvii.) straight off.

Another service which, I think, can be performed by the method of false position is of the following kind. It is well known that the accuracy of both physical and astronomical investigations can be largely influenced by temperature, pressure, or hygrometrical conditions. What are the most suitable conditions to carry on a particular class of observation under? Let such conditions be represented by α, β, γ. Then make four trial sets of observations of the kind under consideration on quantities whose real values may be considered absolutely known by past experience, the values of the physical conditions being varied for the four trials. The method of false position will then give us very closely the most suitable physical conditions for undertaking investigations of the proposed kind.

A very simple extension of these ideas ought to make the method of considerable service to experimental psychology. What are the psycho-physical conditions best suited to mental judgment or to clearness of sense-perception? Interval after food or exercise, external temperature, pulse, &c., &c., are all "constants" whose best values can be found by the "method of false position," and a novel field for research seems to suggest itself here.

Lastly, turning to more mathematical conceptions, the method appears to offer a definite systematical treatment for the combination of the results of different series of observations on the same physical substance. For example, two observers give a pressure-volume formula of the same form for a gas, but with different values of the constants. It is required to modify the constants, so that the formula may fit most closely a new set of data, or the combined data of the previous observations. In such cases the formulæ may be used as trial solutions, and additional trial solutions be made, if required, by very slightly varying the constants.

Another such application will occur to the astronomer, namely, the modification of the constants on which planetary and cometary orbits depend. Here as many observed positions of the body may be used as the calculator can be taxed with, and the six constants of the orbit found by trial solutions differing slightly in their constants from the approximate or hitherto current values. I am not aware that the method of false position has ever been used by astronomers, but I think it possibly might be of assistance to them.

Having indicated some possible uses of the present method, I give an illustration of its application. I limit myself to one case in order that this paper may not be unduly extended. I hope in some experiments about to be undertaken to give later an example of more practical utility.

Illustration.—Let us fit a good circle to the following five points:

$x=0, \quad y_0=0,$

$x=1, \quad y_0=1{\cdot}5,$

$x=2, \quad y_0=1{\cdot}8,$

$x=3, \quad y_0=2,$

$x=4, \quad y_0=1{\cdot}5.$

By simply plotting the points on a piece of decimal paper, and striking circles with a pair of compasses, the following circles were found without difficulty to give moderately close fits :

$$\begin{aligned}(x-2\cdot2)^2+(y-0)^2&=(2\cdot2)^2,\\(x_1-2\cdot3)^2+(y_1+\cdot3)^2&=(2\cdot4)^2,\\(x_2-2\cdot7)^2+(y_2+\cdot8)^2&=(2\cdot8)^2,\\(x_3-2\cdot4)^2+(y_3+\cdot7)^2&=(2\cdot5)^2.\end{aligned}$$

Here there are three constants h_0, k_0, and r_0, the coordinates of the centre and the radius, to be found.

We have at once, using the first circle as a reference-circle :

$$\begin{array}{lll}\Delta_1 h=\cdot1, & \Delta_1 k=-\cdot3, & \Delta_1 r=\cdot2,\\ \Delta_2 h=\cdot5, & \Delta_2 k=-\cdot8, & \Delta_2 r=\cdot6,\\ \Delta_3 h=\cdot2, & \Delta_3 k=-\cdot7, & \Delta_3 r=\cdot3.\end{array}$$

The following are the ordinates found from the four circles :

	Observed.	Reference Circle.	Circle I.	Circle II.	Circle III.
$x=0$ ...	0	0	·386	−·058	0
$x=1$ ...	1·5	1·844	1·717	1·425	1·371
$x=2$ ...	1·8	2·191	2·081	1·911	1·768
$x=3$ ...	2·0	2·049	1·996	1·984	1·727
$x=4$ ...	1·5	1·265	1·394	1·680	1·221

The ordinates show, what was indeed the fact, that our trials were rough, *i. e.*, made without any attempt at great exactitude ; actually they were four out of the first five circles struck. We now form the differences of the ordinates and have :

	y_0-y.	y_1-y.	y_2-y.	y_3-y.
$x=0$	0	·386	−·058	0
$x=1$	−·344	−·127	−·419	−·473
$x=2$	−·391	−·110	−·280	−·423
$x=3$	−·049	−·053	−·065	−·322
$x=4$	+·235	+·129	+·415	−·044

From these we find at once by straightforward arithmetic :

$$\sigma_0=\cdot25645,\quad \sigma_1=\cdot19833,\quad \sigma_2=\cdot29462,\quad \sigma_3=\cdot31883\ ;$$

and fairly easily by using Crelle's Tables :

$$\begin{array}{lll}r_{01}=\cdot470{,}334, & r_{02}=\cdot937{,}925, & r_{03}=\cdot815{,}868,\\ r_{23}=\cdot679{,}835, & r_{31}=\cdot373{,}191, & r_{12}=\cdot403{,}317.\end{array}$$

The coefficients in r of the regression equation are now respectively:

$$\frac{r_{01}(1-r_{23}^2)-r_{02}(r_{12}-r_{31}r_{23})-r_{03}(r_{31}-r_{\ 2}r_{23})}{1-r_{23}^2-r_{31}^2-r_{12}^2+2r_{23}r_{12}r_{31}}=\cdot072{,}327,$$

$$\frac{r_{02}(1-r_{31}^2)-r_{03}(r_{23}-r_{12}r_{31})-r_{01}(r_{12}-r_{23}r_{31})}{1-r_{23}^2-r_{31}^2-r_{12}^2+2r_{23}r_{12}r_{31}}=\cdot692{,}501,$$

$$\frac{r_{03}(1-r_{12}^2)-r_{01}(r_{31}-r_{23}r_{12})-r_{02}(r_{23}-r_{31}r_{12})}{1-r_{23}^2-r_{31}^2-r_{12}^2+2r_{23}r_{12}r_{31}}=\cdot318{,}083.$$

Whence the general numerical formula for modifying the constants of the reference-circle is:

$$\Delta_0\epsilon=\cdot093{,}522\Delta_1\epsilon+\cdot602{,}783\Delta_2\epsilon+\cdot255{,}849\Delta_3\epsilon.$$

Putting $\epsilon=h$, k, r successively we have for the circle of approximately closest fit:

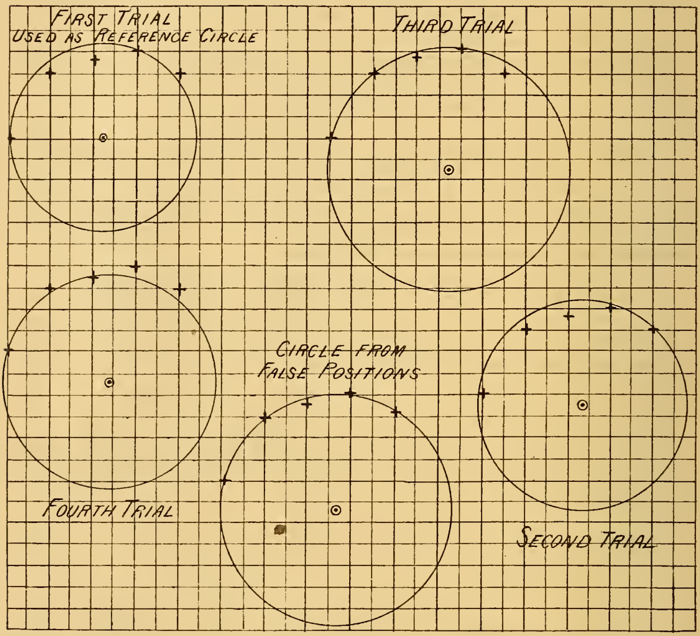
$$h_0=2\cdot562,\qquad k_0=-\cdot689,\qquad r_0=2\cdot657.$$

The accompanying table gives the ordinates, or differences found from this approximate circle of closest fit, and from the four trial circles.

	Ordinates.		Differences.				
	Ob-served.	Closest Circle.	Closest Circle.	1st Trial.	2nd Trial.	3rd Trial.	4th Trial.
$x=0$ ...	0·0	·015	+·015	·000	+·386	−·058	·000
$x=1$ ...	1·5	1·460	−·040	+·344	+·217	−·075	−·129
$x=2$ ...	1·8	1·908	+·108	+·391	+·281	+·111	−·032
$x=3$ ...	2·0	1·932	−·068	+·049	−·004	−·016	−·273
$x=4$ ...	1·5	1·545	+·045	−·235	−·106	+·180	−·279
Square Root of Mean Square Difference ...			·063	·256	·239	·104	·184

It will be observed that tested by the square root of mean square of the differences, the circle obtained by this method of false position is 3 to 4 times as good as all but one of the trial circles. The third trial was a peculiarly lucky one, but even here the false-position circle is more than half as good again. The accompanying diagram gives the four trial circles and the false-position circle. If we wanted a still closer approximation, we should now throw out the worst of the trial solutions, *i. e.* the first, and work from the first approximation and the remaining three trials to get a second approximation. The diagram, however, shows that little

General Method of False Position.—Best Circle through Five Points.



could be gained by this extra labour, and this illustration of the circle fully suffices to indicate the comparative ease with which the new method may be used on a hitherto unsolved type of problem. The labour would not have been much greater had we required a circle (or any other three-constant curve) through even a dozen points.

LXX. *A Potentiometer for Thermocouple Measurements.*

By R. A. Lehfeldt*.

To make a satisfactory potentiometer for thermoelectric work, it is essential that it shall not introduce a high resistance in the circuit of the couple and galvanometer. Most of the potentiometers in the market, which answer well enough for comparing voltaic cells, fail in this respect. I have therefore devised an instrument which is shown schematically in fig. 1. From the positive terminal of the accumulator B current flows to the switch K by means of which it can be

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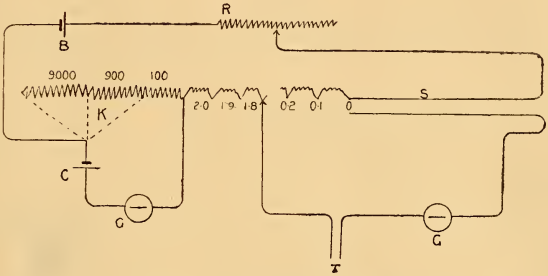
* Communicated by the Physical Society: read March 13, 1903.

sent through 100^{ω} or $100+900$ or $100+900+9000$, in order to get three grades of sensitiveness: it then passes through 20 coils of $0·1^{\omega}$ each, a slide-wire of a little more than 0·1 ohm,

Fig. 1.



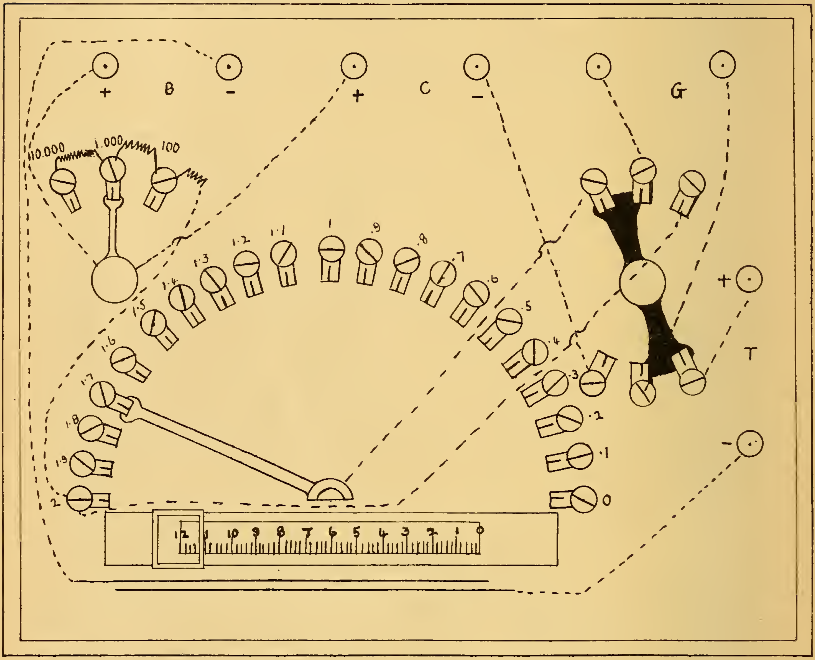
and through the adjustable resistance R back to the accumulator. The fixed resistance of 100, 1000, or 10,000 ohms is shunted by a cadmium cell C and galvanometer G, and R adjusted till the galvanometer is balanced. The thermocouple T with galvanometer G is put across any number of the tenth-ohm coils, and any fraction of the slide-wire. Of course two galvanometers, as shown in the diagram, are not necessary: a double pole-switch puts the actual instrument into either circuit as desired.

The voltage on the ends of one of the tenth-ohms (taken as unit) is then 1000- 10,000- or 100,000th part of the cadmium, *i. e.*, approximately 1000, 100, or 10 microvolts, according to the position of K.

