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CONDUCTED BY

SIR WILLIAM THOMSON, KNT. LL.D. F.R.S. &c.

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AND

WILLIAM FRANCIS, PH.D. F.L.S. F.R.A.S. F.C.S.

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

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VOL. XXX.—FIFTH SERIES.  
JULY—DECEMBER 1890.

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L O N D O N :

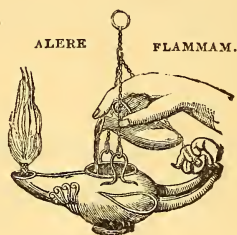
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“Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem.”—*Hugo de S. Victore.*

——· Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condât,  
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.*





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## ERRATA.

- Page 156, line 16, *read* square of the wave-length.  
 — 158, lines 21, 22, and 23, *read*  $n'\nabla^2u$ ,  $n'\nabla^2v$ ,  $n'\nabla^2w$ .  
 — — line 24, *read*  $n'$  for  $n$ .  
 — 429, end of § 6, for *accommodating power* *read* *quantity of accommodation indicated*.

## PLATES.

- I. & II. Illustrative of Mr. A. A. Michelson's Paper on the Application of Interference Methods to Astronomical Measurements.
- III. & IV. Illustrative of Mr. H. Tomlinson's Paper on the Effect of Change of Temperature on the Villari Critical Point of Iron.
- V. Illustrative of Messrs. Maclean and Makita Goto's Paper on some Electrical Properties of Flames.
- VI. Illustrative of Prof. C. V. Boys's Paper on Photographs of Rapidly Moving Objects, and on the Oscillating Electric Spark.
- VII. & VIII. Illustrative of Mr. S. U. Pickering's Paper on the Expansion of Water and other Liquids.
- IX.-XI. Illustrative of Mr. Carl Barus's Paper on the Isometrics of Liquid Matter.
- XII. Illustrative of Messrs. H. E. J. G. du Bois and H. Rubens's Paper on Refraction and Dispersion in certain Metals.



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[FIFTH SERIES.]

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JULY 1890.

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I. *On the Application of Interference Methods to Astronomical Measurements.* By ALBERT A. MICHELSON\*.

[Plates I. & II.]

IN a recent paper on "Measurement by Light-Waves" † it was shown that the limitation of the effective portions of an objective to the extreme ends of a diameter converted the instrument into a refractometer; and although definition and resolution are thereby sacrificed, the accuracy may be increased ten to fifty fold.

The simplest way of effecting this in the case of a telescope is to provide the cap of the objective with two slits adjustable in width and distance apart. If such a combination be focused on a star, then, instead of an image of the star, there will be a series of coloured interference-bands with white centre, the bands being arranged at equal distances apart and parallel to the two slits. The position of the central white fringe can be marked from ten to fifty times as accurately as can the centre of the telescopic image of the star.

One of the most promising applications of the method is the measurement of the angular magnitudes of small sources of light.

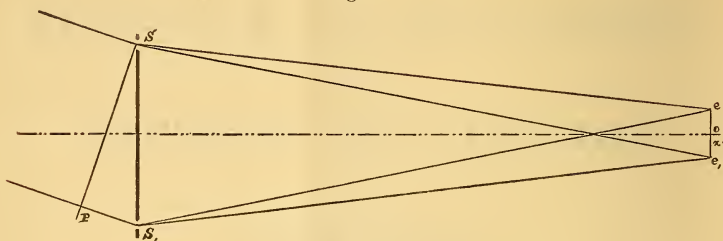
This may be accomplished by taking advantage of the well-known principle that in order to obtain clear interference-

\* Communicated by the Author.

† 'American Journal of Science,' xxxix. Feb. 1890.

bands from two pencils diverging from the same source (width  $a$ ) at an angle  $\beta$ , it is necessary that either  $\beta$  or  $a$  be very small.

Fig. 1.



Thus, in fig. 1, let us take

$a = ee_1$  = width of the source.

$d$  = distance of source from the objective.

$b = SS_1$  = distance between the slits.

Also put  $S_1P = \Delta$ ,  $\frac{a}{d} = \alpha$ ,  $\frac{b}{d} = \beta$ .

Then the usual statement is that the interference-fringes vanish when  $Se_1 - Se = \frac{1}{2}\beta a = \frac{1}{2}ba = \frac{1}{2}\lambda$ , or when

$$\alpha = \frac{\lambda}{b}.$$

But  $\frac{\lambda}{b}$  is the "limit of resolution" of the telescope of aperture  $b$ , and if this be denoted by  $\alpha_0$  we have

$$\alpha = \alpha_0.$$

Or, in words, the fringes disappear when the source subtends an angle which can just be resolved by the telescope.

The experiment was first tried with an objective of 45 millim. effective diameter (distance between the slits) at a distance of ten metres from an adjustable slit which served as the source.

It was found that the first indication of indistinctness occurred when  $a$  was 0.08 millim. wide, and at 0.14 millim. the fringes almost vanished.

*But on continuing to widen the slit they again became clearly visible, to disappear and reappear at regular intervals.*

Now, though it might with truth be urged that the observation of the indefinite vanishing of interference-fringes depends so much on the attendant circumstances, and especially on the condition of the observer, that it can scarcely be called a precise measurement, yet the statement applies no longer

when the disappearance depends on the existence of well-marked *minima of distinctness*; and, as will appear below, it is possible to measure, with accuracy, by the observation of these minima the width of a source of light, which in a telescope can with difficulty be ascertained to have an appreciable size.

The theory of these successive appearances and disappearances is as follows:—

Returning to fig. 1, let  $x$  be the distance of any element of the source from the axis of the telescope,  $dx$  the width of the element, and  $y = \phi(x)$  the length.

Then the difference in the two paths  $xS$  and  $xS_1P$  terminating at the wave-front  $P$ , which makes an angle  $\gamma$  with the plane perpendicular to the axis of the telescope, will be  $\beta x - \gamma b$ , and the resulting intensity in the direction  $\gamma$  for the whole source will therefore be

$$I = \int \phi(x) \left[ 1 + \cos \frac{2\pi}{\lambda} (\beta x - \gamma b) \right] dx. \quad (1)$$

#### CASE I.—*Uniformly Illuminated Slit.*

If the source be a slit whose centre is in the axis, and whose length is parallel to the slits  $SS_1$ , and whose width is  $a$ , then

$$I = a + \frac{\lambda}{\pi\beta} \sin \frac{\pi\beta}{\lambda} a \cos \frac{2\pi\gamma}{\lambda} b. \quad (2)$$

If  $I_1$  be the intensity at the centre of a bright fringe, and  $I_2$  that at the centre of a dark fringe, then the visibility of the fringes may be expressed by

$$V = \frac{I_1 - I_2}{(I_1 + I_2)}. \quad (3)$$

But

$$I_1 = a + \frac{\lambda}{\pi\beta} \sin \frac{\pi\beta}{\lambda} a,$$

$$I_2 = a - \frac{\lambda}{\pi\beta} \sin \frac{\pi\beta}{\lambda} a;$$

$$\therefore V = \frac{\sin \frac{\pi\beta}{\lambda} a}{\frac{\pi\beta}{\lambda} a}$$

or, finally,

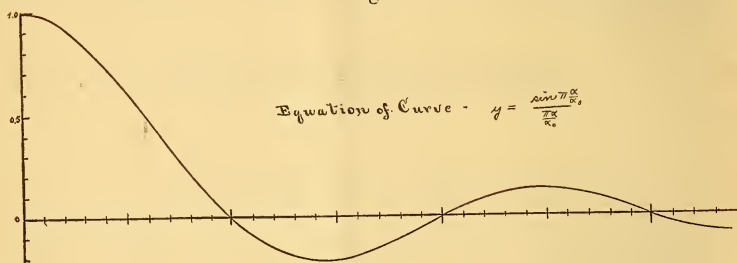
$$V = \frac{\sin \pi \frac{\alpha}{\alpha_0}}{\pi \frac{\alpha}{\alpha_0}} \dots \dots \dots (4)$$

Hence the fringes will disappear whenever  $\alpha$  is a multiple of  $\alpha_0$ . They will be clearest when

$$\alpha = \frac{\alpha_0}{\pi} \tan \pi \frac{\alpha}{\alpha_0} \dots \dots \dots (5)$$

The curve of visibility will be of the form given in fig. 2.

Fig. 2.



The successive values of the maxima, disregarding signs, calculated from the above equation, are :—

$$V = + 1.000$$

$$V = - 0.210$$

$$V = + 0.130$$

$$V = - 0.091$$

The negative values mean that during the corresponding period the fringes are *reversed*\*.

As the expression for  $V$  contains  $\lambda$ , the wave-length of the light employed, the fringes can disappear for that colour (and the complementary one) only; and as this will be most decided for the brightest colour in the spectrum, the yellow or greenish yellow (and therefore also for violet), there will be a residue of red and blue-green mixed with much white light. Both of these deductions have been fully verified by experiment.

\* Probably the expression for  $V$  should be  $\left(\frac{I_1 - I_2}{I_1 + I_2}\right)^2$ , but this will not affect the position of the points for which  $V = 0$ .

Table I. shows well the accordance between theory and observation. Under S is given the nature of the light used : S denotes sunlight, C calcium light, R red light.

The other quantities given in the Table are :—

$\lambda$  = Approximate wave-length in thousandths of a millimetre.

$a$  = Width of slit by direct measurement.

$d$  = Distance to telescope.

$b$  = Distance between centres of slits.

$f$  = Factor depending on the order of the observed disappearance.

$\alpha$  = Angle deduced from the observations.

$\alpha_1 = \frac{a}{d} \times 206265''$ .

$e$  = Error in seconds.

$o$  = Error per cent.

TABLE I.

S.	$\lambda$ .	$a$ .	$d$ .	$b$ .	$f$ .	$\alpha$ .	$\alpha_1$ .	$e$ .	$o$ .
S.	550	240	20,800	50.15	1.00	2.26	2.38	-0.12	- 5
"	"	490	"	23.35	1.00	4.86	4.85	+0.01	0
"	"	740	"	15.45	1.00	7.33	7.33	.00	0
C.	570	197	20,340	65.75	1.00	1.78	1.99	- .21	-10
"	"	365	"	65.75	2.00	3.57	3.69	- .12	- 3
"	"	547	"	65.75	3.00	5.35	5.53	- .18	- 3
"	"	723	"	65.75	4.00	7.14	7.31	- .17	- 2
"	"	900	"	65.75	5.00	8.92	9.11	- .19	- 2
"	"	238	"	53.75	1.00	2.18	2.41	- .23	-10
"	"	442	"	53.75	2.00	4.36	4.47	- .11	- 3
"	"	650	"	53.75	3.00	6.55	6.58	- .03	0
"	"	865	"	53.75	4.00	8.73	8.75	- .02	0
"	"	1.105	"	53.75	5.00	10.91	11.18	- .27	- 3
"	"	277	"	40.75	1.00	2.88	2.80	+ .08	+ 3
"	"	567	"	40.75	2.00	5.76	5.74	+ .02	0
"	"	858	"	40.75	3.00	8.64	8.68	- .04	0
"	"	1.150	"	40.75	4.00	11.52	11.64	- .12	- 1
"	"	1.412	"	40.75	5.00	14.40	14.28	+ .12	+ 1
"	"	388	"	31.15	1.00	3.77	3.93	- .16	- 4
"	"	757	"	31.15	2.00	7.54	7.66	- .12	- 2
"	"	1.160	"	31.15	3.00	11.31	11.73	- .42	- 4
"	"	1.532	"	31.15	4.00	15.08	15.40	- .32	- 2
"	"	1.902	"	31.15	5.00	18.85	19.25	- .40	- 2
R.	623	298	"	44.75	1.00	2.86	3.02	- .16	- 5
"	"	573	"	44.75	2.00	5.73	5.80	- .07	- 1
"	"	852	"	44.75	3.00	8.65	8.62	+ .03	0
"	"	1.108	"	44.75	4.00	11.46	11.21	+ .25	+ 2
"	"	1.415	"	44.75	5.00	14.32	14.32	.00	0
"	"	1.672	"	44.75	6.00	17.18	16.92	+ .26	+ 2
"	"	1.945	"	44.75	7.00	20.05	19.69	+ .36	+ 2
"	"	2.223	"	44.75	8.00	22.91	22.49	+ .42	+ 2



It may be noted that under the observations marked R no less than eight successive disk disappearances were noted, the average error being less than 2 per cent.

CASE II.—*Uniformly Illuminated Disk.*

If the source be a uniformly illuminated disk of radius  $r$ , the expression to be integrated is

$$I = 4 \int_0^r \sqrt{r^2 - x^2} \left[ 1 + \cos \frac{2\pi}{\lambda} (\beta x - \gamma b) \right] dx. \quad (6)$$

Putting  $\alpha$  = angular diameter.

Then

$$\frac{\beta}{\lambda} = \frac{\alpha}{\alpha_0} \frac{1}{r}.$$

Write

$$\frac{x}{r} = w, \text{ and } \pi \frac{\alpha}{\alpha_0} = n.$$

Then omitting the phase constant  $\gamma b$  this reduces to the form

$$I = \frac{\pi}{4} \left[ 1 \pm \frac{4}{\pi} \int_0^1 \sqrt{1 - w^2} \cos nw \, dw \right], \quad (7)$$

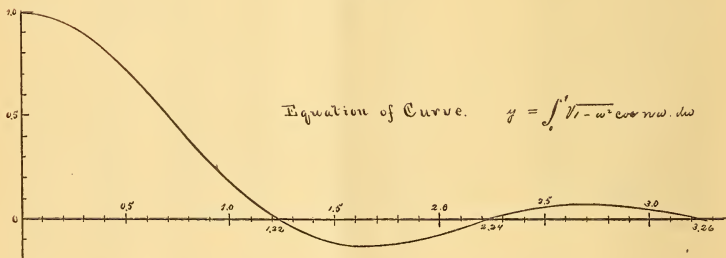
in which the integral is positive for the maxima and negative for the minima.

Putting

$$\int_0^1 \sqrt{1 - w^2} \cos nw \, dw = A, \text{ we have for } V,$$

$$V = A. \quad (8)$$

Fig. 3.



Tables for A are given in Airy's "Undulatory Theory," and give the results expressed in the curve shown in fig. 3.



The values of  $\frac{\alpha}{\alpha_0}$  for which the fringes disappear are

$$1.22, 2.24, 3.26, 4.26, \&c.,$$

and the values of the successive (positive or negative) maxima are :—

$$V = +1.000$$

$$V = -0.130$$

$$V = +0.065$$

$$V = -0.040$$

Here, too, the theory is remarkably well confirmed by experiment. This is shown by Table II., in which the letters have the same meaning as before, save that  $a$  is now the diameter of the circular aperture.

TABLE II.

S.	$\lambda$ .	$a$ .	$d$ .	$b$ .	$f$ .	$a$ .	$a_1$ .	$e$ .	$o$ .
S.	.550	.701	20,800	20.15	1.22	6.85	6.94	-.09	-1
C.	.570	.200	20,340	77.71	1.22	1.85	2.02	-.17	-8
"	"	.271	"	51.95	1.22	2.76	2.73	+.03	+1
"	"	.445	"	32.50	1.22	4.41	4.50	-.09	-2
"	"	.445	"	52.45	2.24	4.52	4.50	+.02	0
"	"	.445	"	81.45	3.26	4.60	4.50	+.10	+2
"	"	.701	"	20.00	1.22	7.17	7.09	+.08	+1
"	"	.701	"	34.85	2.24	7.55	7.09	+.46	+6
"	"	.701	"	52.99	3.26	7.14	7.09	+.05	+1
"	"	1.000	"	25.65	2.24	10.20	10.12	+.08	+1
"	"	1.000	"	14.65	1.22	9.77	10.12	-.35	-4
"	"	1.000	"	27.35	2.24	9.63	10.12	-.49	-5
"	"	1.000	"	38.55	3.26	9.87	10.12	-.25	-2
"	"	1.230	"	21.08	2.24	12.47	12.44	+.03	0
"	"	1.230	"	30.45	3.26	12.58	12.44	+.14	+1
"	"	1.230	"	11.15	1.22	12.85	12.44	+.41	+3
"	"	1.230	"	21.45	2.24	12.23	12.44	-.21	-2
"	"	1.230	"	31.15	3.26	12.25	12.44	-.19	-2
"	"	1.230	"	39.95	4.26	12.49	12.44	+.05	0
"	"	1.465	"	17.42	2.24	14.92	14.82	+.10	+1
"	"	1.465	"	25.99	3.26	14.70	14.82	-.12	-1
"	"	1.690	"	15.14	2.24	17.36	17.10	+.26	+2
"	"	1.690	"	23.40	3.26	16.36	17.10	-.74	-4
R.	.623	0.445	"	35.15	1.22	4.45	4.50	-.05	-1

The curve  $V = A$  (fig. 3) shows that the maxima are considerably smaller than in the case of the slit, and, accordingly, the disappearances are not quite so sharp; but in one case it was possible to note four of them, and in this case also the average error was less than 2 per cent.

CASE III.—*Illumination not Uniform.*

On applying the preceding formulæ to observations on images of the sun's disk the angles obtained were all too small by about 10 per cent., the cause of the discrepancy being the want of uniformity of illumination.

The curve (fig. 4) represents the intensity at any point of the sun's disk as a function of its distance from the centre,

$$i = f(x^2 + y^2)^{\frac{1}{2}}.$$

The ordinates are taken from Vogel's Table\*.

Fig. 4.

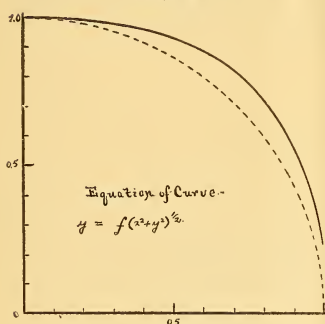
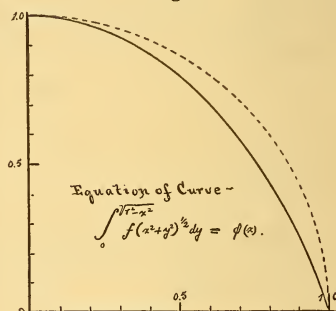


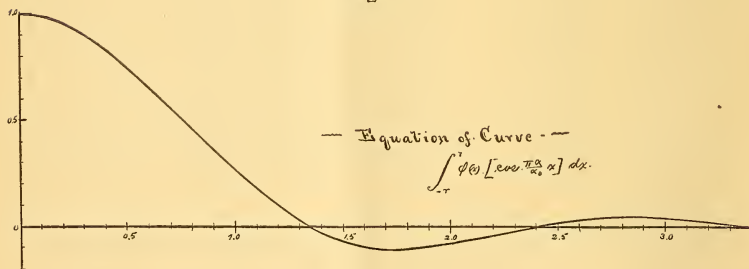
Fig. 5.



From this curve we obtain that shown in fig. 5 by integrating the expression

$$\int_0^{\sqrt{r^2 - x^2}} f(\sqrt{x^2 + y^2}) dy = \phi(x). \quad . \quad . \quad . \quad (9)$$

Fig. 6.



This value of  $\phi(x)$  substituted in (1) gives on integration

\* Young on 'The Sun.'

the value of the intensity of the maxima and minima in the form  $I=1 \pm B$ , whence finally we get for the visibility of the fringes

$$V = B. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The values of  $V$  found from equation (10) are plotted in the curve shown in fig. 6\*.

The fringes disappear at the points for which  $\frac{\alpha}{\alpha_0}$  is

$$1.33, 2.38, \&c.;$$

and the values of the successive (positive and negative) maxima are:—

$$V = +1.00$$

$$V = -0.1$$

$$V = +0.042$$

$$V = -0.028$$

On applying these results to the observations the accordance is very satisfactory, as appears from the following Table:—

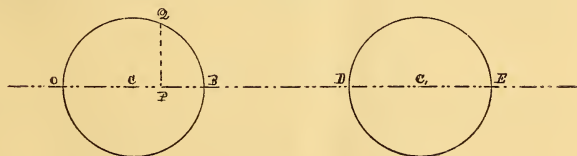
TABLE III.

S.	$\lambda$ .	$a$ .	$d$ .	$b$ .	$f$ .	$a$ .	$a_1$ .	$e$ .	$o$ .
S.	.550	.231	27,800	84.75	1.33	1'.74	1'.71	+0.03	+2
"	"	.377	"	55.25	1.33	2.72	2.79	- .07	-2
"	"	.933	"	22.65	1.33	6.66	6.90	- .24	-3
"	"	.231	21,200	66.15	1.33	2.27	2.24	+ .03	+1
"	"	.377	"	41.75	1.33	3.59	3.66	- .07	-2
"	"	.933	"	16.65	1.33	9.04	9.05	- .01	0

CASE IV.—*Double Source.*

Suppose next that there are two equal symmetrical sources of light whose centres are at  $C$  and  $C_1$  (fig. 7).

Fig. 7.



\* The curves corresponding to Cases I., II., and III. are for convenience of comparison given together in Plate I.

Let  $OC = CB = DC_1 = C_1E = r$ .

$CC_1 = 2s$ ,  $OP = x$ ,  $PQ = y$ .

Then the intensity of the interference-fringes will be

$$I = \int y \left( 1 + \cos \frac{2\pi\Delta}{\lambda} \right) dx \dots \text{as in (1)}.$$

Integrating from O to B and from D to E, we have

$$I = \int_0^{2r} y_1 \left( 1 + \cos \frac{2\pi\Delta}{\lambda} \right) dx + \int_{2s}^{2s+2r} y_2 \left( 1 + \cos \frac{2\pi\Delta}{\lambda} \right) dx; \quad (11)$$

where

$$y_1 = f(x-r) \quad \text{and} \quad y_2 = f[x - (2s+r)]$$

and

$$\Delta = \beta x - \gamma b.$$

In the first integral put  $w_1 = (x-r)$ .

$$,, \quad \text{second} \quad ,, \quad w_2 = x - (2s+r).$$

Then we obtain

$$\begin{aligned} I = & \int_{-r}^{+r} f(w_1) \left[ 1 + \cos \frac{2\pi}{\lambda} (\beta w_1 + \beta r - \gamma b) \right] dw_1 \\ & + \int_{-r}^{+r} f(w_2) \left[ 1 + \cos \frac{2\pi}{\lambda} (\beta w_2 + \beta r - \gamma b + 2\beta s) \right] dw_2. \quad (12) \end{aligned}$$

Expanding the first of these integrals we obtain :—

$$\begin{aligned} & \int_{-r}^{+r} f(w_1) dw_1 + \cos \frac{2\pi}{\lambda} (\beta r - \gamma b) \int_{-r}^{+r} f(w_1) \cos \frac{2\pi}{\lambda} \beta w_1 dw_1 \\ & - \sin \frac{2\pi}{\lambda} (\beta r - \gamma b) \int_{-r}^{+r} f(w_1) \sin \frac{2\pi}{\lambda} (\beta w_1) dw_1; \end{aligned}$$

in which the first term is half the area of the aperture, and the last term (since  $f(w_1)$  is a symmetrical function) is 0. The same is also true of the expansion of the second integral. If, then, we put

$$\int_{-r}^{+r} f(w) dw = \frac{1}{2} Q,$$

$$\int_{-r}^{+r} f(w) \cos \frac{2\pi}{\lambda} \beta w dw = \frac{1}{2} Q A,$$

equation (12) becomes

$$I = Q + \frac{1}{2}QA \cos \frac{2\pi}{\lambda} (\beta r - \gamma b) + \frac{1}{2}QA \cos \frac{2\pi}{\lambda} (\beta r - \gamma b + 2\beta s)$$

or

$$I = Q + QA \left( \cos \frac{2\pi}{\lambda} [\beta s + \beta r - \gamma b] \cos \frac{2\pi}{\lambda} \beta s \right); \quad . \quad . \quad . \quad (13)$$

whence for the visibility

$$V = \frac{I_1 - I_2}{I_1 + I_2} = A \cos \frac{2\pi}{\lambda} \beta s.$$

or finally

$$V = A \cos \pi \frac{\alpha}{\alpha_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

1st. When the sources are two equal uniformly illuminated slits of height  $2h$ ,

$$f(w) = h, \text{ and } Q = 4rh.$$

Hence

$$A = \frac{1}{r} \int_0^r \cos \frac{2\pi\beta}{\lambda} w dw = \frac{\sin \frac{2\pi}{\lambda} \beta r}{\frac{2\pi}{\lambda} \beta r} \quad . \quad . \quad . \quad . \quad (15)$$

Putting  $\frac{2\pi}{\lambda} \beta r = \pi \frac{\alpha_1}{\alpha_0}$ , and substituting for  $A$  in equation (14),

$$V = \frac{\sin \pi \frac{\alpha_1}{\alpha_0}}{\pi \frac{\alpha_1}{\alpha_0}} \cos \pi \frac{\alpha}{\alpha_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

2nd. For the case of two equal uniformly illuminated circular apertures of radius  $r$ ,

$$f(w) = \sqrt{r^2 - w^2}, \text{ and } Q = \pi r^2.$$

Hence

$$A = \frac{4}{\pi r^2} \int_0^r \sqrt{r^2 - w^2} \cos \frac{2\pi}{\lambda} \beta w dw.$$

Putting  $\frac{w}{r} = z$ , this reduces to the form already given for Airy's integral, and the expression for the visibility of the fringes is

$$V = A_1 \cos \pi \frac{\alpha}{\alpha_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

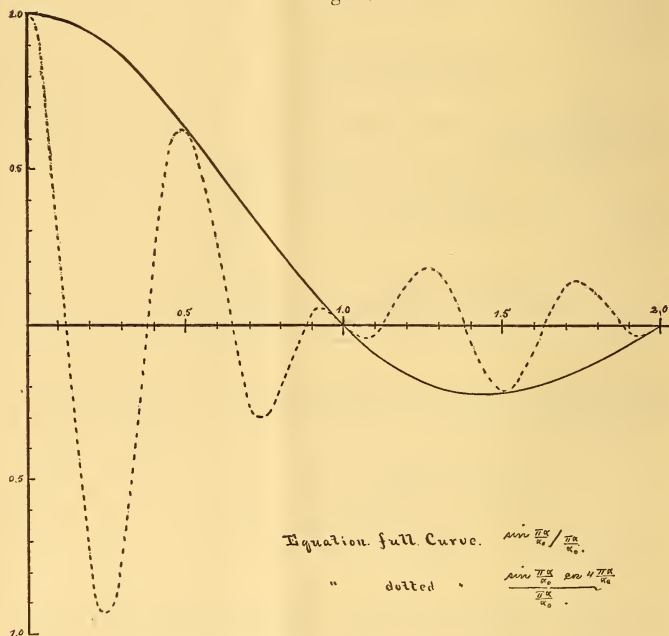


When the distance between the sources is more than five or six times the width, the periodicity of the second term alone is of importance, the term  $A_1$  representing the amplitude of its variation.

The fringes vanish whenever  $\alpha = \frac{2n-1}{2} \alpha_0$ .

The general form of the visibility curve is given in fig. 8.

Fig. 8.



If, on the other hand, the two sources coincide the expression reduces to that previously found for a single circular source.

Table IV. exhibits the results of observations made upon two circular apertures whose diameter is given under the column  $a_1$ , and whose distance between centres under  $\alpha$ . It will be seen that the distance varies from eleven to five diameters, and that the average error of one observation (usually a single setting) is only  $1\frac{1}{2}$  per cent.

TABLE IV.

S.	$\lambda$ .	$a_1$ .	$a$ .	$b$ .	$f$ .	$\alpha$ .	$\alpha_1$ .	$e$ .	$o$ .
C.	·560	·060	·693	25·1	1·50	6 <sup>''</sup> 90	6 <sup>''</sup> 80	+0 <sup>''</sup> 10	+2
"	"	·060	·693	25·3	1·50	6·85	6·80	+ ·05	+1
"	"	·060	·693	25·7	1·50	6·75	6·80	- ·05	-1
"	"	·060	·693	25·7	1·50	6·75	6·80	- ·05	-1
"	"	·060	·666	26·6	1·50	6·53	6·58	- ·05	-1
"	"	·060	·666	26·7	1·50	6·50	6·58	- ·08	-1
"	"	·060	·519	34·4	1·50	5·00	4·99	+ ·01	0
"	"	·060	·465	12·9	0·50	4·48	4·56	- ·08	-2
"	"	·060	·315	18·8	0·50	3·07	3·09	- ·02	-1
R.	·623	·060	·693	27·8	1·50	6·93	6·80	+ ·13	+2
"	"	·060	·693	27·9	1·50	6·90	6·80	+ ·10	+2
"	"	·060	·666	29·5	1·50	6·53	6·58	- ·05	-1
"	"	·060	·666	29·4	1·50	6·57	6·58	- ·01	0
S.	·550	·117	·526	10·75	0·50	5·27	5·18	+ ·09	+2
"	"	·117	·526	11·65	0·50	4·86	5·03	- ·17	-3
C.	·560	·117	·526	10·85	0·50	5·32	5·32	·00	0
"	"	·117	·526	33·24	1·50	5·21	5·32	- ·11	-2
"	"	·117	·526	55·80	2·50	5·18	5·32	- ·14	-3
"	"	·117	·526	80·15	3·50	5·08	5·32	- ·24	-4
R.	·623	·117	·526	36·02	1·50	5·34	5·32	+ ·02	0
"	"	·117	·526	60·20	2·50	5·32	5·32	·00	0
"	"	·117	·526	85·70	3·50	5·24	5·32	- ·08	-2

When the distance between centres is two diameters or less, it is found that the results obtained are much less accurate, being usually too large by about 4 per cent., as shown in Table V.

TABLE V.

S.	.	$a_1$ .	$a$ .	$b$ .	$f$ .	$\alpha$ .	$\alpha_1$ .	$e$ .	$o$ .
C.	·560	·184	·396	42·8	1·50	3 <sup>''</sup> 99	3 <sup>''</sup> 89	+0 <sup>''</sup> 10	+3
"	"	·184	·372	14·8	0·50	3·81	3·66	+ ·15	+4
"	"	·184	·363	16·9	0·50	3·40	3·54	- ·14	-4
"	"	·184	·332	16·6	0·50	3·41	3·22	+ ·19	+6
"	"	·184	·297	19·6	0·50	2·90	2·88	+ ·02	+1
"	"	·184	·266	21·3	0·50	2·71	2·60	+ ·11	+4
"	"	·184	·266	20·4	0·50	2·83	2·62	+ ·21	+8
"	"	·184	·251	23·3	0·50	2·48	2·47	+ ·01	0
"	"	·184	·251	22·8	0·50	2·51	2·47	+ ·04	+2
"	"	·184	·227	24·9	0·50	2·32	2·23	+ ·09	+4
"	"	·184	·219	25·6	0·50	2·22	2·13	+ ·09	+4
S.	·550	·060	·107	56·2	0·50	1·01	1·06	- ·05	-5
"	"	·060	·107	56·8	0·50	1·02	1·04	- ·02	-2
C.	·560	·060	·107	54·0	0·50	1·07	1·08	- ·01	-1
"	"	·060	·107	53·2	0·50	1·09	1·05	+ ·04	+4
"	"	·060	·107	53·5	0·50	1·08	1·05	+ ·03	+3
R.	·623	·060	·107	57·2	0·50	1·13	1·05	+ ·08	+8
"	"	·060	·107	58·7	0·50	1·10	1·05	+ ·05	+5
C.	·560	·060	·075	70·8	0·50	0·79	0·74	+ ·05	+7
"	"	·060	·075	72·0	0·50	0·77	0·74	+ ·03	+4

The measurement of the angular magnitude of sources of light too small to be resolved by the telescope may also be effected with a considerable degree of accuracy by providing the telescope objective with a slit or diaphragm which can be varied in width or size, and measuring the distance between the centres of the diffraction-fringes by means of a micrometer eyepiece. In case the slit is used (as found most convenient in practice), the expression for the intensity of illumination at a distance  $\gamma$  from the centre of the central bright band will be

$$I = \int f(\phi) \frac{\sin^2 \frac{\pi}{\alpha_0} (\gamma - \phi)}{\left[ \frac{\pi}{\alpha_0} (\gamma - \phi) \right]^2} d\phi, \quad \dots \quad (18)$$

where  $f(\phi) = y$  is the ordinate of source of light (of uniform intensity) at the distance  $\phi$  from the axis. If the source has a width  $\alpha$ , the limits of the integral are  $\frac{\alpha}{2}$  and  $-\frac{\alpha}{2}$ .

1st. In case the source is a uniformly illuminated slit,  $f(\phi) = \text{const.}$ , and the expression for  $I$  becomes

$$I = C \int_{-\alpha/2}^{+\alpha/2} \frac{\sin^2 \frac{\pi}{\alpha_0} (\gamma - \phi)}{\left[ \frac{\pi}{\alpha_0} (\gamma - \phi) \right]^2} d\phi,$$

or, substituting  $\frac{\pi}{\alpha_0} (\gamma - \phi) = x$ ,

$$I = C_1 \int_{\pi/\alpha_0 (\gamma - \alpha/2)}^{\pi/\alpha_0 (\gamma + \alpha/2)} \frac{\sin^2 x}{x^2} dx. \quad \dots \quad (19)$$

This integral cannot be found directly, but we may obtain the values of  $\gamma$  for which  $I$  is a maximum or a minimum by differentiating (19) with respect to  $\gamma$ .

This gives

$$\frac{dI}{d\gamma} = \text{Const.} \left[ \frac{\sin^2 \frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right)}{\left[ \frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right) \right]^2} - \frac{\sin^2 \frac{\pi}{\alpha_0} \left( \gamma - \frac{\alpha}{2} \right)}{\left[ \frac{\pi}{\alpha_0} \left( \gamma - \frac{\alpha}{2} \right) \right]^2} \right] = 0.$$

Hence

$$\frac{\sin \frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right)}{\frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right)} = \pm \frac{\sin \frac{\pi}{\alpha_0} \left( \gamma - \frac{\alpha}{2} \right)}{\frac{\pi}{\alpha_0} \left( \gamma - \frac{\alpha}{2} \right)}. \quad \dots \quad (20)$$

Writing this in the form

$$\frac{\sin \frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right)}{\frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right)} = \pm \frac{\sin \left[ \left( \frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right) - \pi \frac{\alpha}{\alpha_0} \right) \right]}{\frac{\pi}{\alpha_0} \left( \gamma - \frac{\alpha}{2} \right)},$$

we see that when  $\frac{\alpha}{\alpha_0} < 1$  the two sides of the equation have opposite signs, because

$$\frac{\pi}{\alpha_0} \left( \gamma - \frac{\alpha}{2} \right) < \pi < \frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right);$$

and we have

$$\frac{\sin \frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right)}{\frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right)} = - \frac{\sin \frac{\pi}{\alpha_0} \left( \gamma - \frac{\alpha}{2} \right)}{\frac{\pi}{\alpha_0} \left( \gamma - \frac{\alpha}{2} \right)}. \quad \dots \quad (21)$$

Expanding and solving for  $\gamma$  we find

$$\gamma \tan \frac{\pi \gamma}{\alpha_0} = \frac{\alpha}{2} \tan \frac{\pi \alpha}{2 \alpha_0}, \quad \dots \quad (22)$$

which gives the condition for a minimum when

$$0 < \frac{\alpha}{\alpha_0} < 1, \quad 2 < \frac{\alpha}{\alpha_0} < 3, \dots 2m < \frac{\alpha}{\alpha_0} < 2m + 1 \dots$$

When  $1 < \frac{\alpha}{\alpha_0} < 2$ , the sign of the two sides is the same, and we have

$$\frac{\sin \frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right)}{\frac{\pi}{\alpha_0} \left( \gamma + \frac{\alpha}{2} \right)} = \frac{\sin \frac{\pi}{\alpha_0} \left( \gamma - \frac{\alpha}{2} \right)}{\frac{\pi}{\alpha_0} \left( \gamma - \frac{\alpha}{2} \right)};$$

and solving for  $\gamma$  as before we find

$$\frac{\tan \frac{\pi \gamma}{\alpha_0}}{\gamma} = \frac{\tan \frac{\pi \alpha}{2 \alpha_0}}{\frac{\alpha}{2}}, \quad \dots \quad (23)$$

which gives the conditions for a minimum for

$$1 < \frac{\alpha}{\alpha_0} < 2, \quad 3 < \frac{\alpha}{\alpha_0} < 4 \dots 2m - 1 < \frac{\alpha}{\alpha_0} < 2m.$$

Finally, when  $\frac{\alpha}{\alpha_0} = 1, 3, 5, \dots 2m-1,$

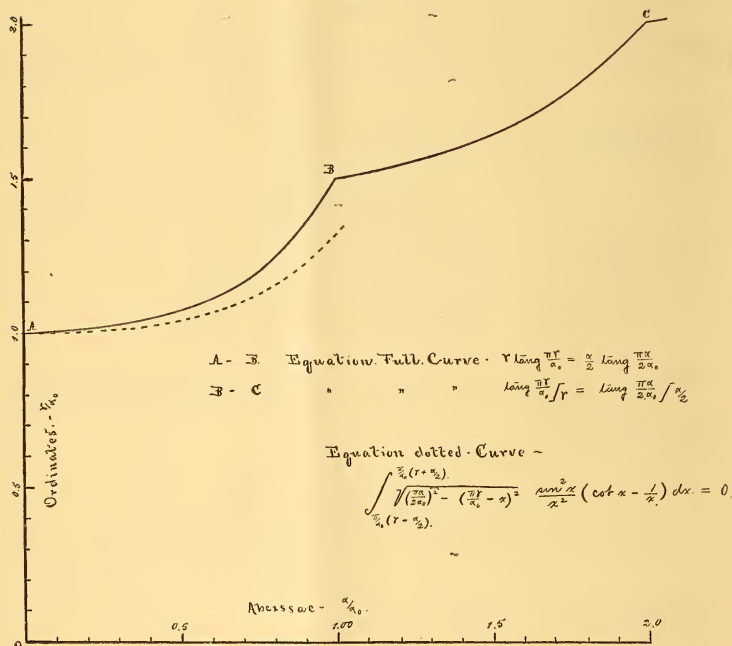
$$\tan \frac{\pi \alpha}{2 \alpha_0} = \pm \infty, \quad \tan \frac{\pi \gamma}{\alpha_0} = \infty, \quad \text{and} \quad \frac{\gamma}{\alpha_0} = \frac{3}{2}, \frac{5}{2} \dots \frac{2m-1}{2};$$

and when  $\frac{\alpha}{\alpha_0} = 2, 4, 6, \dots 2m,$

$$\tan \frac{\pi \alpha}{2 \alpha_0} = 0, \quad \tan \frac{\pi \gamma}{\alpha_0} = 0, \quad \text{and} \quad \frac{\gamma}{\alpha_0} = 1, 2, 3, \dots m.$$

The curve obtained is shown in fig. 9.

Fig. 9.



2nd. When the opening observed is circular, the expression for the intensity becomes

$$I = \int_{-a/2}^{+a/2} \sqrt{\left(\frac{\alpha}{2}\right)^2 - \phi^2} \frac{\sin^2 \frac{\pi}{\alpha_0} (\gamma - \phi)}{\left[\frac{\pi}{\alpha_0} (\gamma - \phi)\right]^2} d\phi. \quad (24)$$



Differentiating with respect to  $\gamma$ ,

$$\frac{dI}{d\gamma} = C \int_{-a/2}^{+a/2} \sqrt{\left(\frac{\alpha}{2}\right)^2 - \phi^2} \frac{\sin^2 \frac{\pi}{\alpha_0} (\gamma - \phi)}{\left[\frac{\pi}{\alpha_0} (\gamma - \phi)\right]^2} \left( \cot \frac{\pi}{\alpha_0} (\gamma - \phi) - \frac{1}{\frac{\pi}{\alpha_0} (\gamma - \phi)} \right) d\phi.$$

Substituting  $x = \frac{\pi}{\alpha_0} (\gamma - \phi)$ , we have finally

$$\frac{dI}{d\gamma} = \int_{\pi/\alpha_0 (\gamma - a/2)}^{\pi/\alpha_0 (\gamma + a/2)} \sqrt{\left(\frac{\pi\alpha}{2\alpha_0}\right)^2 - \left(\frac{\pi}{\alpha_0} (\gamma - x)\right)^2} \frac{\sin^2 x}{x^2} \left( \cot x - \frac{1}{x} \right) dx = 0. \quad (25)$$

Integrating this for different values of  $\frac{\alpha}{\alpha_0}$  and  $\frac{\gamma}{\alpha_0}$ , we obtain the curve shown in fig. 9, which can be expressed very closely indeed for  $0 < \frac{\alpha}{\alpha_0} < 1$  by the simple formula

$$\left(\frac{\gamma}{\alpha_0}\right)_c = \frac{1}{\pi} \left( \pi + 2 \left[ \left(\frac{\gamma}{\alpha_0}\right)_s - 1 \right] \right), \quad \dots \quad (26)$$

where

$\left(\frac{\gamma}{\alpha_0}\right)_c$  is the ordinate to the dotted curve,

$\left(\frac{\gamma}{\alpha_0}\right)_s$  „ „ full curve for any given value of  $\frac{\alpha}{\alpha_0}$ .

The results of some observations by this method on the size of a slit and of circular openings of varying diameters, gave, in the case of the slit, errors varying from one to fifteen per cent., the average error being about eight per cent.; and in the case of circular openings errors of from three to twenty-five per cent., the average error being about twelve per cent. The accuracy of both this and the preceding method would undoubtedly be increased by taking the mean of a number of observations.

Of the two methods, the first is by far the most accurate; but even the second gives results which are from eight to ten times as accurate as those which can be obtained by using the telescope directly.

The apparatus by which the observations in the preceding tables were made is shown in Plate II. fig. 1. The objective of the telescope (a very fine four-inch glass, for the use of which I am indebted to the Worcester Polytechnic Institute) was fitted with a pair of adjustable slits, whose distance apart could be regulated by a right-and-left-hand screw geared to

a rod (as shown in the Plate), so as to be controlled by the observer, and the distance between the slits was read off by a small telescope beside the eyepiece of the large one.

This simple and effective device has but one disadvantage. When the angle to be measured is so small as to be just beyond the power of the telescope, it is necessary, in order to observe the first disappearance of the fringes, that the slits should be separated to the full width of the aperture. Under these circumstances the two pencils meet at a very large angle, usually several degrees, and the corresponding distance between the interference-fringes is but a few thousandths of a millimetre, and in order to be visible as such must be highly magnified and accordingly very faint.

This difficulty may be entirely overcome by using instead of the telescope one of the forms of refractometers shown in figs. 10 and 11.

Fig. 10.

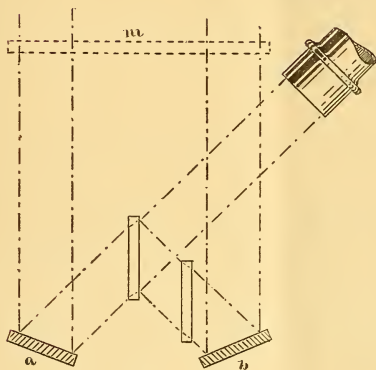
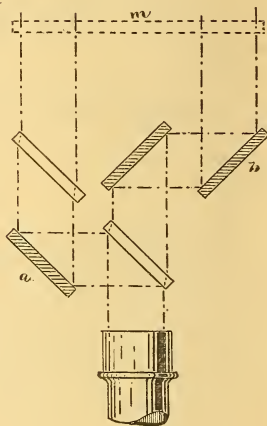


Fig. 11.



The first of these will be recognized as one of the forms already described\*.

The apparatus being adjusted so that interference-fringes are visible, the telescope (a comparatively small one) is adjusted until the two images of its cross-hairs in the mirror *m* coincide with the cross-hairs themselves.

When this is the case, it is clear that when the whole apparatus is pointed at a star (the mirror *m* being now

\* "Measurement by Light-Waves," by A. A. Michelson. American Journal of Science, xxxix. Feb. 1890.

removed) the two pencils will meet in the focus in the same phase, and the breadth of the interference-bands may be regulated by slight alterations of the pieces of the refractometer, *without in any way affecting the intensity of the light*. But beside this incidental advantage is the much more important one, that it is possible, by simply increasing the distance between the mirrors  $a$   $b$ , to enormously increase the effective aperture of the telescope.

Plate II. fig. 2 shows, on a scale of one-fourth actual size, a plan of a proposed instrument for effecting this object. The optical arrangement adopted is that shown in fig. 11.

This form, notwithstanding the greater number of glasses, has some decided advantages over that of fig. 10. In addition to greater facility and ease of adjustment, it has the important advantage of preserving constant the width of the fringes notwithstanding the angular displacement of the whole apparatus\*.

The instrument figured in Plate II. would be used as follows :—The mirrors  $a$  and  $b$  being moved as close together as possible, and the auxiliary mirror  $m$  being in place, the mirror  $a$  is adjusted by the screws SS till the two images of a source of light L as viewed in the telescope T appear to coincide. Next the mirror  $m$  is adjusted in azimuth by the screw K till the paths of the two pencils are equal. (As before mentioned, this angular motion does not affect the mutual inclination of the pencils, and therefore the breadth of the fringes is unaltered.) The telescope T is then adjusted till the two images of its illuminated cross-hairs coincide with the cross-hairs themselves, and is then clamped.

The mirror  $m$  is now detached and the instrument is ready for use.

Suppose the object to be measured is a minor planet or satellite. The whole instrument, which would have to be placed on an equatorial mounting, is pointed so that the image of the body is exactly on the cross-hairs. The interference-fringes will at once appear if the adjustment has been properly made.

Next, by means of a right-and-left-hand screw, the mirrors  $a$  and  $b$  are separated *until the fringes disappear*. If this disappearance is due to an accident, it will immediately become evident by observing any star in the neighbourhood. If the examination of the star shows the fringes while they

\* The same advantage obtains in the use of the instrument as a refractometer for measuring extremely small variations of the angular position of the mirror or mirrors  $m$ .

are absent in the case of the planet, it may be considered certain that the cause of the disappearance in the latter case is its appreciable disk.

The angular diameter of the latter can be found (on the supposition of uniform illumination) by the formula

$$\alpha = 1.22 \frac{\lambda}{b},$$

where  $\lambda$  is the wave-length of the light, and  $b$  the distance between the centres of the mirrors  $a$  and  $b$  \*.

From what has gone before, it will be inferred that the chief object of the method proposed is the measurement of the apparent size of minute telescopic objects, such as planetoids, satellites, and possibly star disks, and also double stars too close to be resolved in the most powerful telescope. But it is clear that interference methods may also be employed for the measurement of star-places.

Thus, in observations for right ascension, the slits would be placed parallel to the meridian, and the instant of passage of the central white fringe across the spider-lines noted; and in observations for declination, the slits would be horizontal, the cross-hair being brought to coincide with the centre of the white fringe.

The increase in accuracy to be expected from this method would, however, be limited by the imperfections of our present means of measuring time and angles; still, it would appear that by its use a one-inch glass may be made to do the work now required of a ten-inch.

### *Conclusion.*

(1) Interference phenomena produced under appropriate conditions from light emanating from a source of finite magnitude become indistinct as the size increases, finally vanishing when the angle subtended by the source is equal to the smallest angle which an equivalent telescope can resolve, multiplied by a constant factor depending on the shape and distribution of light in the source and on the order of the disappearance.

(2) The vanishing of the fringes can ordinarily be determined with such accuracy that single readings give results from fifty to one hundred times as accurate as can be obtained with a telescope of equal aperture.

\* Better, the distance between the centres of the apertures in front of these mirrors.



(3) The principal applications of the methods herein described are the measurement of the apparent magnitudes of very small or very distant sources of light such as planetoids and satellites (though larger bodies are not excluded), and of the angular distances between very close double stars.

(4) On account of the narrowness of the interference-fringes when a very minute body is under examination, the method of obtaining these fringes (by a pair of adjustable slits in front of the objective of a telescope) is open to objection, from which the refractometer method is entirely free. Further, this last modification makes it possible to extend the effective aperture of the equivalent telescope without limit. Thus, while it would be manifestly impracticable to construct objectives much larger than those at present in use, there is nothing to prevent increasing the distance between the two mirrors of the refractometer to even ten times this size. If among the nearer fixed stars there is any as large as our sun, it would subtend an angle of about one hundredth of a second of arc ; and the corresponding distance required to observe this small angle is ten metres, a distance which, while utterly out of question as regards the diameter of a telescope-objective, is still perfectly feasible with a refractometer. There is, however, no inherent improbability of stars presenting a much larger angle than this; and the possibility of gaining some positive knowledge of the real size of these distant luminaries would more than repay the time, care, and patience which it would be necessary to bestow on such a work.

In concluding, I wish to take this opportunity of expressing my appreciation of the disinterested manner in which my efforts have been so ably and zealously seconded by Mr. F. L. O. Wadsworth, Fellow of Clark University.

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## II. *On the Electrification of the Effluvia from Chemical or from Voltaic Reactions.* By J. BROWN \*.

1. FROM the series of very interesting experiments published in the January number of this Journal, p. 56, Mr. J. Enright concludes that nascent hydrogen and other gases become positively electrified by *contact* with acids, and negatively by *contact* with salts in solution. The line of experiment struck out by Mr. Enright will, I think, afford valuable aid in investigating electrochemical hypotheses ; but it would

\* Communicated by the Secretaries of the Electrolysis Committee of the British Association.

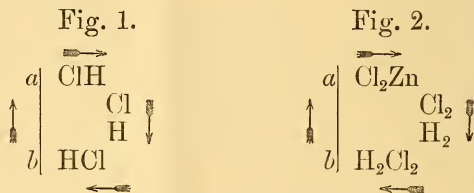


seem improbable that the mere contact of any two substances, without anything further, could perform the work necessary to produce a difference of potential of 42 volts, as found by Mr. Enright, or indeed any considerable fraction of a volt. The experimental evidence appears to be entirely against such a supposition, and I felt that some other explanation would probably be found to be the true one, more especially on considering Mr. Enright's observation that the passage of de-electrified gas through an acid did *not* electrify it, and his statement on page 63 that "whatever tended to electrically connect the charged liquid with the oppositely charged escaping gas, also tended to lessen the charges on both." If "contact" produced the charges, it is difficult to see how further "contact" could lessen them.

2. On carefully reading Mr. Enright's paper, and before making any experiments of my own, the following hypothesis suggested itself to me from consideration of the typical experiment, viz. zinc dissolving in hydrochloric acid, in which, as Mr. Enright shows, the issuing gaseous matter is positively electrified and the acid solution negatively electrified, until finally, owing to the formation of a certain amount of zinc chloride, a reversal of the electrifications of both gas and liquid occurs.

*I use the word "gas" throughout the first part of this paper for convenience. As will appear further on, it is not certain what the nature of the electrified matter is.*

3. Ordinary zinc is always an alloy of zinc and other metals—iron, arsenic, &c.



Suppose *a b*, fig. 1, to represent a portion of the surface of such zinc, where *a* is pure zinc in contact with the foreign metal at *b*, the whole being immersed in hydrochloric acid. The solution of the metal takes place by the formation of little local voltaic circuits, the chlorine combining with the pure zinc at *a*, while the hydrogen is evolved at *b*, and the local current flows with the arrows.

There may of course be a larger number of  $\text{HCl}$  molecules involved than in the circuit shown, in considering which it

seems best to adopt an electrolytic hypothesis similar to that of Grotthus.

A film of zinc chloride is now by the action interposed between the zinc at *a* and the hydrochloric acid, as represented in fig. 2, where (since zinc chloride forms at *a* only, and not at *b*) we have a little double fluid cell, and the current passes successively through zinc-chloride and hydrochloric-acid solutions, instead of through the latter only as in fig. 1.

The only difference in the two actions seems to be, that in fig. 2 certain atoms of zinc take the place of hydrogen in fig. 1, and are intermediate in the decomposition of the acid by the metallic zinc; but there seems at first sight no *à priori* reason why this should cause the negative electrification of the evolved gas.

It may be pointed out, however, that if we think with Faraday that, while the source of the energy of the current in the cell is the potential chemical energy of the active ions, the production of that energy in the form of current instead of heat is closely related to the *decomposition* of the electrolyte, we may presume that the method of the decomposition will probably exercise considerable influence on the electric phenomena. It seemed not improbable that in the case under consideration the reversal of potential in the gas was due to the change in the electrolytic action, as described above.

4. I therefore thought it worth while to test the above hypothesis, and after repeating Mr. Enright's experiment with zinc dissolving in hydrochloric acid, and observing the very remarkable electrification and reversal of sign which he describes, I determined to make trial of a cell with the *b* part of the metallic surface in fig. 2 represented by platinum.

A piece of platinum foil was attached to a small piece of sheet zinc by bending the zinc over it and clipping it tight, and the couple so arranged was placed in a beaker, the zinc lying flat on the bottom, the platinum standing upright. The zinc was covered with strong zinc-chloride solution, on which was carefully placed hydrochloric-acid solution of constant boiling-point, in contact with the platinum only. Gas was given off rather slowly from the platinum. The cell was now placed on an insulated metal plate connected with an electrometer, giving a deflexion of 60 divisions on each side of zero for one Daniell cell. The spot moved very slowly to 10, and showed the cell to be positive. I repeated the experiment, using acid diluted with an equal measure of water, and the spot went to 35, cell positive. In both cases

there was a slight haze of minute bubbles rising from the zinc, which I thought might affect the result.

5. To avoid this and to get a freer evolution of gas from the platinum I platinized it, and clipped it to the end of a strip of zinc 12 centimetres long by  $1\frac{1}{2}$  wide which was bent into a flat spiral and amalgamated. Strong zinc-chloride solution contained in a small beaker covered the zinc to about 3 millimetres above its upper edge, and on this strong hydrochloric acid was carefully poured with a specially constructed pipette, so as to avoid as much as possible any mixture of the two liquids. There was a moderate evolution of gas from the platinum, none visible from the zinc. On connecting the cell as before with the electrometer, the spot went to 350 in four minutes, indicating the cell to be positive, and, by implication, the issuing gas or vapour negative.

6. There was not in any of the trials the slightest indication of any positive electrification of the issuing gas, though it was in two of them evolved in immediate contact with strong hydrochloric acid.

7. The same experiment was now repeated, using strong zinc-sulphate solution surrounding the amalgamated zinc and a 5-per-cent. solution of sulphuric acid in contact with the platinum. Again the cell was positive from the first and the spot went to 350 and off the scale in 9 minutes.

8. When the zinc-platinum couple was immersed in acid only, the sign of electrification of the cell varied according to circumstances. It was positive (*i. e.* the issuing gas negative) for both strong and dilute hydrochloric acid, except in two cases with dilute acid when the zinc had been standing so as to oxidize in the air, and evolved gas from itself. With sulphuric acid the cell became quickly positive with a 5-per-cent. solution, but slowly negative with a 10-per-cent. solution.

Although the results in this form of experiment are not inconsistent with the hypothesis of § 3, the conditions seem not sufficiently determinate or distinct to warrant any certain conclusion beyond the obvious fact that here also negatively electrified gas can be evolved from acid solutions without any admixture of salt.

9. It was felt, however, that the employment of a zinc-platinum couple as an expression of the conditions stated in § 3 was perhaps open to objection, and an endeavour was made to get nearer the supposed conditions. A strip of zinc was cleaned, bent into a spiral, and placed with its lower edge in zinc-chloride solution on which was poured hydrochloric-acid solution. This cell, however, became negative and

subsequently positive, as in Mr. Enright's experiment. The conditions here also were not sufficiently distinct.

A strip of zinc 10 centim. long by about 1 wide had a gutta-percha-covered copper wire soldered to it and the joint protected by a covering of gutta-percha. It was then bent into a spiral to lie on the bottom of the small beaker, the wire rising vertically from it. It was cleaned but not amalgamated, and was covered to a depth of  $1\frac{1}{2}$  centim. with strong zinc-chloride solution. A bent copper sheet was then clamped to the wire with its lower edge about 1 centim. above the zinc chloride, and a solution of hydrochloric acid, containing 20 per cent. strong acid, was carefully poured in until it rose 2 or 3 millim. on the copper. Gas was sluggishly evolved from the copper, and the deflexion altered about 3 divisions in 12 minutes, apparently indicating a feeble negative electrification of the cell. In a second experiment, using a 5-per-cent. acid solution, the cell seemed feebly positive, the index moving 10 divisions in half an hour. But the results of both trials are so small as to be inconsiderable.

10. The copper was now removed and replaced in a new experiment by a piece of zinc cut from the same sheet as that already in the cell, but not cleaned, in order that it might be less active towards the liquid and represent *b* in fig. 2.

Its lower edge was about 3 centim. above the zinc-chloride solution, and was immersed to a depth of 5 millim. in a mixture of 1 part strong hydrochloric acid with 4 of water. Gas was sluggishly evolved from the upper zinc and the spot moved in  $7\frac{1}{2}$  minutes to 35, cell positive. It then returned and the cell became negative, 110 divisions, when the experiment was stopped.

11. The experiment was repeated with a 10-per-cent. acid solution, with the interesting results given in tabular form below, where the first column indicates the number of minutes which elapsed after immersion of the upper zinc in the acid solution, and the second the potential of the cell, positive or negative, in scale-divisions as indicated by the electrometer. No gas was evolved from the lower zinc.

5	+18.	Gas sluggishly evolved from upper zinc.
11	+75.	Striæ of $\text{ZnCl}_2$ solution streaming down from upper zinc. Rather brisker gas-evolution.
15	+101.	
16	+	Positive electrification reaches limit and begins to fall. Probably local action at upper zinc begins to predominate and the Enright effect supervenes.



16½	+85.	
18	+13.	Gas now fizzing off well from local action at upper zinc.
22	-22.	Cell has changed sign of electrification.
25	-62.	Limit of negative deflexion. Action again reverses from effect of locally formed $\text{ZnCl}_2$ on upper zinc combined with that in contact with lower zinc.
26	-50.	
27½	0.	Cell again changes sign of electrification.
28	+43.	
30	+193.	
31	+290.	

Whether these conditions be considered a sufficiently near approximation to those involved in the hypothesis of § 3 or no, it is at all events improbable that the electrification of the gas is due to any effect of "contact" in its nascent state with either solids or liquids. Its electrification is rather connected, in an as yet somewhat obscure but interesting way, with the particular molecular arrangement in the voltaic action by which it is evolved.

12. Some experiments were now made in the hope of deciding whether it be the gas itself that is electrified, or if the charge be on something like spray carried up with the gas. The effluvium experimented on was that from zinc dissolving in hydrochloric acid, which, as is well known, contains much foggy matter. This may be of the nature of fine spray, but it comes up with the gas in the bubbles as they rise through the liquid, and is probably formed at, or nearly at, the same time and place as the gas itself. It is distinct from the larger droplets thrown off from the free surface of the liquid by the effervescence. There was some doubt whether it should be called spray or fog. The latter word has been decided on as best describing its appearance without reference to its origin or actual constitution.

13. A beaker was fitted with a paper hood so as to deflect the issuing gas and direct it upon the jets of an insulated water-dropping funnel, whose drops fell into a separate insulated vessel connected with the electrometer. Now, if the charge were on spray-drops which would adhere to the funnel and so communicate their positive charge to it, the drops falling from it would carry down some of this charge to the receiver and the electrometer would accordingly be affected. The experiment was repeated, with modifications, a number of times, but the results were not uniform, and were apparently complicated by imperfect insulation of the funnel (which was supported on a paraffin bar) permitting negative electricity



to be attracted to the jets by the positively electrified efflu-  
vium\*.

14. Various other forms of experiment all indicated that the efflu-  
vium was highly electrified but did not readily part with  
its charge to bodies immersed in it. Of these the following is  
typical. A large beaker was suspended by silk threads mouth  
downwards, so that it could be filled by gaseous displacement  
with the efflu-  
vium from zinc dissolving in a beaker of hydro-  
chloric acid. An insulating stand, on Mascart's principle,  
was made by cementing with paraffin a glass rod upright on  
a flat-bottomed flask and drying the glass surfaces by strong  
sulphuric acid placed on the paraffin. On the top of the rod  
could be placed either a brass ball 4 centim. in diameter,  
an inverted glass flask about 6 centim. in diameter with  
moistened surface, or a smooth-skinned apple a little smaller  
than the flask. Each of these could be immersed in the freshly  
generated gas for a given time in order to receive any charge  
communicated by contact with the electrified matter, or else  
caused to take a charge inductively by a momentary earth  
connexion while so immersed. They were each then carried  
to the electrometer, and when put in contact with it gave the  
following deflexions:—

Apple immersed in the efflu- vium for 2 minutes.	+ 230.
"                  " $1\frac{1}{2}$ "	+ 180.
"                  and momentarily put to earth. About	— 550.
Wet flask immersed for $1\frac{1}{2}$ minutes.	+ off scale.
Brass ball                  " $1\frac{1}{2}$ "	+ 160.
Brass ball immersed and momentarily put to earth.	— 400.
"                  "                  "                  "	— 45.

In the last experiment five minutes were allowed to elapse  
after filling the large beaker, when the greater part of the  
fog had disappeared. In the others the amount of charge  
was doubtless influenced by the greater or less volume of  
electrified matter that happened to be present.

15. In order to test the electrification of the hydrogen itself  
immediately after its generation and with the fog removed,  
drying by calcium chloride or other substances was suggested.

A small flask was fitted with a chloride-of-calcium tube 1.3  
centim. wide by about 10 centim. long, filled with the chloride  
in the usual granulated form and kept in place by a cotton-  
wool plug at each end. Zinc and hydrochloric acid were  
placed in the flask, and a water-dropping funnel connected

\* The electrification of the proof-plane used by Mr. Enright, as  
described on p. 65 of his paper, was perhaps due to the same cause—  
imperfect insulation allowing leakage.

with the electrometer was employed to test the potential of the gas, after it had passed through the drying-tube, which was bent at the neck to an inclined position, and provided with a paper hood to direct the gas upon the funnel-jets. In the first trial no fog was observed to issue from the tube, and the index moved only about +10 or +12 divisions. In a second trial some fog issued, and the deflexion was about +20, afterwards falling to about +10 while the gas was still forming but no fog visible.

The experiment was repeated with the calcium chloride replaced by particles, of about the same size, of fine clean gravel. Very little fog appeared, and deflexion was +60 to +200.

In a third modification of the experiment with the drying-tube full of cotton-wool there was a slight issue of fog at first with a deflexion of +50; afterwards less fog and no readable deflexion.

16. The results of these experiments point towards the conclusion that the electric charge is on the fog particles. But it is to be remembered that if it be on the hydrogen (supposing a gas can be electrified, which appears to be doubtful\*) the gas particles might themselves become de-electrified by the processes used to remove the fog, or part with their charges by contact with conductors, or, indeed, in this way electrify the fog particles themselves.

The question really is, which was originally electrified—gas or fog? And in considering this it is to be noted that the fog here dealt with is, as explained in § 12, probably formed at the source of evolution of the gas itself, and therefore its electrification (if it be electrified) may be connected with the kind of chemical or voltaic conditions under which the gas is produced.

17. As evidence bearing on this latter point, it was suggested to me to try if any electrification would occur during the evolution of gas without chemical change from an effervescing liquid such as soda-water. The contents of a freshly-opened bottle were quickly poured into an insulated beaker connected with the electrometer. The effervescence produced no sensible deflexion. If, however, a little dilute alcohol was first placed in the beaker there was a slight positive electrification.

18. Among a number of miscellaneous experiments made on the subject in general, it may be noted that barium carbonate thrown into dilute sulphuric acid causes strong electrification, while in dilute hydrochloric acid it produces a much weaker

\* See Nahrwold, "Ueber Luftelectricität," *Wied. Ann.* xxxi. p. 448.

effect; the liquid is negative in both cases. The human breath, although containing visible fog as well as gas resulting from chemical action in the lungs, does not appear to be sensibly charged.

19. From considerations connected with the first series of experiments in this paper, as described in § 3 to § 11, it was thought worth while to try whether there was any similar electrification of a liquid from which gas was evolved by the current from a separate battery as in the voltameter, and some experiments were made with this object.

The battery and decomposing-cell were arranged on an insulating stand and connected to the electrometer. Sometimes the mixed gases were evolved from platinized platinum electrodes in dilute acid; sometimes one or the other gas was absorbed by suitable arrangements. I was, however, unable to arrive at any general law governing either the sign of the electrification or its rate of increase. The latter varied from one division per minute to ten or even twenty times as much in the same time. In a majority of cases the evolution of the mixed gases electrified the cell negatively, and where either oxygen or hydrogen was evolved alone by the use of a double fluid arrangement the cell became positive; but there were exceptions to both rules. The question as to the cause of this electrification is very interesting, and I hope it will not remain long unanswered.

20. Mr. Enright's remark near the end of his paper on the improbability of the so-called "air effect" having any connexion with the theory of the galvanic cell (referring, I presume, to the supposed contact-action between metals and air or free oxygen), prompts me to point out that what I believe will be ultimately adopted as the true theory of Volta's fundamental contact-experiment, or at least the first hint of this theory, was given by De la Rive\*; and considerations relative to its further elucidation and support will be found in papers by the present writer in vol. xli. of the Proceedings of the Royal Society, and in vols. vi. and vii. of this Journal.

My best thanks are due to Professors Everett and Letts, of Queen's College, Belfast, for permission to use the apparatus of the College in these experiments, and for suggestions and advice during the investigation.

#### *Summary of Conclusions.*

When gas is evolved in a chemical or voltaic reaction, the effluvium (*i. e.* this gas or something carried up with it) is

\* *Traité de l'Électricité*, t. i. p. 776.

usually, as shown by Mr. Enright, electrically charged (§ 4). So far as these present experiments show, no electrification is produced by simple effervescence unaccompanied by chemical change (§ 17).

The sign of the electrification is influenced by the kind of chemical or voltaic action taking place, and is apparently not due to any "contact effect" (§§ 4 to 11).

When the effluvium is that given off from zinc dissolving in hydrochloric acid (taken as a typical experiment), and consists of hydrogen accompanied by foggy matter, it is not decided whether the charge is given originally to the gas or the fog particles, though the balance of evidence inclines perhaps towards the latter view (§§ 12 to 16). The fog in question is formed apparently at, or nearly at, the same time and place as the gas (§ 12); and the nature of its charge (if any) is therefore possibly influenced by the voltaic conditions there present.

The gas, or effluvium, from the decomposition of a liquid by a current from the poles of a separate battery immersed in it (voltameter) appears also to be electrified (§ 19).

Belfast, April, 1890.

III. *On Huygens's Gearing in illustration of the Induction of Electric Currents.* By LORD RAYLEIGH, Sec. R.S., Professor of Natural Philosophy in the Royal Institution\*.

AS a mechanical model of the electric machinery at work in the induction of currents Maxwell employed differential gearing; and an apparatus on this principle, designed by him, is in use at the Cavendish Laboratory. Wishing to show something similar in a recent course of lectures, and not having differential gearing at my disposal, I designed more than one combination of pulleys, the action of which should be analogous to that of electric currents. These eventually resolved themselves into Huygens's gearing, invented, I believe, in connexion with the winding of clocks. As this apparatus is easier to understand than differential gearing, and the parts of which it is composed are more likely to be useful for general purposes in a laboratory, I have thought that it might be worth while to give a description, accompanied by an explanation of the mode of action.

Two similar pulleys, A, B, turn upon a piece of round steel fixed horizontally †. Over these is hung an endless cord, and

\* Communicated by the Physical Society: read May 16, 1890.

† Light wooden laths, variously coloured and revolving with the pulleys, render the movements evident at a distance.



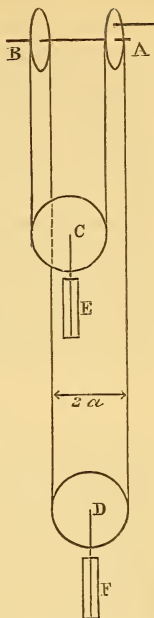
the two bights carry similar pendent pulleys, C, D, from which again hang weights, E, F. The weight of the cord being negligible, the system is devoid of potential energy; that is, it will balance, whatever may be the vertical distance between C and D.

Since either pulley A, B may turn independently of the other, the system is capable of two independent motions. If A, B turn in the same direction and with the same velocity, one of the pendent pulleys C, D rises, and the other falls. If, on the other hand, the motions of A, B are equal and opposite, the axes of the pendent pulleys and the attached weights remain at rest.

In the electrical analogy the rotatory velocity of A corresponds to a current in a primary circuit, that of B to a current in a secondary. If when all is at rest the rotation of A be suddenly started, by force applied at the handle or otherwise, the inertia of the masses, E, F, opposes their sudden movement, and the consequence is that the pulley B turns *backwards*, i. e. in the opposite direction to the rotation imposed upon A. This is the current induced in a secondary circuit when an electromotive force begins to act in the primary. In like manner, if A having been for some time in uniform movement suddenly stops, B enters into motion in the direction of the former movement of A. This is the secondary current on the break of the current in the primary circuit.

It must be borne in mind that in the absence of friction there is nothing to correspond with electrical resistance, so that the conductors must be looked upon as perfect. The frictions which actually enter do not follow the same laws as electrical resistances, and only very imperfectly represent them. However, the frictions which oppose the rotations of A and B have a general effect of the right sort; but the rotations of C and D, corresponding to dielectric machinery, should be as free as possible.

The effect of a condenser, to which the terminals of one of the circuits is joined, would be represented by a spiral spring (as in a watch) attached to the corresponding pulley, the stiffness of the spring being inversely as the capacity of the condenser. The absence of the spring, or (which comes to the same thing) the indefinite decrease of its stiffness, corresponds to infinite electrical capacity, or to a simply closed circuit.





The equations which express the mechanical properties of the system are readily found, and are precisely the same as those applicable in the electrical problem. Since the potential energy vanishes, everything turns upon the expression for the kinetic energy. If  $x$  and  $y$  denote the circumferential velocities in the same direction of the pulleys A, B where the cord is in contact with them,  $\frac{1}{2}(x+y)$  is the vertical velocity of the pendent pulleys. Also  $\frac{1}{2}(x-y)$  is the circumferential linear velocity of C, D, due to rotation, at the place where the cord engages. If the diameter be here  $2a$ , the angular velocity is  $(x-y)/2a$ . Thus, if  $M$  be the total mass of each pendent pulley and attachment,  $Mk^2$  the moment of inertia of the revolving parts, the whole kinetic energy corresponding to each is

$$\frac{1}{2} M \left\{ \frac{(x+y)^2}{4} + \frac{k^2 (x-y)^2}{4a^2} \right\}.$$

For the energy of the whole system we should have the double of this, and, if it were necessary to include them, terms proportional to  $x^2$  and  $y^2$  to represent the energy of the fixed pulleys. The reaction between the pulleys A, B depends upon the presence of a term  $xy$  in the expression of the energy. We see that this would disappear if  $k^2 = a^2$ ; as would happen if the whole mass of the pendent pulleys and attachments were concentrated in the circles where the cord runs. The case discussed above, as analogous to electric currents, occurs when  $k^2 < a^2$ , a condition that will be satisfied, even without non-rotating attachments, if the cord run near the circumference of the rotating pulleys. The opposite state of things, in which  $k^2 > a^2$ , would be realized by carrying out masses beyond the groove, and thus increasing the rotatory in comparison with the translatory inertia. In this case the mutual action between A and B is reversed. If when all is at rest A be suddenly started, B moves forward in the *same* direction. Otherwise C and D would have to rotate, and this in their character of fly-wheels they oppose.

Generally, if  $L$ ,  $N$  be the coefficients of self-induction, and  $M$  mutual induction, we have (constant factors being omitted)

$$L = N = a^2 + k^2,$$

$$M = a^2 - k^2.$$

In order to imitate the case of two circuits coiled together in close proximity throughout, we must have in the mechanical model  $k^2 = 0$ ; that is, the rotatory inertia of the pendent pulleys must be negligible in comparison with the translatory inertia. Also the energy of the fixed pulleys, not included in the above expressions, must be negligible. If these conditions be satisfied, a sudden rotation imposed upon A generates an *equal* and opposite motion in B.

IV. *On Relations between the Lines of various Spectra, with Special Reference to those of Cadmium and Zinc, and a Redetermination of their Wave-lengths.* By JOSEPH SWEETMAN AMES, Assistant in Physics, Johns Hopkins University.\*

IN this paper I shall give a sketch, as complete as possible, of the many theories which have been advanced concerning spectral relations, with a short statement as to their agreement with the most recent investigations; and then I wish to call attention to a few new relations suggested by my own studies.