Fig. 2 represents the actual instrument. The greatest care has been taken to avoid accidental thermoelectromotive forces, which are the chief trouble in using thermocouples. The couple I have actually used so far is constantan copper, which gives about 4000 microvolts between 0° and 100°. The only metals used in the measuring circuit are copper and manganin. All the coils are of the latter metal; the slide-wire is of gilt manganin; the galvanometer connexion is made by a short bridge between the slide-wire and a similar galvanometer wire. (These two wires are shown in the figure by the side of the scale, though actually underneath it.) The slider makes contact always, a separate key being used to put the galvanometer in circuit. The potentiometer is inclosed in a wooden case, lined with thick sheet copper and filled with paraffin-oil to keep the temperature constant, and the two points where the copper thermocouple leads join the manganin measuring circuit are carefully buried deep down in the interior of the box and near together.

The sliding contact is carried by a block sliding on two steel bars: it is moved by a steel rod with clamping and fine adjustment screws, and its position read through a lens by means of a vernier graduated in fortieths of a millimetre.

Fig. 2.



As the wire is 100 millims. long the smallest reading is $\frac{1}{4000}$ of the unit, which, as stated above, may be 1000, 100, or 10 microvolts; and as there are 20 tenth-ohm coils, the smallest reading is $\frac{1}{80,000}$ of the largest.

The fineness of reading is, as a matter of fact, limited by the sensitiveness of the galvanometer used.

All the working parts are inclosed by a plate-glass lid through which only the handles project.

Outside the potentiometer itself the apparatus used consists of the accumulator (sometimes two or more); the adjustable resistance R; the cadmium cell; galvanometer—a highly sensitive D'Arsonval of about 20 ohms, made by the Cambridge Scientific Instrument Co.; and galvanometer key. The latter is of the usual short-circuiting reversing type, but unusually small, made of copper, and inclosed in a box from which only the ebonite studs project, for the better avoidance of thermoelectric effects.

To calibrate the instrument the procedure is as follows:—

(i.) The 100^{ω}, 1000^{ω}, and $10,000^{\omega}$ resistances are compared directly with standards. To allow of this and similar operations, the heads of all the studs in the instrument carry screws. The comparison was kindly made for me at the National Physical Laboratory.

(ii.) Each tenth-ohm is compared with the succeeding one by the usual method for comparing nearly equal resistances; the slide-wire is compared with the first tenth-ohm in the same way. During these operations current is led through the coils and the voltage taken off at the same points as when the potentiometer is ordinarily in use.

(iii.) Groups of ten tenth-ohm coils in series are compared with a standard ohm by the method described in the following paper.

(iv.) Further, as a check on the results, two groups of ten tenth-ohm coils were measured at the National Physical Laboratory in the usual way. These measurements are of no direct use, however, as in making them current is led into and out of the coils at the points ordinarily used for taking off the voltage; hence the result differs from that obtained in (iii.) by the resistance of the studs, which is one or two ten-thousandths of an ohm.

(v.) The slide-wire is calibrated.

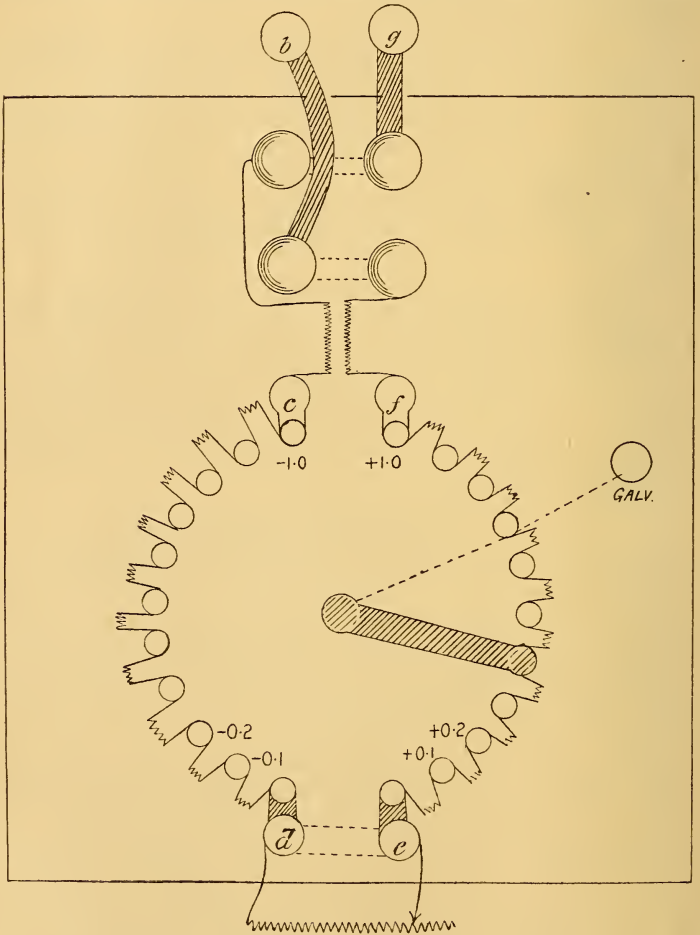
It would be a convenience in calibrating to provide an additional terminal, connected to the point of junction of the last tenth-ohm with the hundred-ohm coil, as this would enable one to lead in current under the usual working conditions without passing the high-resistance coil: this is desirable when calibrating the tenth-ohms, as it is safe to use pretty large currents through them. Otherwise I have found the working of the instrument satisfactory.

Before measuring a thermocouple, two tests should be made. First, the galvanometer-key should be pressed half-way down, so that the galvanometer-circuit is broken. The needle will probably swing a little. If it swings equally on each side of its previous position of rest, there is no thermoelectric effect in the galvanometer. Second, a short piece of copper wire should be put across the thermocouple terminals and the battery-circuit broken: if then (with double-pole switch set to the thermocouple circuit) on pressing the galvanometer-key there is no deflexion, this shows absence of disturbing thermoelectric effects in the rest of the apparatus. The measurement may then be proceeded with.

EDS

LXXI. *A Resistance Comparator.* By R. A. Lehfeldt[*].

OBJECTING to sliding contacts on account of the thermoelectric effects they tend to introduce, and irregularities slide-wires often show when a good deal used, I have designed this comparator without any. It consists of two coils of 99 ohms each (*bcfg*) connected by twenty coils of 0·1 ohm each. The latter are arranged circularly, so that a switch connected to the galvanometer may be set on any one of the intervening studs. When the comparator is to be used in the ordinary way, to make a simple Wheatstone's bridge, the terminals *d e*



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[*] Communicated by the Physical Society: read March 13, 1903.

are connected by a short copper strap. When, as in the potentiometer-coils for the measurement of which this comparator was designed, there is an appreciable connecting resistance between the coils to be compared, the two-point bridge method is used; the strap is then removed and an adjustable resistance inserted. The ends *b g* of the comparison resistances are connected by copper straps to the cups of a mercury commutator, and through that to a pair of large binding screws that project outside the board carrying the coils.

When the galvanometer switch is set on *d* or *e* each arm is 100 ohms; as it is moved round the dial the resistance is altered by steps of $\frac{1}{1000}$ part. The galvanometer deflexions are taken for the two positions nearest balance and interpolation to $\frac{1}{100}$ calculated. In this way I consider that an accuracy of one part in 100,000 is attainable.

To calibrate the comparator the two arms are adjusted to be as nearly equal as possible, and then compared by the use of a pair of nearly equal resistances measured in the usual way. Next the resistances from *b* to *d* and from *e* to *g* are separately compared with a standard 100^{ω}, and *c* to *d* and *e* to *f* with a standard ohm. Finally, a good box is put in parallel with *cd* and *ef* in turn and the ratio corresponding to each stud determined. This need only be done to $\frac{1}{1000}$ part to obtain $\frac{1}{100,000}$ in the final results.

The method of interpolating by the galvanometer has, I think, been unduly neglected. Even when one tries to carry out a strictly null experiment, one is obliged, on account of thermoelectric effects, and so on, to observe accurately minute movements of the galvanometer needle. It therefore does not introduce any new difficulty to read the galvanometer-scale exactly each time, and it may be made, as in this comparator, to avoid reading the position of a sliding contact on a scale. I think therefore that there is gain of accuracy as well as of convenience in using the interpolation method.

The galvanometric arrangements I have adopted for this purpose are as follows:—A plane mirror, 15 mm. diam., is attached to the coil of the (D'Arsonval) galvanometer. A telescope of 25 millim. aperture is placed some 600 millim. in front, and, mounted on the telescope-tube, one of Zeiss's transparent glass scales, backed by ground-glass and illuminated by a small incandescent lamp behind. The mirror and telescope were made by Mr. Hilger: the scale is 100 millim. long, and the graduations are exceedingly fine. Altogether the definition is so good that one can read to $\frac{1}{20}$ millim., *i. e.* to $\frac{1}{2000}$

of the scale-length, with ease and certainty, although the scale is very short. Under these circumstances, to claim one per cent. accuracy in interpolating is well within the mark. I should like to take this opportunity of emphasizing the remark made some years ago by Professor Threlfall, that it is better to attain sensitiveness in a galvanometer by having a big mirror and first-rate optical conditions, than to push the electromagnetic sensitiveness to an extreme.

The apparatus described in this and the foregoing paper is intended for temperature measurements in an attempt at determining the Joule-Thomson effect, and was purchased out of a grant made for that purpose by the Royal Society, and I am glad to express to them my thanks for the liberality which has enabled me to undertake the work.

LXXII. "*Good Seeing.*" *By* S. P. LANGLEY*.

[Plate XVII.]

Astrophysical Observatory, Washington,
November 12, 1902.

EVERY one who has used a telescope knows that our atmosphere is forever in pulsating motion, and troubling our vision of the heavenly bodies, during the most cloudless day or night, so that observatories are put even on high mountains to get rid of the disturbances in this atmosphere, which tend to make the image of every object tremulous and indefinite, and to prevent what the astronomer terms "good seeing."

I desire to speak to the Association about a device which I have recently essayed, for diminishing this universally known and dreaded "boiling" of the telescopic image, a difficulty which has existed always and everywhere since telescopes have been in use, and which has seemed so insurmountable that I believe it has hardly ever been thought of as subject to correction.

Hitherto it has been the endeavour of astronomers, so far as I know, to secure a more tranquil image by keeping the air in the telescope-tube, through which the rays pass, as quiet as possible, and for this purpose the walls of the tube have been made non-conducting, and extreme pains have been taken not to set up currents in the tube. With these precautions the "seeing" is, perhaps, a little better, but very little,

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* Communicated by the Author.—A paper read before the Washington Meeting of the American Association for the Advancement of Science, December 30, 1902.

than if none were used at all, the main difficulty having been always found insurmountable.

I have been led for some years to consider the conditions under which this "boiling" presents itself. It is not necessarily due to a high temperature of the external air, for the most perfect definition I have ever seen of any terrestrial object was obtained by me long since in the Harvard College Observatory, at Cambridge, with its great equatorial telescope, when, on the hottest day that I ever knew in a New England summer, I directed it with a high power on the distant "south mark," which I expected to find almost indistinguishable from the "boiling." I remember my extreme surprise when, under a magnifying power of 300, I found the image as still as the lines of an engraving. This was an extraordinary exception to ordinary experience, and led me to take an interest in the subject. I have since pursued an inquiry to which this circumstance first directed my attention, and I have done so at all altitudes, at one time residing on Aetna for this purpose, noting that even on high mountains vision was so far from being always clear that it was sometimes even much worse than at sea-level.

I have since come to the important conclusion that while the ordinary "boiling" is due to all the air between us and the sun or star through which the rays pass, the greater portion of it is due to the air immediately near us, probably within a few hundred yards, or even feet, from the telescope, and this has led me to ask whether it was not possible that some way to act upon this air could be found. Its non-uniformity leads to deformations of the image too complex to analyse here, which are caused not only by lateral vibrations of the cone of rays, but by its elongation and contraction.

For this purpose I have within the last few months been making experiments at the Smithsonian Astrophysical Observatory, first with a horizontal tube having three successive walls with air-spaces between, which was intended to give the maximum security which freedom from changes of temperature could afford. This Observatory being principally concerned with rays best studied in an image formed by reflexion, has no large dioptric telescope, on which account these experiments have been made with a reflector. I have no reason to suppose, however, that they will not be equally successful with a dioptric telescope.

A large part of the "boiling" of the image is due to air without the tube, but a not unimportant part to the air within it and, in the preliminary experiments the air, kept still in the tube by treating it with the ordinary precautions, was found to have little effect on the ordinary "boiling" of the image, which so seriously prejudices the definition. An image-forming mirror, fed by a coelostat, was placed at the end of this triple-walled tube, which was itself sheltered by a canvas tent and contained the stillest air of the most uniform temperature which could be obtained. The "boiling" was but little diminished merely by inclosing the beam by this tube, which was only what had been anticipated from the ordinary experience of all astronomers.

The device which I had determined to try was one of a paradoxical character, for it proposed to substitute for this still air which gave the usual troubled image, agitated air, which it was hoped would give a still image. For the purpose of this new experiment, the horizontal telescope, using a reflector of 40 feet focus fed by a coelostat through the above tube, was connected with a fan run by an electric motor, which was arranged to draw out the air from the inner tube, at the same time that it forced air in at different points in its length, so as to thus violently disturb and churn the air along all the path of the beam from the coelostat to the solar image.

This first experiment gratifyingly reduced the "boiling" and produced an incontestibly stiller image than when still air was used. As a further test, a series of artificial double stars was now provided, and the concave mirror, acting both as collimator and objective, brought the images to focus, where they were examined by an eyepiece. With the stillest air obtainable, the images were not sharp and only the coarsest doubles were resolvable. Then the blower was started and the definition immediately became sharp. Violently stirring the air in the tube, then, eliminates all, or nearly all, the "boiling" of the stellar image which arises within the tube itself when using ordinary still air. This experiment concerned the air within the horizontal tube only.

I have next taken up the solar image formed by the mirror in the above tube. This is clearly improved by the stirring, but, as a supplementary improvement, I have wished to try a tube something like a prolonged dew-cap, but which is arranged to be inclined toward the sun, so that the beam may pass down it before being reflected by a mirror into the horizontal tube to form the image. This inclined tube is to be connected with the blower like the horizontal one, and the air in both can be stirred together, but experiment has not yet gone far enough to demonstrate whether it has, as is hoped, any superiority commensurate with the special mechanical difficulties involved in the research. Again, there was very marked "boiling" before starting the blower, which largely diminished while the blower was going.

I am not prepared to give quantitative estimates, which I hope to furnish later; but all observers to whom I have shown these early results have agreed, that if the "boiling" was not wholly cured, what remained was but a small fraction of that obtained with still air. I have not completed these experiments, which I am still pursuing at the Observatory, but they seem to me to give promise of an improvement of universal interest to observers, which justifies the making of this early announcement. I had hoped to have shown the Association some photographs of the sun taken, first in the ordinary way, and again with the churned air, but the condition both of the sun and of the sky of late has prevented my obtaining them. I can, to my regret, only give here a photograph (Pl. XVII.) of the images of the artificial double stars as seen through ordinary conditions, as distinguished from those here mentioned, of artificial "good seeing."

LXXIII. *On the Proportion of Argon in the Vapour rising from Liquid Air.* *By* Lord RAYLEIGH, *O.M., F.R.S.*[*]

THE boiling-point of argon being intermediate between those of nitrogen and oxygen, it may be expected that any operations of evaporation and condensation which increase the oxygen relatively to the nitrogen will at the same time increase the argon relatively to the nitrogen and diminish it relatively to the oxygen. In the experiments about to be detailed the gas analysed was that given off from liquid air, either freshly collected, or after standing (with evaporation) for some time—from a day to a week. The analyses were for oxygen and for argon, and were made upon different, though similar, samples. Thus after an analysis of a sample for oxygen by Hempel's method with copper and ammonia, 4 or 5 litres would be collected in a graduated holder, and then the first analysis confirmed on a third sample. In no case, except one to be specified later, was the quantity of gas withdrawn sufficient to disturb sensibly the composition. The liquid was held in Dewar's vessels, but the evolution of gas from below was always sufficient to keep the mass well mixed.

The examination for argon was made in a large test-tube inverted over alkali, into which the gas was fed intermittently from the holder. The nitrogen was gradually oxidized by the electric discharge from a Ruhmkorff coil in connexion with the public supply of alternating current, the

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[*] Communicated by the Author.

proportion of oxygen being maintained suitably by additions of oxygen or hydrogen as might be required. In the latter case the feed should be very slow, and the electric discharge should be near the top of the test-tube. Great care is required to prevent the hydrogen getting into excess; for if this should occur, the recovery of the normal condition by addition of oxygen is a very risky process. After sufficient gas from the holder, usually about 2 litres, had been introduced, the discharge was continued until no more nitrogen remained, as was evidenced by the cessation of contraction and by the disappearance of the nitrogen line from the spectrum of the discharge when the terminals were connected with a leyden-jar. When it was certain that all nitrogen had been removed, the residual oxygen was taken up by ignition of a piece of phosphorus. On cooling, the residue of argon was measured, and its amount expressed as a percentage of the total gas taken from the holder.

The results are shown in the following table. The oxygen, expressed as a percentage of the whole, varied from 30 to about 98. From 43 to 90 per cent. of oxygen, the argon, as a percentage of the whole, scarcely varied from 2·0.

Percentage of Oxygen.	Percentage of Argon.	Argon as a percentage of the Nitrogen and Argon.
30	1·3	1·9
43	2·0	3·5
64	2·0	5·6
75	2·1	8·4
90	2·0	20·0
98	·76	33·0
100	0·0	100·0

The experiment entered under the head of 98 per cent. oxygen is not comparable with the others. In this case 5½ litres of gas were collected as the *last* portion coming away from a stock of liquid as it dried up. Nor was the subsequent treatment quite parallel, for the whole of the oxygen was first removed with copper and ammonia leaving 125 c. c. of mixed nitrogen and argon, of which again by subsequent analysis 42 c. c. was found to be argon. The last entry corresponding to 100 per cent. of oxygen is theoretical and does not represent any actual experiment.

It must be clearly understood that these results relate to the *vapour* rising from the liquid, and *not* to the composition of the liquid itself. So far as the oxygen content is concerned, the comparison may be made by means of Mr. Baly's observations (Phil. Mag. xlix. p. 517, 1900). It will appear, for example, that when the vapour contains 30 per cent. of oxygen, the liquid will contain about 60 per cent., and that when the vapour contains 90 per cent. the liquid will be of 95 or 96 per cent. At every stage the liquid will be the stronger in the less volatile constituents; so that the proportion of argon to nitrogen, or to nitrogen + argon, will be higher in the liquid than in the vapour.

The constancy of the proportion of argon to the whole over a considerable range may be explained to a certain extent, for it will appear that the proportion must rise to a maximum and thence decrease to zero. To understand this, we must remember that "liquid air" is something of a misnomer. In the usual process the whole of the air concerned is not condensed, but only a part; and the part that is condensed is of course not a sample of the whole. As compared with the atmosphere the liquid contains the less volatile ingredients in increased proportion, and the part not condensed and rejected contains the more volatile ingredients in increased proportion. The vapour coming away from the liquid as first collected has the same composition as the gas rejected in the process of condensation. At the beginning of our table, a point, however, which it would be difficult to reach in actual experiment, we should have an oxygen content much below 20 per cent., a ratio of argon to nitrogen + argon below 1 per cent., and in all probability a ratio of argon to the whole also below 1 per cent.

The object which I had in view was principally to obtain information as to the most advantageous procedure for the preparation of argon. So many laboratories are now provided with apparatus for liquifying air, that it will usually be convenient to start in this way if a sufficient advantage can be gained. The above results show clearly that the advantage that may be gained is great. Something depends upon the procedure to be adopted for eliminating the nitrogen. Upon a moderate scale and where there is a supply of alternating current, the method of oxidation, as in the analyses, is probably the most convenient. In this case it may be an advantage to retain the oxygen. If the oxygen content be about 60 per cent., as in the third experiment, the proportion is about sufficient to oxidize the nitrogen. We may compare this with the mixture of atmospheric air and oxygen which behaves in the same manner. In the latter case the proportion of argon would be reduced from 2·0 per cent. to about ·4 per cent., so that the advantage of using the liquid air amounts to about *five* times. In the arrangement that I described for oxidizing nitrogen upon a large scale * the mixed gases were absorbed at the rate of 20 litres per hour.

In the alternative method the nitrogen is absorbed by magnesium or preferably by *calcium* formed *in situ* by heating a mixture of lime and magnesium as proposed by Maquenne †. In this case it is necessary first to remove the oxygen; but oxygen is so much more easily dealt with than nitrogen that its presence, even in large proportion, is scarcely an objection. On this view, and on the supposition that liquid air is available in large quantities, it is advantageous to allow the evaporation to proceed to great lengths. A 20 per cent. mixture of argon and nitrogen (experiment 5) is easily obtained. Prof. Dewar has shown me a note of an experiment executed in 1899, in which a mixture of argon and nitrogen was obtained containing 25 per cent. of the former. In the 6th experiment 33 per cent. was reached, and there is no theoretical limit.

P.S.—I see that Sir W. Ramsay (Proc. Roy. Soc. March 1903) alludes to an experiment in which the argon content was doubled by starting from liquid air.

LXXIV. *Radioactivity of Ordinary Materials. By the* Hon. R. J. Strutt, *Fellow of Trinity College, Cambridge* ‡.

It is now well recognized that the air in any ordinary vessel possesses the power of conducting electricity, under electromotive forces insufficient to produce luminous discharge, although only to a very slight extent. It has been usual to refer to this effect as the "spontaneous ionization" of the air. This name suggests that the conductivity is in some way an essential property of the air, just as the electrical conductivity of metals is inseparably connected with the nature of those bodies.

Mr. C. T. R. Wilson, however, has found (Proc. Roy. Soc. vol. lxix. p. 277) that when other gases are substituted for air, the relative ionizations are in nearly the same ratio as those which I observed (Phil. Trans. 1901, p. 507) for the same gases under the action of Becquerel radiation. Further, Mr. J. Patterson has found (Proc. Camb. Phil. Soc. xii. p. 44)

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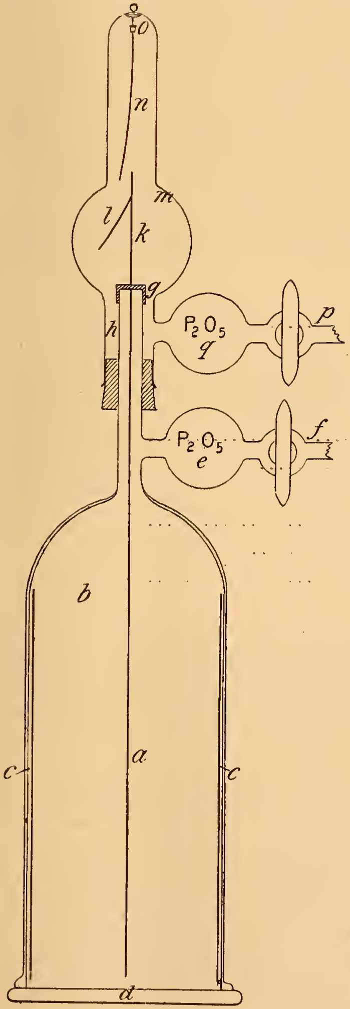
* Chem. Soc. Journ. lxxi. p. 181 (1897); Scientific Papers, vol. iv. p. 270.

† I employed this method successfully in a lecture before the Royal Institution in April 1895 (Scientific Papers, vol. iv. p. 188). In a subsequent use of it I experienced a disagreeable explosion, presumably on account of the lime being insufficiently freed from combined water.

‡ Communicated by the Author. Part of the above was published in 'Nature,' Feb. 19, 1903. It appeared afterwards that some of the results had been anticipated by Prof. MacLennan and also by Prof. Rutherford and Mr. Cook, in papers read before the American Physical Society in Dec. 1902, although no account of their experiments had then appeared in print. I have thought it best to confine myself to the description of my own results, so as to give an independent view of the subject.

that, when a large vessel is used, the amount of ionization is not proportional to the pressure, but tends towards a limit, when further increase of pressure no longer affects it. This is exactly the behaviour that might be expected if the effect was due to a feeble radioactivity of the walls of the vessel, the radiation being easily absorbed by the air. I have recently carried out a series of experiments, with a view to decide whether the nature of the walls of the vessel had any influence on the rate of discharge of a charged body inside it.



The figure represents the experimental arrangement adopted. *a* is a charged wire in the axis of the cylindrical vessel *b*. The walls of *b* could be lined with any desired material by inserting a cylinder *cc* composed of it. This could be done by removing the glass plate *d* at the end, which was cemented on. The vessel could be exhausted through the stopcock *f* if desired. *e* was a drying-bulb containing phosphoric anhydride. The wire *a* passed air-tight through the brass cap *g*, cemented on to the neck *h* of *b*; *h* was made of lead-glass, on account of the superior insulating qualities of this kind of glass. The cap *g* carried a brass strip *k* carrying a gold leaf *l*. The whole was surrounded by a vessel *m* as shown. *n* was an iron wire attached to a platinum wire *o*. This iron wire could be brought into contact with *k* by means of an external magnet in order to charge the system. *m* could be exhausted through the stopcock *p*, and dried by means of the phosphoric anhydride contained in *q*. The position of the gold leaf was read by a microscope with micrometer eyepiece focussed upon it.

Before making an experiment the insulation, which is all important, was tested. *m* was permanently exhausted, and the stopcock *p* closed. *b* was also exhausted, for the time, and a charge given to the brass strip *k*, so that the leaf *l* diverged. An interval of one hour was allowed in order that any absorption of the charge by the glass insulation *h* should have time to take place. After that it was found that there was no measurable movement of the leaf over the scale-divisions in two or three hours; $\frac{1}{5}$ of a division would have been visible.

When the vacuum test of insulation had been made, dry air was admitted into the vessel *b*. It was assumed that the glass insulation, which was satisfactory in a vacuum, remained so when air which had been dried by passage through phosphoric anhydride was admitted in contact with it. As soon as the air was admitted into *b*, a leakage of electricity from the wire *a* was observed.

The amount of this leakage, in scale-divisions per hour, with various materials surrounding the charged wire, is given below.