*Relations between Different Spectra.*

Alex. Mitscherlich† was the first, apparently, to seek numerical relations between the spectra of different substances. Having proved, independently of Roscoe, that the spectra of compounds were different from those of the elements themselves, he examined and compared the spectra of the haloid salts of barium, calcium, and strontium. He selected certain lines in each as most prominent, and found in the case of the salts of barium that the distance apart of these lines was directly proportional to the atomic weight of the salts themselves, while in the calcium and strontium salts the proportionality was an inverse one. He could find no relations in the spectra of the elements. Those found in the compounds were chance ones; for, using a prism spectroscope, his wave-lengths are arbitrary. A few years later, Mascart‡ called attention to the series of doublets in the spectrum of sodium and to one of triplets in the spectrum of magnesium. He thought there was some connexion between the relative distances of the lines in these similar groups, which could not be attributed to chance, and which might point to some "harmonic" relations.

In the same year M. Lecoq de Boisbaudran§ announced, as the result of his study of the flame-spectra of the alkalies and the alkaline earths, a simple law. He selected certain lines in each spectrum, which he called "homologous," as they appear (with certain changes) in the spectra of homologous substances, such as barium, calcium, and strontium. These lines do not, however, have the same wave-length in the different spectra; and his law was that the heavier the mole-

\* Communicated by the Author.

† Pogg. Ann. cxxi. (1864); Phil. Mag. September 1864.

‡ Comptes Rendus, lxix. (1869).

§ Tom. cit.

cule of the element, the more were these lines shifted towards the red end of the spectrum. The main objection to all this is that until recently the selection of homologous lines has been a purely personal matter: any observer has had the privilege of calling "homologous" any lines he saw fit; and even now, as I shall show, it is mainly in the ultra-violet part of the spectrum that homologous lines and series can be definitely determined. To verify his law, M. de Boisbaudran takes the average of wave-lengths lying often far apart. This process can be justified only when each line separately obeys the law. But far more important than this relation is one which M. de Boisbaudran deduced some years later\*. He states it as follows:—

"In the natural families (of elements), the variation in the increment of atomic weights is proportional to the variation in the increment of the wave-lengths of homologous rays (or groups of rays) in the 'third harmonic' of the spectra."

I cannot better explain the meaning of his terms than by giving in detail the application of the law to the determination of the atomic weight of germanium†.

Aluminium, gallium, and indium belong to the same "natural family;" and their atomic weights and spectra are known, so the ratio of the "variations in the increments" can be determined once for all. The average of the wave-lengths of a prominent pair of aluminium lines is, according to him, 3952; and homologous pairs in the spectra of gallium and indium give similarly 4101 and 4306. He takes as the atomic weights of the three metals 27·5, 69·9, and 113·5 respectively.

Hence we have:—

	$\lambda$ .	$\Delta\lambda$ .	$\Delta^2\lambda$ .	Variation in Increment.
Al.	3952			
		149		
Ga.	4101		56	$\frac{56}{149} = \cdot 37584$
		205		
In.	4306			

Atomic weight.

Al.	27·5			
		42·4		
Ga.	69·9		1·2	$\frac{1·2}{42·4} = \cdot 0283$
		43·6		
In.	113·5			

\* *Comptes Rendus*, cii. p. 1291 (1886).

† *Ibid.*

Then, the ratio of these variations,

$$\frac{\cdot 37584}{\cdot 0283} = 13\cdot 28,$$

must be a constant for all the natural families.

The spectrum of germanium is partially known ; and it can be shown chemically that it belongs to the same family as silicon and tin. So, treating its atomic weight as an unknown quantity, and assuming certain values for the wave-lengths and atomic weights of silicon and tin, we have :—

	$\lambda$ .	$\Delta\lambda$ .	$\Delta^2\lambda$ .	"Variation."
Si.	4010			
		443		
Ge.	4453		181	$\frac{181}{443} = \cdot 4051$
		624		
Sn.	5077			

Atomic weight.

Si.	28			
		$x - 28$		
Ge.	$x$		$146 - 2x$	$\frac{146 - 2x}{x - 28} \equiv X$
		$118 - x$		
Sn.	118			

By his law,

$$\frac{\cdot 4051}{X} = \frac{\cdot 37584}{\cdot 0283} = 13\cdot 28,$$

$$\therefore X = \cdot 03051,$$

$$\therefore x = 72\cdot 32.$$

So M. de Boisbaudran succeeds in getting identically the same value for the atomic weight as Winckler afterwards found by chemical means. This is surely a wonderful confirmation of the law, if the lines assumed to be homologous are so in reality. It is true that the atomic weights of the elements are not known so accurately as to justify M. de Boisbaudran in attributing such exactness to his deductions ; and so the method ought not to be applied to the determination of atomic weights. But, if the law is correct, it may well serve to identify homologous lines. Let us apply it to the case of magnesium, zinc, and cadmium. The ratio of the "variations," which is a constant for all natural families, is not known more accurately than 13·0 ; but this will do very well for our purposes. The variation in the increment of the



atomic weights of magnesium, zinc, and cadmium is  $\cdot 146$ . Hence the variation in the increment of the wave-lengths is  $\cdot 146 \times 13 = 1\cdot 898$ . I have recently studied the spectra of zinc and cadmium with much care; and, as will be shown later, each line in the one spectrum has an homologous one in the other. Two of these lines have the wave-lengths  $2800\cdot 9$  and  $2980\cdot 8$  respectively. This law of M. de Boisbaudran should enable us to find the corresponding line in the magnesium spectrum. Calling it  $x$ , the variation in the increment is

$$\frac{x - 2621\cdot 0}{2800\cdot 9 - x}.$$

But this must equal  $1\cdot 898$ . Hence  $x = 2738\cdot 8$ . In reality there is a line  $2736\cdot 9$ ; but its physical properties do not correspond to those of the two zinc and cadmium lines. Two other lines of zinc and cadmium, which are undoubtedly homologous, are  $3345\cdot 1$  and  $3610\cdot 6$ ; and the hypothetical magnesium line corresponding to these would have the wave-length  $3253\cdot 6$ . There is, however, no line in this neighbourhood which can possibly be homologous with the zinc and cadmium lines. Therefore, while this law may apply roughly to certain lines, it surely cannot be considered general.

After M. de Boisbaudran several investigators, including Ditte and Troost and Hauteville\*, endeavoured to trace relations between atomic weights and "displacement" of the spectra. But, as remarked above, it was impossible at this time to make any accurate statements as to homologous lines or their displacement. This fact is clearly shown by the disagreement of observers of the same spectra in regard to homologous lines. Cimician† examined the spectra of a great many substances in search of lines, and tried by a study of them to prove the compound nature of the elements. The dispersion of his instrument was, however, so feeble that he could not properly decide upon similarities in different spectra. He opposes M. de Boisbaudran's law of the shifting of the spectra, and says that instead of increasing with the atomic weight the wave-lengths increase with the intensity of the "chemical kinetic energy." (See Mohr, *Mech. Th. der Chem. Affinität*, Wien, 1867.) The first really scientific work on the relations between the lines of spectra was that of Hartley‡. In studying the spark-spectra of the elements, his attention was attracted to the many points of resemblance between the spectra of chemically similar elements, notably magnesium,

\* *Comptes Rendus*, lxxii. (1871).

† *Wien. Sitzber.* 1877, 1878, 1880.

‡ *Journ. Chem. Soc.* 1882, 1883.



zinc, and cadmium. But it is hardly safe to draw inferences from spark-spectra; for, although they are undoubtedly characteristic, yet the state of affairs in the spark-discharge is so unnatural, if I may use the term, that similar molecules could not be expected to act alike. The study of the arc-spectra of the elements leads to many modifications and additions, as will be shown later. Prof. Hartley called attention also to a most remarkable relation connecting the lines in the series of triplets in the spectra of magnesium, zinc, and cadmium. He corrected the wave-lengths for atmospheric refraction, and then calculated their reciprocals; that is, he deduced quantities proportional to the frequencies of the waves. He then found that the differences of these frequencies for each triplet in any one series is a constant quantity. This law holds also for series of doublets. I will return to this point when the spectra of cadmium and zinc are discussed. That there are mathematical expressions connecting the many series of rays in the spectra of the elements no one can doubt. Their regularity and analogy are evidently not accidental. But there are two ways of arriving at such a mathematical formula: one is to deduce it from theoretical considerations and to test it by experiment; the other is to give up all preconceived ideas and simply to "guess," as Kepler did. Cornu\* advises the latter method. He thinks that relations are to be found, if at all, between the lines which are "reversed." It is true that most of the lines in these series which obviously obey some common law are reversed; but different observers are continually finding different reversals. The conditions must be specified. While studying, then, the reversed lines of aluminium and thallium, Cornu noticed the resemblance between the series which they formed and the one of hydrogen lines. He thought he could trace a linear relation between them. That is, for all the ultra-violet reversed lines of aluminium (and of thallium) the following formula held:—

$$\lambda = a + b \lambda_1,$$

where  $\lambda_1$  is the wave-length of one of the lines in the hydrogen series, beginning with wave-length 4340. That this formula is not true will be shown later when the wave-lengths of the aluminium lines are given.

In the spectra of zinc and cadmium some new points of resemblance were noted by Mr. Bell † quite recently; but he worked with the spark-spectra, and so was at a disadvantage. For the sake of completeness some notice must be taken of

\* *Comptes Rendus*, c. (1885).

† *Amer. Journ. Sci.* [3] xxxi. (1886).

the recent attempt by Prof. Anton Grünwald \* of Prague to deduce a mathematical theory of spectra and spectral relations. A synopsis of his theory and the objections to it have been given by myself †, and later by Kayser ‡. In his last paper Prof. Grünwald claims to find coincidences between lines in the spectra of antimony, tellurium, and copper, and then to deduce the proof of a new element. In fact, there is not a single coincidence between these three spectra. It is evident from his writings that Prof. Grünwald has never had the benefit of using and working with a spectroscope.

### *Harmonic and Combinational Lines.*

There has been an attempt to solve the question of the origin of lines in spectra, which is quite different from the theories and relations already discussed. Since the motion imparted to the æther and known to us as light is a periodic one, it seems but natural to apply Fourier's series and to see if the presence of the various harmonics of the fundamental can be found. The first to find such simple relations was M. Lecoq de Boisbaudran §. He thought that line for line the two visible bands of nitrogen were related to each other in the ratio 3:4. Later and more accurate measurements have shown this relation to be inaccurate. Soon after Prof. G. Johnstone Stoney || pointed out some harmonic relations in the spectrum of hydrogen. At the same time he studied the absorption spectrum of  $\text{CrO}_2\text{Cl}_2$  with a view to testing his theory; but the result was not satisfactory. At the best all the harmonics are never present; all the lines are not accounted for; and several fundamentals have often to be supposed. The ultra-violet lines of magnesium and cadmium were examined by Soret ¶ in the search for harmonic ratios; but his coincidences are very rough.

Liveing and Dewar \*\* also engaged in the quest for these harmonic relations in the spectra of lithium, sodium, and potassium, but with indifferent success. A few such relations can be found in every spectrum; but is this number greater than that which a chance-distribution would give? This question occurred to Schuster, while he was working on the spectrum of iron. He proposed the following problem:—

\* *Astr. Nach.* p. 2797 (1887); *Wien. Sitzb.* 1887, 1888, 1889.

† *Amer. Chem. Journ.* xi. (1889); '*Nature*,' xl. (1889).

‡ *Chem. Ztg.* xiii. pp. 1655 and 1687 (1889).

§ *Comptes Rendus*, lxix. (1869).

|| *Phil. Mag.* [4] xlii. (1871); '*Nature*,' xxi. (1830).

¶ *Bibliot. Univ. Archives des Sci. Phys. et Nat.* Sept. 1871; *Phil. Mag.* [4] xlii. (1871).

\*\* *Proc. Roy. Soc.* xxix. (1879); xxx. (1880).

“ Given  $n$  quantities distributed arbitrarily between 1 and  $A$ , what is the probable number of quotients of two of these  $n$  quantities, which will be equal to  $\alpha \pm \delta$ , where  $\delta$  is small ? ”

He finds\* the probable number to be

$$\frac{n(n-1)(A^2\alpha^2-1)\delta}{(A-1)^2\alpha^2},$$

where  $A \approx \frac{1}{\alpha^2}$ . Applying this result to the spectrum of iron

he finds, on the whole, fewer harmonics actually present than the formula demands. His conclusion, however, is that the law of distribution, although a complicated one, may in special cases resolve itself into the harmonic one. Since this investigation of Schuster's, the search for harmonic ratios has nearly ceased ; but, giving a broadened meaning to the word, Liveing and Dewar† have called attention to certain “ harmonic ” relations in spectra. These are, the repetition of similar groups, a certain sequence in distance, and a law of physical quality such as intensity and clearness.

A more recent attempt to apply dynamical reasoning and formulæ to the spectra of the elements has been made by M. V. A. Julius‡. On dynamical grounds there should be, he thinks, present in spectra lines whose frequencies are the sums or differences of the frequencies of other lines (the combinational tones of Helmholtz). So he deduces the probable number of coincidences, within limits  $\pm \delta$ , if the differences are taken between each two of  $n$  quantities lying at random between  $P$  and  $Q$ . He then actually calculates the differences in the case of eight spectra, and finds more coincidences than his formula says mere chance would give him. This theory of combinational rays would account also for the regularity of doublets and triplets, which was first noticed by Hartley, but which M. Julius apparently rediscovered. Until the wavelengths of the lines in the various spectra are known much more accurately than they are at present, such work as this is almost thrown away. The objective existence of combinational tones is now generally acknowledged, however ; and we may certainly expect corresponding phenomena in light-waves. This idea is not a new one ; but M. Julius is the first to elaborate it. In doing so, however, he neglects too much, I think, the physical properties of the lines. We would expect the strongest lines, if any, to be the ones to produce combina-

\* Proc. Roy. Soc. xxxi. (1881).

† Phil. Trans. clxxiv. (1883).

‡ *Ann. de l'Ecole Polyt. de Delft*, 1889.

tional lines; but M. Julius gives equal importance to each line, faint or strong, hazy or sharp. The spectrum of calcium has some very strong lines in the red; and, as their wave-lengths have recently been carefully determined by Prof. Rowland, I thought I would test this theory by means of them. My search was in vain: not a combinational line could I find.

### *Distribution of Lines.*

For many years spectroscopists have sought to reduce the distribution of lines in any one spectrum to a mathematical formula, but without much success. There are, however, one or two brilliant exceptions.

In 1885 J. J. Balmer\* gave a formula for the lines in the hydrogen spectrum, which is most simple and which, as will be seen later, is remarkably accurate. His formula is

$$\lambda = \lambda_0 \frac{m^2}{m^2 - 4},$$

where  $\lambda_0$  is a constant and  $m$  takes in succession the values 3, 4, 5.... More will be said of this formula when the hydrogen spectrum itself is discussed.

A formula was also advanced by Nordenskiöld†, the Arctic explorer; but it is quite inaccurate.

These two formulæ were found by trial; but it is interesting to note that one similar to Balmer's has been deduced theoretically. A general theory of radiation has been devised by Herr Kövesligethy‡, and in the course of this he arrives at the following wave-length formula:—

$$\lambda^2 = \mu_0^2 \frac{1}{R - 1},$$

where  $\mu_0$  is the value of  $\mu$  for the temperature of dissociation,  $\mu$  being a function of the temperature and constitution of the body; and  $R$  is a function containing a parameter which must be determined for each substance. This formula is most suggestive; and the appearance of the elaborate treatise on the general theory, which is promised us, is eagerly expected.

In their first contribution to the "Spectra of the Elements"§ Kayser and Runge announce that they have found a general law for all spectra, which includes Balmer's as a special case. The uncertainty of the measurements of the

\* Wied. Ann. xxv. (1885).

† Comptes Rendus, cv. (1887).

‡ Astr. Nachr. p. 2805 (1887); Beibl. xii. pp. 346 and 579 (1888).

§ Abhd. Berlin Acad. 1888.



wave-lengths of the elements is so great, though, that they have been unable to test it sufficiently. In a more recent paper\* they give a formula for one of the cyanogen bands; but this is not, I judge, their general formula, nor even a special case of it.

The various bands found in the spectra of carbon and its compounds, and of many other substances also, seem at sight to be especially suitable for mathematical investigation; and many of them have been studied most carefully.

The first to hit upon an approximate law was Prof. A. S. Herschel† of Newcastle-on-Tyne. On seeing Piazz Smyth's map of the green band of CO, which was plotted in wave-numbers or frequencies, he at once noticed that the differences of the lines were in arithmetical progression. This was in November 1883. He announced his intention of studying other bands; but I can find no record of his having done so. Prof. Rowland, independently, detected a similar law as soon as he began his work on the solar spectrum, which was in 1885. He investigated the A, B, and  $\alpha$  bands first, and afterwards all the carbon bands. He found that the law was not so exact as the accuracy of his measurements demanded, and so never published his work.

Later on, M. H. Deslandres, working in Cornu's laboratory, came upon the same approximate law. Cornu‡ had noted that the reciprocals of the wave-lengths of the homologous lines in the three bands A, B, and  $\alpha$  were nearly in arithmetical progression; and in his monograph on these telluric bands (Paris 1886) he says that the law of distribution of the doublets is sensibly the same in all three. This law, stated analytically, is

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta\lambda'}{\lambda'} = \frac{\Delta\lambda''}{\lambda''},$$

where  $\Delta\lambda$ ,  $\Delta\lambda'$ ,  $\Delta\lambda''$  are the distances from the homologous lines to the "isolated" ones; and  $\lambda$ ,  $\lambda'$ ,  $\lambda''$  are the averages of the rays whose intervals are  $\Delta\lambda$ ,  $\Delta\lambda'$ ,  $\Delta\lambda''$ . This law is only the roughest approximation. Cornu does not seem to have thought of testing the lines of each group separately. But in 1886 Deslandres§ published his investigation of the nitrogen bands; and stated that for all of them, and in fact for all bands so far examined, the following law is true:—"In general, the rays composing a band can be divided into

\* *Abhd. Berlin Acad.* 1889; *Wied. Ann.* xxxviii. (1889).

† *Trans. Roy. Soc. Edinb.* xxxii. [3] (1884).

‡ *Comptes Rendus*, xcvi. (1884).

§ *Comptes Rendus*, ciii. (1886); also vol. civ. (1887), and vol. cvi. (1888).



several overlapping identical series ; and in each series the intervals from one ray to the next (measured in wave-numbers) form approximately an arithmetical progression.” As Deslandres remarks, for most bands it is immaterial which we use,  $\lambda$ ,  $\frac{1}{\lambda}$ , or  $\frac{1}{\lambda^2}$ ; but  $\frac{1}{\lambda}$  seems to apply most generally. In a later paper Deslandres says that the bands themselves form groups, and that the same law governs the distribution of bands as governs the lines in any one band. Thus for any ray,

$$\frac{1}{\lambda} = Am^2 + Bm + C, \quad m = 0, 1, \dots$$

$$C = Dn^2 + En + F, \quad n = 0, 1, \dots$$

$$\therefore \frac{1}{\lambda} = Am^2 + Bm + Dn^2 + En + F.$$

Deslandres gives reasons for believing the general formula is of the form :—

$$\frac{1}{\lambda} = f(n^2, p^2) m^2 + Bn^2 + \phi(p^2).$$

This he compares with that of a vibrating rectangular prism, which likewise is a function of three positive parameters. These laws of Deslandres apply fairly well to all banded spectra ; but they are only approximations. I had made measurements of many of the bands of carbon and cyanogen to test their accuracy, but have been anticipated in their publication by Kayser and Runge\*. They find, as I had done, that these laws fail in some cases. They study with particular care the most regular of the cyanogen bands, the one at wave-length 3883.5, and find that the empirical formula

$$\frac{1}{\lambda} = a + be^{cn} \sin(dn^2),$$

where  $a, b, c, d$  are constants and  $n=0, 1, 2, \dots$  applies reasonably well. But in testing this formula they make no correction for atmospheric refraction, which would, I think, make some difference. They come to the conclusion that no exact formula, which is reasonably simple, can be found by trial. If one is ever to be known it must be deduced theoretically.

#### *Some New Relations.*

The two elements between whose spectra there is the most striking resemblance are, as is well known, zinc and cadmium.

\* *Abhd. Berlin Akad.* 1889; *Wied. Ann.* xxxviii. (1889).

Their great similarity has often been noted ; but, as the spark-spectra have nearly always been studied, the exact correspondence between them has so far escaped notice. It is to be regretted, too, that in general so little attention has been paid to the physical properties of the lines, when homologous groups or series were selected. It is only, I think, by means of the physical similarities that correct inferences can be made. For these two reasons a great many of the relations given by Prof. Hartley are inaccurate. All of my measurements and descriptions of the zinc and cadmium spectra are taken from the photographs of the arc-spectra recently made by Prof. Rowland. My measurements are only provisional and do not possess a greater accuracy than 0.1 of a unit (*i. e.*  $0.01\mu\mu$ ). This is sufficient for present purposes, and Prof. Rowland, who has nearly completed a systematic study of the spectra of the elements, will soon publish his tables of wave-lengths, which will be accurate to 0.01 of a unit. There will be noticed a discrepancy between my wave-lengths of cadmium and those given by Mr. Bell\* The reason for this was discovered by Mr. Bell and myself, when we were working on the spark-spectrum of cadmium two years ago. A mistake of one unit in one of Mr. Bell's micrometer-readings vitiated one of the standard wave-lengths (which were used for the determination of the others). The scale of my wave-lengths is that of Rowland's map, as its superiority is now universally acknowledged. The wave-lengths are afterwards corrected for atmospheric refraction by means of interpolations in Ketteler's † determinations. These corrections become very uncertain in the extreme ultra-violet ; but no better values are known.

### Zinc.

Wave-length in Air.	Wave-length in vacuo.	Wave-numbers.	
6362.5	6364.4	$1571.2 \pm .02$	
4810.7 r. } $\alpha$ .	4812.2	$\left\{ \begin{array}{l} 2078.0 \pm .04 \\ 2117.0 \end{array} \right.$	Strong and sharp.
4722.3 r. }	4723.7	$\left\{ \begin{array}{l} 2136.0 \\ 2159.1 \pm .05 \end{array} \right.$	
4680.3 r. }	4681.7	$\left\{ \begin{array}{l} 2197.5 \pm .09 \\ 2987.9 \end{array} \right.$	
4630.1	4631.5	$\left\{ \begin{array}{l} 2988.5 \\ 3026.4 \end{array} \right.$	Very strong and nebulous.
3346.2 } $\beta$ .	3347.3	$\left\{ \begin{array}{l} 3026.8 \\ 3045.6 \end{array} \right.$	
3345.7 } $\left. \begin{array}{l} \\ \end{array} \right\}$	3346.8		
3345.1 r. } $\left. \begin{array}{l} \\ \end{array} \right\}$	3346.2		
3303.1 } $\left. \begin{array}{l} \\ \end{array} \right\}$	3304.2		
3302.8 r. } $\left. \begin{array}{l} \\ \end{array} \right\}$	3303.8		
3282.35 r. }	3283.4		

\* Amer. Journ. Sci. [3] xxxi. (1886).

† Phil. Mag. [4] xxxii. (1866).

Zinc (*continued*).

Wave-length in Air.	Wave-length in vacuo.	Wave-numbers.	
3076.1 r.	3077.1	3249.8 $\pm$ .11	
3072.1 r.	3073.1	3254.0	
3035.9 } $\gamma$ .	3036.9	3292.8	Sharp.
3018.5 } }	3019.5	3311.8	
2800.9 r. d. } $\delta$ .	2801.8	3569.1 $\pm$ .13	
2770.9 r. d. }	2771.8	3607.8	Strong and nebulous.
2756.5 r. }	2757.4	3626.6	
2712.6 }	2713.5	3685.3 $\pm$ .14	
2684.2 } $\epsilon$ .	2685.1	3724.3	Sharp and faint.
2670.7 }	2671.6	3743.1	
2608.7 }	2609.6	3832.0 $\pm$ .15	
2582.5 } $\zeta$ .	2583.4	3870.9	Strong and nebulous.
2570.0 }	2570.9	3889.7	
2516.2 }	2517.0	3973.0 $\pm$ .16	
2491.6 } $\eta$ .	2492.4	4012.2	Nebulous.
2479.9 }	2480.7	4031.1	
2463.7 }	2464.5	4057.6 $\pm$ .17	
2440.4 } $\theta$ .	2441.2	4096.3	Hazy.
2429.0 }	2429.8	4115.6	
2138.3 r.	2139.0	4675.1 $\pm$ .22	

This last line is a broad reversal.

## Cadmium.

Wave-length in Air.	Wave-length in vacuo.	Wave-numbers.	
6438.8	6440.7	1552.6 $\pm$ .02	
5086.1 r. } $\alpha$ .	5087.6	1965.6 $\pm$ .05	
4800.0 r. }	4801.5	2082.7	Strong and sharp.
4678.3 r. }	4679.7	2136.9	
4413.1 }	4414.5	2265.3	
3614.6 } }	3615.7	2765.7 $\pm$ .08	
3613.1 } }	3614.2	2766.9	
3610.6 r. } $\beta$ .	3611.7	2768.8	Very strong and
3467.7 }	3468.8	2882.8	nebulous.
3466.15 r. }	3467.3	2884.1	
3403.7 r. }	3404.8	2937.0	
3261.1 r.	3262.2	3065.4 $\pm$ .09	
3252.6 r. } $\gamma$ .	3253.6	3073.5 $\pm$ .10	
3133.2 }	3134.2	3190.6	Sharp.
3081.0 }	3082.0	3244.7	
2980.8 r. d. } $\delta$ .	2981.8	3353.7 $\pm$ .12	
2881.0 r. d. }	2881.9	3469.9	Strong and nebulous.
2837.0 r. }	2837.9	3523.7	
2868.2 }	2869.1	3485.4 $\pm$ .13	
2775.0 } $\epsilon$ .	2775.9	3602.4	Sharp and faint.
2733.8 }	2734.7	3656.7	
2763.9 d. } $\zeta$ .	2764.8	3616.9 $\pm$ .14	
2677.6 d. }	2678.5	3733.4	Strong and nebulous.
2639.4 }	2640.3	3787.4	
2660.3 }	2661.2	3757.7 $\pm$ .15	
2580.2 } $\eta$ .	2581.1	3874.3	Nebulous.
2544.8 }	2545.7	3928.2	
2602.1 }	2603.0	3841.7 $\pm$ .16	
2525.3 } $\theta$ .	2526.1	3958.7	Hazy.
2491 }	2492	4012.5	
2288.1 r.	2288.9	4368.9 $\pm$ .19	

This last line is a broad reversal; and 2980·8 is probably triple. As usual, “r” means reversed; and “d” double.

This list of lines does not pretend to include *all*; for a very few faint ones could not be measured as accurately as I wished.

The two spectra, as will be noticed, consist mainly of groups of three lines; these triplets overlap in the cadmium spectrum, but owing to the physical similarity of the lines forming any one triplet it was a matter of perfect ease to select them. Thus it is evident that line for line, group by group, the two spectra correspond. The only possible exception is in group  $\xi$ . In cadmium the first two lines are plainly double, while in zinc they are not resolved. The lines are broad and nebulous; and the zinc lines will, I think, be proved double. The more closely the two spectra are examined the more perfect does their agreement appear.

If we observe either spectrum, it is at once evident that groups  $\beta$ ,  $\delta$ ,  $\xi$ ,  $\eta$ ,  $\theta$  form a series. Taking the differences of the wave-numbers of the last lines in each of these triplets, we have for zinc:—

581·0, 263·1, 141·4, 84·5;

for cadmium:—

586·7, 263·7, 140·8, 84·3.

The correspondence is again evident. These series resemble greatly the series of hydrogen lines; and, as so many spectra have these series, it may be well to describe them in detail. These series always run in the same direction; that is, the relative distances of the lines grow smaller as the wave-lengths become smaller. The lines forming the series are always nebulous; they are strong towards the red end, but rapidly become faint and hazy as we go down the series. The spectrum of the substance has, in general, other lines than those forming the series: the latter are the ones that always appear in the solar spectrum, the former ones may not. Their regularity is perfect. Returning to the zinc and cadmium spectra, and taking differences in wave-numbers between the first and second and the second and third lines of each triplet in the two spectra, excepting  $\beta$  and  $\delta$ , we have:—

For zinc,

39·0	38·8	39·0	38·9	39·2	38·7
19·0	19·0	18·8	18·8	18·9	19·3

For cadmium,

117·1	117·1	117·0	116·5	116·6	117·0
54·2	54·1	54·3	54·0	54·1	53·8



Groups  $\beta$  and  $\delta$  are excluded because, containing doublets and triplets, it is impossible to determine just what wave-number should be used.

It is difficult to say whether or not the agreement in the above figures would be better if the wave-numbers were known more accurately; but I am inclined to think that natural constants for the two metals are indicated by them.

It will be noticed that nearly all the homologous groups are in the ultra-violet. This seems to be true of all spectra. It is only, apparently, when the wave-numbers, or frequencies, are sufficiently large, that the similar modes of vibrations of the molecules become evident.

The resemblance of the spectrum of magnesium to those of zinc and cadmium is much less marked than the one just noted. In fact, I think nearly all the points of similarity given by Prof. Hartley are wrong. Magnesium has, it is true, ten groups of triplets; but their physical properties bear no apparent relation to those of the zinc and cadmium triplets. The beautiful series of five lines at wave-length 2779.9 in the magnesium spectrum surely has no companions in the zinc and cadmium spectra. There is, however, one striking feature common to all three. This is the presence of one broad reversed line. In magnesium it is at wave-length 2852.2; in zinc, at wave-length 2138.3; in cadmium, at wave-length 2288.1. Liveing and Dewar have observed the line at wave-length 2852.2 in the arc-, spark-, and flame-spectra of magnesium; so it is evidently in some sense a fundamental line. The differences of the wave-numbers in each magnesium triplet are also nearly constant, being close to 4 and 2.

The spectra of calcium, strontium, barium, and mercury also contain triplets; but their number is small in comparison with that of the lines not so included.

It is hardly necessary to refer to the series of pairs in the spectra of sodium, copper, and silver; but it may be well to note that each of these spectra has in the ultra-violet one prominent pair, always occurring as impurity lines, very "persistent," and coinciding with the solar spectrum. The sodium pair has the wave-length 3303.0 and 3302.4; that of copper, 3274.0 r. and 3247.7 r.; that of silver, 3282.9 r. and 3280.7 r. The presence of silver in the sun is at last proved. From a study of their physical properties I think the series of sodium pairs is in reality made up of two overlapping series, thus bearing a resemblance to the two series of potassium pairs.

The spectrum of lithium is similar to that of hydrogen. It has a series similar to the hydrogen one and obeying almost identically the same law, beginning at wave-length 3232.8.



In order to test Cornu's theory of the connexion between aluminium and hydrogen, I have measured with some care the wave-lengths of the aluminium pairs as photographed by Prof. Rowland. The wave-lengths of the hydrogen lines were determined by myself. Cornu's theory, stated concisely, is that for aluminium

$$\lambda = a + b \lambda_1,$$

where  $\lambda_1$  is the wave-length of a hydrogen line. According to Cornu the following lines correspond :—

Al.	H.
2373·2	4340·66
2269·2	4101·85
2210·15	3970·25
2174·0	3889·15
2150·4	3835·6

If his theory is true, the ratios of the differences of each two consecutive lines should be the same for each series. Taking the first three lines of each, we find the ratio 1·76 for aluminium and 1·81 for hydrogen. The other ratios agree better ; but still the difference is too great.

As noted above in the historical sketch, the law that the second differences of the wave-numbers of the lines forming a band is constant, is approximately true. No general law more exact than this can, I think, be deduced with our present knowledge. But there seems to be some connexion between the lines forming a band and those in a series like the hydrogen ones : the former may be regarded as forming the "head" of this latter series. There is this true, however : the bands can run in either direction, towards the red or towards the ultra-violet ; while the series always turn one way. But, in spite of this, it may not be without use to show that the bands and the series are connected mathematically.

Balmer's law for the distribution of the hydrogen lines, stated in a slightly more general form, is :—

$$\frac{1}{\lambda} = a \left( 1 + \frac{b}{c + m^2} \right), \quad m = 0, 1, 2 \dots$$

If we substitute in this

$$m = M - n, \quad n = 0, 1, 2 \dots,$$

where  $M$  is a constant many times as great as  $n$ , we have

$$\frac{1}{\lambda} = A + Bn + Cn^2 + \&c.,$$

where the coefficients rapidly grow smaller. This formula is, of course, the analytical statement that for lines near the head of a band the second differences of the wave-numbers are constant. So, if these series and bands represent in any degree the fundamental or original vibrations of the "molecule," as I think probable, it is of interest to note that a similar law applies to both. The exact law of distribution which must come from theoretical considerations will therefore include this as a special case.

*Addendum.*—Since writing the above the Philosophical Magazine for April (1890) has reached me, and it contains an article by Dr. Rydberg, of the University of Lund, "On the Structure of the Line-Spectra of the Chemical Elements," which demands notice. In this paper, which is only preliminary, Dr. Rydberg calls special attention to the many series in the spectra of the elements, divides them into various classes, gives formulæ for their distribution, and states that the wave-lengths are periodic functions of the atomic weights. This last relation, which is barely indicated in the article, seems to be nothing but the one of M. de Boisbaudran, which has already been discussed\*. The law of distribution is nothing but Balmer's slightly generalized. The valuable part of the paper lies in the division of the lines of the spectra into different series and in showing the relations between them. He does not state how he gets his wave-lengths; but they seem to be a combination of Hartley's and Liveing and Dewar's. So he has confused the spark- and arc-spectra.

V. *On some Gaseous Spectra:—Hydrogen, Nitrogen.* By JOSEPH SWEETMAN AMES, Assistant in Physics, Johns Hopkins University†.

MY investigations on the spectra of gases were begun at the suggestion of Professor Rowland, and were designed primarily to ascertain the exact wave-lengths of the line-spectrum of hydrogen. Incidentally some other spectra have also been studied.

#### *Method and Apparatus.*

A concave grating, mounted in the well-known Rowland manner, was used. It was ruled especially for this research, was 6 inches (15.2 centim.) wide with 20,000 lines to the inch, and had a radius of curvature of 13.5 feet (4.11 metres).

The experiments were conducted according to the method

\* Pp. 33 *et seq.*

† Communicated by the Author.

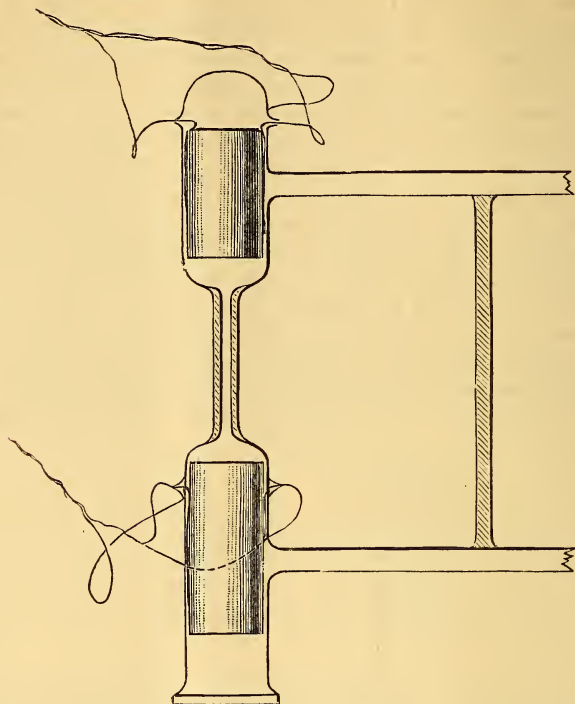
designed by Prof. Rowland for concave gratings, and described in my paper in the Johns Hopkins University Circular 73, 1889\*. Photographs were taken of the gaseous and solar spectra on the same plate. Some of the hydrogen plates were measured on a dividing-engine; but in most cases the wave-lengths were simply read off from the coincidences between the gaseous lines and certain places in the solar spectrum, the wave-lengths of which were taken from Rowland's map. The error in any wave-length is, I think, not more than 0.05 of a unit (*i. e.*  $0.005\mu\mu$ ), or about one part in one hundred thousand. To guard against any displacement of the gaseous spectra, the positions of certain mercury-lines, which were present on all the plates, were carefully noticed and measured. The complete arc-spectrum of mercury has recently been photographed by Prof. Rowland; and so the lines are accurately located on the map. No plate was used in the present work in which these lines were not exactly in their proper places. Their wave-lengths are:—

2653.80	
2652.15	
3650.28	4077.98
3654.96	4347.71
3663.03	4358.50
3663.41	4451.09
4046.67	

Several forms of spectrum-tubes were tried, but that finally adopted was the one shown in the cut (p. 50). As is apparent, it was used "end on." It consists essentially of two tubes containing thin cylinders of aluminium and connected by a finer tube. This tube was in one case circular, having a bore of about 1 millim., and in another it was elliptical. This latter form is preferable, because it keeps the light in the tube better, and because it produces an elongated image on the slit. The use of the aluminium cylinders was suggested by Prof. Rowland. They were in connexion with an induction-coil by means of platinum wires which entered each end-tube, and which were bent so as to make good contact. The cylinders make, as it were, a lining for the two end-tubes; and since, when the vacuum is high, the discharge takes place from the whole surface of the electrode, the brilliancy of the light in the capillary tube is much greater than in the ordinary form of apparatus. A quartz plate was fastened to the

\* Also *Phil. Mag.* [5] xxvii. (1889).

end of the spectrum-tube by a cement of sodium silicate (liquid glass). The light from the tube was focused on the



slit by a quartz lens, having an aperture of 1 inch (2.54 centim.) and a focal length of 6 inches (15.2 centim.). The air-pump used was an ordinary Sprengel; and the arrangement for admitting gases into the tube was the one recommended by Cornu\*. In this there is, in connexion with the spectrum-tube, a barometer-tube whose lower end is joined to a movable cup by a rubber tube. When the spectrum-tube is exhausted, the mercury which is poured into the movable cup rises in the barometer-tube and forms a trap. A U-shaped tube in which water can be electrolysed is in communication with this barometer-tube near the bottom. So, if the cup is lowered, a bubble of gas or air will be forced into the spectrum-tube by the atmospheric pressure. Drying-tubes of caustic potash were introduced; and on each side of the spectrum-tube several inches of sulphur, held between plugs of glass-wool,

\* *Journ. de Phys.* [10] v. (1886).



were placed so as to stop the mercury-vapour. In my entire apparatus there were only three joints where the glass tubes were not fused together. In each of these the following plan was adopted to render it air-tight. One tube was slightly coned out, the other inserted for about an inch, and the entire joint was filled and covered with a preparation of Venice-turpentine and beeswax, known in the laboratory as "universal." This "universal" is easy to mould when slightly warmed, is quite tough, and sticks closely to glass which has been thoroughly heated. These joints proved to be absolutely air-tight, and no gases of any kind were given off after a few days' use. In some cases, for greater security, I put "universal" over the sodium-silicate joint between the spectrum-tube and the quartz-end. The apparatus was cleaned and filled by first pumping dry air through, then washing the interior with ozone as proposed by Cornu, and finally admitting the gas desired. There were, however, certain impurities always present. Mercury and sulphur, and sometimes traces of air, could be detected; but in no case was I troubled with any bands of carbon or its compounds.

The induction-coil was driven by a storage-battery of twenty volts, and was most regular and satisfactory.

The photographs were taken on dry plates made specially for this research by the M. A. Seed Dry-Plate Company of St. Louis, Mo. Lantern-slide glass was used, as the plates must be held bent to a radius of 6.75 feet (2.06 metres). I cannot speak too highly of the quality of the plates, or of their fitness for photographing gaseous spectra. Ten seconds' exposure was sufficient for the solar spectrum at w.-l. 3700; and an exposure of an hour was more than sufficient for the weakest gaseous spectrum. The plates were 1 inch wide and 11.5 inches (29 centim.) long. The dispersion of the instrument was such that, using the second spectrum of the grating, one plate included wave-lengths differing by 400 units ( $40\mu\mu$ ). The definition was perfect over the entire length.

### *Hydrogen.*

The spectrum of hydrogen is of unusual importance owing to its supposed presence in the light emitted by the white stars, and also because of Balmer's formula for the distribution of its lines which form a series.

Huggins\* has measured the lines in the stellar spectra, and Cornu† has investigated the spectrum of hydrogen with a view to their identification. The so-called "secondary"

\* Phil. Trans. clxxi. part ii. (1880).

† Journ. de Phys. [10] v. (1886).



spectrum of hydrogen has been shown by Hasselberg\* to be due to this gas, and the wave-lengths of many of its lines have been measured by him. Cornu does not say whether he observed the secondary spectrum as well as "the stellar series" or not, but I judge from a chance remark that he did. I was entirely unable to get the stellar series by itself, although my hydrogen was pure I am confident, and I varied the tubes, the current, the vacuum, and the exposure. I also introduced large condensers without any noticeable change. Cornu's plates were 5 centim. long, and one was sufficient for the entire hydrogen spectrum from  $G'$  to  $\theta$ . His time of exposure was often three and a half hours. My plates were surely more sensitive than his; and, as the secondary spectrum includes the stellar series, I think the lines observed by him appear on my photographs, especially as he speaks of the "brilliant rays" coming from his tube, in contrast with the nebulous lines in the spectra of the stars. If his lines had been faint and hazy, I might suppose my dispersion too great.

The wave-lengths of the most important hydrogen-lines, as measured on my plates, with their intensities, and the corresponding wave-lengths as given by Hasselberg and Cornu are as follows:—

Hydrogen.		
	C (6563·042).	Hasselberg.
	5084·9	5084·56
	5055·2	5054·22
	5013·15	5012·21
	4973·3      6	4972·51
	4928·8      6	4927·95
	4876·1      4	4875·23
F	4861·49    20	4860·60
	4838·3      4	4837·31
	4797·9      4	4796·81
	4764·0      3	4762·53
	4719·2      5	4718·33
	4683·95      5	4683·00
	4634·15      6	4633·10
	4580·1      4	4579·44
	4534·8      2	4533·72
	4498·75      4	4497·53
	4461·1      5	4460·62
	4447·85      3	4447·24
	4412·35      5	4411·75
G'	4340·66    15	4340·06
	4212·65      7	4211·83
	4205·2      8	4204·39
	4195·9      6	4194·98
	4177·25      8	4176·47
	4171·35      7	4170·66
		Cornu. 4339·5

\* *Mém. de l'Acad. imp. St. Pétersb.* xxx. p. 7 (1882), xxxi. p. 14; *Bull. de l'Acad. imp. St. Pétersb.* xi. p. 203 (1884).

Hydrogen (*continued*).

			Hasselberg.	Cornu.
<i>h</i>	4101·85	10	4101·18	4101·0
	4079·0	5	—	
	4069·75	7	4069·17	
	4067·0	7	4066·40	
	4062·6	6	4062·07	
	3997·25	4		
	3992·2	4		
	3992·0	4		
	3990·15	6		
	3987·0	3		
	3982·75	4		
<i>H</i>	3970·25	8		3968·9
	3963·3	3		
	3962·4	2		
	3944·5	3		
	3924·5	3		
	3889·3	4		
<i>α</i>	3889·15	7		3887·8
	3879·7	3		
	3872·45	4		
	3871·8	5		
	3867·2	4		
	3863·3	5		
	3861·7	4½		
	3858·85	4		
	3836·6	3		
<i>β</i>	3835·6	Nebulous.		3834·5
	3804·9	6		
	3803·2	4		
<i>γ</i>	3798·0	Nebulous ground.		3796·9
	3797·7	4		
	3796·8	5		
	3771·7	3		
<i>δ</i>	3770·7	Faint and nebulous.		3769·4
	3770·3	2		
	3752·05	3		
<i>ε</i>	3750·15	Very faint.		3749·8
	3741·3	2		
<i>ζ</i>	3734·15	Very weak.		3733·6
	3732·2	3		
	3722·2	2		
<i>η</i>	3721·8	Very weak.		3720·6
	3716·05	1		
<i>θ</i>	3711·9	(?)		3710·7
	3702·2	3		
	3684·3	5		
	3682·05	4		
	3674·5	5		
	3644·8	1		
	3633·5	2		

As Cornu does not describe his lines, I can only conjecture with which of my lines his last five correspond.

The stellar series observed by Huggins consists of nebulous

lines rapidly growing fainter towards the ultra-violet end. If the lines which are marked with letters in my list are actually these same lines, and if Cornu's measurements apply to them also, we have the following measurements for the series :—

	Ames.	Cornu.	Huggins.
C	6563·04		
F	4861·49		
G'	4340·66	4339·5	
<i>h</i>	4101·85	4101·0	4101·0
H	3970·25	3968·9	3968·9
$\alpha$	3889·15	3887·8	3887·5
$\beta$	3835·6	3834·5	3834·0
$\gamma$	3798·0	3796·9	3795·0
$\delta$	3770·7	3769·4	3767·5
$\epsilon$	3750·15	3749·3	3745·0
$\zeta$	3734·15	3733·6	3730·0
$\eta$	3721·8	3720·6	3717·5
$\theta$	3711·9	3710·7	3707·5
$\iota$	—	—	3699·0

Of course my scale is different from Cornu's ; but it seems remarkable that the measurements of Cornu and Huggins should vary so much, as they used the same standards. I have marked  $\gamma$  (3798·0) nebulous ; but besides this background there is a sharp line there, which undoubtedly belongs to the secondary spectrum. It is strange, too, that the first four lines of the series should coincide with solar lines, while none of the others do. There are, however, on Rowland's map certain hazy places which are approximately where the most nebulous hydrogen-lines fall ; but there are no lines corresponding to H,  $\alpha$ , and  $\beta$ , which are strong and clear on my photographs.

Knowing that Balmer's formula applied most exactly to the visible hydrogen-lines, I calculated the constant and used it to foretell lines. Indeed it was in this way that I selected the last three of the lines in the series. There was never any ambiguity in the selection. These lines were the only nebulous ones in the spectrum ; but they were so faint as sometimes to escape notice until looked for.

Correcting my wave-lengths for atmospheric refraction as best I could, I found that the constant in Balmer's formula should be 3647·20. Making the calculations, then, with this constant, and comparing the deduced wave-lengths with mine (corrected) we have :—

Calc. $\lambda = 3647 \cdot 20 \frac{m^2}{m^2 - 4}$		Observed.
C	6564.96	6564.97
F	4862.93	4862.93
G'	4341.90	4342.00
h	4103.10	4103.11
H	3971.4	3971.40
$\alpha$	3890.3	3890.3
$\beta$	3836.7	3836.8
$\gamma$	3799.2	3799.2
$\delta$	3771.9	3771.9
$\epsilon$	3751.4	3751.3
$\zeta$	3735.6	3735.3
$\eta$	3723.2	3722.8
$\theta$	3713.2	3712.9

The agreement is striking; and it is possible that atmospheric refraction may fully account for most of the discrepancies.

As stated before, the formation of series similar to this one of hydrogen is a feature common to many spectra. Balmer's law with slight modifications probably applies to all. The similarity between them is evident at once to the eye; but mathematically it is more apparent if we consider the wave-numbers, or rather their differences. So, for purposes of comparison, I will give these for the hydrogen series. The values are corrected, as before, for atmospheric refraction.

N.	$\Delta N.$
C 1523.32	
F 2056.37	533.05
G' 2303.09	246.72
h 2437.18	134.09
H 2518.00	80.82
$\alpha$ 2570.50	52.50
$\beta$ 2606.34	35.84
$\gamma$ 2632.13	25.79
$\delta$ 2651.18	19.05
$\epsilon$ 2665.74	14.56
$\zeta$ 2677.16	11.42
$\eta$ 2686.15	8.99
$\theta$ 2693.32	7.17

As to the secondary spectrum of hydrogen, Hasselberg has shown, conclusively I think, that it is not due to impurities, but to hydrogen itself. All of my observations on this point are in complete accord with his. But in his list of lines there are two mistakes. That the line at w.-l. 4347.71 (4347.10 on his map) is a mercury one is now certain, as it appears strong in the arc-spectrum as photographed by Prof. Rowland. Then, on Hasselberg's map and in his list of wave-lengths,

the lines at w.-l. 4790.0 and 4077.98 (4078.31 and 4077.32 on his scale) are interchanged: 4079.0 is the hydrogen-line, 4077.98 the mercury one. This is at once seen on viewing Prof. Rowland's photographs.

There is the possibility that some of the lines which I have attributed to hydrogen are due to sulphur, as its ultra-violet spectrum is not known. I am at present engaged on this spectrum, however, and shall soon be able to decide whether or not my present list of hydrogen-lines is correct.

### *Nitrogen.*

The spectra of air and its constituents have been studied with special care by Wüllner\*, Hasselberg†, and Deslandres‡. In this paper I do not wish to refer to any of the disputed points concerning the immediate cause of the different groups of bands in the spectrum of ordinary air or nitrogen, but merely to give measurements of the lines which form the "second group" of nitrogen, and to mention some of its properties.

In this group there are nearly fifty bands, each band consisting of three series, the three first lines of each forming a "head" for the band. The bands all have their heads towards the red end of the spectrum, while the group itself is turned the opposite way. At first sight the bands are gathered in companies of five, except towards the head of the group, where there is a series of two bands, then one of three, one of four, and finally the sequence of fives. It seems as if the group should begin with a single band; but I have sought it in vain. The three lines forming the heads are double for all the series, without exception I think.

In the following Table the wave-lengths refer to the second line in each head. The first column gives my measurements of the wave-lengths in air; the second the corresponding wave-numbers; the third the measurements of the wave-lengths by Hasselberg and Deslandres.

\* See Wied. *Ann.* xxxviii. (1889) for references.

† *Mém. de l'Acad. imp. St. Pétersb.* xxxii. p. 15 (1885).

‡ *Ann. Chem. et Phys.* [6] xiv. (1888).



$\lambda$ .	N.	
4975.0	2010.05 $\pm$ .04	4974.0 H.
4917.1	2033.72	4916.72
4813.9	2077.32	4813.01
4722.6	2117.48	4721.61
4666.35	2143.00 $\pm$ 0.5	4665.22
4648.4	2151.28	4647.30
4573.7	2186.41	4572.78
4489.6	2227.37	4488.60
4415.7	2264.65	4414.68
4356.3	2295.53	4355.80
4344.4	2301.81	?
4269.15	2342.39	4268.83
4200.85	2380.47 $\pm$ .06	4200.26
4141.2	2414.76	4140.24
4094.0	2442.60	4093.69
4059.0	2463.66	4058.27
3998.0	2501.25	3997.22
3942.55	2536.43	3941.5 D.
3894.25	2567.89 $\pm$ .07	3893.5
3856.9	2592.76	3856.2
3804.85	2628.22	3804.2
3755.15	2663.01	3754.45
3710.15	2695.31	3709.3
3671.35	2723.79	3670.5
3642.0	2745.74 $\pm$ .08	3640.9
3576.85	2795.76	3576.0
3536.5	2827.65	3536.4 (?)
3500.15	2857.02	3499.1
3469.05	2882.61	3468.1
3446.2+	2901.75	3445.3
3371.2	2966.30 $\pm$ .09	3370.8
3338.6	2995.27	3338.1
3309.4	3021.70	3308.7
3284.8	3044.325	3284.2
3267.5	3060.44	3267.1
3158.9	3165.66 $\pm$ .10	3158.3
3135.7	3189.08	3134.9
3116.4	3208.83	3115.75
3103.8	3221.86	3103.2
2976.7	3359.42 $\pm$ .11	2976.1
2961.9	3376.21	2960.8
2953.0+	3386.38	2952.4
2819.7	3546.48 $\pm$ .13	2818.7
2814.15	3553.47	2813.1

The study of these bands is most interesting. We have here the best means of testing the accuracy of Deslandres's so-called laws. Measurements show that the series of lines in each band obey his law fairly well, and in this sense are identical. The physical properties of the series are not always, however, the same. We can also arrange the bands themselves in five series as Deslandres\* did, and in each of these series the same law of distribution holds with considerable accuracy.

\* *Comptes Rendus*, civ. (1887).

This arrangement is not an obvious one, as I can discover no physical property common to one such series alone which would lead us to make the proper selection.

The Table of wave-numbers so grouped is :—

I.	II.	III.	IV.	V.
				2010·05
				2151·28
			2117·48	2295·53
		2077·32	2264·65	2442·60
	2033·72	2227·37	2414·76	2592·76
	2186·41	2380·47	2567·89	2745·74
2143·00	2342·39	2536·43	2723·79	2901·75
2301·81	2501·25	2695·31	2882·61	3060·44
2463·66	2663·01	2857·02	3044·325	3221·86
2628·22	2827·65	3021·70	3208·83	3386·38
2795·76	2995·27	3189·08	3376·21	3553·47
2966·30	3165·66	3359·42	3546·48	

In each of these series the first differences are the same nearly, so they are “identical;” and the second differences are constant to a certain degree.

Physical Laboratory, Johns Hopkins  
University, April 1890.

VI. *Galvanometers.* By Prof. W. E. AYRTON, *F.R.S.*,  
T. MATHER, and W. E. SUMPNER, *D.Sc.\**

IN order that a number of students may be able to work at the same time in the Physical Laboratories of the City and Guilds of London Central Institution we have endeavoured, as far as possible, to arrange the apparatus so that each of the many experiments should be complete in itself. This has led to the necessity of our constructing, and having constructed for us, a large number of galvanometers of various types, and from the specimens that are on the table it will be seen that several of the galvanometers contain points of novelty. A long series of comparative tests has been carried out with all the more important types that are in our laboratories, and we have therefore thought that a record of the results obtained by the students, and by ourselves, will be of value in affording data to guide others in the selection of instruments most suitable for the objects in view, as well as in suggesting future improvements in the manufacture of galvanometers.

I. *Astatic or Non-Astatic.*

One of the first questions that arises is whether it is desirable to employ the astatic type in the construction of sensitive

\* Communicated by the Physical Society: read January 17, 1890.

galvanometers. Prof. A. Gray, in his treatise on 'The Theory and Practice of Absolute Measurements in Electricity and Magnetism,' maintains that it is not, for he says (page 311):—"Sensibility is sometimes obtained by the use of astatic galvanometers, but these are rarely necessary and are more troublesome to use than ordinary non-astatic instruments."

This opinion carries special weight as it may be very probably taken as expressing Sir William Thomson's view on this subject, seeing that the usual method adopted by Sir William for measuring small currents is to employ a galvanometer with a single set of magnetic needles, and to weaken the magnetic controlling field as far as requisite by means of adjustable magnets. Theoretically there is no limit to the sensibility obtainable in this way; but with any strength of the resultant controlling field due to the earth and the adjustable magnets an astatic combination of magnetic needles must give a more sensitive arrangement than a non-astatic one. For let  $F$  be the resultant strength of this controlling field, let  $M$  be the magnetic moment of a needle within the coil whose magnetic constant is  $G$ , and let  $C_1$  be the current flowing, then, if  $\alpha$  be the deflexion, we have for small deflexions

$$\alpha = \frac{C_1 G}{F}.$$

Next, let a needle of moment  $m$  be attached to the suspended system outside the coil, so as to form an approximately astatic system with the needle inside, then, even if we neglect the action of the coil on the needle outside, an action which of course assists the action of the coil on a needle inside, we have, if  $C_2$  be the current now flowing,

$$\alpha = \frac{C_2 G M}{F(M-m)}.$$

Hence, if the deflexions be the same in the two cases,

$$C_2 = C_1 \frac{M-m}{M}.$$

Now  $M$  may be made large, and  $M-m$  small, hence  $C_2$  may be a small fraction of  $C_1$ . Consequently for any adjustment of the controlling magnet, the current required to produce a given deflexion can be much diminished by using an astatic combination instead of a non-astatic one.

But, perhaps, the most important advantage of an astatic over a non-astatic instrument is its much greater freedom from outside magnetic disturbance. In order that  $C_1$ , the

current with the non-astatic galvanometer, may be small for a given value of the deflexion  $\alpha$ , the resultant controlling field  $F$  must be small; whereas with the astatic combination there is no necessity to make  $F$  small in order that  $C_2$  may be small, since  $\frac{M}{M-m}$  may be made large. Now the disturbance that an

extraneous magnetic body can bring about depends on the strength of the magnetic field it sets up compared with that of the field  $F$  produced by the earth and the adjusting magnet combined. Hence the moving about of a magnetic body in the neighbourhood of the galvanometer will produce more disturbance on a non-astatic galvanometer than on an astatic galvanometer of the same sensibility. The preceding are very important considerations; hence, so far from agreeing with Prof. Gray that it is more troublesome to work with astatic galvanometers than with non-astatic ones, the preceding considerations, which we find fully borne out by experience, have led us to regularly employ the astatic principle with sensitive galvanometers.

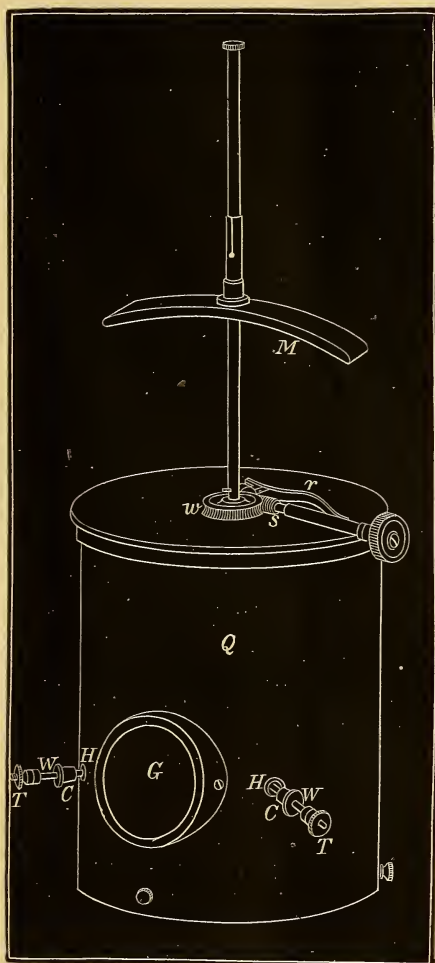
And generally we may conclude that when it is desired to utilize a magnetic control, for example, with electrometers, &c., it is better, when a small controlling moment is required, to obtain this by the use of a weak magnet on the suspended system than by attempting to simply weaken the controlling field. Indeed, we may mention that even in the case of electrometers, where there is no question of the action of currents on magnets, and where (when a magnetic control has been employed in place of a bifilar or torsional control) it has been usual to attach a single little magnet to the aluminium electrometer-needle, to be acted on by a stationary outside magnet, we have found it more convenient to attach an *astatic* combination of magnets to the moving needle, and to direct the system by a fairly strong permanent magnet, which acts of course differentially on the suspended astatic system of magnets, since with such an arrangement great freedom from outside magnetic disturbance is secured, combined with the power of employing a wide range of sensibility.

It is worth noticing that in galvanometers, where the distance of the controlling magnet from the needles is varied by simply raising the magnet  $M$ , as in the case of the galvanometer seen in fig. 1, it is more convenient to place the galvanometer so that the plane of the coils is in the magnetic meridian of the laboratory when the controlling magnet is removed; or, in other words, to place the galvanometer so that the spot of light comes to the zero of the scale for no current



passing through the instrument and with no controlling magnet. For in that case the sensibility of the instrument can be subsequently varied by simply raising or lowering the

Fig. 1.



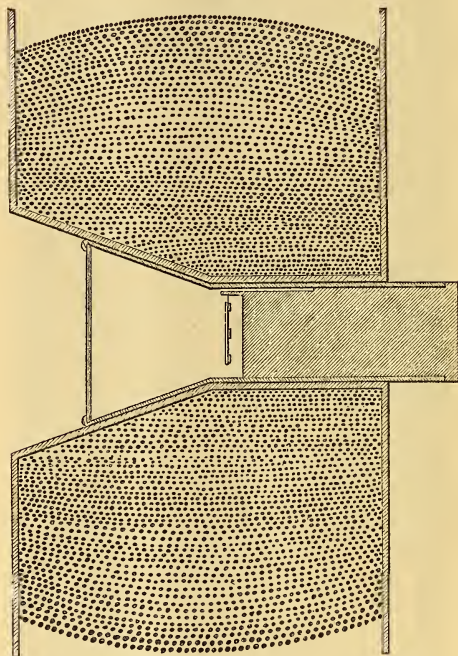
controlling magnet *parallel to itself*; whereas, if the galvanometer be fixed in any other position, it is necessary, when raising or lowering the controlling magnet, to give it a careful screwing motion to prevent the spot of light going off the scale.



## II. *Position of Mirror.*

According to the ordinary method of constructing a Thomson's reflecting-galvanometer, a tubular space at the centre of the coil is left unwound, and the mirror, with the magnets at the back of it, hung at the centre of this unwound space (see fig. 2, which illustrates a well-known form of this type of galvanometer). To allow the ray of light to pass out

Fig. 2.



of the coil after reflexion at the mirror, when the mirror is deflected, the end of the tubular space has to be made trumpet-shaped, which leads to still more space in the neighbourhood of the needle being left unwound. And when the galvanometer is an astatic one, a somewhat similar tubular space is left unwound on each side of the lower coil to allow room for the diamond-shaped aluminium vane to turn.

In this way the most valuable part of each coil, viz. that close to the magnetic needles, is left unwound. This disadvantageous mode of construction so impressed itself on Mr. Mudford, while a student at the City Guilds' Institute, that he suggested that the needles alone should be placed within

the coil, and that the mirror (which is, of course, employed to reflect a ray of light, and not, as its position *inside* the coil would seem to infer, to be acted on electromagnetically) should be placed outside the coil, or between the upper and lower sets of coils when two pair of coils are employed. A specimen of a galvanometer constructed in this way and containing certain other improvements, which will be referred to later on, was submitted some years ago by Mr. Mudford to Sir William Thomson, who expressed approval of the devices employed, and, since that time, many galvanometers differing in other details, but all embodying the principle of not wasting valuable space in the coils, have been constructed for the Central Institution.

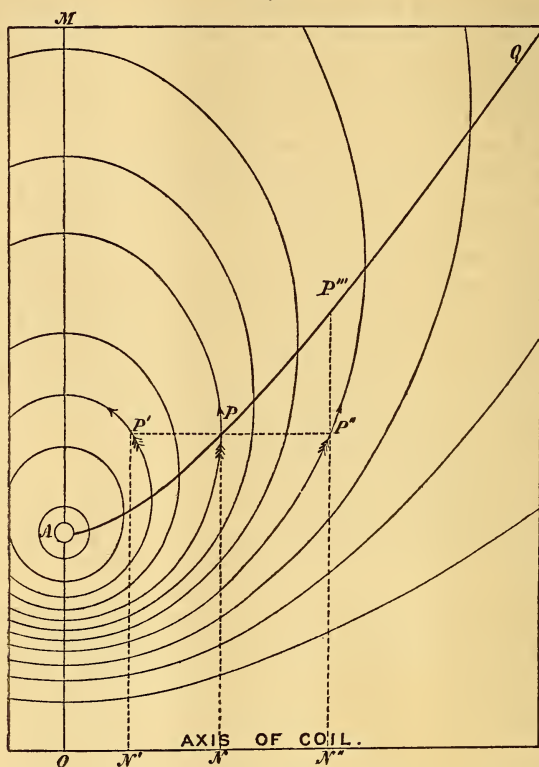
It is interesting to notice that the common method of placing the mirror inside the coil is an irrational survival of an old custom kept up, like the two buttons at the back of a coat, when its use is almost forgotten. Gauss and Weber put their mirror inside the coil because the mirror was made of polished steel and was also the magnetic needle. Sir William Thomson put the mirror inside the coil in his "speaking galvanometers," for receiving messages on submarine cables, because he desired to render the space near the mirror as air-tight as possible in order to obtain great damping. And the ordinary maker of astatic galvanometers puts the mirror inside the coil, because he has seen it there in other galvanometers, and it has never occurred to him to put it anywhere else.

If the ray of light has not to go into the coil no hole need be left and the coil may be wound practically to the centre. It is necessary, however, that the space left unwound inside the coil should be somewhat larger than is required simply to allow the needle to turn through a small angle, because if the windings were carried to the axis of the coil in the immediate neighbourhood of the needle the effect on the latter of the current passing through the innermost coils would be opposed to that of the rest of the coil. To find the shape and volume of the least space that should be left unwound we proceeded as follows:—

Let OA (fig. 3) be the radius of a convolution of wire whose plane is perpendicular to the paper, the section of the convolution being represented by the small circle at A, then, from Maxwell's 'Elect. and Mag.' vol. ii. plate xviii., the lines of force due to a current passing round this convolution are as indicated. Therefore, if a magnet whose half length is NP be placed at a distance ON from the plane of the convolution such that NP is a tangent to the line of force at P, no torque will be exerted on the magnet by a current passing round the

convolution, since the direction of the force at  $P$  is along the magnet  $NP$ . But if the magnet be placed nearer to the convolution, as at  $N'P'$ , or farther from it, as at  $N''P''$ , there will

Fig. 3.



be a torque exerted on it due to this convolution of radius  $OA$ ; the two torques, however, will be in opposite directions. Now as the radii of the greater number of convolutions contained in the coil are greater than the half length of the magnet, it is clear that the torque exerted by the convolution  $OA$  when the magnet is to the right of  $NP$  is in the same direction as that exerted by the coil as a whole, and that the torque exerted on the magnet by this convolution when the magnet is between  $OA$  and  $NP$  is opposed to the torque exerted by the rest of the coil. In other words, if  $NP$  be the position of the half-magnet in the coil, a convolution of smaller radius than  $OA$  must not be wound in the plane that passes through  $OAM$  at right angles to the paper. And if a line  $APQ$  be drawn so as to cut all the lines of force at points

where the tangents are perpendicular to the axis of the coil, OA gives the smallest radius that a coil must have in the plane passing through OAM at right angles to the paper, whether the magnet be at N and its half length be NP, or the magnet be at N'' and its half length be N''P'''.

For our purpose, however, we have not to consider the problem of magnetic needles of different lengths at different distances from a fixed plane, but the converse problem of a magnetic needle of a fixed length in a fixed position, which is at different distances from different planes, the critical radius of convolution in each of which we wish to determine.

If NP were the fixed half length of the magnet, then, as already seen, OA would be the critical radius of a convolution at a distance NO from N, and the critical radius of a convolution for another distance can be obtained by imagining the figure 3 reduced in the proportion of NP to N''P''', in which

case a critical radius  $\frac{NP}{N''P'''} \times OA$  will be obtained at a dis-

tance  $\frac{NP}{N''P'''} ON''$  from N. Or, lastly, if we take OA as the

half length and position of our magnetic needle, the critical radius of convolution at every distance from O will be obtained by taking every such ordinate as N''P''' and multiplying OA by the ratio of OA to N''P''', and the distance from

O for which this is the critical radius is equal to  $\frac{OA}{N''P'''} \times ON''$ .

A curve giving the locus of such critical radii of convolution is shown in fig. 4 for a needle of length 2, shown therefore in the figure about twelve times its full size, and we learn from it that at a distance from the centre of the coil equal, say, to 0.4 of the half length of the needle, the smallest convolution should have a radius about 0.75 of the half length of the needle, and that the wire must not be wound close to the axis until the distance from the centre along the axis is about 0.72 of the half length of the needle.

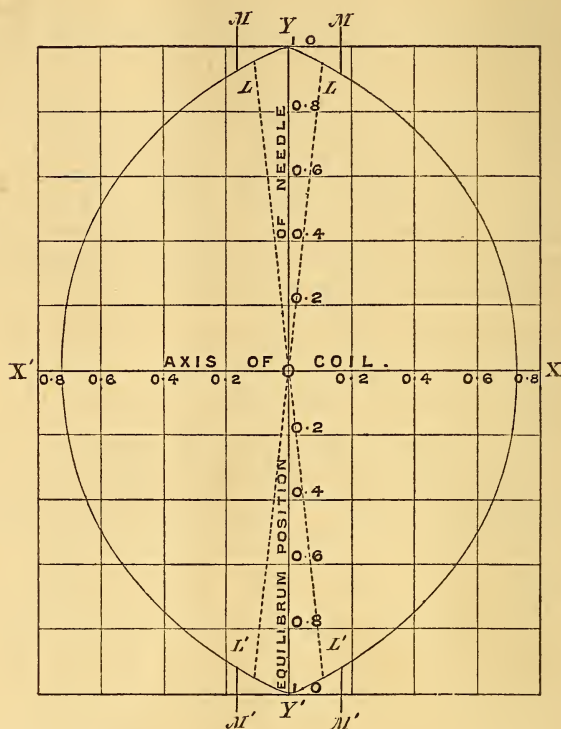
With an ordinary reflecting-galvanometer the needle requires to have a free angular space for turning of about 15°, represented by the space between the two lines LOL'. In this region the radii of the smallest convolutions must be a little greater than theory allows, otherwise the needle would touch the coils, and generally a sufficiently near approximation can be made to the cavity which theoretically ought to be left unwound by making it an oblate spheroid with a polar axis about 0.72 of its equatorial diameter, the latter being of course slightly larger than the length of the needle.

*Phil. Mag.* S. 5. Vol. 30. No. 182. July 1890. F



Since winding wire inside the surface whose section is given in fig. 4 would oppose the effect of the wire wound outside this surface if the current flowed in the same sense

Fig. 4.



Shape of cavity to be left unwound inside the coil when the length of the magnetic needle is 2.

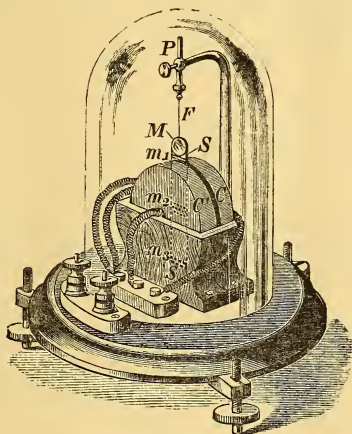
throughout the whole coil, it is possible, by causing the current to circulate in opposite directions in the two portions, to wind all the space and to cause all the convolutions to help one another. This we have not yet tried, but in view of the fact that the space which has been left unwound in the galvanometers constructed according to Mr. Mudford's suggestion is very near the needle, and therefore very valuable, it seems important to try and utilize it in the way just suggested. In that case the surface we have theoretically determined would be the surface separating the coil into two parts, wound respectively in opposite directions.

As the coils of a reflecting-galvanometer have to be supported by a central framework, there is necessarily a certain distance left between the coils when they are in position. This space we find when drawn to scale is that contained between the two vertical lines  $MM'$ , and which therefore allows more than sufficient room for the needle to turn. Hence if the plan of opposite winding that we have suggested be tried, the face of the coils may be made quite plane and no portion whatever of the coils left unwound, even to allow the needle space to move.

### III. *Damping the Oscillations.*

Since no hole is left in the lower coil for the aluminium damper, as is the case with Messrs. Elliott's reflecting-galvanometers, a different mode of damping is adopted. The plan we find best is to attach the mirror  $M$  (fig. 5) to the

Fig. 5.



middle of a long vertical strip of mica,  $S$ , across the upper and lower ends and the middle of which the magnets  $m_1$ ,  $m_2$ , and  $m_3$  are fixed. Such an arrangement is also seen in position in the galvanometer shown in figure 6 later on. With this arrangement, which requires very little space, we find that when the controlling magnet is adjusted so that the periodic time of vibration is 7 seconds or more the spot of light does not visibly pass through the zero or the instrument is dead-beat, and even when the period is much shorter than this, the spot of light does not pass

through the zero more than twice\*. With galvanometers in which less damping is desired, a portion of the strip of mica is cut away, so as to make it narrower, and in extreme cases, when for example no damping is required, as in the case of a ballistic galvanometer, the mica strip is replaced by a vertical piece of wire.

With a ballistic galvanometer, especially when intended for teaching-purposes, it is desirable to have some easy means of adjusting the amount of damping. In the case of the galvanometer used by our students for experimenting on the variation produced in the swing of the needle of a ballistic galvanometer by variations in the amount of damping, this variable damping is effected by enclosing the mirror in a cell whose glass ends can be simultaneously made to approach or recede. This motion of the ends of the cell is effected by turning a milled head outside the instrument which works a right-and-left-handed screw inside.