Tinfoil	3·3
Ditto, another sample	2·3
Glass, coated with phosphoric acid	1·3
Silver, chemically deposited on glass	1·6
Zinc	1·2
Lead	2·2
Copper (clean)	2·3
Ditto, thoroughly oxidized	1·7
Platinum (various samples)	2·0, 2·9, 3·9
Aluminium	1·4

It appears, then, that there are very marked differences in the rate of leak when different materials constitute the walls of the vessel. There can, therefore, be little doubt that the greater part, if not the whole, of the observed ionization of air is not spontaneous at all, but due to Becquerel rays from the vessel.

It is, I think, interesting to find that the phenomena of radioactivity, which have hitherto been regarded as rare and exceptional, are really everywhere present. The rate of leak with various pieces of tinfoil from the same stock was always the same, as nearly as the experiments could show. But, as may be seen in the table, a piece from another stock gave a different amount of leakage. The same holds good for platinum, one specimen tried being twice as active as another

It was found that ignition did not affect the radioactivity of a given sample of platinum.

In order to compare the activity of the substances mentioned above with that of uranium salts, a small crystal of uranium nitrate measuring 12 × 4 mm. was cemented to the inside of the cylinder. The rate of leak due to it was found to be thirteen times that due to the most active specimen of platinum. The area of the uranium nitrate was only $\frac{1}{240}$ part of that of the platinum, so that its activity for an equal area would be no less than 3000 times greater.

It is possible that the radioactivity of ordinary materials may be due to traces of the more active substances. This would explain the varying activities of different samples of the same material. Only an infinitesimal proportion of radium would be required. Radium is at least 100,000 times more active than uranium, and uranium 3000 times more active than the most active common material that I have experimented with. So that one part of radium in three hundred million would suffice to account for the observed effects.

It was evidently important to compare the quality of the Becquerel rays emitted by the various substances. This can be done, in the case of powerful radiators like uranium or radium, either by examining the deflexion in a magnetic field, or by observing the amount of absorption by solid or gaseous media. In the case of very feeble radiators it would be quite impracticable to attempt the magnetic experiment, while the absorption by solids can scarcely be examined, since the solid absorbent would give off radiation of its own comparable in amount with that due to the original radiating substance. We are reduced, then, to examining the absorption by air*.

In order to compare various radiations in this way we have only to examine the variation of leak with pressure. In the case of the more absorbable radiations less pressure will be required to make the current sensibly independent of a further increase of pressure, or, what is the same thing, to absorb practically all the radiation.

In the experiments the apparatus used was similar to that

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* It may be remarked that in all probability some part of the observed ionization of air may be due to radioactivity of the surrounding air in the other parts of the vessel. But it is not apparent how this can be experimentally distinguished from the ionization due to the walls. In all probability this ionization due to surrounding air is small, since it is scarcely possible to understand otherwise how the ionization for large pressures could be sensibly independent of pressure.

described above, except that the current was taken between coaxial cylinders, diameters 2·7 and 9·8 cms. respectively. The outer cylinder was provided with ends of the same material as the walls, so that the air between the walls was not exposed to the radiation of any other substance than that which it was desired to examine. Experiments were made with walls of zinc and of two samples of tinfoil of different activities.

The results are tabulated below.

Zinc.		More active tinfoil.		Less active tinfoil.	
Pressure (inches).	Leak.	Pressure (inches).	Leak.	Pressure (inches).	Leak.
3·9	·66	·95	·7	·9	·26
10·7	1·6	3·0	1·8	9·8	1·1
16·8	2·0	5·41	3·4	14·4	1·9
21·8	2·7	10·6	6·0	20·2	2·5
24·7	2·6	16·6	5·5	24·5	2·6
29·0	2·6	23·1	6·0	30·1	2·3
30·1	2·8	29·8	6·2	38·6	2·3
38·6	3·2	39·2	5·5		

These measurements are less accurate than might be wished as they were made under somewhat unfavourable conditions, at the Royal Institution. The vibration from the machinery running in the basement made it impossible to take exact readings*.

It is clear, however, that the current due to radiation from the zinc walls does not reach a limit within the range of pressure experimented upon. With the more active tinfoil the limit is reached at about 10 inches pressure, while with the other specimen of tinfoil 20 inches are required before the current reaches its full value. We may infer that the radiation from different samples of the same material varies, not only in quantity, but in quality also.

It was desired to compare the radiation from tin and zinc with that from uranium nitrate. Some small fragments of the latter were cemented at intervals over the surface of the cylinders, and the rate of leak taken for various pressures. It was found that the leak began first to diminish considerably at 20 inches pressure, although, owing to the presence of a small proportion of penetrating rays in uranium salts, the limit was not very definite. It appears that the α radiation from uranium has about the same penetrating power as the radiation from the second specimen of tinfoil.

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* This remark does not apply to the measurements with the first apparatus, which were much more accurate.

Prof. Rutherford's experiments* show that the α radiation of thorium and radium differ somewhat from that of uranium, being more penetrating. In all probability the radiations from the tinfoil, and perhaps from the zinc also, are of the same general nature as the α radiations from uranium, thorium, and radium, though differing somewhat in quality.

LXXV. *Secondary Radiation from Gases subject to X-Rays.*

By Charles G. Barkla, *M.Sc.* (*Vict.*), *B.A.* (*Cantab.*), *King's College, Cambridge; Oliver Lodge Fellow, University College, Liverpool*†.

RADIATION from air through which X-radiation was passing was first noticed by Röntgen ‡, through the effect produced on a photographic plate which was screened from the direct radiation.

Sagnac §, who studied secondary radiation from metals subject to X-rays, also obtained a much smaller effect from air, and concluded it was more easily absorbed than the primary radiation producing it. The following is an account of a more complete investigation of the subject of secondary radiation from gases subject to Röntgen rays.

An X-ray bulb and exciting induction-coil were placed inside a large wooden box which was completely covered with thick sheet lead. A small rectangular aperture in the side of the box near the bulb permitted the radiation to pass in a definitely bounded beam through air or any other gas outside the box.

In the first experiments no attempt was made to inclose the air through which the radiation was directed, so that

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* Phil. Mag. July 1902, p. 11. Every one must recognize the merit of Prof. Rutherford's most valuable experiments on the absorption of Becquerel rays by air. But I must confess I cannot follow the reasoning by which he seeks to deduce from them the coefficient of absorption. His calculation starts on the assumption that if I be the intensity of radiation close to an infinite radioactive surface, the intensity at a distance x is $Ie^{-\lambda x}$, where λ is the coefficient of absorption. No doubt if the radiation were emitted wholly in a direction normal to the surface this would be so. But, as a matter of fact, an element of area of the surface emits much of its radiation in an oblique direction. This obliquely emitted radiation has to pass through a greater thickness of air before it has reached the distance x from the infinite radioactive plane. Thus the relation between intensity and distance becomes greatly complicated. It is impossible to calculate it without knowing the relation between the intensity of radiation from an element of area, and the angle between that element and the direction of propagation.

† Communicated by Prof. L. R. Wilberforce.

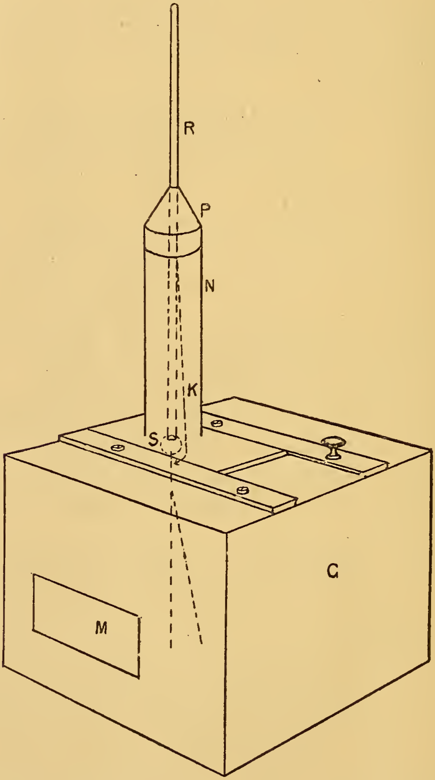
‡ *Annal. Phys. Chem.* lxiv. 1, pp. 18–37 (1898).

§ *Comptes Rendus*, cxxvi. pp. 521–523 (1898).

after passing through another rectangular aperture in a lead screen placed several centimetres from the side of the box and parallel to it, the X-rays were not intercepted by any solid body for a considerable distance—about two metres—but passed merely through air.

To detect the secondary radiation, a special form of electroscope was used. It consisted of a case (as shown in fig. 1), with four sides of stout brass. One end G was of glass, and at the opposite end a face of any desired material and thickness could be placed. As in C. T. R. Wilson's* experiments on Spontaneous Ionization, the gold-leaf and brass plate to which it was attached were suspended in this case by a bead of sulphur S, which was fixed to the lower end of a vertical brass rod R. This passed axially through a cylindrical brass neck N, whose lower end was movable along grooves in a

Fig. 1.



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* Roy. Soc. Proc. vol. lxviii. pp. 151–161 (1901).

direction perpendicular to the two ends, and from which it was separated by an ebonite plug P. Connexion could be made between this rod and the insulated plate and gold-leaf by means of a light spring K which was attached to the rod, and which when set in vibration made contact with the insulated portion of the electroscope. The capacity of this was exceedingly small in the later experiments, the brass plate being replaced by a straight piece of copper wire to which was attached a narrow strip of gold-leaf. The deflexion of the gold-leaf was observed through a microscope with graduated eyepiece, which was fixed just outside a small glass window M in one side of the case.

When the rod was connected to one terminal of a battery, while the other terminal was earth-connected, the insulated plate and gold-leaf could be charged by means of the contact-maker, which made momentary connexion between the rod and plate, leaving the plate and gold-leaf charged and insulated.

When this was the case, a leak of electricity from the plate and gold-leaf was only possible by the sulphur support or through the air in the electroscope. It was shown that the leak by the support was negligible by first discharging the electroscope completely, and then charging the cylindrical supporting rod to a high potential, by connecting to one terminal of a battery the other terminal of which was earthed, and then leaving the apparatus for a number of hours. The amount by which the leaf and plate charged was (the amount of leak through the support) − (the amount of leak through the air). The latter was very small, as the potential of the plate and gold-leaf was little different from that of the case, which was earth-connected. There was no perceptible change in the position of the gold-leaf.

When the rod was kept at a higher potential than the insulated portion, and this again was at a considerably higher potential than the earthed case, the leak through the gas was not negligible, and the amount by which the leaf and plate charged was

$$\text{(amount of leak through the support)} - \text{(amount of leak through the air)} = \alpha.$$

When, on the other hand, the leaf and plate were charged to a higher potential than the supporting rod the loss of charge by the former was

$$\text{(amount of leak through the support)} + \text{(amount of leak through the air)} = \beta.$$

When the potential of the leaf and plate was the same in each case, the leak through the air was of course the same ; and when the difference of potential between the supporting rod and the gold-leaf and plate was the same, the leak by the support was also the same.

The potentials of the rod, plate and gold-leaf, and the case may in the two experiments be written $2n$, n, 0, and 0, n, 0 respectively.

The leak by the support was thus $\frac{1}{2}(\alpha+\beta)$, and the leak through the air $\frac{1}{2}(\beta-\alpha)$.

The support leak, however, in the following experiments was to the leaf and plate from the supporting rod, and was excessively small as the potential of the leaf and plate was not allowed to sink much below that of the supporting rod.

Any leak then must have been due to the conductivity of the air in the electroscope. In its steady normal state, when the potential was high enough to produce a saturation current, this measured the spontaneous ionization of the air. Anything more than this must have been due either to the introduction of ions from outside, or to the formation of ions in the inclosed air itself by radiation from outside.

In the preliminary experiments made upon air which was not inclosed, care was taken that the beam of X-rays emerging from the second screen did not fall upon any solid in the neighbourhood. It was shown by putting screens much nearer and measuring the secondary radiation from these that the secondary radiation from the wall (distant 2 metres), upon which the beam fell, was inappreciable. The electroscope was placed well out of the direct beam (through the two rectangular apertures in the box and screen) with a thin paper face parallel to the near bounding-plane of the beam. The electroscope-case, box, and screens were earthed.

The rate of motion of the gold-leaf was noted when the induction-coil was not working, so that this measured the spontaneous ionization of the air. When the bulb was worked the leaf fell much more rapidly.

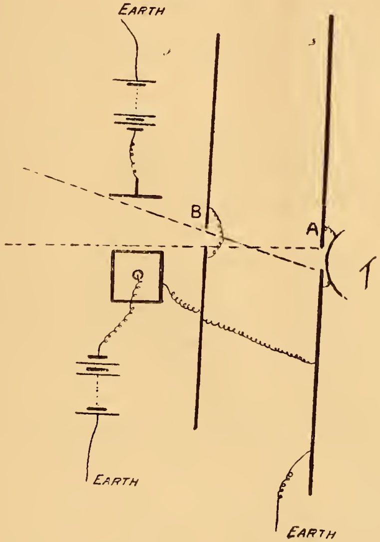
The aperture A (fig. 2) in the box was then covered with lead, and the effect on the electroscope was again normal, showing that the rapid fall was not due to direct radiation through the lead covering of the box inclosing the bulb and induction-coil and through the second opening B to the paper face of the electroscope. The effect was therefore caused by radiation proceeding through A.