In order to correct the throw of a ballistic galvanometer for the damping of the oscillations of the needle, it is well-known that it is necessary to multiply the sine of half the angle of throw by the expression

$$V = \frac{1}{\sqrt{1 + \frac{\lambda^2}{\pi^2}}} \sum \frac{\lambda}{\pi} \tan^{-1} \frac{\pi}{\lambda},$$

where  $\lambda$  is the logarithmic decrement of the oscillations. The value of this quantity when  $\lambda$  is so small that its square may be neglected is

$$V = 1 + \frac{1}{2}\lambda.$$

It seemed, however, desirable to work out the value of  $V$  more fully and also to express it in terms of the numerical ratio of each amplitude to its successor, since in this way the need of finding the Napierian logarithm is avoided. This we did at first by direct calculation, but while forming a table of values connecting  $V$  and the decrement we observed that the matter could be treated much more simply as follows:—

By taking logarithms of the complete expression for  $V$  we have

\* Quickness in the needle coming to rest, which is produced by using a powerful controlling field, must not, of course, be confounded with considerable damping, since, other things being the same, the decrement is the greater the weaker the controlling field and the slower the motion of the needle.

$$\log V = -\frac{1}{2} \log (1 + x^2) + x \tan^{-1} \frac{1}{x},$$

where

$$x = \frac{\lambda}{\pi}.$$

Differentiate both sides of this equation once, twice, and thrice with respect to  $x$  and substitute for  $x$  the value 0. We then obtain successively,

$$\frac{dV}{dx} = \frac{\pi}{2}; \quad \frac{d^2V}{dx^2} = \frac{\pi^2}{4} - 3; \quad \frac{d^3V}{dx^3} = \frac{1}{8}\pi^3 - \frac{9}{2}\pi.$$

By Maclaurin's theorem we then have

$$V = 1 + \frac{\pi}{2}x + \left(\frac{\pi^2}{4} - 3\right)\frac{x^2}{2} + \left(\frac{1}{8}\pi^3 - \frac{9}{2}\pi\right)\frac{x^3}{6} + \&c.;$$

or substituting for  $x$ , and working out numerically, we obtain

$$V = 1 + 0.5\lambda - 0.027\lambda^2 - 0.054\lambda^3,$$

which shows that until  $\lambda$  approaches unity the approximate value for  $V$  generally used is sufficiently accurate. Now if the ratio of the amplitude of any swing to that of its successor is  $(1+y)$  we have

$$\lambda = \log (1+y) = y - \frac{y^2}{2} + \frac{y^3}{3} - \&c.,$$

$$\lambda^2 = y^2 - y^3,$$

$$\lambda^3 = y^3.$$

Neglecting powers higher than the third, we obtain by substitution

$$V = 1 + 0.5y - 0.277y^2 + 0.130y^3,$$

from which we can at once calculate the value of the complete correcting factor when we have observed the decrement.

It is usual to determine the sensibility of a ballistic galvanometer either by the employment of an earth-inductor, or by discharging through the galvanometer a condenser charged to a known P.D. The first method, however, necessitates an *exact* knowledge of the horizontal or vertical component of the magnetic intensity at the spot, while the second requires an *exact* knowledge of the value of the capacity of the condenser and of the P.D. employed. But now that it is possible to obtain an ammeter calibrated with a high degree of accuracy, the simplest method of determining the sensibility of a ballistic galvanometer is to first calibrate it absolutely as a



galvanometer for measuring currents by direct comparison with the ammeter. Its absolute calibration as a ballistic galvanometer can then be determined from the fact that

The swing per micro-coulomb in scale-divisions

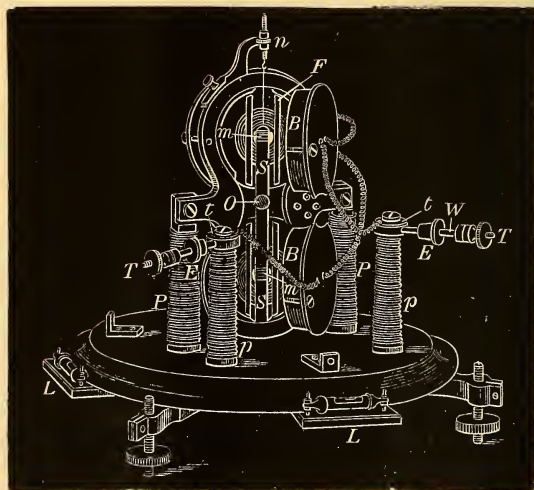
$$= \text{the deflexion per micro-ampere} \times \frac{2\pi}{T},$$

where T is the periodic time of oscillation of the needle in seconds.

#### IV. *Supporting the Coils.*

In olden days Messrs. Elliott supported the coils in their galvanometers by simply employing three long screws to squeeze each coil between a brass plate and the framework of the instrument to which the plate was screwed. The disadvantage, however, of such an arrangement was made painfully clear in the use of a galvanometer constructed by this firm for one of the authors in 1868. For on transporting this galvanometer across India, soon after it was made, the brass screws expanded more than the coils, and the coils consequently slipped down, shearing away the needles, the mirror, and the aluminium vane. It was therefore suggested to Messrs. Elliott that

Fig. 6.



the coils should be supported in boxes B, preferably hinged, as shown in fig. 6, so that when the coil-boxes are opened, as in this figure, the suspended system S could be got at and

even removed without detaching the connecting wires from the coils. The galvanometer shown in fig. 6 is, when in use, covered up by the brass case supporting the controlling magnet, illustrated in fig. 1.

Hinged boxes containing the coils of a reflecting-galvanometer appear to have been employed even earlier than this by Mr. Pepper, at the Polytechnic, but that form of construction was, apparently, in 1868 unknown to, or at any rate unused by, instrument makers.

In the case of galvanometers intended to be highly insulated, these hinged boxes may with great advantage be made of ebonite, and to prevent the boxes becoming electrified and acting on the suspended needle electrostatically, one terminal of the galvanometer should be joined to the outside brass case.

In the galvanometer shown in fig. 6, the boxes are kept closed by a screw which is screwed into the framework of the instrument, but in the galvanometer shown in fig. 7 this screw is replaced by a spring button, which is a more convenient arrangement.

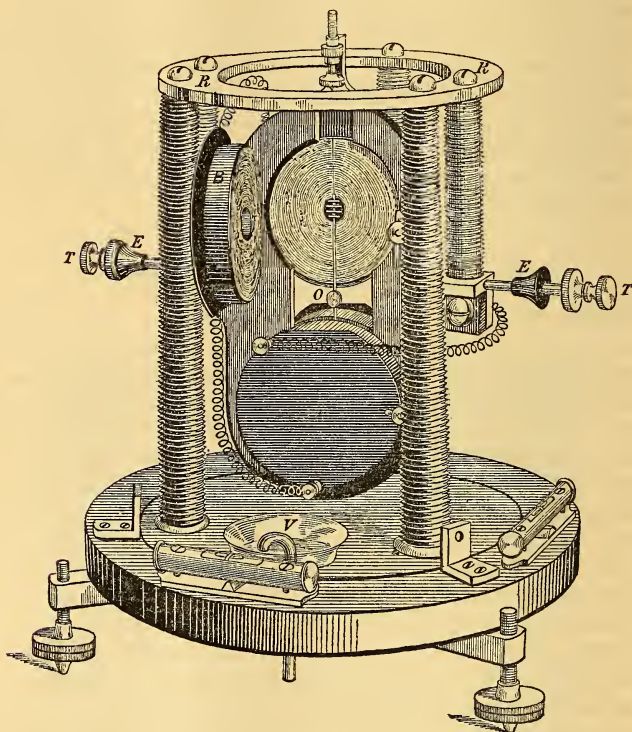
#### V. *Insulation of Coils and Terminals.*

In the ordinary method of constructing reflecting-galvanometers the wires are brought under the base to terminals fastened on to it. But such an arrangement is most unsatisfactory, since, no matter how thoroughly the upper part of the ebonite base may be cleaned and dried, leakage is almost sure to take place between the two wires, between the terminals, and between both the wires and the terminals to the ground along the inaccessible under surface of the ebonite base. In fact, when one of the authors was engaged, on behalf of the Indian Government, in 1872 testing telegraph insulators at Messrs. Siemens's works at Charlton, it was the common practice every morning to light a gas-burner near the galvanometer to dry it, and to diminish the leakage to a workable amount. And it appears to the authors that the form of expensive astatic reflecting-galvanometer, that is still made by some firms, with the wires underneath the base, is but a survival of the antiquated type of leaky electrostatic apparatus, to use which required that the whole air of the room should be first dried. Fig. 6 shows the obvious way of overcoming this difficulty, and which consists in supporting the framework and the coils of the apparatus as well as the terminals on paraffined corrugated ebonite pillars *p*, which are maintained clean and dry by their being kept entirely inside the brass cover of the instrument *Q* (fig. 1). The terminals *T* at the

ends of the wires W project through holes H in the brass case, these holes being kept closed by tightly-fitting ebonite collars C, fig. 1, E, fig. 6, when the galvanometer is not in use, or when it is being employed for some test where a small amount of leakage is not important.

Still higher insulation is obtained with the galvanometer shown in fig. 7, since in this instrument the coils are supported from two corrugated ebonite rods which hang from a brass ring R, carried on the top of three corrugated ebonite

Fig. 7.



Very high resistance galvanometer with brass case removed.

pillars fixed to the slate base-plate. This instrument, the four coils of which have a joint resistance of nearly 400,000 ohms, was constructed by Messrs. Nalder Bros.; but the device, by means of which the shortest path along which surface-leakage can take place from the coils, or from the terminals, to the base of the instrument is between 30 and 40 inches of ebonite

artificially dried by sulphuric acid, is due to Messrs. Eidsforth and Mudford. To prevent any possible overflowing of the sulphuric-acid vessel, a syphon passes through the base on the Tantalus cup principle, and which empties the liquid when it rises to the level of the bend of the syphon.

## VI. *Proportionality of Deflexion and Current.*

Some authorities are of opinion that it is of comparatively little consequence what is the law connecting deflexion and current, since for very accurate work any galvanometer must be carefully calibrated experimentally, and the exact law connecting deflexion and current thus ascertained. But, on the contrary, although the necessity of calibration for accurate work is perfectly true, experience has shown us that for ordinary practical work much time is saved if the readings on the scale are approximately, even if not quite accurately, proportional to the currents producing them. This latter result can, of course, be obtained either by fitting the lengths of the divisions on the scale to the peculiarities of the galvanometer, or by starting with a uniformly divided scale and constructing the galvanometer in such a way that equal additions to the current produce equal angular deflexions.

In certain cases, when, for example, the galvanometer is mainly employed for measuring currents all having about one definite value, as for example in the case of a voltmeter used on an electric-lighting circuit, it is obviously desirable to have the scale widely extended at the part where it is most used, and to obtain this result it is better to have the divisions crowded together elsewhere. But, since the power of accurately subdividing the spaces on a scale by eye is much increased if all the spaces be of equal length, it is preferable, in the case of galvanometers for general use, and when all parts of the scale are equally valuable, to judiciously construct the galvanometer in such a way that the whole scale may be divided into equal distances which are directly proportional to equal increments of current, than to give the coils and needle a shape arrived at in a haphazard fashion, and then attempt to experimentally subdivide the scale to suit the vagaries of the galvanometer.

In a former paper communicated by Prof. Perry and one of the authors to this Society, it was pointed out that while a galvanometer may be a "proportional" instrument if the zero for no current be that corresponding with the needles being in a symmetrical position to the coils, the same instrument may be very far from proportional if the zero for no current



be taken at one end of the scale and the spot of light deflected right across the scale for increasing currents, since in this latter case a variation in the law occurs as the plane of the needles passes through the symmetrical position. This want of proportionality is exhibited by the following figures :—

Ordinary Reflecting-Galvanometer.

Deflexion from one end of the Scale.	Relative Strength of Current.	Error.	Percentage Error.
0	0	0	
60	62.0	+2.0	3.4
120	121.0	+1.0	0.8
180	181.5	+1.5	0.9
240	242.5	+2.5	1.0
300	303.0	+3.0	1.0
360	363.5	+3.5	1.0
420	423.5	+3.5	0.8
480	483.0	+3.0	0.7
540	542.0	+2.0	0.4
600	600.0	0	

This defect is even more marked in some parts of the scale with the ordinary d'Arsonval galvanometer when the zero for no current is at one end of the scale. This instrument, as usually made by Messrs. Carpentier, has a tubular iron core supported from a standard which carries the top suspension of the coil, and the stationary permanent magnets are not provided with pole-pieces. In consequence of the core and the suspension not being supported independently, there is great difficulty in centering the coil relatively to both the core and the stationary magnets ; further, neither the core nor the coil can be readily removed. And partly because of this difficulty of centering the coil, partly because its centre of gravity is generally not in the line of suspensions, and partly because the stationary magnets have no properly shaped pole-pieces, there is (as may be seen from the following sample of the results of many experiments we have made on d'Arsonval galvanometers) an error in different parts of the scale far less regular in its value than in the case of the ordinary reflecting-galvanometer with stationary coil.

## Ordinary d'Arsonval Galvanometer.

Deflexion from one end of Scale.	Relative Strength of Current.	Error.	Percentage Error.
0	0	0	
60	59	-1	-1.7
120	118.5	-1.5	-1.3
180	180	0	0
240	240.6	+0.6	+0.2
300	300	0	0
360	359.8	-0.2	-0.06
420	416.5	-3.5	-0.8
480	473.5	-6.5	-1.4
540	537	-3	-0.6
600	600	0	

We find that it is possible, however, to obtain with a d'Arsonval galvanometer a far more exact proportionality between the deflexion and the current than is given in the preceding table by:—

Supporting the coil independently of the iron core, so that fairly accurate centering becomes possible. This result has been to a certain extent accomplished in the small type of d'Arsonval galvanometer constructed by Messrs. Nalder.

Allowing the coil to hang freely from the top suspension so that the centre of gravity of the coil is always in the axis of rotation. Electric continuity at the bottom of the coil is then maintained by a spiral of fine wire offering little torsional rigidity.

Fitting iron pole-pieces to the stationary magnets, and shaping these pole-pieces so that the rate of cutting lines of force by the moving coil is practically constant.

The following gives the results of tests made on a d'Arsonval galvanometer constructed in this way, each divisional length on the scale being 1.05 millim., so that the total deflexion of 600 divisions represented a motion of the spot of light over about 63 centimetres, or about 25 inches. The deflexion could be read easily to 0.2 of a division, and it will be observed that the greatest want of proportionality is only 0.15 per cent., which occurs with a deflexion of 480 scale-divisions.

## Improved d'Arsonval Galvanometer.

Deflexion from one end of Scale.	Relative Strength of Current.	Error.	Maximum Percentage Error.
0	0	0	0.15
60	60	0	
120	119.9	-0.1	
180	179.8	-0.2	
240	239.9	-0.1	
300	299.8	-0.2	
360	360.2	+0.2	
420	420.5	+0.5	
480	480.7	+0.7	
540	540.5	+0.5	
600	600	0	

To improve the magnetic circuit in d'Arsonval galvanometers some English makers replace the original tubular core by a solid iron core; and Messrs. Jolin of Bristol form the core of a series of short horizontal magnets laid vertically one above the other. A comparison that we have made of the sensibilities of the instruments constructed in these different ways has not shown that the English instruments are superior in this particular respect to the French. This may be, however, due to the fact that the horseshoe permanent magnets employed by the English manufacturers are inferior to those used by Messrs. Carpentier.

The ordinary methods adopted for attaching the suspension wires of the d'Arsonval coil to the supports seem to have been designed with total disregard of the fact that these wires convey the current into and out of the coil. This is particularly serious when a d'Arsonval galvanometer is used as a voltmeter, especially when it is employed to measure a small fraction of a volt, and when therefore the total resistance in the circuit must be small.

In fact we have found that before any reliance can be placed on the indications of a d'Arsonval galvanometer employed in this way, it is necessary to solder all the joints. And instead of trusting to contact through the supports to which the torsional suspension-wires are attached, we have found it desirable to solder wires coming from the terminals of the instrument directly to the hooks to which the suspension-wires are attached. Perhaps the best plan is to solder wires at one of their ends to the terminals of the instrument, and at their other ends to an extension of the torsional suspension-wires.

In devising very low-resistance d'Arsonval galvanometers

careful consideration must be given to the suspension-wires which lead the current into and out of the moving coil, since being usually made of German silver they may easily become slightly heated by the relatively large current employed with a very low resistance-galvanometer, and in consequence their elasticity temporarily diminished. This would of course have the effect of making the instrument more sensitive for large currents than for small; but as the sensibility for large currents would, until a limit was reached, increase with the time the current was kept flowing through the galvanometer, such an instrument could not be used for accurate measurement. One method of overcoming this difficulty is to make the suspension of very thin phosphor-bronze strip, such as is employed in the construction of delicate "Ayrton and Perry magnifying-springs." For a thin strip has, for its cross-section, a very small torsional rigidity and a very large radiating surface, and therefore is the very thing to employ when we want a conductor with small torsional rigidity, and which will be very slightly raised in temperature by the passage of a current through it.

D'Arsonval galvanometers, when used as voltmeters, are subject to the error that affects all electromagnetic voltmeters arising from a variation of the resistance of the coil due to a variation in the temperature of the room; if, however, both the coil and the suspension-wires are made of platinum-silver, a very curious compensating effect is brought about, since the percentage increase of resistance with temperature of platinum-silver is almost exactly equal to the percentage diminution in its torsional rigidity. Hence when a rise of temperature diminishes the current flowing through the instrument for a given P.D. maintained at its terminals and so diminishes the deflecting couple, a proportional diminution in the torsional rigidity of the suspending wires, and therefore in the controlling couple, is produced at the same time. *It is thus possible to construct an electromagnetic voltmeter of one metal only, which has no temperature error.*

## VII. Sensibilities of Different Types of Galvanometers.

Apart from differences in detail (as, for example, in the size, shape, or number of the coils, &c.), galvanometers may be divided into four distinct classes, viz.:—

1. Galvanometers in which the moving system consists of one or more magnetic needles turning about an axis at right angles to the magnetic axes of the needles.
2. Galvanometers in which the needles have a motion of



translation along their own magnetic axes, the magnetic needles being drawn into, or pushed out of, coils acting like solenoids.

3. Galvanometers in which the magnetic system is stationary, and the moving system consists of a coil turning about an axis on its own plane.
4. Instruments based on the heating of a conductor by the passage of a current through it.

Type 1 includes tangent-galvanometers, Thomson's reflecting-galvanometers—in fact, so many well-known instruments that further description is unnecessary. In addition to galvanometers with straight magnetic needles, it may be noticed that

Fig. 8.

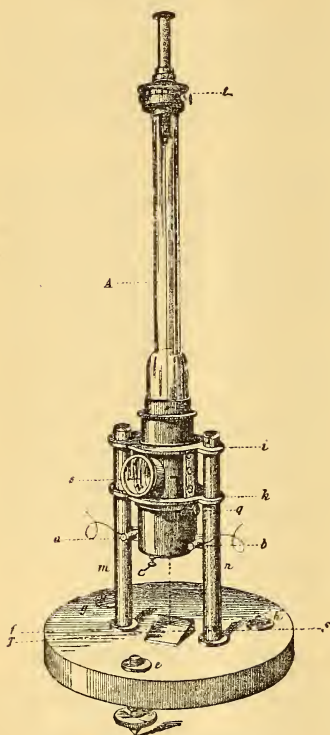
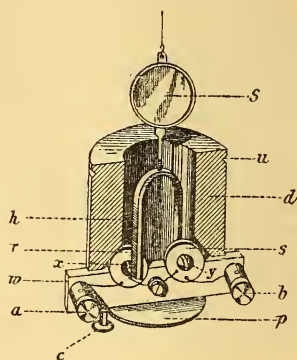


Fig. 9.

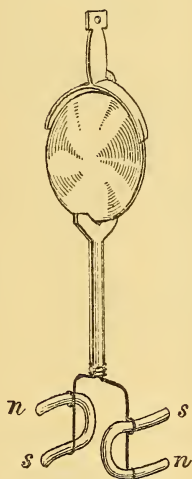


type 1 also includes instruments containing a bell-shaped horseshoe-magnet; since the bell-shaped magnet is only a device for producing the equivalent of a very powerful and permanent short flat magnet.

We may here mention that the instrument shown in fig. 5 is spoken of in this paper as a galvanometer with "one pair of coils," while those illustrated in figs. 6 and 7 are referred to as having each "two pairs of coils."

Type 2 has been employed by Lord Rayleigh, the Profs. Gray, Mr. Rosenthal, by ourselves, and others. Figs. 8 and 9 illustrate an instrument of this type, constructed by Messrs. Edelmann of Munich, and called a Rosenthal Micro-galvanometer, since this instrument has the peculiarity that the coils into which the ends of the magnet are sucked are extremely small, having an *outside* diameter of only 11 mm. and a thickness of 2 mm. Fig. 9 shows the suspended magnet of the Rosenthal galvanometer as constructed by the makers, the arrangement being non-astatic; but we have also made and used with this galvanometer an astatic combination, constructed as in fig. 10.

Fig. 10.

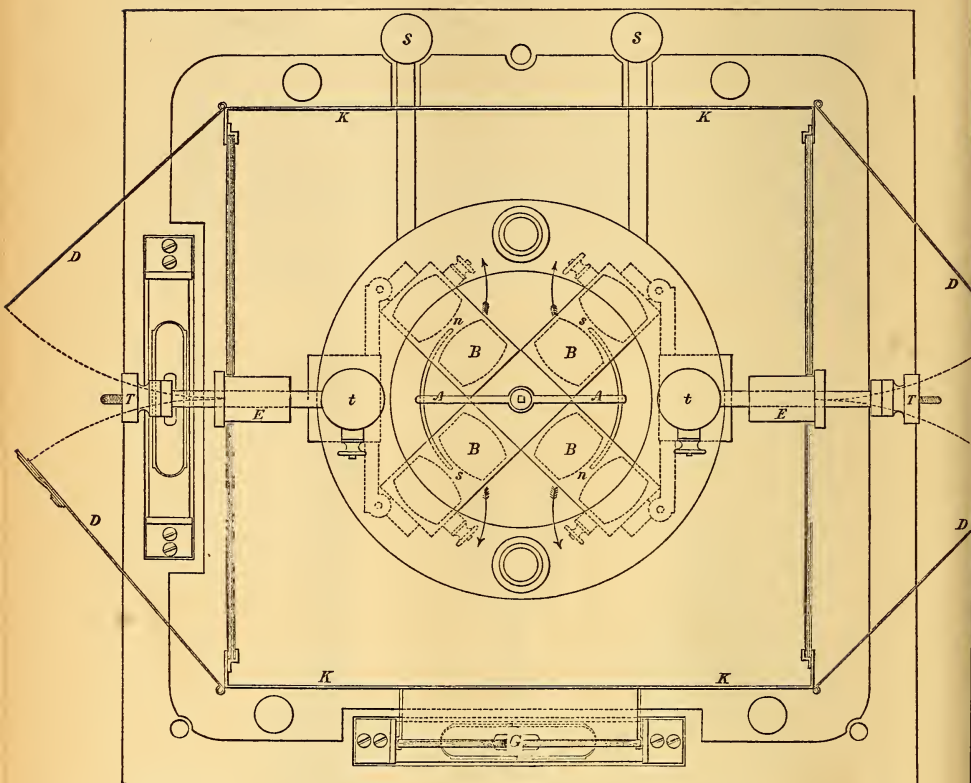


Mirror and astatic pair of needles for the Rosenthal Micro-galvanometer.

Figs. 11 and 12 show, in plan and elevation, a ballistic galvanometer constructed for the Central Institution by Messrs. White of Glasgow, from drawings made by us in consultation with Prof. T. Gray. The needles *ns, ns*, which are arranged so as to produce an astatic combination, are each at one end sucked into a coil and at the other end pushed out of a coil, the coils being contained in four small, rectangular, hinged boxes, *B*, which are kept closed by spring catches. The vertical

aluminium wire, to which is screwed the aluminium bridge AA (fig. 11), supporting the needles, carries on one side

Fig. 11.

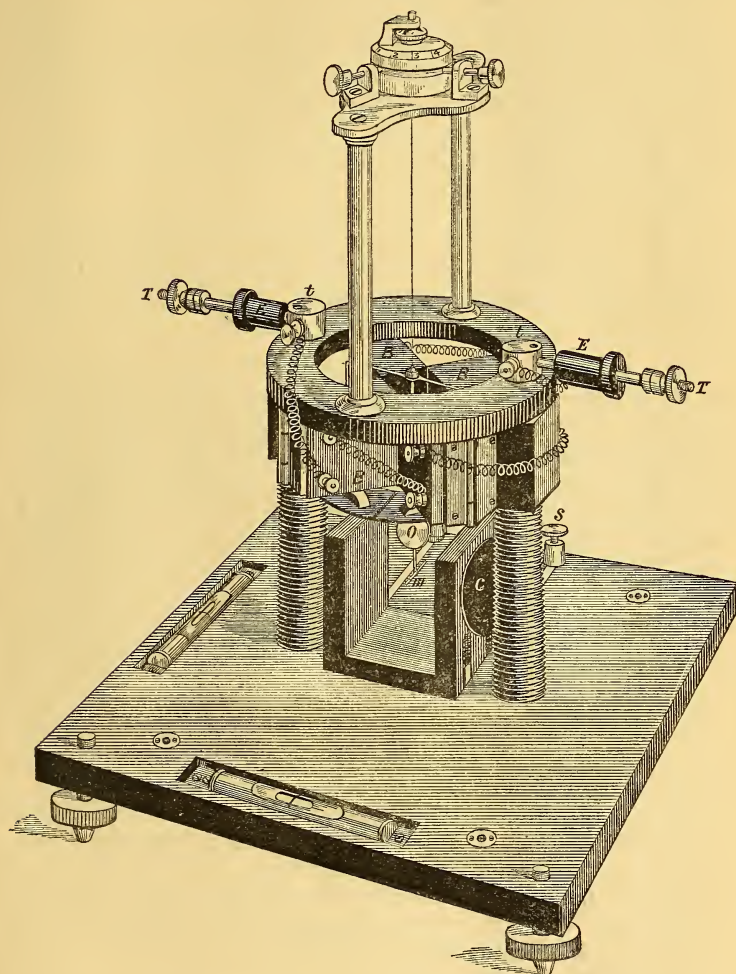


Plan of Ballistic Galvanometer.

of its lower end a concave mirror O (fig. 12) to produce a spot of light on a scale, and on its other side a truly plane mirror, to be viewed with a telescope, if desired. At its lower end it carries a small magnetic needle, *m*, to be acted on by a pair of coils, C, joined up in series and having their ends led to the terminal screws, *s*, *s*. These coils are quite independent of the main coils of the instrument, and are employed for damping the oscillations of the suspended system. With ballistic galvanometers previously made for us we have not had any such damping-coil attached; but since to all our galvanometers

which are used ballistically it has been found convenient to provide a damping-coil, operated with an auxiliary small cell and roughly-made reversing-key, for the purpose of expediting

Fig. 12.



Perspective elevation of Ballistic Galvanometer with brass case removed.

measurements, we think that such a damping-coil should be attached, by the makers, to every ballistic galvanometer.

The brass case, K, has hinged brass doors D, D, D, D at its sides, to protect the glass windows; and both doors and  
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windows have holes in them to allow the terminals T, with their ebonite collars E, to be screwed into the brass terminal blocks, *t, t*. At the front of the instrument there is a circular plate-glass window G, to allow the light to pass through, and protected by a brass cap when not in use.

Type 3 includes the well-known d'Arsonval galvanometers, with the modification described to this Society some two years ago for obtaining "invariable sensibility" by replacing the ordinary torsional suspension with one having extremely small torsional rigidity, and inserting a number of small magnets in the moving coil, which, being attracted by the large stationary magnet, produce the control.

Type 4 we do not propose touching on in this paper, as that type of instrument formed the subject of communications previously made to this Society by Prof. Perry and by one of the authors on "Hot-Wire Voltmeters" and "Twisted Strip Voltmeters."

It is important that the results of the numerous tests on many specimens of each of the first three types of galvanometer that have been carried out in the laboratories of the Central Institution, as well as the tests that have been made elsewhere, and the results of which we have collected together, should be reduced to the same standard; so that the relative merits of the different types of galvanometer, as well as of the different specimens of each type, should be able to be usefully compared. A satisfactory standard of comparison, however, cannot easily be arrived at; and we are not aware that the question of comparing galvanometers of totally different types has previously received much attention. The "figure of merit" of a galvanometer is sometimes defined as "the amount of current which will produce one division or degree of deflexion"\*. But although the figure of merit, so defined, tells us the sensibility of a particular galvanometer with a particular adjustment of the controlling magnet, and with a particular distance of the scale, it gives us no means of comparing this galvanometer with other forms, since this figure of merit can be varied by altering the position of the controlling magnet &c.—in fact, is not a constant of the particular galvanometer. Something much more definite than this is therefore required for our purpose.

A little consideration shows that the sensibility of a galvanometer in actual practice is made up of many factors, some of which depend on the skill of the experimenter himself. In view of the sensibility of any particular galvanometer being a

\* 'A Handbook of Electrical Testing,' by H. R. Kempé.

complex result depending on many factors, it is desirable to record the results of experiments on galvanometers in such a form that the influence of each factor can be separately estimated. We have therefore endeavoured to distinguish, as far as possible, the three chief causes that affect the sensibility of reflecting-galvanometers, viz. the arrangement and winding of the coils, the construction of the magnetic system, and the optical method of magnifying the angular deflexion produced. With the same view the question of the susceptibility of various galvanometers to outside magnetic disturbances has been considered separately, since, first, the electrical qualities of the instrument are not altered by such disturbances, and, secondly, their influence is dependent, not only on the kind of instrument, but on the place of test. In the Table that is given later on recording the results of a large number of experiments, we have classified galvanometers in four divisions of decreasing susceptibility to outside magnetic disturbance, comprising :—

*Non-astatic instruments working in a weak field having strongly magnetized needles.*

*Non-astatic instruments working in a strong field and having somewhat weakly magnetized needles.*

*Astatic galvanometers, working in a fairly strong field.*

*Galvanometers of the d'Arsonval type, working in an extremely strong field.*

At the end of the Table are given the constants of a collection of non-reflecting instruments. These instruments, being all of a rougher type, have been simply grouped together at the end of the list ; consequently their position on the list has no reference to their sensitiveness or unsensitiveness to outside magnetic disturbance.

The optical sensitiveness of an instrument is dependent on many conditions that have no necessary connexion with the electromagnetic qualities of the instrument ; for example, the goodness of the mirror, the brightness of the light, the distance of the scale, &c. are important factors. We have therefore given the number of scale-divisions per micro-ampere or per micro-coulomb, assuming the scale to be placed at a distance from the mirror equal to 2000 scale-divisions. As the scale-distance most generally used is a metre, and as the scale-divisions are frequently in half-millimetres, the conditions assumed are often fulfilled in practice. The sensibilities for a steady current, and for a discharge, are thus directly expressed in angular measure, irrespective of optical magnification.

An important and difficult question to decide is whether the factor of merit of a galvanometer should be stated for a constant periodic time of oscillation of the suspended system, or for a constant controlling-moment for unit angle-deflexion, or for a constant controlling-field irrespective of the magnetic moment of the suspended system. The first condition is the most simple to realize experimentally with different instruments, and the results so obtained are the most convenient for use in subsequent calculations; this condition is, further, the one most easily understood. We therefore give, in columns 3 and 4, the values of  $D$  and  $S$ , which respectively denote the deflexion per micro-ampere and the swing per micro-coulomb, each in scale-divisions, when the period is 10 seconds and the scale-distance is 2000 scale-divisions. The corresponding values at any other period  $T$  are of course  $DT^2/100$  and  $ST/10$ . It would, however, be unfair to rest satisfied with the results given in these tables for the purpose of comparing different galvanometers. For a galvanometer having a large mirror, and intended to be used at a considerable distance from the scale, would appear to be an inferior instrument, because on the one hand the large moment of inertia of the mirror would necessitate the controlling-moment being large to reduce the period to 10 seconds, while, on the other hand, the magnification arising from the much greater distance that separated, in practice, the scale from this particular galvanometer would have no weight in the values given in the columns for  $D$  and  $S$ . We have therefore given in column 2 the values of  $M$ , which are the millimetres deflexion per micro-ampere when the period is 10 seconds and the scale placed as in the ordinary use of the instrument. We have further, in the following way, reduced the numbers to their corresponding values under the condition of *constant controlling-moment*, the condition of constant controlling-field being rejected, because it is inapplicable to instruments of the d'Arsonval type.

The periodic time  $T$  equals

$$2\pi\sqrt{\frac{\text{Moment of inertia} \times \sin \theta}{\text{Controlling-moment for a deflexion } \theta}};$$

therefore, in order to obtain the comparative deflexions that would be obtained with the same controlling-moment per unit angle, we must find the deflexions that would be produced with periodic times proportional to  $\sqrt{I}$ , where  $I$  is the moment of inertia of the suspended system, the values of which for the various galvanometers are given approximately in C.G.S. units in column 6. Hence, to obtain the values in columns 7 and 8, which give numbers respec-



tively proportional to the steady deflexion per micro-ampere and the first swing per micro-coulomb for the same controlling-moments for all galvanometers, we must multiply  $D$  by  $I$  and  $S$  by  $\sqrt{I}$ . Now the stability of the zero of any galvanometer depends on the controlling-moment per unit angle of deflexion; hence columns 7 and 8 give numbers proportional to the angular deflexion per micro-ampere and the angular swing per micro-coulomb for the same amount of stability of the zero for all the instruments. The periodic times, however, will be very different for the different numbers either in column 7 or for the different numbers in column 8, the periodic time corresponding with any particular number being equal to  $10\sqrt{I}$  seconds, where  $I$  is the moment of inertia given in column 6 for the particular instrument in question. For example, the numbers 3200 and 283, given in columns 7 and 8 for Profs. T. and A. Gray's galvanometer, correspond with a periodic time of  $10\sqrt{50}$ , or about 70 seconds; while the numbers 542 and 3400, given in the same columns for the 360,000-ohm galvanometer at the Central Institution, correspond with a periodic time of only  $10\sqrt{0.01}$ , or 1 second. The numbers, then, in columns 7 and 8 give a fair comparison between the various galvanometers when the time required to take an observation is unimportant.

The influence of resistance has next to be considered. If two galvanometers differ only in the gauges of wire with which they are wound, and the convolutions are similarly distributed, then the sensibilities should be proportional to the number of turns. If, again, the thickness of the insulating covering bears a constant proportion to that of the wire, then the resistance of the coils would be proportional to the square of the number of turns; so that the values of  $D/r^{\frac{1}{2}}$ ,  $S/r^{\frac{1}{2}}$  would be constants for the same pattern of instrument, where  $D$  and  $S$  are the number of scale-divisions per micro-ampere and micro-coulomb respectively, and  $r$  is the resistance of the galvanometer. The proportion in question, however, varies not only for coils of different resistances, but also in the same coil, for several different gauges are generally used in winding the various portions. To get some idea of the relation between resistance and sensibility, we have made tests on galvanometers of the same pattern but of different resistances, the same suspended system of magnets being used successively in each instrument, the controlling magnet being adjusted to produce the same periodic time in each experiment, and, when the galvanometers were reflecting ones, the scale being placed at the



same distance from each of the instruments. The following were the results obtained with three astatic reflecting-galvanometers having coils of exactly the same size in each case, but of very different resistance.

Resistance of Galvanometer, in ohms.	D.	$D/r^{\frac{1}{2}}$ .	$D/r^{\frac{2}{3}}$ .
26	349	68.5	94.4
2457	2160	43.5	95.4
6410	3360	42	101

From this it would appear that, if the only thing altered in a galvanometer be the gauge of wire with which it is wound, the sensibility is more nearly proportional to the resistance raised to the power  $\frac{2}{3}$  than to the resistance raised to the power  $\frac{1}{2}$ .