When B was covered with lead the motion of the gold-leaf was again normal, so that the fall was not due to direct radiation from A through the lead of the screen.

The electroscope being out of the direct beam, the leak was due indirectly to radiation passing through A and B.

When the length of the aperture B was kept constant and the width altered, the rate of motion of the gold-leaf was

Fig. 2.



approximately proportional to the width of the slit and therefore to the breadth of the beam. This proved that the effect was not due to secondary radiation from the edges of the lead round B, for when the slit was very narrow, doubling its width added little to the length of the edge, while the motion of the gold-leaf was twice as rapid.

The same thing was also proved by screening the paper face of the electroscope from direct radiation from B by a sheet of lead, which was so arranged as to intercept very little radiation proceeding from the air through which the primary beam passed.

When the paper face was covered with a sheet of lead, the electroscope was perfectly screened.

It was at first (when very thin paper was used for the face of the electroscope) doubtful whether some of the ions formed in the air by the primary radiation were not pulled through pores in the paper into the electroscope. The paper was moistened with acidulated water, so that it could be kept perfectly at zero-potential with the other parts of the case, and hence so that there was no electric field outside due to the charge on the plate and gold-leaf. There was thus no electric field drawing the ions into the electroscope. The moisture, however, affected the normal fall of the gold-leaf*; but the great increase produced in the rate of motion by what appeared to be a secondary radiation was not materially affected.

A very thin leaf of aluminium was put over the paper face and was connected to earth with the brass case, and it was found that the ionization produced inside was not appreciably reduced.

It was therefore evident that the ionization inside was produced by a radiation proceeding from the gas which was subjected to primary X-radiation, or that there was still a *diffusion* of ions through the paper and aluminium leaf.

An aluminium plate was then placed on the side of the primary beam opposite to the face of the electroscope but outside the beam. This was connected first to the positive, then to the negative terminal of a battery of 100 cells, whose other terminal in each case was earthed. As the electroscope-face was at zero-potential, there was in each case an electric field of about 40 volts per centimetre across the beam in opposite directions in the two cases. The ions which would discharge the electroscope were in one case attracted away from the electroscope to the plate, and in the other case attracted to the face of the electroscope. But it was found that there was no appreciable difference between the two leaks in the two cases, showing:—

(1) That there was not a diffusion of ions through the paper and aluminium face; and

(2) That the radiation which came from the gas was not in any way the result of recombination of the ions, for the ions were withdrawn before they had sufficient time to recombine.

The ionization of the air in the electroscope was therefore the result of radiation from the gas upon which primary radiation fell, and this secondary radiation was independent of the subsequent behaviour of the ions in the primary beam.

The absorbability of the secondary radiation was then investigated. To ascertain the order of magnitude of this absorption, the electroscope was placed with aluminium and paper face just outside the primary beam. When this face was covered with lead no ionization was detected. The rate of ionization was measured when there was no protecting plate and when the face was covered with a sheet of

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* Probably due to a radioactive substance in the water.

aluminium ·012 cm. thick. The difference showed the amount of secondary radiation previously absorbed by the air in the electroscope now absorbed by the aluminium. The secondary beam was, however, in this case not directed, so that the effective thickness of the plate was greater than ·012 cm. With one bulb the absorption amounted to 47 per cent. of the initial intensity—taking the amount of ionization in the electroscope as proportional to the intensity of the radiation passing through—while the absorption of the directed primary beam (in this case falling perpendicularly on the absorbing plate) was 30 per cent. Thus the absorption was of the same order of magnitude as that of the primary beam.

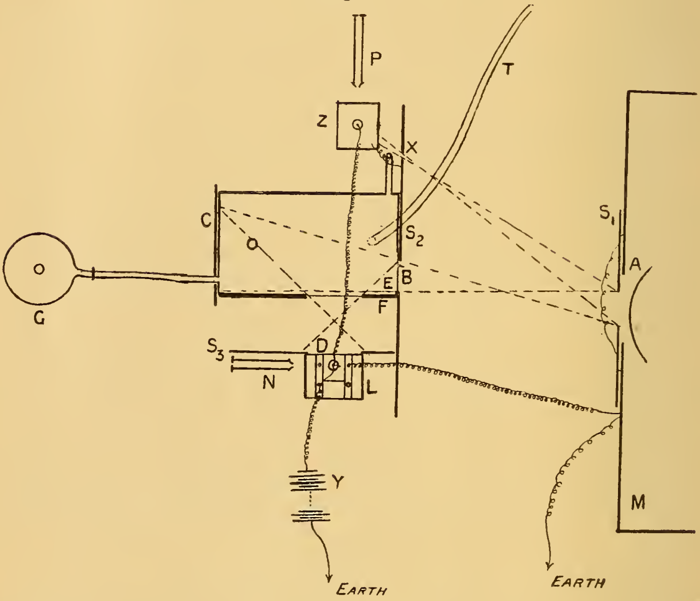
To test this more accurately, the electroscope was placed several centimetres away from the primary beam, and received the secondary radiation which passed through rectangular apertures in two parallel lead plates. All the rays entering the electroscope through the second aperture passed through the first, so that the effective thickness of a protecting plate was very little greater than the actual thickness. As the beam was more perfectly directed in successive experiments, the proportional absorption by similar plates of aluminium of the direct and secondary beams was found to come closer and closer into agreement. The absorption-coefficients for the primary and secondary radiations cannot differ by more than 10 per cent. of their value, for the radiations experimented upon. I conclude that the penetrability of the primary and secondary rays is practically the same.

In order to investigate the subject more fully—more particularly to ascertain what the intensity and the penetrability of the secondary radiation were dependent upon—different gases were used in place of the air through which the primary beam was directed. As the gas had to be inclosed, it was of course necessary to guard against secondary effects from the containing chamber reaching the electroscope. The shielding from this secondary radiation made it impossible to expose the electroscope to radiation from a large quantity of gas, and made it necessary to place the electroscope some little distance from the gas the radiation from which was being studied. The effects were thus considerably diminished. A metal box 14 cms. × 10 cms. × 10 cms. was constructed with inlet and outlet tubes for the gases, and with two parchment windows, one at the end and the other at the side. In some experiments the former was of thin aluminium (·011 cm.). This was for the admission of primary radiation from the bulb. The secondary radiation passing through the side window was studied.

The arrangement was then as follows:—

A bulb and induction-coil were placed inside a lead-covered box M (fig. 3) in one side of which was a rectangular aperture A through which a beam of Röntgen rays passed. Immediately outside this aperture were lead shutters S_1, so that the width could be varied as desired. Two large lead shutters S_2 were placed at a distance of 17 cms. from this aperture and parallel to the side of the box, so that the width of a second aperture B was adjustable.

Fig. 3.



The gas chamber described above was placed with its end window immediately behind the second screen, with its end face against the two shutters and in such a position that a beam of X-rays passed through the parchment window and the opposite end of the box while the sides were perfectly protected. The electroscope L, which was placed with its thin face opposite and parallel to the side window F, was protected by lead from radiation which might otherwise have entered it through its other faces. The thin face was protected from radiation from all directions except through the window of the gas chamber.

The primary beam did not fall upon this window, so that no primary radiation was received by the electroscope.

Again, the two sources of secondary radiation from solids were the thin window through which the primary beam entered the box, and the end C through which it left. To protect against any effect from these, a leaden screen S_3 with rectangular aperture D was placed at a distance of 5 cms. from the side window F, and with the aperture opposite this window. In that position no rays from the end window, or from that portion of the opposite end of the chamber which was subjected to the primary rays, passed through the side window and through the aperture in the screen, so that the electroscope, which was placed immediately behind this screen, did not receive any secondary radiation from solids.

But it was obvious that it would receive tertiary radiation from at least one source. To properly guard against this would have necessitated a considerable diminution in the energy of secondary radiation from the gas which it was desired to measure. Instead of this, then, the tertiary radiation falling on the thin face of the electroscope was made as small as possible, and was afterwards proved to be negligible.

This tertiary radiation arose from the secondary rays from the first window E falling on the side window F of the gas chamber and on leaden screens surrounding the thin face of the electroscope, also from the secondary rays from the other end of the gas chamber falling on the side window and leaden screens.

To ascertain the magnitude of this effect, experiments were made with air. In the first case the parchment side window F was removed and placed immediately in front of the thin face of the electroscope, so that no secondary radiation fell upon it; also the leaden screens protecting the thin face from other radiations were placed a considerable distance from the electroscope so that the tertiary radiation received by this must have been excessively minute. In the other case these were brought as near as possible and the parchment window was placed in its normal position in the gas chamber, so that it was a source of tertiary radiation.

In the first case the electroscope measured the ionization arising from the secondary radiation from the air and from the very weak tertiary radiation from the leaden screens. In the other case the ionization arose from the secondary radiation from the gas and a maximum tertiary radiation from screens and windows. The difference between the intensities of the total radiation received in the two cases was too small to be observed.

The conclusion was therefore that the tertiary radiation from solids was negligible, so that the ionization measured by the electroscope was produced by secondary radiation from the gas inclosed in the gas chamber.

As the intensity of the primary radiation was not constant throughout the experiments, a second similar electroscope Z was placed behind a leaden screen with a small hole X in it opposite the thin face of this electroscope, and primary radiation from the aperture A in the large box containing the induction-coil and bulb passed through this small hole into the electroscope. The rate of motion of the gold-leaf was a measure of the rate of ionization produced in air by the primary radiation, or for rays of the same kind it was a measure of the intensity of primary radiation. The total deflexions in a given time were then used to standardize the intensity of primary radiation.

The two charging-rods of the electroscopes were connected to one terminal of a battery Y whose other terminal was earthed. Momentary contact was made with the insulated portions by means of the contact-makers and the gold-leaves were deflected. Both electroscope-cases were earth-connected so that a definite deflexion corresponded to a definite potential of the gold-leaves. The deflexions were read by the microscopes N and P. Readings were taken at intervals for several hours in order to measure the constant fall due to spontaneous ionization of the air in the electroscopes. The induction-coil was then worked for thirty or, in some cases, twenty seconds, during each whole minute for another period —usually an hour. Readings were taken at intervals and a constant proportionality between the deflexions of the gold-leaves was found. The electroscope subjected to primary radiation was then used to standardize the intensity of the radiation proceeding from the bulb.

When another gas was experimented upon, everything remained in position as before. A gas generator G was connected to an inlet tube which was at the top or bottom of the gas chamber according as the gas was lighter or heavier than the gas which it was replacing. An outlet tube T conducted the gas from the opposite end of the chamber. The insulated portions of the electroscopes were recharged and the same experiments repeated when the gas to be experimented upon filled the box. The deflexions of the standardizing electroscope in a given time did not vary much, but those of the other electroscope varied considerably with the gases used, as the following table shows :—

	Duration of Experiment.	Deflexion of Standardizing Electroscope.	Deflexion of Secondary Electroscope.
Air . . .	31 min.	16·85	6·2
Hydrogen .	32 min.	16·5	·95
. . . .	. . . .	. . . .	. . . . [*]
Hydrogen .	34 min.	17·5	·95
Air . . .	33 min.	18·35	6·35

It should, however, be remembered that when different gases occupy the box, equally intense primary radiations entering the box are only equally intense at the end of the box by which they enter, and that the gases of higher absorption-coefficient are really subjected to less intense radiation than those which are more transparent. A correction must therefore be made for this loss of intensity due to absorption by the gas contained in the chamber. Taking the path of the middle primary and secondary rays as approximately giving the average distance travelled in the chamber, the correction necessary was that due to transmission through about 10 cms. of gas.

The absorption by the different gases was approximately as follows[†] :—

Air	1·5 per cent.
Hydrogen	0 ,,
Sulphuretted Hydrogen .	6 ,,
Carbon Dioxide	2 ,,
Sulphur Dioxide	4 ,,

The following table gives the relative intensities of ionization of the air in the electroscope produced by the radiation from different gases subjected to equally intense primary radiation. Corrections have been made for spontaneous ionization and for absorption of radiation in the gas chamber.

Assuming the penetrability of the radiations from the different gases to be approximately the same—(justified later)—the second column gives the relative intensity of secondary radiation from the gases subjected to similar and equally intense primary radiation from the bulb. The effect from air has been taken as unity, the possible percentage error in the case of hydrogen being very great.

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[*] Experiments were made on spontaneous ionization and any stray effect reaching the electroscope. Corrections have been made for these in the above table.

[†] Rutherford, Phil. Mag. [5] vol. xliii. no. 263, pp. 241–255, April 1897.

Gas.	Rel. Intensity of Sec. Radiation.	Density of Gas.	Relative Ionization of Gas *.
Air	1	1	1
Hydrogen	·17	·07	·33
Sulphuretted Hydrogen	1·075	1·18	6
Carbon Dioxide	1·45	1·53	1·4
Sulphur Dioxide	2·11	2·19	6·4

From these results there is obviously a proportionality between the intensity of secondary radiation and the density of the gas, while there is no obvious connexion with the rate of ionization.