Another set of experiments was now made with four non-astatic galvanometers, the coils of each of which were made in the same mould, totally different, however, in shape from that employed in constructing the coils of the three reflecting-galvanometers given in the last list. When tested with the same suspended system, the controlling magnet being adjusted to produce the same periodic time in each case, the following results were obtained :—

Resistance of Galvanometer, in ohms.	M, Fraction of one degree per micro-ampere.	$M/r^{\frac{1}{2}}$ .	$M/r^{\frac{2}{3}}$ .
0.87	0.0149	0.01597	0.0157
4.30	0.0333	0.01604	0.0185
64.23	0.1120	0.01397	0.0246
399.25	0.2700	0.01352	0.033

In this case the sensibility appears to be more nearly proportional to  $r^{\frac{1}{2}}$  than to  $r^{\frac{2}{3}}$ . We have, therefore, in the large table given two columns, one (No. 9) for  $D/r^{\frac{1}{2}}$  and one (No. 10) for  $D/r^{\frac{2}{3}}$ , which represent (according as  $r^{\frac{1}{2}}$  or  $r^{\frac{2}{3}}$  may be regarded as the more accurate divisor to employ) the deflexion per micro-ampere on a scale whose distance is

2000 scale-divisions for a periodic time of 10 seconds that would be obtained if all the different forms of galvanometers were wound with such a gauge of wire that the resistance of each instrument was 1 ohm. Column 11 gives the swing per micro-coulomb on the same hypothesis, but in this case we have only used  $r^{\frac{2}{3}}$  as the divisor.

And whereas columns 9, 10, and 11 give the relative values for the same periodic time, columns 12 and 13 give the deflexion per micro-ampere and the swing per micro-coulomb on a scale whose distance is 2000 scale-divisions for *the same controlling-moment* that would be obtained if all the galvanometers had 1 ohm resistance—the periodic time in any case being equal to  $10 \sqrt{I}$  seconds,  $I$  being the moment of inertia of the suspended system given in column 6.

Another question to be considered is the factor of merit in connexion with the volume of the coils. As this is important as regards the cost of high-resistance galvanometers, a separate column (5) is therefore given, showing the approximate volume in cubic centimetres occupied by the wire in each instrument, and other columns (14, 15, 16, 17) give the values obtained by dividing this quantity into the various factors of merit. The results of comparison in these latter columns are very interesting. It appears that galvanometers of the Rosenthal or Gray and the d'Arsonval types are by far the most sensitive in proportion to the volume of coil; and we believe that the best way to make a very sensitive galvanometer with a movable magnetic system is to employ several small coils, instead of one or two large ones\*, and that the magnets should be horse-shoe-shaped, with the line joining the poles vertical, as in Prof. Gray's instrument, but modified so as to give smaller moment of inertia. Such a magnetic system can be made very delicately astatic, and the weakening of the magnets with time does not greatly influence the astaticism. We also conclude from our investigations that the most sensitive galvanometer of all would be one of the d'Arsonval type suitably modified. The poles of the magnet should be very close together, the coil should be very long and narrow, and no stationary iron core should be used inside the coil as in the ordinary d'Arsonval galvanometer. The sensitiveness could be further increased by employing electro-magnets instead of permanent ones to produce the deflecting field, the current flowing round the electro-magnet being kept constant by means of an auxiliary reflecting

\* Mr. C. V. Boys, F.R.S., in his Cantor Lectures on "Instruments for Measuring Radiant Heat" (April 1889), has also shown that galvanometers with small coils may be made very sensitive (pp. 22, 23).

"set-up ammeter" producing an image on the same scale as is used for the electromagnetic d'Arsonval galvanometer. With a "set-up ammeter" the suspended system is supported by means of an almost torsionless phosphor-bronze strip, requiring many twists to be given to it to bring the spot of light on to the scale when the current, that is to be kept constant, is flowing through it. A motion, then, of the spot of light over 100 divisions of the scale corresponds perhaps to a variation of only  $\frac{1}{210}$  in this current; and consequently, by means of such an instrument and a suitable adjustable resistance, a current can be kept constant to a very small fraction per cent.

It might be objected to our conclusions that, in the papers read by Prof. Threlfall before this Society, and published in the 'Philosophical Magazine' for December 1889, he comes to the conclusion that coils used in what we may shortly call the Mudford way (figs. 5, 6, and 7) give greater sensibility than when used in the Gray way (figs. 8-12). But on studying Prof. Threlfall's papers we find that, from various numerical errors, he makes his coils when used as a Gray galvanometer one ninth as sensitive as they really were, and when used as a Mudford galvanometer seventeen times as sensitive as they were; so that Prof. Threlfall's ratio of the sensibility of the Gray galvanometer to the sensibility of the same coils when used as a Mudford galvanometer requires to be multiplied by the very large number 153\*.

In order to correct Prof. Threlfall's calculations, the following alterations must be made:—

Phil. Mag., Dec. 1889: Page 465, line 11, *for* "The current was therefore  $1.26 \times 10^{-7}$  amperes," *read* "The current was therefore  $1.43 \times 10^{-8}$  amperes."

Same page, line 25, *for* " $2.5 \times 10^{-8}$  amperes" *read* " $2.8 \times 10^{-9}$  amperes."

Page 469, line 1: "The galvanometer having been brought to a state of sensitiveness of 5 scale-divisions for  $10^{-11}$  amperes, the measurement of the resistance of the sample of sulphur in question became a tolerably easy matter." On examining, however, the results obtained in the actual measurements with the sulphur (p. 471), we find that the sensibility of the galvanometer was not as above stated, 500,000 divisions per micro-ampere, but 34,200. And, as his scale was 3 metres away from the galvanometer, and his scale-divisions 1 millim., this number 34,200 reduced to our standard becomes 22,800†.

\* These errors were also noticed by Prof. A. Gray, and referred to in an article in the Phil. Mag. for February 1890.

† Prof. Threlfall says, in a letter published in the Phil. Mag. for June 1890, in reply to these criticisms, that his galvanometer was not in a state

EXPLANATION OF TABLE.

$r$ =resistance in ohms.

$M$ =millimetres deflexion per micro-ampere when the period is 10 seconds, and the scale is placed as in the actual use of the instrument.

$D$ =deflexion in scale-divisions per micro-ampere when the period is 10 seconds, and the scale-distance is equal to 2000 scale-divisions.

$S$ =swing produced per micro-coulomb under the same conditions as in last.

$V$ =volume occupied by the convolutions of wire, in cubic centimetres approximately.

$I$ =moment of inertia of the suspended system, in C.G.S. units approximately.

$DI$ =deflexion in scale-divisions (scale-distance equal to 2000 scale divisions) per micro-ampere for constant controlling moments, and for a periodic time equal to  $10\sqrt{I}$  seconds.

$SI^{\frac{1}{2}}$ =swing per micro-coulomb under the same conditions as in last. Columns 9, 10, and 11 give the deflexion per micro-ampere, and the swing per micro-coulomb, when the period is 10 seconds and the resistance of each instrument one ohm.

Columns 12 and 13 give the deflexion per micro-ampere and the swing per micro-coulomb, for the same controlling moment, and for the resistance of each instrument equal to one ohm.

Columns 14 and 15 give the deflexion per micro-ampere and the swing per micro-coulomb per cubic centimetre of coil, when the period is 10 seconds and the resistance of each galvanometer one ohm.

Columns 16 and 17 give the deflexion per micro-ampere and the swing per micro-coulomb per cubic centimetre of coil, for the same controlling moment, and the resistance of each galvanometer equal to one ohm. Periodic time of any instrument is  $10\sqrt{I}$  seconds.

C.I., Central Institution.

F.T.C., Finsbury Technical College.

† The constants of these instruments have been kindly furnished by the makers.

‡ These instruments were tested after being in use for some time and without their needles being remagnetized.

\* These numbers are calculated from those given in column 3.

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of maximum sensibility when used for these experiments on sulphur. Granting this, and looking at the observations given on page 472 of the *Phil. Mag.*, vol. xxviii., from which the constant of the galvanometer was determined, we find that there was considerable vagueness of the zero, amounting in some cases to more than 4 per cent. of the double deflexion, as well as a gradual change in the position of the zero from 105 to 78. If, then, the control were diminished to about  $\frac{1}{1.7}$  of the value it then had, and which would be necessary to give the galvanometer the sensibility claimed for it, the vagueness of the zero would probably become too serious for the instrument to be used for any but the very roughest measurements.



		1.	2.	3.	4.
Type.	Description.	r.	M.	D.	S.
Thomson. One pair of coils.	Elliott's Tripod (F.T.C.) † .....	0.6	3.8	7.6	4.76*
	Tripod " † .....	50	102	204	128*
	Elliott's Tripod. Specially light needles † .....	3860	7550	15,400	9,700*
	.....	6000	15,750	32,000	20,000*
Thomson. Two pairs of coils.	Elliott's Glass Cylinder (F.T.C.) † .....	4600	1220	2440	1520*
	Latimer Clark & Muirhead (F.T.C.) † .....	20,000	8700	10,700	6720*
	Elliott's Stock pattern † .....	7000	4300	7110	4450*
	" Large Coil pattern † .....	12,300	7680	15,200	9550*
	" " " .....	30,000	10710	21,800	13,700*
	" Special form † .....	30,000	20,000	40,000	25,000*
	" Ayrton & Perry ballistic (Japan) .....	20,000	1070	1430	900
	Langley's Bolometer .....	20	125	250	156*
Mudford's Thomson. One pair of coils.	Figure 5 (C.I.) .....	26	347	349	220*
	" " .....	2,457	1375	2160	1360*
	" " † .....	6,410	2720	3360	2110*
	Bell Magnet Ballistic † .....	2086	880	1720	1080*
	" " " .....	7800	720	1350	850*
	Figure 5 (C.I.) " .....	10,000	640	1200	755*
	.....	5330	.....	2280	1440*
Mudford's Thomson. Two pairs of coils.	Figure 6 (F.T.C.) † .....	700	1720	2970	1860*
	" (C.I.) .....	686	1660	1600	1010*
	Variable damping Large Coils (C.I.) .....	9744	4200	4280	2640
	Figure 7 (C.I.) .....	360,000	50,000	54,200	34,000*
	" " † .....	350,000	15,700	31,400	19,700*
Rayleigh, Gray, or Rosenthal.	Figure 8, Non-astatic (C.I.) .....	44	22.9	25.4	16
	Figure 9, Astatic (C.I.) .....	44	25	27.7	17.4
	Non-reflecting (C.I.) .....	5.2	.....	9.06	5.7*
	Gray's (Proc. Roy. Soc. 1884, p. 287) ...	30,000	32	64	40*
	Figures 11 & 12 (C.I.) .....	4090	54	63	39.2
	Threlfall's (Phil. Mag. Dec. 1889, p. 460) .....	15680	2.90	3.74	2.35
d'Arsonval.	Jolin's High-resistance (C.I.) .....	750	137	260	163*
	Carpentier's ordinary .....	208	286	375	236*
	Jolin's Low resistance (C.I.) .....	3.8	39	42	26.4*
	Invariable sensibility, Large type (C.I.) ...	21	190	181	114*
	Nalder's type fitted	Pole pieces in (C.I.) " out "	.....	169	106*
	with Invariable-sensibility device.				
	Carpentier milliamperemeter (C.I.) .....	183	.....	73	45.7*
Flat Coil or Multiplier type.	Single Needle Post-office pattern (C.I.) ...	800	.....	190	119*
	Coils 6 centim. long outside	400	.....	303	190*
		350	.....	146	91.7*
		64	.....	125	78.7*
		4.3	.....	14.8	9.3*
		4.3	.....	35.2	22.1*
	Winding 0.6 " thick.	.87	.....	6.8	4.27*
		.87	.....	16.7	10.5*
	Detector nearly astatic † .....	2000	.....	490	308*
	" partially astatic † .....	2000	.....	42	26.4*

5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.
V.	I.	DI.	SI <sup>1/2</sup> .	D/r <sup>1/2</sup> .	D/r <sup>2/3</sup> .	S/r <sup>2/3</sup> .	DI/r <sup>2/3</sup> .	SI <sup>1/2</sup> /r <sup>2/3</sup> .	D/r <sup>2/3</sup> V.	S/r <sup>2/3</sup> V.	DI/r <sup>2/3</sup> V.	SI <sup>1/2</sup> /r <sup>2/3</sup> V.
.....	.....	.....	.....	10	9.4	5.9	.....	.....	.....	.....	.....	.....
.....	·04	81.6	25.6	28.7	42.8	26.9	17.1	5.4	.....	.....	.....	.....
125	·01	154	970	248	566	356	5.66	35.6	4.53	2.85	·045	·29
125	·01	320	2000	413	986	616	9.86	61.6	7.89	4.93	·079	·49
.....	.....	.....	.....	36	83	52	.....	.....	.....	.....	.....	.....
.....	.....	.....	.....	76	203	128	.....	.....	.....	.....	.....	.....
30	0.013	92	507	85	205	129	2.68	14.7	6.8	4.3	0.089	0.049
240	0.013	198	1090	137	350	220	4.53	25.2	1.46	0.91	0.019	0.10
240	0.013	284	1560	126	353	220	4.6	25.3	1.47	0.91	0.019	0.10
250	.....	.....	.....	231	648	405	.....	.....	2.67	1.60	.....	.....
.....	.....	.....	.....	10.5	27.3	17.1	.....	.....	.....	.....	.....	.....
.....	.....	.....	.....	56	76	47	.....	.....	.....	.....	.....	.....
72	·042	14	45	66.5	94.4	60	3.92	12.2	1.31	0.83	0.055	0.16
72	·042	91	284	43.5	95.5	60	4.00	12.3	1.33	0.83	0.055	0.16
72	·042	142	435	42	101	63	4.25	13.0	1.40	0.87	0.059	0.17
72	.....	.....	.....	37.6	81	51	.....	.....	1.12	0.71	.....	.....
.....	.....	.....	.....	15.3	37.3	23.5	.....	.....	.....	.....	.....	.....
.....	.....	.....	.....	12.0	30.2	19.0	.....	.....	.....	.....	.....	.....
72	·042	95.5	295	31.0	74.0	46.6	3.1	8.9	1.03	0.65	.....	.....
.....	.....	.....	.....	112	215	136	.....	.....	.....	.....	.....	.....
88	·084	134	293	61	118	74	9.81	21.5	1.34	0.84	0.011	0.24
200	·052	222	602	43.5	108	67	5.61	15.3	0.54	0.34	0.028	0.076
236	·01	542	3400	90	324	202	3.24	20.2	1.37	0.86	0.014	0.086
.....	.....	.....	.....	53.1	190	119	.....	.....	.....	.....	.....	.....
0.29	1.5	38	19.6	3.82	5.6	3.5	8.4	4.3	19.3	12.1	29.0	14.8
0.29	0.7	19.4	14.5	4.2	6.1	3.8	4.27	3.2	21	13.1	14.7	11.0
2.0	·21	1.91	2.61	4.0	4.7	2.94	·98	1.35	2.35	1.47	0.49	0.67
51	50	3200	283	0.37	1.04	0.6	52	4.6	0.02	0.012	0.10	0.09
36	17	1070	165	1.0	2.26	1.4	39	6.0	0.06	0.04	1.1	0.17
72	.....	.....	.....	·03	·078	·049	.....	.....	·00108	·00068	.....	.....
2.8	3.0	7800	895	9.5	18.4	11.5	55.1	6.3	6.6	4.1	19.8	2.2
.....	.....	.....	.....	26	44.3	27.9	.....	.....	.....	.....	.....	.....
0.6	5.5	230	62	21.5	25	15.5	134	36.3	42	26	225	61
0.96	13	2360	410	39.5	54	33.6	700	122	56	35	730	126
·2	1.5	254	129	10.2	17.7	11.2	27	13.7	88.5	56.0	135	68.5
.....	.....	.....	.....	14.6	25.5	16.1	.....	.....	.....	.....	.....	.....
3.2	25	1820	228	5.4	9.0	5.6	225	28	2.8	1.74	70	8.7
.....	.....	.....	.....	6.7	131	82	.....	.....	.....	.....	.....	.....
.....	.....	60.6	85	15.1	27.6	17.3	5.5	7.75	1.26	0.79	0.25	0.35
22	·2	29.2	41	7.8	14.0	8.8	2.82	3.94	0.64	0.40	0.13	0.18
.....	.....	25	35	15.6	23.8	14.9	4.75	6.65	1.08	0.68	0.21	0.30
.....	.....	2.96	4.1	7.1	8.25	5.18	1.65	2.28	0.37	0.23	0.07	0.10
.....	.....	7.04	9.9	17.0	19.6	12.3	3.92	5.5	0.85	0.56	0.18	0.25
.....	.....	1.4	1.9	7.3	7.2	4.53	1.49	2.02	0.32	0.21	0.07	0.09
.....	.....	3.3	4.7	18	17.9	11.1	3.5	5.0	0.82	0.50	0.15	0.23
.....	.....	.....	.....	1.1	23.4	14.7	.....	.....	.....	.....	.....	.....
.....	.....	.....	.....	·09	2.0	12.6	.....	.....	.....	.....	.....	.....

VIII. *Self-Induction of Galvanometer-Coils.*

We have already seen that the sensibilities of two precisely similar galvanometers, which differ only in resistance, cannot easily be predicted from their resistances, since, in consequence of the varying thickness of the insulating covering of the wire, there is no simple connexion between resistance and the number of convolutions of wire occupying a given space. It therefore occurred to us to consider whether, since the self-induction of a coil of a given size and shape depends mainly on the square of the number of convolutions, and but little on the thickness of the wire or of the insulating covering, the square root of the self-induction would be proportional to the magnetic constant of the coil. The following table gives the results of the tests on the three astatic reflecting-galvanometers already referred to :—

Galvanometer.	Resistance, in ohms. <i>r</i> .	Self-Induction, in secohms. <i>L</i> .	Time Constant, in seconds.	<i>D</i> .
A .....	26	0.052	0.002	349
B .....	2457	1.75	0.00071	2160
C .....	6410	4.72	0.00074	3360

*D*, as before, standing for the number of scale-divisions of deflexion produced by the same current with the same distance of the scale, the same system of mirror and magnets being used in each case, and the controlling magnet adjusted to give the same periodic time of oscillation. The following gives the ratio of the values of *D*, of the square roots of the self-inductions, of the square roots of the resistances, and of the resistances to the power  $\frac{2}{3}$  :—

$$\frac{D_B}{D_A} = 6.190; \sqrt{\frac{L_B}{L_A}} = 5.801; \sqrt{\frac{r_B}{r_A}} = 9.721; \left(\frac{r_B}{r_A}\right)^{\frac{2}{3}} = 6.167.$$

$$\frac{D_C}{D_B} = 1.555; \sqrt{\frac{L_C}{L_B}} = 1.643; \sqrt{\frac{r_C}{r_B}} = 1.615; \left(\frac{r_C}{r_B}\right)^{\frac{2}{3}} = 1.468.$$

$$\frac{D_C}{D_A} = 9.627; \sqrt{\frac{L_C}{L_A}} = 9.526; \sqrt{\frac{r_C}{r_A}} = 15.70; \left(\frac{r_C}{r_A}\right)^{\frac{2}{3}} = 9.051.$$

From the preceding list it appears that the ratio of the square roots of the self-inductions gives the ratio of the galvanometer-constants of coils, not only much more accurately than the ratio of the square roots of the resistances,

but, on the whole, even more accurately than the ratio of the resistances to the power  $\frac{2}{5}$ .

In view, then, of the importance of knowing the self-induction of galvanometer-coils, we give the results of some measurements made by means of the secohmmeter :—

Reflecting-Galvanometer with One Pair of Coils.			
	Resistance, in ohms.	Self-Induction, in secohms.	Time-Constant, in seconds.
Front coil .....	3007	3.75	0.00125
Back coil .....	2830	3.16	0.00112
Front and back coils, joined up as in actual use .....	5837	9.6	0.00164
Mutual induction of the two coils in position .....	.....	1.35	
Reflecting-Galvanometer with Variable Damping.			
Four coils in series, but separated so as have little Mutual Induction .....	9680	12.48	0.00129
Reflecting High-Resistance Galvanometer (fig. 7).			
Top front coil .....	105,600	40.72	0.000386
Top back coil .....	101,200	39.50	0.000390
Bottom front coil .....	90,000	27.51	0.000306
Front top and back coils joined up in position .....	207,000	109.8	0.000531
Reflecting Ballistic Galvanometer (fig. 11).			
One Coil only .....	1003	0.166	0.000166
Flat Single-Coil Galvanometer. (Nobili type.)			
The one Coil .....	64	0.0324	0.000506

From the above it appears that a coil of the ordinary size and shape used in Thomson galvanometers has a coefficient roughly equal, numerically, to one thousandth of its resistance in ohms. If the coils of the instrument are in series and placed near each other, as in actual use, the coefficient is increased by about half its former amount, owing to mutual induction ; so that,



for Thomson galvanometers whose resistances vary between 1000 and 10,000 ohms, the time-constant is about 0.0015 second. With very high-resistance instruments the time-constant falls to 0.0005 second, in consequence of the increasing importance of the insulating covering of the wires.

### IX. *Effect of Time and Use on Galvanometer-Needles.*

The following give the values of *D*, the deflexion in divisions of a scale, placed at a distance from the galvanometer equal to a length occupied by 2000 scale-divisions, produced by one micro-ampere, the controlling magnet being adjusted to give a periodic time of oscillation equal to 10 seconds.

#### Double-Coil Astatic Reflecting-Galvanometer. Resistance, 686 ohms.

	<i>D</i> .
Needles magnetized and tested the same day . . . . .	1600
After about two years' use . . . . .	366
Needles remagnetized and then used for about one year .	826

#### Single-Coil Astatic Reflecting-Galvanometer. Resistance, 26 ohms.

As obtained from the makers . . . . .	198
After about three years' use . . . . .	170
Needles remagnetized and tested the same day . . . . .	243

#### Double-Coil Astatic Reflecting-Galvanometer ; Variable Damping. Resistance, 9744 ohms.

As obtained from the makers . . . . .	4200
After about three years' use . . . . .	3000
Needles remagnetized and tested the same day . . . . .	4280

#### Rosenthal Non-astatic Reflecting Micro-Galvanometer. Resistance, 44 ohms. (Figs. 8 and 9.)

As obtained from the makers . . . . .	25.4
After four years' use . . . . .	5.16

The needles of the first and last of these four galvanometers have lost much more magnetism than have the needles of the second and third galvanometers. As regards the Rosenthal instrument it might have been expected, in view of the powerful nature of its magnetic needle (see fig. 9) and of the fact that the current only acts on small projections of this magnet, that the magnetism would not be much diminished by use. But it has to be remembered that, whereas with the ordinary reflecting-galvanometers the zero-position of the needles is that in which the lines of force due to the coil are at right

angles to the axes of the magnetic needles, and therefore the needles are not in a position to have their magnetism much altered by the passage of a current, unless that current be very strong, the suspended magnet of the Rosenthal galvanometer will tend to have its magnetism diminished by every current sent through the instrument in such a direction as to push the poles of the suspended magnet out of the coil, since the lines of force of the two coils will pass along the axis of the suspended magnet. Care not having been taken to send the current round the Rosenthal galvanometer, so as to always suck the ends of the magnet into the coils, is probably the explanation of the weakening of its suspended magnets during four years in the ratio of 5 to 1. Whereas the falling-off in the sensibility of the first of the four galvanometers in the preceding list in the ratio of 4·3 to 1 during a shorter time is probably due to inferior steel having been used in the construction of its magnetic needles.

In view of the great difference which exists between various specimens of magnet-steel, it is most important that only the very best magnet-steel should be employed in the construction of galvanometers which are intended to have a high sensibility, since the factor of merit of the instrument depends largely on the goodness of the magnetic needles.

VII. *Note on Boltzmann's Kinetic Theory of Gases, and on Sir W. Thomson's Address to Section A, British Association, 1884. By E. P. CULVERWELL, M.A., Fellow of Trinity College, Dublin\*.*

**B**OLTZMANN has shown that, whatever be the law of force between the particles of a gas, the configuration of the gas will remain unchanged provided the number of particles moving in a particular way be proportional to  $e^{-\frac{I}{\lambda}}$ , where  $I$  is the total energy of a particle moving in that way. This may be termed a permanent configuration. Mr. Watson has extended this to a system of molecules with any number of degrees of freedom.

But, so far as I know, no one has attempted to show that a set of particles having any given initial conditions will, as time goes on, approximate more and more to this permanent configuration. Sir William Thomson indeed has stated (see Montreal Presidential Address, Section A) that he believes it "to be rigorously demonstrable that the whole translational energy [of a perfectly elastic molecule] must ultimately

\* Communicated by the Author.

become transformed [by repeated collisions] into vibrational energy of higher and higher nodal subdivisions, if each molecule is a continuous elastic solid." If this were true there is, I think, no doubt that the proof would involve also a proof that Boltzmann's permanent configuration is that which all dynamical systems will finally assume.

Barely touching on the difficulty, dwelt on by Sir W. Thomson at Montreal, that elastic molecules would not on his theory, or indeed on Boltzmann's theory either, possess the known properties of a gas, I will take as an example the only case in which the equations of motion can be integrated in finite terms, *i. e.* that in which the stress between two particles varies directly as the distance. Taking attractive action, each particle moves harmonically round the centre of Mass of the system, *and the mutual actions of the particles do not on the whole tend to distribute the energy equally among all the degrees of freedom.* For instance, let there be a system comprising any number, great or small, of balls or points following this law, the balls being in motion with, say, very small velocities. Let two of the particles be given very violent blows in opposite directions, so that the total momentum of the system is unaltered, then the interaction of the balls will not cause any of the energy given to the two balls to be shared among the other balls. Observe that the particles must either be mathematical points or else able to move through each other, but this makes no difference to my argument, which is that there is nothing in the nature of dynamical *equations* in virtue of which their solutions tend to a permanent average distribution of energy.

This instance shows that it is impossible to prove in general that a set of particles will tend to the Boltzmann configuration, in which the energy is equally distributed among all the degrees of freedom (though it does not show that they would not do so for certain laws of force other than the direct distance); and it shows also that the assumption commonly made, that permanent states are independent of initial conditions, is really not based on dynamical grounds but on physical experience, and that it *involves* some principle analogous to the second law of thermodynamics.

But surely no instance is required to show the impossibility of proving that, *whatever be the initial conditions*, the effect of repeated intermolecular collisions is to equalize the energy among the different degrees of freedom. For the well-known property of reversal, which all complete and purely dynamical systems fulfil, shows that for every configuration which tends to an equal distribution of energy, there is another which

tends to an unequal distribution, for a considerable time at all events, and this quite independently of the number of degrees of freedom, or the continuity, of the molecules; and it is safe to state that no demonstration such as Sir William Thomson has hinted at can be given as a result of dynamical equations, in which a simultaneous reversal of velocities is equivalent to a mere change in the sign of  $t$ .

This may be tested by examining in a common-sense way the case of a molecule striking a rigid wall, for it would be too laborious to calculate the circumstances of the collision even for the law of direct distance among the particles of the molecule, because fresh equations would be necessary after each collision of any particle of the molecule with the wall. For, taking a molecule formed of two particles only, which attract with any law of force, let the collision take place against a wall perpendicular to  $X$ ; then, if when the first particle  $P_1$  hits the wall, the other particle  $P_2$  happens to be at rest relatively to the wall, it is evident that after  $P_1$  has hit the wall,  $\bar{x}$ , the  $x$  velocity of the Centre of Mass, is exactly reversed (and should  $P_2$  reach the wall,  $\bar{x}$  will be increased). Hence whether  $P_2$  hit the wall or not, *and whatever be the law of force*, the numerical value of  $\bar{x}$  will be *increased* whenever  $P_2$  is moving from the wall at the instant  $P_1$  hits it, and similarly if  $P_2$  were moving rapidly towards the wall when  $P_1$  hit it, and if  $P_2$  did not hit the wall violently, then  $\bar{x}$  would be smaller than before the collision. In fact if to  $P_1$  and  $P_2$  be given the positions and reversed velocities that they have after the collision, then the result would be a new collision after which  $\bar{x}$  would have its original value. Hence it is as likely that the energy of the particle relative to its Centre of Mass will be transformed into translational energy as that the translational energy will be transformed into relative energy; and it seems evident that similar reasoning would apply to a molecule formed of 3, or of 4, or of any number of particles.

The conclusion I draw from these observations is that no success can attend an attempt to prove that the temperature-equilibrium results from dynamical actions between molecules alone. I can see no reason for supposing that, if the particles of a gas could be enclosed in a vessel not containing æther (and such that no energy were transferred to the vessel in its collision with the particles), the gas would ever attain a temperature-equilibrium at all. If it did *always* attain such an equilibrium, it would be to my mind a proof that the ultimate particles of matter did not individually obey those laws which they are known to obey when collected in the



enormous numbers which compose the bodies for which the laws of motion have been experimentally proved.

But when one of the most important purposes for which the existence of the æther is required is the communication to, or abstraction of, heat-energy from material particles, it seems absurd to try to derive temperature-equilibrium from molecular action. We know that by means of the æther, bodies at a distance and wholly prevented from acting on each other molecularly, come to exactly the same temperature-equilibrium as the particles of a gas are expected to do by intermolecular collisions, although the æther between them is perfectly competent to settle their temperature-equilibrium without any assistance from their collisions. Hence there is every reason to suppose that it is by the molecules interacting through the æther that the temperature-equilibrium is determined. Hence taken by themselves the molecules do not form a *complete* dynamical system, for we cannot consider the æther (or any medium having kinetic properties) as merely limiting the number of degrees of freedom of the molecules, and thus replace it by (geometrical) equations of condition. Indeed it is no harm to observe here that equations of condition should not be employed in *atomic* theories, though perhaps they may have a place in *molecular* theories. For an equation of condition either indicates that the force between two particles  $P_1$  and  $P_2$  is not a function of the distance between them (and is therefore inadmissible) or else it is resolvable into  $f(r_{12})=0$ , and then it should be discarded, and a distinct expression of the law of force it implies should be substituted for it.

It would be very interesting if Sir W. Thomson would give some outline of the way in which the initial conditions could be introduced in a demonstration such as he believes possible, for it appears to me that the fundamental error in all assumptions about permanent states is that they persistently ignore the initial condition on which obviously the whole theory must depend, *if the system be reversible*. It is interesting, too, to remark that in the case of vortex motion (in which one attends simply to the dynamical equations and does not reason from preconceived physical ideas), Sir W. Thomson "has found no indication of the dissipation of translational velocities, or of vibrations of slow period, into those of shriller and shriller vibrations." Of course I do not mean to say that things do not actually come to a permanent state, but only to assert that permanence is a consequence of the *interaction of molecules and æther* and not of the interaction of molecules among themselves. No doubt the mode in which

the æther produces those permanent states in which there is no transference of energy from one place to another is difficult to explain, but it is an experimental fact which any theory of the æther must necessarily explain, for it must explain the radiation-equality of temperature.

If the views here put forward be correct, Sir W. Thomson's objection to the kinetic theory of gases is disposed of, and the many difficulties arising from the nature of the Boltzmann permanent configuration are avoided\*. But the difficulties are only avoided; all that is done is to reduce the number of properties explained by the kinetic theory, and to shift the temperature difficulties to the æther, so that in some shape or other they will crop up again.

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VIII. *The Elastic Constants of Quartz Threads.* By RICHARD THRELFALL, *Professor of Physics in the University of Sydney*†.

SINCE there can be little doubt as to the great superiority of quartz over silk threads for all purposes of suspension where accuracy is required, I have thought it worth while to obtain some detailed numerical information of their elastic properties. My attention has been directed to the following points suggested by the needs of instrument-making:—

1. The determination of the strength of quartz fibres.
2. The determination of the modulus of torsion and the modulus of simple rigidity from vibration experiments.
3. The determination of the temperature-coefficient of the coefficient of torsion‡.
4. The determination of the coefficient of expansion of fused quartz for the purpose of enabling a calculation of the temperature-coefficient of the simple rigidity to be carried out.
5. An investigation of the amount of "Nachwirkung" exhibited by quartz fibres with the view of finding a practical limit to the rate of twist which may be safely applied.

\* I mean such difficulties as those connected with specific heats and with the proportion of the energy in the different radiations of gases; for instance, it may be urged that the molecules of sodium gas must have an infinite number of degrees of freedom, since when heated sufficiently and in sufficient numbers per unit volume they give out a continuous spectrum, and yet in ordinary states of vibration they give out merely, or at all events chiefly, the characteristic sodium-line.

† Communicated by the Author.

‡ By "coefficient of torsion of a thread" I mean the moment of forces requisite to twist the lower end of the thread through one radian, the upper end being fixed.

6. An attempt to discover elastic fatigue by keeping threads vibrating for many days in succession.

7. A determination of the Young's modulus of quartz fibres by the method of bending, leading to a calculation of the compressibility of fused quartz.

I shall describe the experiments and computations made under each of these heads in order.

*Production of Threads, and Conditions of Experiment.*

For the purpose more especially of the experiments on Young's modulus it was necessary to make threads much thicker than those usually employed for purposes of suspension. This was partly due to the fact that in determining both the rigidity and the Young's modulus the diameter of the threads requires to be known with greater accuracy than any of the other data, as it enters the result raised to the fourth power. On the other hand, it is probable that the properties of thick threads are not quite identical with those of thin ones. This is certainly the case with the breaking-strength, but whether the relative difference of strength of thin and thick threads is to be attributed to the difference in thickness *per se*, or to the consequent difference in annealing, which necessarily accompanies difference of thickness, I cannot say, but I incline to the latter view. In experimenting therefore it becomes a matter of judgment and experience to decide what thickness of threads it is best to work with. I have endeavoured to proceed in such a way as to have the threads neither too thin for tolerably accurate measurement, nor so thick as to be entirely removed in properties from the thin threads which are used in practice. I have in general found that it is impossible, with my apparatus, to be sure of the thickness of threads of about  $\cdot 015$  centim. diameter within less than three or four per cent. by a single measurement, and have consequently adopted the plan of making many observations of each thickness, with a view to eliminating the accidental errors—which, I have satisfied myself, are of the chief importance. I have also experimented in each case on several samples of threads so as to eliminate any possible individual peculiarity of the threads employed.

I have to thank Mr. Adair for making all the observations of time of vibration, and computing most of the results; Mr. Pollock for determining the coefficient of expansion of fused quartz and the coefficient of expansion of a brass vibrator, and also for determining the breaking-strength of many

threads, and their limits of perfect torsional elasticity. The measurements of the threads, as well as the rest of the work, has been attended to by myself.

I have found it convenient to abandon the bow-and-arrow method of making threads in favour of a rather more manageable method—applicable to the production of comparatively short, thick thread-. On a board about seven feet long a brass rod three quarters of an inch in diameter and six feet long was fastened so as to lie parallel with the board at a distance of about an inch and a half above it. On this brass rod a light boxwood traveller was adjusted to slide freely, and this traveller carried a rough and ready clamp. A clamp was also established on the board at one end of the brass rod. A bit of quarter-inch catapult elastic was fastened to the slider, and fixed as to its other end to a hook screwed into the board at the end furthest from the fixed clamp. This elastic was brought into tension by pulling the slider up towards the clamp. When in position the slider was held by a trigger, actuated by foot. A combination of springs and india-rubber was arranged near the hook, so as to act as a break on the slider, and also to jam it in such a way that there was no rebound. The slider was prevented from turning round by its proximity to the board. In order to draw a thread, a bar of quartz of the required thickness was clamped as to its ends in the two clamps and was heated in the middle. Of course, on pulling the trigger, a thread of any desired thickness and about 5 feet long was produced. From the middle of this thread a portion of the required length for the experiment in hand was cut, and the diameters of the two ends were measured. If the difference in diameter observed was within the range of experimental error of measurement, the thread was considered sufficiently uniform for the work in hand. Some threads shot in the ordinary way were also used in the breaking and vibration experiments. I venture to think that in practice the catapult method of production will be found useful, as it is certainly possible by means of it to get a thread about four feet long at least as fine as I can manipulate, though one improves in manipulation so much that the experimental limit is continually moving away. It must be admitted, however, that a little practice is necessary in order to draw fine threads by the catapult method. The strength of the fibres is such that for galvanometric purposes the limit of thinness is imposed by our skill in manipulating the fibres, not by their inability to carry a load. For this reason, and also because the strength of fibres appears to differ



according to the amount of annealing they have received, and possibly also according to their thickness, *per se*, the measurement of breaking-strength was only comparatively rough.

### *Breaking-Strength of Fibres.*

Two methods were used. In one a small paper bucket was fastened to a fibre by a silk thread, so as to avoid giving the fibre any lateral strain. The load was applied by allowing mercury spray from a fine pipette to gradually pass into the bucket. The weight of the bucket of mercury was ascertained as soon as the fibre broke. The second method was certainly more convenient, and considerably more accurate, in that it did not lead to vibration being set up in the thread. In it use was made of a brass spring. A microscope stand was taken, and the top of a spiral hard brass spring (made of wire .044 centim. diameter of some thirty-one convolutions, and having a diameter of .95 centim.) was fastened to the structure which normally carries the sliding-tube of the microscope. The upper straight part of the spring had a point of reference moving over a scale engraved on looking-glass, and to the bottom of the spring the top of the thread was attached by hard paraffin or shellac; the bottom of the thread was fastened to the base of the apparatus, and the rack and pinion was worked till the spring was just on the point of beginning to be stretched. The position of the point of reference on the scale was then noted, and the rack screwed slowly and steadily up till the thread broke. Watch was of course kept on the point of reference, and its position when the thread broke was noted. By afterwards loading the spring with known weights—the mercury-bucket for instance—the tension exerted by the spring could be estimated. It elongated 1.45 centim. with 5 grammes weight, and 2.9 centim. with 10 grammes weight. The method is open to the objection that a twisting couple, due to the uncoiling of the spring, as well as a pull, acts on the fibre. This was eliminated as far as possible by making the convolutions close together, and the twist was not in any case more than a few degrees per inch of length of fibre. The length of the thread varied in different experiments, as will be seen from the table. The fracture was sometimes curious, and in one instance, owing presumably to splitting, the lower end of the thread was found to present a perfect point at the position of fracture. The following abstract of results will be sufficient:—

No. of thread.	Length in cm.	Diameter in centim.	Breaking weight in grammes.	Fracture.
3.	30	·0036	34·34	Close to bucket and half inch from top, irregular.
7.	12	·0020	10·2	Half inch from end.
Same thread. {	Not noted.	·0016	10·5	Close to attachment (probably due to vibration of bucket).
		·0016	14·0	In the middle.
		·0014	10	One inch from lower end, very clean.
		·0014	9·2	Half inch from top, clean.
Same thread. {	10	·0014	9·2	Close to upper attachment.
		·0014	11·7	Quarter inch from bottom, perfect point.
		·0014	8·2	Quarter inch from top, not clean.
		·0014	8·2	About the middle, clean.

The diameter of these threads was measured with the help of a stage-micrometer by Zeiss, which was afterwards found to be correct by stepping it with a measuring-microscope against the millimetre-divisions of a standard metre-scale, and of a scale by the Darling, Brown, and Sharp Co.

It is rather an interesting question as to what finally determines the point where fracture shall take place. All the threads were from very long pieces which had been shot, and were very uniform. Some of the fractures indicate that at the instant of fracture the material near the exact point of fracture was in a very unstable condition. This is strengthened by the observation that the pieces afterwards broke more easily as a rule. The results are of value only as showing what sort of loads can be carried by quartz threads of moderate thickness, and as showing that Boys's estimate of a breaking-strength of from fifty to seventy tons weight per square inch of quartz section is confirmed.

#### *Measurement of Diameter of Threads.*

As the measurement of the thread-diameter was the fundamental operation in all the other experiments, it is as well to

state at once exactly how it was done. A thread having been selected by preliminary trial for uniformity, was broken to the required length. A sample about a quarter of an inch long was then broken off each end and placed on a microscope slide. The refractive index of quartz is about the same as that of Canada balsam, which therefore had to be avoided; consequently the ends were mounted in 50-per-cent. glycerine stained with aniline blue, and a carefully chosen cover-slip placed over all as in ordinary microscope practice. The object of colouring the glycerine was to make the quartz more visible. The objective used was a Zeiss D, giving a magnifying power of about 230 diameters with the eyepiece used. The ordinary camera was employed to give a simultaneous view of a scale pinned to a stand on the table at such a height that parallax was almost entirely avoided. The thread to be measured was then brought to the centre of the field, and a reading of the scale was taken. The process was repeated with the other end, and finally the threads were replaced by the micrometer. It was found necessary to use the same part of the field for the micrometer that had been occupied by the thread in making the comparison by the aid of the step-scale. A most laborious preliminary examination was made in order to avoid constant errors due to the micrometer. The Zeiss scales divided into hundredths of a millimetre were compared with a very fine scale by Powell and Lealand. The Zeiss scales were found to agree, but to give readings differing from the Powell and Lealand scale by about 3 per cent. in the direction of making the divisions of the latter too large. The millimetres of each of these scales (*i.e.* the end divisions) were then compared directly by means of a very fine comparing-microscope by the Cambridge Scientific Instrument Co. The screw of this instrument had been minutely examined previously by Mr. Pollock for another purpose, and had been found more correct than it was possible to set the head (to  $\cdot 0001$  inch) for a certain short part of its run. The result of this comparison again showed that the Powell and Lealand differed from the Zeiss micrometers by from 3 to 4 per cent. The divisions of all the micrometers were then stepped on the stage and found to be all correct as nearly as could be estimated; in other words, they were identical in length, or did not differ from each other by more than 3 per cent. of their whole length. The sensitiveness is indicated by the observation that at the centre of the field  $3\cdot 76$  division of the step-scale corresponded to  $\cdot 01$  on the micrometer. Finally, to decide which micrometer was the best to use, the Cambridge Instrument Co.'s comparing-microscope was used to compare the milli-

metres of the various scales with several millimetres taken from the standard metre, with several taken from a callipers by the Darling, Brown, and Sharpe Co., and with several from a large callipers by Elliot Bros. The result was to show that the Zeiss scales were as nearly right as I found possible to estimate, and the Powell and Lealand wrong by about 3 per cent. In order to check the method some very thick threads, up to .3 millimetre diameter, were measured under the microscope, and callipered directly both with American and English micrometer-callipers. The result was entirely satisfactory, though the experiment involved using a lower power on the microscope. Some thin threads were also measured, and though less suited to the callipers allowed the high power to be used on the microscope and gave, as nearly as could be read, identical results. At first there was a want of consistency because care had not been taken always to use the middle of the field. The advantage of using the glycerine mounting was that it was much easier to focus on the edge of the thread with certainty than was the case in air. It is perhaps fair to say that the engraving of the Powell and Lealand scale was very superior to that of the Zeiss, but it was not so convenient, as only one tenth of a millimetre was divided into hundredths, and, as has been said, was wrong by 3 per cent. I have to thank Professor Haswell and Dr. Wright for the use of these scales. To get the best results I found it necessary to use a variety of shades and screens so as to obtain uniform illumination. In the thread measurements the divisions and parts of a division occupied by the image of the thread on the step-scale were estimated first, and then the micrometer having been substituted for the threads the value of a step-scale division was got by taking the number of divisions occupied between the two nearest coincidences, covering the part of the scale previously occupied by the image of the thread. This is more accurate than using pencil marks. I have dwelt on this measurement with more detail than is perhaps necessary, because as the accuracy attained here really conditions the final accuracy of the results, I have wished to give an idea of what sort of accuracy I have succeeded in reaching. Most, if not all, of the threads were too coarse for the optical method of measurement.

*Determination of the Coefficient of Torsion and of its  
Temperature-Coefficient.*

In these experiments an arrangement was made permitting the torsion to be investigated by the method of vibration at



all temperatures up to  $98^{\circ}\text{C.}$ , and at pressures ranging from 76 to one or two centimetres of mercury.

A cube of brass, measuring about four inches on the side, was bored through the centre of one face to a depth of about three inches, the diameter of the bore being about one inch. This block served as a support to the vibration-tube, which was jacketed and projected into the hole in the block. The tube was provided with a flange so that it could be connected air-tight to the block. A hole about one inch in diameter, and whose axis was horizontal when the vibration-tube was vertical, was cut through the block and opened into the bore. This hole was glazed with carefully selected glass and allowed the motion of the vibrator to be observed. In order to get the window air-tight, the necessity for considerable pains was anticipated and experienced. Rubber washers, coated with white lead, and compressed against the glass by a good and powerful screw, enabled me finally to dispose of the difficulty. Additional light was let into the cavity in the block by means of a solid glass rod running horizontally into the block at an angle of about  $40^{\circ}$  to the axis of the window-hole. This bar was secured by screw-packing in the usual manner. Everything was straight and all the parts true, so that the vibration-tube could be made truly vertical by setting the brass block horizontal. This was done in the usual way. The vibration-tube was about 24 inches long, and was furnished with a small side tube so as to allow of its being put in connexion at will with a Bunsen pump, a Sprengel pump, and an air-drying apparatus. The jacket was furnished in a similar manner with an inlet and outlet for steam or other vapour, and was wrapped in cotton-wool and paper to a thickness of about half an inch all round. The ordinary brass-rod suspender was passed through a rubber bung, fitting the top of the vibration-tube, and surrounded by a movable circular wooden trough which could be filled with mercury, and thus form a mercury seal for the bung. In spite of all the trouble taken, the apparatus was never absolutely air-tight, the high temperature at which it was used preventing me from reaping the advantage of covering doubtful places with marine glue. The vibrators used were (1) :—A pure silver anchor-ring supported by a disk of aluminium foil, through the centre of which passed a short bit of aluminium wire to which the thread was attached. (2) A cylindrical vibrator of brass, vibration being about the axis of the cylinder. (3) A similar but larger vibrator for measuring the temperature-coefficient with thick threads. (4) A disk vibrator of brass, vibration taking place about its axis of revolution.

Let  $\alpha$  be coefficient of expansion of brass (linear).  
 $\alpha_1$                    "                   "                   quartz (linear).  
 $m$  be mass of vibrator of brass.  
 $k$  be radius of gyration of vibrator.  
 $l$  be length of fibre.

$$\tau = \frac{\pi}{2} n r^4,$$

where  $n$  = rigidity of quartz,  
 $r$  = radius of fibre.

Let  $T_1$  be time of a complete oscillation at temperature  $t_1$ ;  
 then

$$T_1 = 2\pi \sqrt{\frac{m k^2 l}{\tau}} = 2\pi \sqrt{\frac{m k^2 l \cdot 2}{n \pi r^4}}.$$

Let the temperature of both brass and quartz change to  $t$   
 and the time to  $T_2$ ; then

$$T_2 = 2\pi \sqrt{\frac{m k'^2 l'}{n' \pi r'^4}},$$

where  $k'$ ,  $l'$ ,  $r'$ ,  $n'$  denote the corresponding values of these  
 quantities. Whence

$$\frac{T_1}{T_2} = \frac{k}{k'} \sqrt{\frac{n'}{n}} \left(\frac{r}{r'}\right)^{\frac{3}{2}} \left(\text{since } \frac{l}{l'} = \frac{r}{r'}\right).$$

Now  $k' = k \{1 + \alpha(t_2 - t_1)\}$  and  $r' = r \{1 + \alpha'(t_2 - t_1)\}$ .

$$\begin{aligned} \therefore \frac{T_1}{T_2} &= \{1 - \alpha(t_2 - t_1)\} \sqrt{\frac{n'}{n}} \{1 + \frac{3}{2} \alpha'(t_2 - t_1)\} \\ &= \sqrt{\frac{n'}{n}} \{1 + (\frac{3}{2} \alpha' - \alpha)(t_2 - t_1)\}. \end{aligned}$$

Now neglecting any possible change in  $n$ , *i. e.* putting  
 $n = n'$ ,  $T_2$  will be greater than  $T_1$  if  $\frac{3}{2} \alpha' - \alpha$  is negative. If,  
 on the other hand, the rigidity changes,

$$\frac{n'}{n} = \left(\frac{T_1}{T_2}\right)^2 \{1 - (3\alpha' - 2\alpha)(t_2 - t_1)\}.$$

If the temperature of the brass is less than the temperature  
 of the fibre when both are heated, as was the case in some of  
 the experiments, we have

$$\frac{T_1}{T_2} = \sqrt{\frac{n'}{n}} \left[1 + \frac{3}{2} \alpha'(t_2 - t_1) - \alpha(t_2 - t_1)\right],$$

allowing us to estimate the change in  $n$  when  $\alpha$  and  $\alpha'$  are  
 known.

The following experiments were made on various fibres to find the value of  $n$  :—

*Fibre A.*

Let  $I$  = moment of inertia of a flat circular disk  
 $= \cdot 36407$  (gm. cm.<sup>2</sup>) ;  
 $l = 10\cdot 51$  cm. ;  $r = \cdot 000927$  cm.

$T = 24\cdot 79$  secs. ; mean of eight observations on sixty vibrations and of three observations on 30 vibrations. From which

$$n = 2\cdot 119 \times 10^{11} \text{ C.G.S.}$$

at a temperature of about  $23^{\circ}$  C. and under a pressure in the vibration-tube of about three and a half centimetres of mercury. From other experiments it was found that the pressure in the vibration-tube made no appreciable difference in the period of vibration. The log decrement was very small and was of no consequence in any case.

*Fibre B.*

Same vibrator.  $l = 21\cdot 2$  cm.  $r = \cdot 0021135$  cm.

Time deduced from 11 sets of 200 oscillations. Each was  $5\cdot 3313$  seconds. Temperature  $22^{\circ}$  C. Whence

$$n = 3\cdot 4205 \times 10^{11}.$$

The experiments to test effect of pressure were made on this fibre.

*Fibre C.*

$I = \cdot 31115$  {gm. cm.<sup>2</sup>} (silver ring),  
 $l = 27\cdot 8$  cm.

$r = \cdot 00075$  cm. (Rather doubtful owing to microscope-field distortion not having been taken into account.) Temperature about  $21^{\circ}$  C. Whence

$$n = 7\cdot 7573 \times 10^{10}.$$

This value has not so much weight as the others.

*Fibre D.*

$I = \cdot 36407$ .  $l = 13\cdot 047$ .  $r = \cdot 000775$ .

$T$  from four sets of 50 vibrations each  $= 33\cdot 852$  seconds. Temperature about  $23^{\circ}$  C.

$$n = 2\cdot 8877 \times 10^{11}.$$

*Fibre E.*

$$I = \cdot 36407. \quad l = 16\cdot 976. \quad r = \cdot 002455.$$

T from five sets of 200 vibrations each.  $T = 3\cdot 7148$ . Temperature  $24^{\circ}$  C.

$$n = 3\cdot 0987 \times 10^{11}.$$

Discarding the value got for fibre C, for the reason given, the mean value for  $n$  at the temperature of  $21^{\circ}$  to  $23^{\circ}\cdot 5$  C. is

$$n = 2\cdot 8815 \times 10^{11}.$$

*Determination of Change produced in Modulus of Torsion of Quartz Fibre by Heating.*

For this experiment it was not essential that the fibre should be uniform. On the other hand, the vibrator required to be heavy, or rather to have a large moment of inertia, so that the energy possessed by it might be sufficient to carry it through a good many vibrations. The cylinders were used in these experiments. One was about  $\cdot 8$  centim. in diameter and weighed about 10 grammes. The other, similar in figure, weighed about 25 grammes. It was very necessary to devise a means of fastening the fibre rigidly to the suspender and to the vibrator, as, of course, at the upper temperature all ordinary cements become unreliable.

I finally hit on a method which I have since found useful for some purposes in the case of glass. It was suggested by Professor Kundt's method of preparing metal surfaces on glass. Two thin needles of quartz, each about two centim. long and one millim. in diameter, were coated each on one end for a distance of, say, five millim. with metallic platinum. This was done by dipping the end in strong solution of platinum tetrachloride, and subsequently reducing the same by heating in a Bunsen flame. The heating requires to be done with judgment. If the oxyhydrogen jet is used the platinum gathers into drops; if, on the other hand, the temperature be below a good red heat, the platinum does not reduce or stick properly. Having got the ends of the quartz needles platinized, they are dipped in solution of chloride of zinc and then tinned in the ordinary way with a small iron. A hole is drilled in the vibrator and another in the suspender, and these holes are tinned. It is then easy to solder each needle into its respective hole, just as if it were a wire. Unless care be taken not to cool the soldered parts too rapidly, the quartz will be found to be rotten near the



points of soldering. The thread is prepared by simply drawing down a needle by hand, leaving the thicker portions attached. The thin part was generally about 12 inches long. The ends are then easily joined to the similar ends, projecting from the brass work. The whole having been clamped so as to let the vibrator swing freely, it is brought into order by heating the thick portions till they become soft and stretch slightly. Two sets of observations were made with threads prepared and supported in this way. Of these, one was much better than the other—that with the heavy vibrator—and that alone will be used, for the reason that the small vibrator was of unknown brass; while the coefficient of expansion of the other was determined from a sample cut from the same rod. The time of vibration (taken from sets of two hundred vibrations each) was first determined under a pressure of a few centim. of mercury, and at a low temperature. Steam was then turned through the steam-jacket, and after a known period the time of vibration was again taken. The temperature inside the vibration-tube and in the hollow in the block was determined in a subsequent experiment, where the conditions as to steam-supply were made as nearly identical as possible with those obtaining during the vibrations. The observations made were very numerous and very concordant. Two hundred vibrations took about 11 minutes 39 seconds, and the sets differed only by two or three tenths of a second. Time was taken from a rated stop-watch. Nineteen sets were taken at a mean temperature of  $22^{\circ}$  C., and fourteen sets at a mean temperature of  $98.5^{\circ}$  C. for the fibre, and  $67^{\circ}$  C. for the brass. In order to obtain a result from these measurements we require to know the coefficient of expansion of the brass, and for some purposes of the quartz also. The coefficient of linear expansion of the brass was found, by the method of Matthiessen (Phil. Trans. 1866), in a manner that will be described, to be .000020264 between  $79^{\circ}$  and  $35^{\circ}$  C. This was considered to be the coefficient of expansion over the range  $23^{\circ}$ – $68^{\circ}$  used in the observation. For most practical purposes we are only concerned to know the change in the torsion produced by heating a twisted quartz fibre, and for this it is sufficient to know the expansion of brass. To get the coefficient of the modulus of rigidity we require to know besides the expansibility of fused quartz and the length of the thread used. The former we have attempted to get by Matthiessen's method applied to masses of fused quartz, but with only partial success. Even assuming that an extension to threads of the coefficient so found were admissible, the

actual length of the active part of the fibre is also uncertain ; but of course it is easy to see that almost all the work must be done by the thin part, since the resistance to torsion varies as the fourth power of the diameter. This enables the results to be applied to really uniform cylindrical fibres without appreciable error. We can easily estimate the total change in the force of torsion induced in any thread by raising its temperature one degree. In any instrument, such as a gravity-meter, this coefficient of total change is all that is required, and, as will be seen, is the same for all fibres of similar figure. Let  $\phi t_1$  be the "moment of forces" exerted by the fibre under given conditions at temperature  $t_1$ , *i. e.*  $\frac{\pi n r^4 \theta}{2l}$ ,  $\phi t_2$  be the corresponding value at  $t_2$ . Let  $T_1$  and  $T_2$  be the time of a given number of vibrations at the lower and upper temperatures respectively ; and let  $\alpha$  be the coefficient of linear expansion of brass.

Then

$$\phi t_2 = \phi t_1 \left( \frac{T_1^2}{T_2^2} \right) (1 + 2\alpha t),$$

where  $t$  is range of temperature through which the brass vibrator is heated.

In the experiments

$$\begin{aligned} t_1 &= 22^\circ \text{ C.}, \\ t_2 &= 98^\circ.5 \text{ C.}, \\ \therefore t_2 - t_1 &= 76^\circ.5 \text{ C.}, \end{aligned}$$

range through which quartz is heated.

The brass was heated from  $22^\circ$  to  $67^\circ \text{ C.}$ ; therefore  $t = 45^\circ$ ,  $T_1 = 11^m 39.2417^s$ , and  $T_2 = 11^m 36.3425^s$ . Whence

$$\frac{\phi t_2}{\phi t_1} = 1.01018 = 1 + 76.5e \text{ say, or } e = .00013307; \text{ and may be}$$

called the temperature-coefficient of torsional stiffness of cylindrical fibres. Neglecting the increase in length of the fibres this will be the same as the temperature-coefficient of the modulus of torsion. In order to get the temperature-coefficient of the rigidity one requires to know in addition the coefficient of expansion of quartz, as has been said, and this has not yet been obtained to our satisfaction, *i. e.* Mr. Pollock's and mine. The degree of reliability that is to be placed on our estimate may be judged from the table (see below) which embodies the result of our researches. The probability, however, is that by taking  $\alpha' = .0000017$  we shall not be very far

out. Using this number in the equation for  $\frac{n}{n'}$  we find that  $n' = (1.009790)n$ , or the temperature-coefficient of the absolute rigidity appears to be about  $+0.00012797$  per degree Centigrade.

### *Determination of Coefficients of Expansion.*

The method of Matthiessen (Phil. Trans. 1866) was employed. I have in my possession a very fine set of copper vessels fitted into one another, one of them being silvered outside and one inside. Consequently I can maintain five or six litres of water at a high temperature with a very slow rate of cooling. It was with this apparatus that the experiments were made. As the method is well known it will perhaps suffice to say that infinite pains were taken to get as good results as the method will allow of. Everything that thoughtfulness could suggest was done, except the purchase of a special balance, and yet the expansion of quartz appeared irregular to a degree. In the final experiments the amount of fused quartz available in the form of short thick rods was more than 14 grammes—a quantity involving no inconsiderable expenditure of time and oxygen in its preparation. In the course of the work we plotted curves from various tables giving the expansibility of water, and finally used the values given by Matthiessen (*loc. cit.*). The small table in Everett's 'Units and Physical Constants,' p. 39, is subject to a misprint (discovered from the curves) in that it gives the density of water at temperature  $35^\circ$  as 0.99469 instead of 0.99419. We are inclined to believe that sticks of fused quartz are in general in such a state of strain that the real expansion due solely to rise of temperature is masked by other effects. This suggests that the proposed use of fused quartz for thermometer-bulbs may turn out to present a purely illusory advantage, though on this point we would prefer to speak with all reservation. The accompanying table will give an idea of the work done and the results arrived at. I ought to say that many previous experiments had been made in my laboratory by a student, Miss Robinson, and that my attention was really drawn to the matter by the anomalous results she obtained. The table gives the results of only the more reliable experiments, *i. e.* those against which nothing is known; any want of sensitiveness of the balance will not account for the abnormalities.

## Observations on the Expansion of Quartz.

Date 1889.	Weight <i>in vacuo</i> .	Corrected mean weight in water.	Mean temp. of water.	No. of obs.	Coefficient of cubical expansion.
Dec. 5.	grammes. 2·6971	grammes. 1·4897	71·3 C.	1	
		1·4877	68·4	1	+0·000017
		1·4842	63·2	1	+0·000008
		1·4776	51·8	1	+0·000032
		1·4749	46·5	1	+0·000034
		1·4651	22·7	1	-0·000003
		1·4897	71·3	1	
		1·4749	46·5	1	+0·000026
Dec. 13.	9·1179	5·0255	74·08	6	+0·000037
		5·0159	69·85	5	+0·000007
		5·0015	63·59	8	+0·0000004
		4·9536	38·6	19	-0·000022
		4·9360	26·0	7	
		5·0255	74·08	6	+0·000006
		4·9536	38·6	19	
Dec. 19.	14·2170	7·8703	83·1	11	+0·000004
		7·7027	29·8	3	
Dec. 20.	14·2170	7·8709	83·5	10	+0·000014
		7·7397	45·3	4	-0·000008
		7·6885	21·5	5	
		7·8709	83·5	10	+0·000005
		7·6885	21·5	5	

Precisely similar experiments on brass left nothing to be desired: in the first set the brass was more or less polished; in the second it was carefully but lightly gilt. It must be said, however, that here we dealt with a weight of about 73 grammes of material, and that consequently with the balance



used the method was more accurate. The range was from about  $80^{\circ}\text{C.}$  to  $36^{\circ}\text{C.}$  The first experiment gave  $3\alpha = \cdot 000060616$ , and the second,  $3\alpha = \cdot 000060666$ . Whence we deduce  $\alpha = \cdot 0000202$ .

*Experiments on "Nachwirkung."*

The fibre used was pulled out by hand so as to leave the ends thick for attachment. The length of the "uniform" part may be taken as about twelve inches, and its thickness at  $\cdot 0102$  centimetre. One of the thick ends of the fibre was rigidly clamped, and the other carried a fine mirror ground and polished in the laboratory for galvanometer-purposes. A cross bar was fastened to the lower thick portion below the mirror, and this was twisted in the usual manner by a glass cell. The subjective method was used. One complete rotation corresponds to 2500 scale-divisions, and the scale was easily read with certainty to tenths of a division. At first the twist was put in by successive additions of five complete turns at a time. The fibre was usually left twisted for five minutes and then slowly allowed to come back to its original position. No distinct "Nachwirkung" was observed till the fibre had been twisted through fifteen turns (*i. e.* 37,500 scale-divisions) and left in its place for 16 hours 40 minutes. On releasing the thread it seemed to take 3 hours 40 minutes to come back to near its zero position, and thus untwisted by 3.7 divisions. This creeping back seemed regular and normal. We deduce from this and other experiments that one may safely twist a thread of  $\cdot 01$  centim. diameter through one turn per three centimetres of length, and leave a good margin of safety, since Nachwirkung first appeared when the rate of twist rose to about one turn per two centimetres of length. Since the intensity of the strain is proportional to the diameter for a given rate of twist, this result allows us to estimate the maximum twist that may be used with safety with fibres of any thickness. Number of turns per centimetre must not be greater than

$$\frac{\cdot 01}{\text{Diameter in centimetres}} \times \frac{1}{3}.$$

*Torsional Fatigue.*

After vibrating the thread that had been used for the temperature-coefficient of the rigidity, continuously (in the daytime) for a week, Mr. Adair failed to discover any signs of torsional fatigue. The period of vibration remained the same as ever. The experiments, however, were too rough to enable us to say more than that torsional fatigue, if it exists, is too small to affect the readings of any instrument in which threads are likely to be used.

## Young's Modulus.

Method used :—Bar loaded in the middle.

Two excellent steel knife-edges were fastened rigidly to a block of boxwood which was flat at the bottom, so that when the bottom was horizontal the knife-edges were the same, as tested by a spirit-level. The knife-edges were parallel and 4.043 centim. apart; the thread to be tested was drawn out by the catapult method and measured as to diameter by means of the Zeiss scale in the manner before mentioned. The weight was applied in the form of a rider of round platinum wire, which was brought to the central point of the thread by a gauge. The deflexion produced was measured by a micrometer-microscope (the one mentioned above as having a practically correct screw). Twelve observations, with the weight alternately on and off, were made on each thread and were always very consistent. Errors due to "loss of time" in the micrometer-screw were of course eliminated. The errors, however, in estimating the deflexion were in any case wholly insignificant compared with the errors of measurement of the thread diameter. No observations of temperature-coefficient were made, as the method was not suitable. A long thread hung down a jacketed tube would be necessary, and in view of our ill success in determining  $\alpha$  would be hardly worth experimenting on. The results which I obtained are exhibited in the following table. They were calculated from the formula

$$\mu = \frac{FL^3}{12 \cdot \pi \cdot l \cdot m^4}$$

	L.	m.	F.	l.	
Thread.	Distance apart of knife- edges.	Radius of thread in centi- metres.	Weight of Rider in grammes multiplied by "g."	Deflexion in centimetres.	Resulting value of $\mu$ .
Thick.	4.043	.008375	$3114 \times 979.65$	$.1024 \times 2.54$	$4.1792 \times 10^{11}$ C.G.S.
X.	"	.008771	" "	$.08623 \times 2.54$	$4.1255 \times 10^{11}$ C.G.S.
Y.	"	.0061015	$1572 \times 979.65$	$.10079 \times 2.54$	$7.6086 \times 10^{11}$ C.G.S.
Z.	"	.005593	" "	$.18674 \times 2.54$	$5.8164 \times 10^{11}$ C.G.S.
X.	"	.008771	" "	$.04316 \times 2.54$	$4.1628 \times 10^{11}$ C.G.S.

Mean value of  $\mu = 5.1785 \times 10^{11}$ .

The resistance to compression can now be found by the usual formula—assuming that the threads are isotropic,

$$K = \frac{\mu n}{9n - 3\mu}.$$

This gives  $K = 1.435 \times 10^{11}$ .

The results of the investigation can now be summed up as follows (the numbers refer to the C.G.S. system):—

Simple rigidity of quartz fibres at  $22^\circ \text{C.}$ ,

$$n = 2.8815 \times 10^{11}.$$

Young's modulus of quartz at  $23^\circ \text{C.}$ ,

$$\mu = 5.1785 \times 10^{11}.$$

Bulk modulus,

$$K = 1.435 \times 10^{11}.$$

Temperature-coefficient of stiffness  $22^\circ$ – $98^\circ \text{C.}$ ,

$$e = .000133.$$

Approximate coefficient of linear expansion of quartz  $80^\circ \text{C.}$ – $36^\circ \text{C.}$ ,

$$\alpha' = .0000017.$$

Corresponding approximate temperature-coefficient of  $n$

$$= +0.00013.$$

**Limit of allowable twist in round numbers, one third turn per centimetre in a fibre .01 centimetre diameter.**

Sydney, March 26, 1890.

*Note on Prof. Threlfall's Paper "On the Elastic Constants of Quartz Threads." By C. V. Boys, F.R.S.*

As Prof. Threlfall has asked me to look over the proofs of his paper on the Elastic Constants of Quartz Threads, I am taking the liberty of sending, by way of comparison, the results obtained at South Kensington, which were published for the first time at one of the Cantor lectures delivered at the Society of Arts in the spring of 1889. It will be seen that though we have not investigated the subject quite so systematically as Prof. Threlfall, our results and his agree within the limits of experimental error.

Diameter of fibre	{ in inches . . . .	.00069	.00019
	{ in centimetres . . .	.00175	.00048
Tenacity	{ tons to the square inch . .	51.7	74.5
	{ dynes to the square centim. .	$8 \times 10^9$	$11.5 \times 10^9$

Quartz fibres, whether thick or thin (*i. e.* weak or strong), all increase in tenacity as they are dissolved by hydrofluoric acid; so that no matter whether a thick or thin fibre was used at first, the diameter is found to be the same at the moment that it is broken by the pull of a given weight suspended from it, showing that it is neither a vitreous skin nor an effect of annealing that gives the fine fibres so great a tenacity. Quartz fibres dissolve very slowly in hydrofluoric acid in comparison with spun glass.

The experiments on the elasticity of quartz threads were made with a machine, for a description of which I must refer those interested to the Journal of the Society of Arts.

The mean value of Young's modulus found was  $6 \times 10^{11}$   
 „ „ the modulus of torsion . . . .  $3.74 \times 10^{11}$   
 „ „ the rigidity . . . . .  $2.38 \times 10^{11}$

I also gave (p. 17 of the reprint) full directions for mounting quartz fibres, which will possibly be worth referring to by those who may wish to acquire the easy act of handling these delicate filaments.

I should like to take this opportunity of publishing measures of the refractive power of fused quartz recently made by Mr. W. Watson in the Physical Laboratory at South Kensington, using a prism of this material that had been ground and polished by my friend Mr. Cunynghame. This piece of quartz I had annealed by allowing it to cool slowly in the centre of a furnace of pure broken quartz heated by a large oxyhydrogen-flame. Mr. Watson also measured the refractive index of a piece of crystalline quartz at the same time for the purpose of comparison.

Fused Quartz prism. Angle $57^{\circ} 7' 40''$ .			Crystalline Quartz prism. Angle $60^{\circ} 12' 50''$ . (Mean of two lines.)
Metal used to give line.	Wave-length.	Refractive index.	Refractive index.
Lithium.....	6705	1.4560	1.5415
Sodium .....	5892	1.4587	1.5443
Thallium .....	5349	1.4608	1.5469
Strontium .....	4607	1.4647	1.5507
Rubidium .....	4209	1.4681	1.5556



It will be seen that the refractive power of fused quartz is very low ; its dispersive power is the same as that of crystalline quartz. The material is perfectly transparent, it works as pleasantly as the crystal, and is certainly more permanent than any glass. Perhaps the makers of microscope-objectives might find it of some use. Examined by polarized light the prism appears isotropic.

C. V. BOYS.

South Kensington.

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### IX. *Notices respecting New Books.*

*A Short Course of Experiments in Physical Measurements.* By HAROLD WHITING, *Instructor in Physics at Harvard University.*  
—Part I. *Density, Heat, Light and Sound.*

THE above volume is issued as the first portion of an Elementary Course of Practical Physics, and deals with the subject in a manner differing somewhat from that adopted in the ordinary English text-books. The line of teaching indicated in it is one which has been more extensively followed in Germany than in the English colleges.

The author has chosen for his purpose only such experiments as can be performed without very elaborate apparatus, but which by applying care and a few special precautions can be made to give fairly accurate results. At the outset the student is expected to acquaint himself with the chief sources of error in any determination, and to learn how these can be got rid of either by careful manipulation or by suitable correction. He is thus taught at the very beginning of his course to attach more importance to his own carefulness than to the possession of what is often only apparently more accurate apparatus. In some respects this system possesses an advantage over the ordinary method of teaching, in which the student's first course of practical physics usually consists in repeating for himself the experiments which he has seen performed in the lecture-room. At the same time some difficulties arise from the fact that the methods of correction often involve a greater knowledge of physics than the student is supposed to possess when he performs the experiment. A good instance of this is to be found in the case of calorimetric measurements, where the application of a correction for the rate of cooling of a calorimeter involves an acquaintance with the laws of cooling ; and these laws would scarcely be treated of in an elementary course of lectures.

But perhaps the difference in the systems of examination furnishes the greatest objection to the adoption of foreign methods of teaching. At the end of his first year's course an English student is expected to know how to use almost every piece of apparatus which he has seen exhibited in the lecture-room, and he is thus

prevented from giving to each experiment the additional time which would be necessary in order to secure a good result.

The experiments described in the book before us are well arranged, and under each experiment the methods of procedure, the principles involved, and the nature and methods of correcting the various errors are all clearly set forth. In this respect the book is all that could be desired. The amount of mathematics involved is trifling, and is stated clearly and concisely, so that it could be followed easily by most students.

Among the experiments described in this first part we notice one or two that are entirely new, and other older experiments have been slightly modified in form. Foremost among the new experiments is a method of determining the specific heat of air at constant volume. A wire heated electrically by a measured current is used to heat the air, and the rise in temperature of the air is calculated from the observed increase of its pressure. We have not yet had an opportunity of trying this experiment, but if it yields a satisfactory result it will certainly form a valuable addition to the existing calorimetric methods. A good modification is also introduced into Dulong and Petit's apparatus for determining the absolute coefficient of expansion of mercury. In order to more easily compare the heights of the two columns of mercury they are brought nearer together at the top than is usually the case in the text-books. Several modifications of this kind appear throughout the book, and furnish valuable suggestions for obtaining increased accuracy in the results of experiments.

The illustrations and diagrams in the book have not been designed with a view to artistic excellence, but they show in most cases all the essential details of the apparatus. There is, however, room for improvement in this respect. In conclusion we believe that this work will be found useful by those teachers who wish to give their students a good training in practical physical measurement, without rushing through the subject at the pace usually required by those who are candidates for examination.

JAMES L. HOWARD.

## X. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from vol. xxix. p. 289.]

February 26, 1890.—J. W. Hulke, Esq., F.R.S., Vice-President,  
in the Chair.

THE following communication was read :—

“On the Relation of the Westleton Beds or ‘Pebbly Sands’ of Suffolk to those of Norfolk, and on their extension inland, with some observations on the Period of the final Elevation and Denudation of

the Weald and of the Thames Valley.”—Part III. On a Southern Drift in the Valley of the Thames, with Observations on the Final Elevation and Initial Subaerial Denudation of the Weald, and on the Genesis of the Thames.” By Prof. Joseph Prestwich, D.C.L., F.R.S., &c.