It should be noted that the discrepancy in the case of hydrogen can be accounted for by the presence of a small quantity of air or other impurity in the gas chamber. As the gas was introduced by simply displacing the gas previously occupying the box, this impurity was undoubtedly present. The same consideration would bring the other gases into even closer agreement.

During the course of these experiments, the changes in the density of the gases experimented upon due to variations in atmospheric pressure and temperature between the observations were insignificant.

To examine the absorption of the radiation from different gases, plates of aluminium of thickness ·0105 cm. were placed before the side window of the gas chamber. The intensity of ionization produced by the radiation which passed through the aluminium was compared with that produced when no plates intercepted the secondary radiation. Experiments were made with the radiation from hydrogen and from sulphuretted hydrogen, and the differences due to absorption of the secondary radiation in the two cases amounted to 36 per cent. and 37·5 per cent. of the normal ionization. This was much smaller than the possible error, and in later experiments with air and carbon dioxide no difference in the penetrability of the rays was found.

The experimental results may be stated as follows:—

(1) All gases subject to X-rays are a source of secondary radiation.

(2) The absorbability of the secondary radiation is (within the limits of possible error—about 10 per cent.) the same as that of the primary radiation producing it.

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* J. J. Thomson, Cambridge Phil. Soc. Proc. x. pp. 10–14 (1898).

(3) For a given primary radiation the intensity of secondary radiation is proportional to the density of the gas from which it proceeds—the temperature and pressure being practically constant.

(4) The secondary radiation is not due to recombination of the ions.

Sagnac concluded from his experiments that the secondary rays from *air* are more easily absorbed than the primary rays, but his paper does not give an idea of the amount by which they differ. As the secondary radiation is relatively weak, a beam of considerable cross-section must be studied, so that the rays do not pass normally through the absorbing plate. In the experiments described above, the plates of aluminium placed in the path of the secondary beam produced greater proportional diminution of the resultant ionization than was produced on the ionization caused by the primary, when this beam was intercepted by similar plates. The difference, however, was small, and not more than might be accounted for by the greater thickness through which most of the rays had to pass by striking the plate obliquely.

The fact of the ionization produced in the electroscope by the radiation from different gases being so accurately proportional to the density of the gas from which it proceeds is significant in this connexion, for the ionization depends upon the intensity of the radiation and upon its nature. The difference in the absorbability of the radiations is easily proved insufficient to account for the difference in intensity of ionization ; also it is extremely improbable that differences in the intensity together with differences of the absorbability would produce so accurate a law. It is much more probable that differing intensities of secondary radiation *alone* account for the differing intensities of ionization, and that the secondary radiation has the same penetrability from whatever gas it proceeds. This again leads to the probability that the secondary radiations from different gases are of the same nature as the primary rather than that the primary is similarly transformed by the different gases.

As the primary and secondary radiations only differ appreciably in intensity, we may reasonably conclude that the radiation proceeding from gases subject to X-rays is due to scattering of the primary radiation.

As this scattering is proportional to the mass of the atom, we may conclude that the number of scattering particles is proportional to the atomic weight. This gives further support to the theory that the atoms of different substances are different systems of similar corpuscles, the number of which in the atom is proportional to its atomic weight.

In conclusion I wish to thank Profs. J. J. Thomson and Wilberforce for their advice and interest in this work.

University College, Liverpool.

LXXVI. *Specific Ionization produced by Corpuscles of Radium.*

To the Editors of the Philosophical Magazine.

Gentlemen,

MR. DURACK has given an account (Phil. Mag. May 1903) of some experiments on the specific ionization produced by corpuscles given out by radium, from which he concludes that the number which I obtained for the same quantity was too large. The specific ionization produced by the corpuscles is the number of ions that a single corpuscle will generate in going through a centimetre of gas at a millimetre pressure.

From the experiments which I have made with ultra-violet light I have shown that negative ions, when moving with a sufficiently high velocity, produce others by collisions with molecules of the gas. The number of ions produced by a single ion increases as the force is increased, and reaches a maximum when the force is above a certain value depending on the pressure. The voltage in these experiments was comparatively low, as it seldom exceeded 300 volts. For air at a millimetre pressure the maximum number of ions which a single ion generates is 15.

I also made some experiments with radium which led me to conclude that each of the corpuscles which are given out generates at least 13 ions per centimetre in air at a millimetre pressure.

Mr. Durack finds from his experiments that this number ought to be ·4, and he attributes the difference between his result and the result which I obtained with ultra-violet light to the very high velocity of the corpuscles given out by radium, the velocity of these corpuscles being large compared with the velocity corresponding to a fall of potential of 300 volts.

According to this theory the probability that new ions should be produced by a collision would diminish when the velocity is increased above a certain value.

Mr. Durack states that the result of my experiments is wrong as it does not agree with his number ·4.

It is easy, however, to explain the discrepancy between these results, if the theory which Mr. Durack has proposed is the true explanation of the difference between his experiments with radium and my experiments with ultra-violet light. The velocity of the corpuscles will depend on the thickness of the aluminium between the radium and the gas which is examined. In my experiments the aluminium through which the radiation had to pass was much thicker than that used by Mr. Durack, so that the corpuscles which passed through the gas must have been travelling with a diminished velocity, and consequently they would each produce a larger number of ions per centimetre in the gas through which they pass.

If we accept this theory we might expect to obtain any value less than 15 for the specific ionization by varying the thickness of the aluminium through which the radiation has to pass.

Yours very truly,
John S. Townsend.

LXXVII. *Some Experiments on the Electrical Conductivity of Atmospheric Air.* *By* J. C. McLennan *and* E. F. Burton, *University of Toronto*[*].

I. *Introduction.*

In a paper by H. Geitel[†] reference is made to a gradual increase observed in the conductivity of a mass of atmospheric air after being confined in an air-tight chamber. This effect was found to require from four to five days to reach its maximum value, and was observed in localities where no thorium compounds or other known radioactive substances existed.

In a subsequent investigation Elster and Geitel[‡] found that the air which had been confined for some time in closed caves or house-cellars possessed an abnormally high conductivity. This phenomenon, together with the observed increase in conductivity mentioned above, they concluded, could not be due to the presence of dust or water-vapour. They traced it rather, in both cases, to the existence of some undetermined radioactivity in the confining walls.

More recently these physicists discovered that atmospheric air possessed the property of exciting induced radioactivity in

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[*] Communicated by Prof. J. J. Thomson. Read before the meeting of the American Physical Society in Washington, Dec. 31st, 1902.

[†] *Phys. Zeit.* ii. pp. 116–119 (1900).

[‡] *Phys. Zeit.* ii. pp. 560–563 (1901).

bodies exposed under negative electrification. This phenomenon of induced or excited radioactivity had been previously observed by Rutherford in bodies exposed to air drawn from the neighbourhood of thorium compounds, and had been connected by him very directly with an emanation which these salts emit. This emanation he found possessed the property not only of exciting radioactivity in all solid substances in its neighbourhood, but also of ionizing any gas with which it was in contact.

Since atmospheric air has been shown by Elster and Geitel*, C. T. R. Wilson†, and others to be continually ionized by some agent, and since it has also been shown to possess the property of exciting radioactivity, one is forced to conclude there is present in the air an emanation possessing properties similar to that emitted by thorium compounds.

Hitherto the source of such an emanation has not been determined, but, as the phenomena of induced radioactivity and spontaneous ionization universally characterize atmospheric air, it seems evident, since thorium compounds are but sparsely distributed in nature, that sources other than these must exist.

Recalling the experiments of Elster and Geitel, it seems probable that the earth's surface, and possibly too the materials used in the construction of their apparatus, are sources of this emanation. As but little evidence existed in favour of this conclusion, the writers recently made a series of observations upon atmospheric air confined in air-tight vessels of different metals. The result of the investigation showed that the conductivity of the inclosed air depended very largely upon the material of which the receiver was made, and the effects observed would seem to indicate that all metals, in varying degree, are the sources of a marked though feeble radioactive emanation.

2. *Apparatus.*

In these observations the air whose conductivity was to be measured was confined in a cylinder, 125 cms. in length and 25 cms. in diameter, similar to that shown in fig. 1. In the first experiment it was made of sheet-iron coated with zinc, and in the later experiments linings of various metals were inserted in order to examine their effect upon the conductivity of the inclosed air. The bottom and cover were removable, and, when in position, were made air-tight by means of cement. Into a flanged opening in the cover was fitted an

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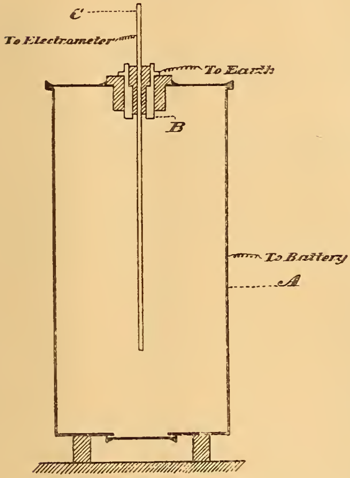
* *Loc. cit.*

† Proc. Roy. Soc. March 1901.

ebonite plug about 5 cms. in diameter, a brass tube B was passed through this, and into it a second ebonite plug was tightly fitted. This second plug carried a brass rod C, which extended almost to the bottom of the cylinder. The brass tube B, which was earthed throughout the measurements, served as a guard-ring, and prevented any leak from the vessel to the rod C across the ebonite plugs.

The conductivity was measured by placing the cylinder upon an insulated platform, charging it by means of a set of small storage-cells to a potential of 165 volts, which sufficed for the saturation current, and observing the rise in potential of the electrode D, which was joined to a quadrant electrometer in the usual manner. The sensibility of the electrometer was such as to produce a deflexion of 1000 mms. on a scale at one metre distance for a potential-difference of one volt between the quadrants.

Fig. 1.



3. *Conductivity Measurements.—Time Effect.*

Before inclosing air for examination the cylinder was placed in an open window in the laboratory, with the ends removed and the air allowed to blow through it for some time. The top and bottom were then replaced, cemented in position, and the cylinder connected with the electrometer as quickly as possible.

Measurements on the conductivity were made at intervals of a few minutes at first, and it was invariably found that a rapid decrease in the ionization took place until a minimum value was reached. The conductivity then slowly increased and approached a limiting value in the course of two or three days.

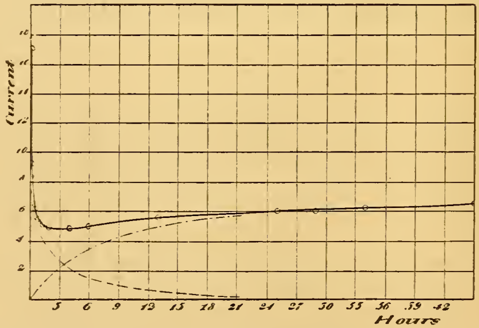
In repeated tests carried out in this manner with the zinc cylinder it was found that, while the initial conductivity varied from day to day, there was always observed a rapid decrease to a constant minimum, followed by a gradual rise to a constant limiting value.

A typical set of values for the conductivity of air confined in the zinc cylinder at atmospheric pressure are given in column 3 of Table I., the currents being expressed in arbitrary units, and the times being taken from the closing of the cylinder.

TABLE I.

Time.	Current : Arbitrary Scale.	
	Pressure, 501·0 cms.	Pressure, 74·2 cms.
Column 1.	Column 2.	Column 3.
10 mins.	30·0	17·1
15 ,,	...	9·3
30 ,,	17·5	6·2
50 ,,	13·2	5·5
1·0 hour	12·0	—
1·25 ,,	...	5·13
1·50 ,,	9·9	—
1·75 ,,	6·9	5·1
2·00 ,,	8·0	4·9
4·00 ,,	6·6	4·8
5·00 ,,	7·6	—
6·00 ,,	...	5·0
10·00 ,,	...	5·8
22·00 ,,	19·2	—
25·00 ,,	...	6·0
29·00 ,,	...	6·0
32·00 ,,	22·0	—
34·00 ,,	..	6·3
44·00 ,,	24·0	—
45·00 ,,	...	6·5

Fig. 2.

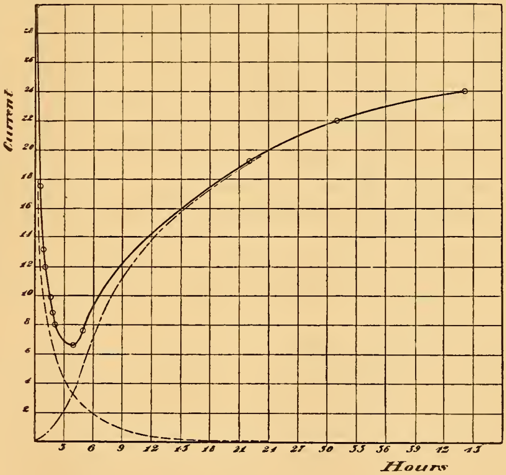


The ionization curve for these values (fig. 2) shows that the minimum current, 4·8, was reached in about four hours after the air was inclosed. After about eighteen hours the curve indicates that the conductivity was tending towards a limiting value, which the reading taken after forty-four hours showed to be about 6·5.

As a variation in the experiments, a series of tests were made in air confined in a receiver at high pressures. The cylinder in this case was of heavy rolled iron coated with zinc, and was of the same dimensions as that used in the first measurements.

The results of observations on the conductivity of air confined at a pressure of about seven atmospheres are given in column 2, Table I., the scale used being the same as before. The curve representing these values is shown in fig. 3, and exhibits the same characteristics as that for the lower pressure.

Fig. 3.



We have again the rapid decrease to a minimum followed by a gradual rise tending towards a limiting value. The minimum conductivity in this case was about 6·6, and was reached in about four hours after the required pressure in the cylinder had been obtained. The time occupied in pumping the air was about one hour.

In seeking for an explanation of the curves shown in figs. 2 and 3, their two-fold origin, as indicated by the dotted lines, is at once suggested, the conductivity in the initial stage being due to an agent subject to rapid decay, and that in the second to one whose power shows a gradual increase.

The first of these dotted curves is similar to that given by Rutherford* for the conductivity of the air in a chamber

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* Rutherford, Phil. Mag. Jan. 1900, p. 6.

which had been cut off from a second containing thorium oxide, after the two had been in communication for some time, while the second is similar to that given by him for the increase in the conductivity of the air in one chamber when *placed* in communication with another containing thorium oxide.

It will thus be seen that the first portion of the curves in figs. 2 and 3 can be explained upon the supposition that a radioactive emanation, probably having its origin in the earth's surface, was introduced into the cylinder with the air, the decay of this emanation being the cause of the decrease in the conductivity, and the second portion upon the supposition that a radioactive emanation is given off by the walls of the containing vessel. On this view the limiting value to which the conductivity curves tend would represent a condition of equilibrium, where the rate of decay of the emanation was equal to the rate at which it was produced.

As both the low and the high pressure cylinders were made of the same material and were of the same size, one would expect the same amount of the emanation to be present in both when the steady state was reached. With an easily absorbed radiation from this emanation, we should obtain a limiting conductivity independent of the pressure. But, since a very great difference was found in the limiting conductivities at the two pressures, it would appear that the radiation possesses considerable power of penetration and is not easily absorbed.

The difference in the initial conductivities given in columns 2 and 3, Table I., may also be readily explained by the difference in the air-pressures. The time required to fill the high-pressure cylinder, and the decay taking place during that time in the emanation introduced with the air, preclude a comparison of the amounts of active emanation present in each cylinder when the first observations upon their conductivities were made ; but, if the amount in the high-pressure cylinder were equal to or greater than that in the low-pressure cylinder, the difference in the initial conductivities is explained, while, if it were less, the greater density of the air in the high-pressure cylinder, and the consequent greater absorption, would still account for the higher conductivity.

4. *Effect of Different Metals.*

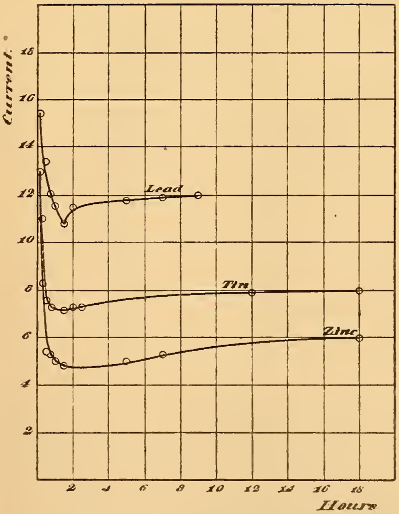
To ascertain whether the conductivity of the inclosed air was affected by a change in the metal composing the walls of the receiver, linings of tin and lead were in turn fitted into the zinc cylinder used in the first experiment.

Tests of the conductivity were made both with and without the tin and lead linings. Before each test the cylinder was well aired and sealed in the manner already described. As soon as the air was inclosed, measurements on the conductivity were begun and continued at stated intervals as before.

TABLE II.

Time.	Current: Arbitrary Scale.		
	Zinc.	Tin.	Lead.
10 minutes	13·0	13·0	15·4
15 ,,	8·3	11·0	—
30 ,,	5·4	7·6	13·4
45 ,,	5·3	7·3	12·1
1·0 hours	5·0	...	11·55
1·5 ,,	4·85	7·2	10·8
2·0 ,,	...	7·3	11·5
2·5 ,,	...	7·3	—
5·0 ,,	5·0	...	11·8
7·0 ,,	5·3	...	11·9
9·0 ,,	...	...	12·0
12·0 ,,	...	7·9	—
18·0 ,,	6·0	8·0	—

Fig. 4.



The values obtained for the conductivity with each of the metals are given in Table II., and curves representing these values are shown in fig. 4.

The curves for the different metals, it will be seen, have the same characteristics. In each there is a rapid drop to a minimum and a gradual rise towards an ultimate limiting value. It is interesting to note that a considerable difference was found in the minimum conductivities for the three metals and that the final limiting values also varied.

The decay of an emanation introduced into the cylinder with the air would again account for the first portion of the curves, a radioactive emanation from the metallic walls would explain the existence of the second portion, while the differences in the minimum and limiting values may be considered to have their origin in variations in the rate at which the emanation is given off by the different metals.

In this connexion it will be noted that the limiting values of the conductivities range according to the atomic weights of the metals, lead having the highest, tin the next, and zinc the lowest.

5. *Effect of Variations in Pressure.*

In order to investigate the relation between the conductivity of air and the pressure at which it was confined, the heavy cylinder was filled to a pressure of about seven atmospheres, and allowed to stand for some days until its conductivity assumed a constant value.

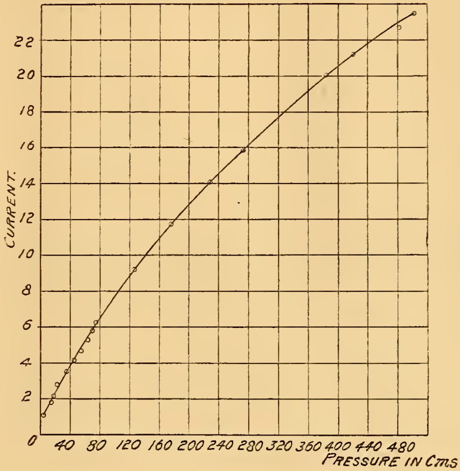
Table III.

Pressure in cms.	Current: Arbitrary Scale.	Pressure in cms.	Current: Arbitrary Scale.
501·0	23·5	69·3	5·8
481·0	22·7	62·0	5·4
420·0	21·2	53·0	4·7
384·0	20·3	44·2	4·2
272·0	15·8	35·0	3·5
227·0	14·1	22·4	2·7
176·0	11·7	18·2	2·2
125·0	9·3	14·0	1·8
74·2	6·5	4·4	1·1

The air was then allowed to escape gradually, and the pressure reduced from 501·0 cms. to 4·4 cms of mercury, the conductivity being measured at these and at various intermediate pressures. The results are given in Table III., and the conductivity curve in fig. 5.

The ionization curve so nearly approaches a straight line that we may almost conclude, in view of the wide range of the pressures examined, that the conductivity was proportional to the pressure. This result is what we should expect to obtain with an emanation maintained at a constant strength and emitting a radiation of a penetrating nature.

Fig. 5.



6. *Penetrating Rays from External Sources.*

While the effects described up to the present may be explained by supposing the ionization to be caused by a radioactive emanation sent off from the metals, it has been found that part of the conductivity cannot be accounted for in this way, but must be attributed to an active agent external to the receiver.

The heavy cylinder referred to above was filled with air to a pressure of about 400 cms. of mercury and allowed to stand until its conductivity had become steady. It was then placed in an insulated galvanized iron tank, 150 cms. in height and 75 cms. in diameter, which was gradually filled with water so as to surround the cylinder with a layer 25 cms. in thickness. The initial conductivity before the water was admitted was 21·1. As the water rose the conductivity decreased and fell to 13·3 when the tank had been filled. The values for the conductivity during the experiment are given in Table IV., and they show that the loss was almost directly proportional to the rise of the water. The total fall in conductivity, it will be seen, was about 37 per cent.

TABLE IV.

Depth in cms.	Current: Arbitrary Scale.
0·0	21·1
15·0	20 5
60·0	18·0
77·0	17·0
97·0	14·3
110·0	13·75
120·0	13·3

The experiment was repeated with the cylinder placed in a tank 50 cms. in diameter. This tank permitted the cylinder to be surrounded by a layer of water 12·5 cms. in thickness, and it was found when the water was poured in that the conductivity fell off 17·5 per cent.

From these results it is evident that the ordinary air of a room is traversed by an exceedingly penetrating radiation, such as that which Rutherford* has shown to be emitted by thorium, radium, and the excited radioactivity produced by thorium and radium.

In order, therefore, to reach definite conclusions regarding the extent and true character of the effect of various metals upon the conductivity of the air which they inclose, it will be necessary to entirely cut off the inclosing vessel from the action of this external radiation, and the writers have not yet carried their experiments to this point.

Physical Laboratory,
University of Toronto.

LXXVIII. *Notices respecting New Books.*

Text-Book of Electrochemistry. *By* SVANTE ARRHENIUS, *Professor at the University of Stockholm.* *Translated by* JOHN McCRAE, Ph.D. London: Longmans, Green, & Co., 1902. Pp. xii+344.

IN the English edition of this text-book by one of the leading authorities on electrochemistry, we find much to praise and not a little to blame. We shall probably best discharge our duties towards the author and the translator by stating that no one interested in the subject can afford to ignore the book, written as it is by one whose name will ever remain associated with the epoch-making theory of ionization.

Having said so much, we think that both the translator's and the reader's interests will be best served if we draw attention to some of

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* Rutherford, 'Nature,' vol. lxvi. p. 318 (1902).

the blemishes which disfigure the book, and which could easily be removed in a future edition, a demand for which is certain to arise.

In the introductory chapter on "Fundamental Physical and Chemical Conceptions" the treatment of electrical units is extremely slovenly. It is a pity that the translator has not adopted the terms "resistance," "resistivity," "conductance" and "conductivity" in the meanings now generally attached to them, and prefers to use "specific resistance" etc. On p. 5, it is stated that "the term 'potential difference' is frequently used in place of electromotive force"—a statement which, alas! is only too true, but true by reason of the very general ignorance which refuses to recognize the essential difference between the two terms. An exceptionally bad example of negligence is to be found on p. 6, where we come across the following two statements: "The difference of the potentials at two points is called the potential difference *or* electromotive force, and is that *force* which tends to make the electricity pass from one point to the other"; and lower down, "the potential corresponds, in a certain sense, to *work*" (the italics in both cases are ours). Such crude and, to a learner, extremely confusing statements might be excused in a popular exposition of a difficult subject; in a serious scientific text-book they are intolerable. On p. 11, the horse-power is stated to be equivalent to 75 kilogramme-metres per sec.; this is true of the Continental, but not of the British horse-power, which is about 1·36 per cent. larger. On p. 124, the E.M.F. of the Clark cell is wrongly given as 1·438 volts at 15°. On p. 114, the author adopts the method commonly followed by advocates of the dissociation theory, and boldly states that the very smallest E.M.F. is sufficient to produce chemical decomposition. "This fact," it is added, "was proved by Buff with *currents* so small that it was only after months that a cubic centimetre of explosive mixture was obtained." There is here clearly a confusion of E.M.F. and current. We are not aware of any perfectly trustworthy experiments which have shown that any E.M.F., however small, is capable of evolving an explosive mixture of hydrogen and oxygen from acidulated water. It is the fashion, with many electrochemists, entirely to neglect considerations of energy in dealing with this matter.

We have taken up so much space in pointing out some of the more important errors in the book, that its excellences must be but briefly referred to. Where the author is on more purely chemical ground his exposition is admirably clear and to the point. An immense number of references are given to original sources of information, and there is a useful index at the end of the book.

Meteorologische Optik. *Von* J. M. PERNTER, *Professor an der K. K. Universität und Director der K. K. Centralanstalt für Meteorologie und Erdmagnetismus.* Mit zahlreichen Textfiguren. II. Abschnitt. Wien und Leipzig: Wilhelm Braumüller. 1902. Pp. 55–212.

SOME time ago we had occasion to review briefly the first part of this excellent and comprehensive treatise by Professor Pernter.

who is well known as an authority on meteorology. The present section of the work is concerned with those phenomena which are attributable to the gaseous constituents of the atmosphere, and which are brought about by refraction and total reflection. These phenomena are dealt with under three heads, corresponding to the three chapters of the present section of the work. To the first class are referred the effects produced by the normal distribution of density in the atmosphere—*i. e.*, by a uniform decrease of density in an upward direction. The second class comprises phenomena which result from irregular density distributions, and the third relates to effects in which more or less rapid fluctuations in the density of the various layers take place. The discussion of the various problems presented by such abnormal phenomena is a very thorough one, and the volume should prove interesting to the general reader, as it contains a large number of vivid accounts by eye-witnesses of the phenomena dealt with, and is well illustrated.

Physico-Chemical Tables. For the use of Analysts, Physicists, Chemical Manufacturers, and Scientific Chemists. *By* JOHN CASTELL-EVANS, *F.I.C.*, *F.C.S.*, *Superintendent of the Chemical Laboratories and Lecturer on Inorganic Chemistry and Metallurgy at the Finsbury Technical College.* Vol. I. Chemical Engineering and Physical Chemistry. London: Charles Griffin & Company, Limited. 1902. Pp. xxxii + 548.

GREAT credit is due to Mr. Castell-Evans for the extraordinary amount of labour which the compilation of the present volume, the first half of the complete work, must have cost him. One cannot but admire his courage in persevering in his formidable task, in spite of, as he informs us in the preface, the warning given him by a friend that he was making himself "a hewer of wood and a drawer of water for other people." But if so, it is now only fair to add that probably the "other people" feel deeply grateful.

The volume is divided into three parts. Part I. contains various mathematical formulæ and tables; it may be suggested that physicists would probably welcome, in addition to the tables given, tables of exponentials and the hyperbolic functions, which are so frequently useful. Part II. contains tables relating to mechanics (gravitation, elasticity, &c.). Part III., which occupies by far the largest portion of the book, deals with physics and physical chemistry: thermometry, expansion coefficients, calorimetry, densities, barometry, thermal constants and volumes of gases, vapour-densities, fusion, vaporisation, vapour *pressures* (we regret to notice the term "vapour tension"), boiling-points, and latent heats of vapours.

We hope that the book will find the recognition it deserves among all those whose scientific work would be much lightened by the use of such tables.

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END OF THE FIFTH VOLUME.

Printed by Taylor and Francis, Red Lion Court, Fleet Street.

Fig. 1.

Fig. 2.

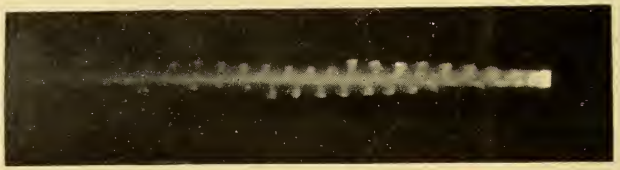
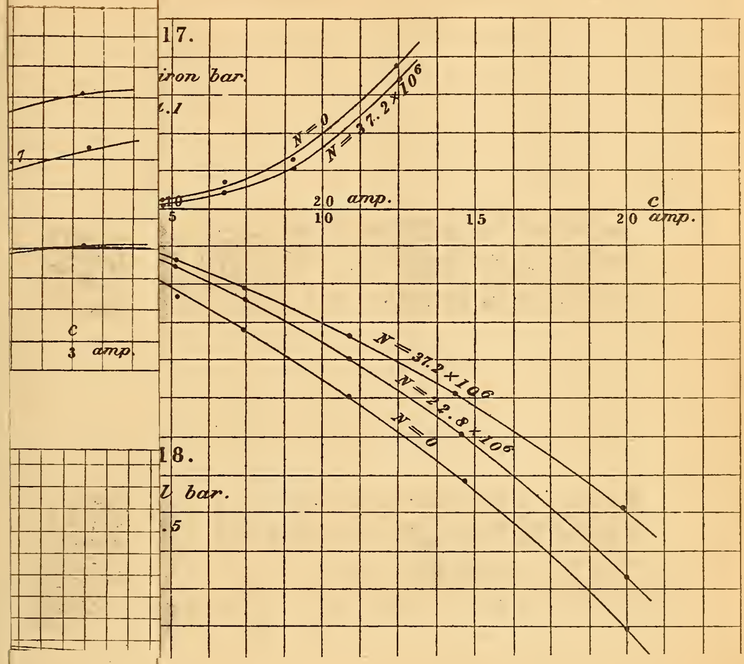


Fig. 3.

Fig. 4.



sical Observatory, Smith

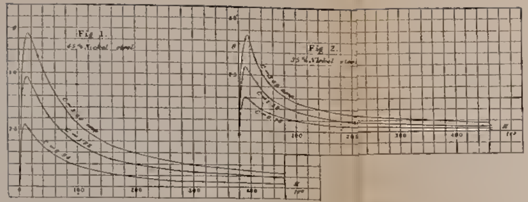


Fig. 1. 45% Nickel steel.

Fig. 2. 35% Nickel steel.

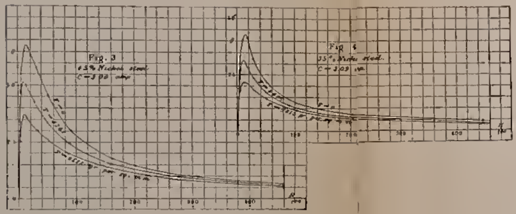
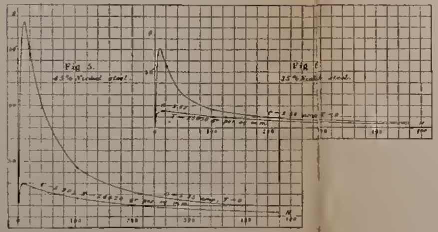


Fig. 3. 45% Nickel steel. C=3.03 amp.

Fig. 4. 35% Nickel steel. C=3.03 amp.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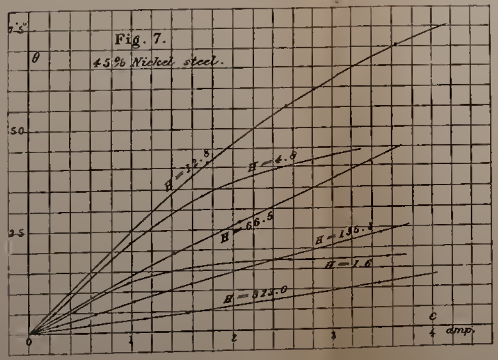


Fig. 7. 45% Nickel steel.

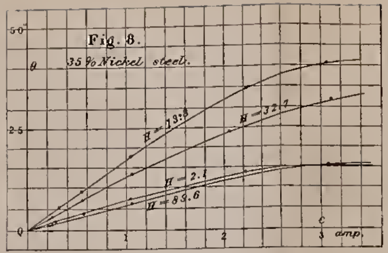


Fig. 8. 35% Nickel steel.

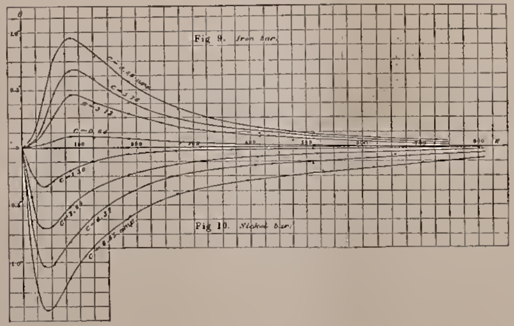


Fig. 9. Iron bar.

Fig. 10. Nickel bar.

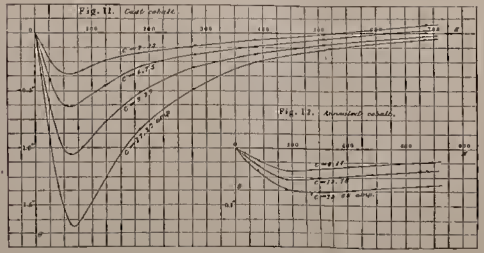
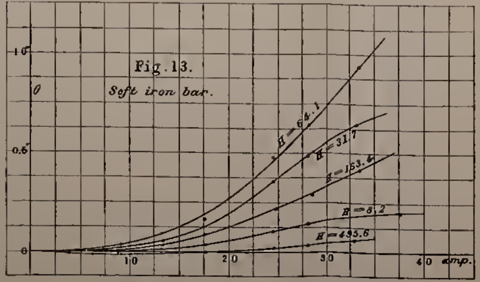


Fig. 11. Cast cobalt.

Fig. 12. Annealed cobalt.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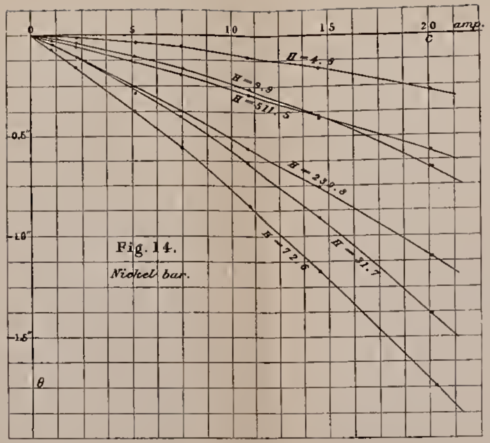
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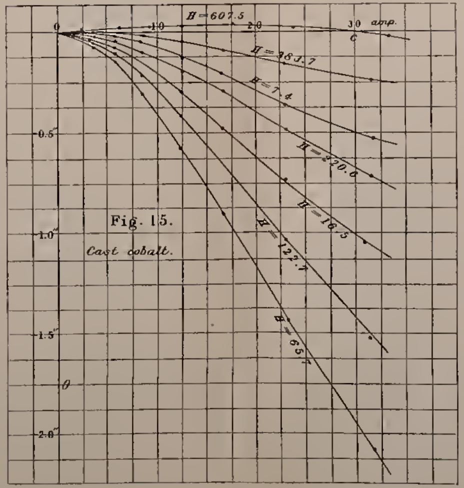
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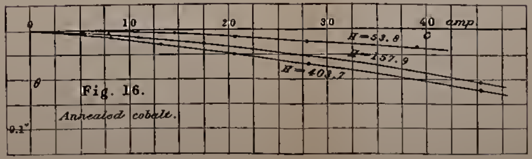


Fig. 16. Annealed cobalt.

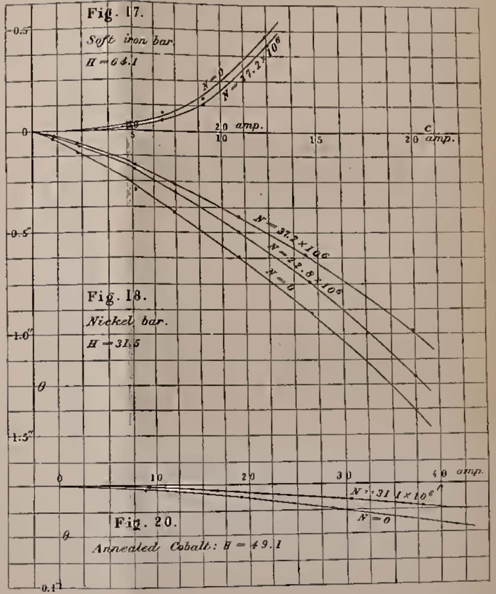


Fig. 17. Soft iron bar. H=64.1

Fig. 18. Nickel bar. H=31.5

Fig. 20. Annealed Cobalt: H=49.1

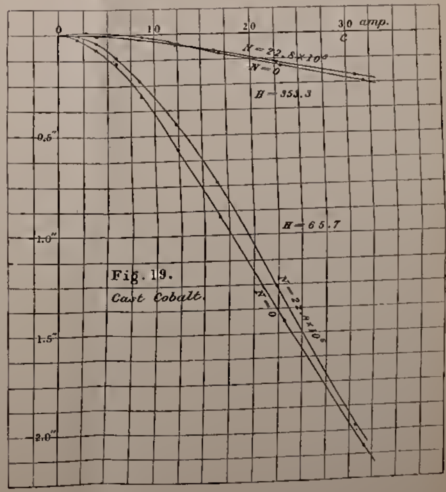
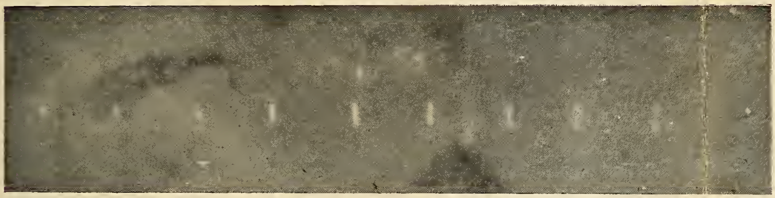


Fig. 19. Cast Cobalt.

1.

The object,—a series of artificial stars.

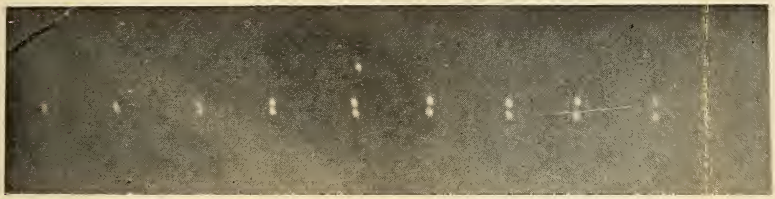
2.



Without stirring

Images of above object, exposures 3 minutes.

3.



With stirring.

4.

Without stirring

Images of above object, exposures 4 minutes.

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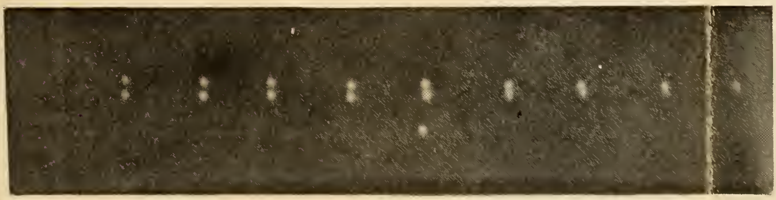

With stirring.

Photographs illustrating Artificial Good Seeing.
Astrophysical Observatory, Smithsonian Institution.