In this third part of his paper the author gave a description of the characters of the Southern Drift, showing how it differs from the Westleton Beds in the nature of its included pebbles, which consist of flints from the Chalk with a large proportion of *chert* and *ragstone* from the Lower Greensand, while there is a total absence of the Triassic pebbles and Jurassic *débris* characterizing the Northern Drift. He traced the drift through Kent, Surrey, Berkshire, and Hampshire, and described its mode of occurrence.

Another preglacial gravel was then discussed under the title of the Brentwood group, and its age was admitted to be doubtful.

The author then entered into an inquiry as to the early physiological conditions of the Wealden area, and gave reasons for supposing that a hill-range of some importance was formed in the Pliocene period after the deposition of the Diestian beds. From the denudation of this ridge, he supposes that the material was furnished for the formation of the Southern Drift, which may have been deposited partly as detrital fans at the northern base of the range.

The relation of the Southern Drift to the Westleton Shingle and other preglacial gravels was considered, and the Westleton Beds were referred to a period subsequent to that of the formation of the Southern Drift.

The influence of the meeting of the earlier Wealden axis with that of the folding which produced the escarpments of central England was discussed, and it was suggested that the result would be the genesis of the Thames valley and river.

The following summary gives the results of the author's inquiry as developed in the other parts of the paper. He holds :—

1. That the Westleton shingle ranges from Suffolk to Oxfordshire and Berkshire, rising gradually from sea-level to 600 feet.

2. That the lower Tertiary strata were coextensive with this shingle.

3. That the upraising of the Westleton sea-floor, with its shingle, preceded the advance of the glacial deposits, and that the latter become discordant to the former when traced westward, occupying valleys formed after the rise of the Westleton Beds.

4. That the Tertiary strata and Westleton Beds on the north border of the Chalk-basin were continuous until the insetting of the Glacial period, when they were broken through by denuding agencies.

5. That none of the present valleys on the north of the Thames Tertiary basin date back beyond the Preglacial period.

6. That the same date may be assigned to the Chalk, and probably to the Oolite escarpments.

7. That in the Thames basin, besides the Northern Drift, there is

a Southern Drift derived from the Lower Greensand of the Wealden area, and from the Chalk and Tertiary strata formerly extending partly over it.

8. That during the Diestian period the Weald was probably partly or wholly submerged, and that between this and the insetting of the Glacial period, the Wealden area and the Boulonnais underwent upheaval resulting in the formation of an anticlinal range from 2000 to 3000 feet high.

9. That from the slopes of this range the materials of the Southern Drift were derived, and spread over what is now the south side of the Thames basin.

10. That this denudation commenced at the time of the Red Crag, and went on uninterruptedly through successive geological stages.

11. That consequently, though the Southern Drift preceded the Westleton shingle, the two must at one time have proceeded synchronously.

12. That the valley-system of the Wealden area dates from Pliocene times,—the initial direction of the transverse valleys from Preglacial times,—and of the longitudinal valleys from Glacial times.

13. That the Thames basin results from the elevation of the Weald and the flexures of the Chalk and Oolites of the Midland counties, and dates from a period subsequent to the Westleton Beds.

14. That the genesis of the Lower Thames similarly dates from early Pleistocene times, whilst its connexion with its upper tributaries and the Isis, which possibly flowed previously north-eastward, took place at a rather later period.

March 12.—J. W. Hulke, Esq., F.R.S., Vice-President,  
in the Chair.

The following communications were read:—

1. "On a Deep Channel of Drift in the Valley of the Cam, Essex." By W. Whitaker, Esq., B.A., F.R.S., F.G.S.

In Scotland and in northern England long and deep channels filled with Drift have been noticed, but not in southern England.

For some years one deep well-section has been known which showed a most unexpected thickness of Glacial Drift in the higher part of the valley of the Cam, where that Drift occurs mostly on the higher grounds and is of no very great thickness. Lately, further evidence has come to hand, showing that the occurrence in question is not confined to one spot, but extends for some miles. The beds found are for the most part loamy or clayey.

At the head of the valley various wells at Quendon and Rickling show irregularities in the thickness of the Drift, the Chalk coming to or near the surface in some places, whilst it is nearly 100 feet below it in others.

Further north, at Newport, we have the greatest thickness of Drift hitherto recorded in the South of England, and then without reaching the base. At one spot a well reached Chalk at 75 feet;



whilst about 150 feet off that rock crops out, showing a slope of the Chalk-surface of 1 in 2. In the most interesting of all the wells, after boring to the depth of 340 feet, the work was abandoned without reaching the Chalk, the Drift in this case reaching to a depth of about 140 feet below the level of the sea, though the place is far inland. The Chalk crops out about 1000 feet eastward, and at but little lower level, so that there is a fall of about 1 in 3 over a long distance.

At and near Wenden the abrupt way in which Drift comes on against Chalk has been seen in open sections. Two wells have shown a thickness of 210 and 296 feet of Drift respectively; and as the Chalk comes to the surface, at a level certainly not lower, only 140 yards from the latter, the Chalk-surface must have a slope of 1 in less than  $1\frac{1}{2}$ , and this surface must rise again on the other side, as the Chalk again crops out. The Drift here reaches to a depth of 60 or 70 feet below the sea-level.

At Littlebury, in the centre of the village, a boring 218 feet deep has not pierced through the Drift, which reaches to 60 feet below the sea-level. As in a well only 60 yards west and slightly higher, the Chalk was touched at 6 feet, there must here be a fall of the Chalk-surface of about 1.2 in 1. Eastward too, on the other side of the valley, the Chalk rises to the surface.

The places that have been mentioned range over a distance of 6 miles. How much further the Drift-channel may go is not known, neither can we say to what steepness the slope of the underground Chalk-surface may reach; the slopes given in each case are the lowest possible.

The author thinks that the channel has been formed by erosion rather than by disturbance or dissolution of the Chalk.

## 2. "On the Monian and Basal Cambrian Rocks of Shropshire." By Prof. J. F. Blake, M.A., F.G.S.

In a previous paper the author had suggested that the Longmynd rocks were referable to the Upper Monian. He now finds that they are divisible into two groups, of which the lower only can be thus referred.

This lower group is divisible into five parts:—1. Dark Shales; 2. Banded Series; 3. Purple Slates; 4. Hard Greywackés; 5. Pale Slates and Grits. These are shown to have a real dip to the west, and not to be thrown into any folds. It is in these only that fossils have been found. The lowest dark shales are not basal rocks, nor derived from the eastern volcanic series.

The junction of the upper group, which represents the true Cambrian, is unconformable, as shown by detailed stratigraphy. It consists of three members, the middle one being slates which die out northwards. There is neither synclinal nor anticlinal fold, but a regular sequence and dip; and pale slates follow on the west. The base is brought into connexion with each division of the lower series except No. 2. The conglomerates contain:—1. Quartz;

2. Rhyolites ; 3. Gneissic rocks ; 4. Slates like those of the underlying group. The supposed Archæan masses on the western border are non-existent, being intrusive and transgressive igneous rocks.

The volcanic group on the east is not bounded by the main fault, the dark shales lying to the east of that fault. Evidence is given that the volcanic rocks have been protruded through these shales, which they have altered. The Eurite of the Wrekin is of later date, and the only possible older rocks are the Rushton Schists and the fragments of schistose rocks on Primrose Hill.

At several places patches of red grit and conglomerate are seen on the Volcanic hills ; these are referred to the Cambrian, and their connexion also with earlier conglomerates forming part of the Volcanic series is suggested. The Cambrian quartzite is later than all these, but may be synchronous with the upper part of the western Grits.

The Volcanic rocks are not, therefore, Middle Monian, as formerly supposed, but represent the interval between Monian and Cambrian. If classed with either, the author inclines rather to place them with the Cambrian, in spite of the unconformity of the quartzite. He regards them as probably the equivalents of the Bangor Series, and possibly of the St. David's Volcanic Group. If this classification be adopted, then the Monian system will be entirely separated from the Pebidian, and be established on distinct and independent observations.

3. "On a Crocodilian Jaw from the Oxford Clay of Peterborough." By R. Lydekker, Esq., B.A., F.G.S., &c.

4. "On two new Species of Labyrinthodonts." By R. Lydekker, Esq., B.A., F.G.S., &c.

March 26.—J. W. Hulke, Esq., F.R.S., Vice-President,  
in the Chair.

The following communications were read :—

1. "On a new Species of *Cyphaspis* from the Carboniferous rocks of Yorkshire." By Miss Coignou, Cambridge.

2. "On Composite Spherulites in Obsidian from Hot Springs, near Little Lake, California." By Frank Rutley, Esq., F.G.S., Lecturer on Mineralogy in the Royal School of Mines.

The spherulites which form the subject of the present communication have been previously noticed, and it was then suggested that a smaller spherulitic structure was set up in the large spherules after their formation. In the present paper evidence was adduced in favour of a different mode of origin. It was argued that the small spherulitic bodies (primitive spherulites) were developed in the obsidian before it assumed a condition of rigidity, and that they floated towards certain points in the still viscid lava, and segregated in more or less spherical groups, though there is no evidence to show what determined their movements ; furthermore, that from a point or points situated at

or near the centre of each group, crystallization was set up, giving rise to a radiating fibrous structure, which gradually developed zone after zone of divergent fibres until the entire mass of primitive spherulites was permeated by this secondary structure—a structure engendering a molecular rearrangement of the mass, such as would obliterate any trace of structure which the primitive spherulites might have originally possessed.

In a supplementary note the views of Mr. J. P. Iddings with reference to the spherulites in question were given. Mr. Iddings considers that the structures here described as primary are of secondary origin. The author stated in detail his reasons for adhering to the conclusions given in this paper.

3. "A Monograph of the Bryozoa (Polyzoa) of the Hunstanton Red Chalk." By George Robert Vine, Esq.

4. "Evidence furnished by the Quaternary Glacial-Epoch Morainic Deposits of Pennsylvania, U.S.A., for a similar mode of formation of the Permian Breccias of Leicestershire and South Derbyshire." By William S. Gresley, Esq., F.G.S.

The author noted that nodules of ironstone occurring in the Pennsylvanian glacial deposits of Quaternary age are scratched in precisely the same manner as those which he has described from the Permian deposits of Leicestershire and Derbyshire, and concluded that one and the same agency, viz. ice, has been instrumental in producing the observed results in both cases.

## *XI. Intelligence and Miscellaneous Articles.*

DIAMAGNETISM TESTED BY CARNOT'S PRINCIPLE. THEORETICAL PREDICTION. BY J. PARKER, M.A., FELLOW OF ST. JOHN'S COLLEGE, CAMBRIDGE.

IN May 1889 I published a short paper in the Philosophical Magazine in which Carnot's principle was applied to diamagnetism. An oversight occurs in the paper which has since been corrected by M. Duhem, who has adopted and extended the substance of the paper.

The present state of experiment and theory on diamagnetism may be briefly stated thus:—

(1) If a piece of bismuth be placed near a strong iron magnet in the open air, the bismuth behaves as if repelled by the iron.

(2) If the same experiment were performed in a vacuum, it is shown by Carnot's principle that the bismuth would not be repelled and might be attracted.

We therefore conclude that if the experiment were performed in a place from which the air could be pumped away at will, the repulsive force on the bismuth would become zero when the pressure of the air was sufficiently reduced, and by continuing the exhaustion still further it would probably become attractive.



The action of the bismuth in the open air will be explained if we remember that both the iron and the bismuth are surrounded by a mass of magnetized air, so that the behaviour of the bismuth is due to three causes:—

- (1) The attraction of the iron magnet.
- (2) The attractions of the magnetized atoms of air.
- (3) The resultant of the unequal pressures of the air over the surface of the bismuth.

The conclusions of this paper naturally lead us to question the propriety of making our “absolute” units of electricity and magnetism depend on the actions between bodies surrounded by electrified or magnetized air about which all that is known is that, at some distance away, the air with which it is in equilibrium has a measurable pressure.

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AN EASY MODE OF PRODUCING THE ACTIVE SPARK IN HERTZ'S  
EXPERIMENTS. BY H. CLASSEN.

In repeating Hertz's experiments in the State Physical Laboratory at Hamburg, an observation was made which shows how in a simple manner we can overcome the difficulty experienced by many observers of keeping the primary spark effective for a long time together. In the same manner in which Rijke\* used the action of a current of air on the make-and-break spark of an induction-coil in order to produce a stronger action in the secondary coil, so may the spark of the coil itself, and therefore also its inductive action on any other conductor, be similarly influenced.

In the experiments a large Ruhmkorff's coil was used which had a very rapid contact-maker, and which gave sparks up to 14 centim. If the ends of the secondary coil are loaded with conductors, and the discharging-knobs are brought within a distance of a few centimetres, the discharge takes place mostly in the form of a continuous rose-coloured strip of light, and is useless for Hertz's experiments. But when this band is blown away so that flames a centimetre in length project on the side, sharp brightly luminous sparks occur between the knobs. The current of air produced by a Münke's water-pump was now blown continuously between the knobs, and thus a series of sharp cracking sparks passed quite continuously, and could without difficulty be continuously maintained for hours. A series of Hertz's experiments could now be repeated, and even when the current of air was replaced by one of steam the action was the same. The whole process suggests the idea that, in the ordinary discharge with a luminous band of light, detached metallic particles effect a permanent conduction, and that the essential discharge-spark is only produced as these particles are blown away. The influence of the ultra-violet illumination, too, which has been designated by various observers as highly disturbing, would, after the researches of Lenard and Wolf on the pulverization of bodies

\* Pogg. *Ann.* cxvii. p. 276 (1862).



by illumination, in this find an explanation.—Wiedemann's *Annalen*, xl. p. 647 (1890).

ON THE EXPERIMENTS OF HERTZ. BY L. BOLTZMANN.

I have successfully demonstrated to a large audience the sparks which pass between a knob and a point in Hertz's experiments on rays of electrical force, by connecting the knob with a very sensitive electroscope, and the point with the pole of a suitable galvanic battery, the other pole of which was put to earth. As long as there were no minute sparks or *scintilla* (Fünkchen\*) the electroscope remained uncharged; but when these were formed they established a connexion between the knob and the point and caused the leaves to diverge. In this manner I was able to show with certainty the scintilla produced by a single primary spark when the primary and secondary inductors were at a distance of 36·8 metres apart, the greatest distance available.

At a distance of 8·7 metres all the Hertz experiments could be most conveniently demonstrated before an audience of about 200, so as to be visible to every one; only three or four primary sparks were required for each experiment, by which the electrodes could be kept brightly polished. Dust, cracks in the metal, or an impure greasy condition of the surface appeared more injurious than the layer of oxide: cleaning with dilute sulphuric acid, distilled water, and then dry rubbing was found to be best; a thicker layer of oxide is removed by polishing with French chalk (moistened with spirit), in which case dry rubbing is sufficient. I was not able to perceive any advantage in a current of air as recommended by Dr. Classen.

The length of the secondary spark produced at the great distance of 36·8 metres I estimated at  $\frac{1}{5000}$  millim. as the maximum. As the dry pile which served to charge the electroscope had a potential of 200 volts, the knob and the point were adjusted at a distance which exceeded by about  $\frac{1}{5000}$  the striking distance of the dry pile, the discharge of which was then set up by the addition of Hertz's waves to the tension of the dry pile. By using a much more feebly charged battery instead of the dry pile, and a much more delicate galvanoscope, Hankel's for example, the rays might be perceived at still greater distances. In the latter case it might not be impossible to measure the deflexion with a view to quantitative determinations. The regulation of the distance between the knob and the point must then be made so much the finer.

I also made experiments on interference by reflecting the waves from the primary parabolic mirror through two plane mirrors, which, like those of Fresnel, formed an obtuse angle, and whose planes were at a distance of fourfold a half wave-length. This method

\* It may be convenient to use the word *scintilla*, spark, or little spark, to denote the very minute spark produced in the secondary circuit in Hertz's experiments.—E. ATKINSON.

seems well suited for accurate measurements of the wave-length and of the decrement of the vibrations.—Wiedemann's *Annalen*, xl. p. 399 (1890).

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LECTURE-EXPERIMENT TO DEMONSTRATE THE EXCITATION OF  
ELECTRICITY BY LIGHT. BY WILHELM HALLWACHS.

In the first experiments on the excitation of electricity by light, only very feeble positive charges were obtained of the magnitude of a volt. MM. Bichat and Blondlot then found a method of increasing the charges by directing a current of air against the irradiated plate by which they obtained increases of potential up to 30 volts. This method of increasing the excitation afforded at the same time an insight into the connexion between the excitation of electricity by light and the discharge of electricity by light, which latter was increased by the electrostatic power of the negative charges imparted to the plates, just as by a current of air. This connexion was made clear by the experiments of Prof. Righi, who demonstrated the proportionality between the potential produced by radiation and the electrostatic forces which occur at the surface. In repeating the experiments of Bichat and Blondlot, I have obtained charges up to 100 volts by blowing against the bottom of a brass vessel suspended in a sheath.

In order to show in a lecture the excitation of electricity by light we take advantage of the current of air; for then, if the field of observation is sufficient and the lamp does not burn too long, we may dispense with the troublesome screens against induction. By means of the following arrangement I have been able to show the phenomenon to a large circle of hearers. In the luminous cone of the electric light, after removing any glass lenses in the lantern, a freshly polished zinc plate fixed to a shellac support is introduced laterally. The rays of light which pass by on the side strike a lens at some distance, which concentrates them on the gold leaf of a Hankel's electrometer. After removing the eyepiece, the object-glass of the microscope of the electrometer projects an image of the gold leaves on a screen, on which a scale is affixed to observe the displacement of the gold leaves. When the electrometer was charged with 20 chromic-acid elements and when the plates of the electrometer were tolerably near, the desired sensitiveness was obtained. In order to measure the latter a rigid wire was placed on the electrometer-battery, a few elements removed from the point put to earth, and connected by the conductor with the gold leaf.

In order to make the experiment, the gold leaf and the zinc plate are connected with each other, a disk of mica is introduced in the path of the rays coming from the lamp, the zinc plate is put to earth for a moment, and after removing the mica disk no perceptible change is observed in the adjustment of the gold leaves if the sensitiveness of the electrometer is not exceptionally great. If

there is no deflexion, it shows that the space in which the observations are made is free from the products of combustion of the lamp. When the mica disk has been again pushed forward the zinc plate is blown on from a hand-bellows, when there is no deflexion of the gold leaf. If then the mica disk is withdrawn, a few separate puffs with the bellows are sufficient to produce considerable deflexions, so as to drive the leaf off the scale. That the direction of the deflexion corresponds to a positive electrification follows from the sign of the potential when the electrometer is charged for determining its sensitiveness, and from the deflexions thereby produced. Wiedemann's *Annalen*, xl. p. 343 (1890).

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## INVESTIGATION OF ELECTRICAL RESONANCE.

BY DR. ERNEST LECHNER.

The author describes first of all a method of observing electrical vibrations in wires. Opposite each of the two terminal plates of a Hertz's arrangement for vibrations an equally large insulated plate is arranged, and from each plate is led a wire several metres in length, the two wires being parallel. Over the end of the wire a rarefied tube, without an electrode, is placed, which becomes luminous in consequence of the electrical oscillations in the wires. If the parallel wires are connected by a cross wire the luminosity in general ceases. If this bridge is moved backwards and forwards along the parallel wires, a few very sharply defined places are found where the tube suddenly becomes luminous; these are the ventral segments of the electrical motion.

After the author had studied the conditions of the experiment, and had shown that the whole is an electrical phenomenon of resonance, the shape and position of the electrical wave was precisely determined by seeking the common ventral segment. The influence of the introduction of capacities at the end of the wires was also examined.

The author invariably found that Hertz's observations were always confirmed; in one important point, however, he obtained a different result. While Hertz found for the velocity of electricity in wires 200,000 kilometres per second, the author obtained within 2 per cent. of the exact velocity required by Maxwell's and all other theories; he cannot, however, explain why his results differ from that of Hertz. A possible source of error in the experiments of Hertz was found on closer inquiry to be too small. As the method used by the author is very simple and comprehensive, and can be very easily made, in the form even of a lecture-experiment, he considers his value not only theoretically but also practically the most probable.—*Wiener Berichte*, May 8, 1890.

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[FIFTH SERIES.]

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AUGUST 1890.

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XII. *Some Experiments on the Velocity of Transmission of Electric Disturbances, and their Application to the Theory of the Striated Discharge through Gases.* By J. J. THOMSON, M.A., F.R.S., Cavendish Professor of Experimental Physics, Cambridge\*.

THE velocity of transmission of an electric impulse along a wire is, according to Maxwell's theory, equal to the velocity with which light passes through the dielectric surrounding the wire. The velocity is thus determined by the surrounding dielectric, in which the energy resides, and the function of the wire seems merely to be that of guiding the discharge, which travels at a rate fixed by the dielectric.

The equality between the velocity of light through air and the rate of transmission of an electric impulse along a wire surrounded by air has been roughly verified by observing the lengths along a wire of electric waves generated by an electric vibrator: it was found that the wave-length divided by the calculated time of vibration was very nearly equal to the velocity of light. In order to test Maxwell's theory more fully, and to illustrate the influence of the dielectric and the subordinate part played by the conductor, I have made some experiments to compare the velocity of transmission of electric impulses along wires surrounded by different dielectrics.

If an electric vibrator AC attached to an induction-coil has connected with it a wire AB which bifurcates at B into two circuits, BL, BM, and if the ends L, M are connected to a spark-micrometer the sparking-distance of which can be adjusted by means of a screw, the sparking-distance will depend

\* Communicated by the Author.

*Phil. Mag.* S. 5. Vol. 30. No. 183. August 1890. K



upon the relative lengths of the wires BL, BM. If these wires are both surrounded by air, the sparking-distance is a minimum when the lengths are equal. This is the case whatever the material or cross section of the wires. This is also the case if one of the wires is placed between two large zinc plates at a small distance apart; though in this case the electrostatic capacity of one of the wires is very much greater than that of the other.

If  $\phi_0 \cos nt$  represents the potential of B,  $l, l'$  the lengths of the wires BL, BM respectively,  $v$  and  $v'$  the velocities of transmission of electric impulses along them, then the potentials of L, M are respectively

$$\frac{\phi_0 \cos nt}{\cos \frac{nl}{v}}, \quad \frac{\phi_0 \cos nt}{\cos \frac{nl'}{v'}}.$$

These potentials will be equal, and the sparks therefore have a minimum length, when  $l/v = l'/v'$ . When  $v = v'$ ,  $l = l'$ , which agrees with the effects observed when both wires were surrounded by air. But if  $v$  and  $v'$  are different, then the lengths of the circuits for minimum spark-length will be unequal, and the ratio of the two lengths will be the ratio of the velocities of transmission of electric impulses along the wires. We have thus a method of finding the rate of transmission of electric waves along different wires\*.

In order to compare the velocity along a wire surrounded by air with that along one surrounded by paraffin or sulphur, one of the wires BM was placed inside and insulated from a brass tube connected with the earth at each end. The tube was filled either with paraffin which was poured in in a melted condition and allowed to set, or with sulphur melted down so as to form a solid mass. The length of the circuit BL could be altered by successively adding pieces of wire each  $\frac{1}{4}$  of a metre in length. The length of the wires when the spark-length was least are given in the following Table, where the different numbers refer to experiments made on different days :—

Wire surrounded by paraffin.	Wire surrounded by air.
4 metres.	5, $5\frac{1}{4}$ metres.
4     "	5.5     "
4     "	6       "
4     "	5       "
Mean . . 4 metres.	5.4 metres.

\* I have found since this paper was in type that exactly the same method was used by von Bezold twenty years ago to prove that the velocity of transmission of electricity along wires is not affected by the material or diameter of the wire (Poggendorff's *Annalen*, cxl. p. 541).

The velocity along a wire in air is thus  $5\frac{1}{4}$ , or 1.35 times the velocity along a wire surrounded by paraffin.

Wire surrounded by sulphur.	Wire surrounded by air.
4 metres.	6.25 metres.
4     "	6.5     "
4     "	7     "
4     "	7.5     "
<hr/> Mean . . 4 metres.	<hr/> 6.81 metres.

Thus the velocity along the wire surrounded by air is 1.7 times the velocity along the wire surrounded by sulphur.

These experiments show that the velocities along wire surrounded by air, paraffin, and sulphur are approximately proportional to the reciprocals of the square roots of their specific inductive capacities.

When the tube surrounding the branch BM of the circuit was filled with powdered glass, the sparks were least when the lengths of the wires BL, BM were equal. This was also the case when the tube was filled with flowers of sulphur. I believe the explanation of this to be that the small pieces of glass and sulphur are coated with a conducting film of moisture which prevents the waves entering the glass or sulphur, so that the waves in this case are really transmitted through air.

#### *Velocity of Transmission along Electrolytes.*

To determine the velocity along an electrolyte, an electrolytic cell filled with a solution of zinc sulphate and having zinc electrodes was placed in one of the arms of the fork. The cross section of the cell was about 1 square inch, and the distance between the electrodes about 2 inches. In this case the sparks were least when the arms were of the same length, though the effect produced by increasing the length of one of the circuits was not so great as when both arms were entirely metallic. The velocity of propagation of a rapidly alternating current along an electrolyte surrounded by air can thus not differ much from the rate along a wire.

When a vacuum-tube was substituted for the electrolytic cell, the sparking-length did not seem to be affected, however the relative lengths of the arms BL and BM were altered. I believe that this, however, is not because the velocity of the discharge through a vacuum-tube is very much less than the velocity along a wire, but on account of the retardation of the discharge at the electrodes. The velocity across an air-space cannot be very different from that along a wire, otherwise the periods of electrical vibrators would vary with the length of

the spark very much more rapidly than seems to be the case. I am endeavouring by the aid of a rotating mirror to measure the velocity of the discharge along a vacuum-tube 50 feet long, and though the experiments are not yet completed, they have gone far enough to show that the velocity through the gas is comparable with that of light. The results of experiments on the rate of propagation of electricity along wires leads us to regard the conductor as merely guiding the discharge, the correlation between the æther and the conductor compelling the discharge to travel along the latter with the velocity of light.

The very rapid rate with which the electric discharge is propagated through a rare gas compels us to admit that the electricity is not carried by charged atoms moving with this velocity. For if it were, then if the discharge were to take place in air at atmospheric pressure between two parallel plates one centimetre apart, charged to a potential difference of approximately 30,000 volts, the kinetic energy which would have to be communicated to the atoms to make them move with this velocity would be greater than the original potential energy of the charged plates: assuming that the charge on each atom is that deduced from electrolytic considerations.

The evidence in favour of the view that the conduction of electricity takes place by means of the atoms of the substance through which the discharge passes appears to me to be so strong, that I think it important to see whether this view of the electric discharge cannot be reconciled with the very rapid rate at which the electric discharge passes through a gas. The following view of the behaviour of the gas seems to explain both the rapid propagation of the discharge and some of its most striking features, such as stratification.

Before the electric field is intense enough to cause discharge, the induction in the field polarizes the gas. We may regard this polarization as being equivalent to the formation of chains of molecules analogous to the "Grotthus chain" in electrolysis. As the intensity of the field increases, suppose the molecules in one of these chains near an electrode, say the negative, interchange their atoms; and that *it is not merely those molecules which are next the electrode which split up, but that the decomposition of the molecules extends along an appreciable length of the chain.* The positively electrified atoms will cling to the negative electrode, and after a time, depending upon the number of free atoms, the distance between them, and their mutual attractions, the chain will resume its original molecular condition. This time may vary slightly from atom to atom. Let us, however, for the sake of clearness, suppose



that the atoms recombine simultaneously after a time  $T$ . Then, when the atoms have recombined as far as possible, since there are a certain number, say  $N$ , of positively electrified atoms sticking to the negative electrode, there must be  $N$  negative atoms left free : in order that the discharge should travel with the velocity  $V$ , these  $N$  negative atoms must be situated along the line of discharge at a distance  $VT$  from the negative electrode. Hence if we suppose that the molecules along a length  $VT$  of the Grotthus chain were split up before discharge commenced, the free negative atoms would appear at the end of this chain, and the discharge would travel with the velocity  $V$ ; and thus, by properly choosing the length of the chain, we can make the velocity what we please.

The  $N$  free atoms at the end of the chain would act as a new negative electrode, and other Grotthus chains of length  $VT$  would decompose at the end of this, and so on. The discharge would thus be broken up into a series of separate currents, each of length  $VT$ ; and in this way the discharge through each element would be able to satisfy the condition imposed on it by the surrounding dielectric and travel with the velocity of light.

According to our view, this breaking-up of the current into a series of separate pieces shows itself in the stratifications observed when the discharge passes through a gas at low pressure. The behaviour of a striated discharge in a magnetic field seems almost to prove that it is made up of a series of separate discharges. For "if a magnet be applied to a striated column, it will be found that the column is not simply thrown up or down as a whole, as would be the case if the discharge passed in direct lines from terminal to terminal, threading the striæ in its passage. On the contrary, each stria is subjected to a rotation or deformation of exactly the same character as would be caused if the stria marked the termination of flexible currents radiating from the bright head of the stria behind it, and terminating in the hazy inner surface of the stria in question. An examination of several cases has led the authors of this paper to conclude that the currents do thus radiate from the bright head of a stria to the inner surface of the next, and that there is no direct passage from one terminal of the tube to the other." (Spottiswoode and Moulton, *Phil. Trans.* 1879, part i. p. 205.)

Goldstein, and Spottiswoode and Moulton, from the study of the behaviour of the striated discharge, have independently arrived at the conclusion that each stria represents a separate discharge. Thus Goldstein (*Phil. Mag.* [5] x. p. 183) says :—  
"By numerous comparisons, and taking account of all appa-



rently essential phenomena, I have been led to the following view :—

“The kathode-light, each bundle of secondary negative light, as well as each layer of positive light, represent each a separate current by itself, which begins at the part of each structure turned towards the kathode, and ends at the end of the negative rays or of the stratified structure, without the current flowing in one structure propagating itself into the next, without the electricity which flows through one also traversing the rest in order.

“I suspect, then, that as many new points of departure of the discharge are present in a length of gas between two electrodes as this shows of secondary negative bundles or layers—that as, according to experiments repeatedly mentioned, all the properties and actions of the discharge at the kathode are found again at the secondary negative light and with each layer of positive light, the intimate action is the same with these as it is with those.”

Spottiswoode and Moulton (Phil. Trans, part i. 1879, p. 201) express much the same opinion :—“If, then, we are right in supposing that the series of artificially produced hollow shells are analogous in their structures to striæ, it is not difficult to deduce from the explanation above given the *modus operandi* of an ordinary striated discharge. The passage of each of the intermittent pulses from the bright surface of a stria towards the hollow surface of the next may well be supposed, from its inductive action, to drive from the next stria a similar pulse, which in its turn drives one from the next stria, and so on. Thus the procession in the naturally and artificially striated columns are precisely similar; save that in the case of the latter the pulses from the several striæ are excited by induction from without the tube, while in the case of the former the induction is that of the discharge itself in its passage from stria to stria. The passage of the discharge is due in both cases to an action consisting of an independent discharge from one stria to the next; and the idea of this action can perhaps be best illustrated by that of a line of boys crossing a brook on stepping stones, each boy stepping on the stone which the boy in front of him has left.”

The laws governing striation seem to be in accordance with those which follow from the view expressed above, that the distance between two striæ is the distance passed over by light during the time taken by the atoms split up in the chain to recombine.

Thus the distances between consecutive striæ increase when the pressure of the gas diminishes; but when the pressure

diminishes the mean distances between the atoms increase, and therefore  $T$ , the time required for recombination, will increase; but as on the above view the distance between two striæ is  $VT$ , where  $V$  is the velocity of light, the diminution of the pressure will cause a separation of the striæ. Again, the distance between two striæ increases as the diameter of the tube in which the discharge takes place increases; since in the wider parts of the tube we have the same number of molecules split up as in the narrower, the average distance between the atoms will be greater in the wide part of the tube than in the narrow, so that the time required for recombination, and therefore the distance between two striæ, will be greater in the wide part of the tube than in the narrow.

We have not the requisite data for calculating the time required for the recombination of the atoms, but we may perhaps suppose it is of the same order as the time required for a particle moving with the average molecular velocity to travel over half the average distance between the molecules: this time for air at the pressure of 1 millim. of mercury is about  $2 \times 10^{-11}$  seconds, which would correspond to a distance between the striæ of 6 millimetres, which is a length quite of the same order as the actual one.

An interesting point arises when the electrodes are separated by a distance less than  $VT$ . In this case the discharge cannot be propagated from one electrode to the other with the velocity  $V$  unless the velocity of the atoms is very much increased. This increase in the energy which has to be communicated to the gas to allow the spark to pass will increase the resistance which the gas opposes to the passage of electricity along the line joining the electrodes; that is, it will require a greater electromotive intensity to produce the discharge. If, however, instead of taking the straight line of force between the electrodes, we consider one of the longer curved lines, and choose one whose length is  $VT$ , or a multiple of it, then along this line a Grotthus chain could be formed, which would convey the discharge with the velocity  $V$ ; and since in this case it is not necessary to increase the velocity of the atoms in order to attain the requisite velocity of propagation, the resistance opposed by the curvilinear path per unit length will be less than that offered by the straight path. Thus, when the electrodes are separated by a shorter distance than  $VT$ , the shortest distance between them need not be the path of least resistance, and we might expect to find the discharge taking place along curvilinear paths of such length as would enable the discharge to travel at a rate  $V$  without increasing the kinetic energy of the molecules.

Very striking examples of this effect have been given by Hittorf and others. Hittorf (Wied. Ann. xxi. p. 90) describes an experiment in which when the electrodes were very near together the discharge passed along a curved path of very much greater length, leaving the short space between the electrodes free from glow. In Lehmann's *Molekularphysik*, vol. ii., many illustrations of the discharge between electrodes very near together are given. Some of these are very remarkable, the space immediately between the electrodes being free from glow, while the discharge when the electrodes are plane passes between the faces of the electrodes which are most remote from each other.

The view we have taken of the electric discharge requires the molecules to be split up for a finite distance along the line of force: the electromotive intensity has to maintain over this length the value required to split up the molecules; thus, if the field of force is not uniform, it will require a greater electromotive intensity at the surface of the electrode to produce a spark than if the field were uniform. However, at ordinary pressures  $VT$  is so small that it would be very difficult to produce a sufficiently rapid variation of the field to make this effect felt.

The striations on this view of the electric discharge may be regarded as forming little electrolytic cells, the beginning and end of a stria corresponding to the electrodes of the cell. Let us consider one of these cells. Suppose the unit of electricity passes through it, then the work done by the electric field is  $F\lambda$ , if  $F$  is the electromotive intensity, and  $\lambda$  the length of the stria. The passage of this unit of electricity will be accompanied by definite chemical changes in the space between two striations. Let  $w$  be the increase in the potential energy due to these changes, then, if there is no increase in the kinetic energy of the gas, we must have

$$F\lambda = w.$$

Thus, when the chemical change is the same, the electromotive intensity varies inversely as the distance between two striæ. Thus, if we can diminish in any way the distance between the striæ without altering the chemical action, the electromotive intensity required to force electricity through the gas will be increased. If we have gas at the same pressure in tubes of different diameter, after the exhaustion has passed a certain point, the distance between the striæ will be greater in the wide tubes than in the narrow ones, so that the resistance offered to the discharge ought to be greater in the narrow tubes than in the wide ones. Hittorf (Wied.



*Ann.* xxi. p. 90) has observed this effect to a very striking extent: at a pressure of .03 centim. of mercury it took 1100 elements of his battery to force the discharge through a tube 1 centim. in diameter, while 300 elements were sufficient to force it between similar electrodes in a tube 11 centim. in diameter.

In the structure round the negative electrode, consisting of the glow over the electrode, Crookes' dark space, and the negative glow, which, according to our view, is only a stria differing from other striæ merely by the special arrangement of the lines of force near the electrode, the chemical and other changes produced by the discharge seem to be more complicated than those which take place in the rest of the field: one obvious reason for this is the presence of the metal, which makes many chemical changes possible which could not take place in striæ where nothing but gas is present. This stria is thus under special conditions, and may differ in size, fall of potential, &c. from the remaining striæ.

Hittorf's experiments show that there is an exceptionally large change in potential close to the kathode. If we take the preceding view of the spark-discharge this will explain the very striking increase in the electromotive intensity necessary to produce a spark across a layer of air when the thickness of the layer is diminished beyond a certain amount. For let us consider the case when the spark passes between two infinite parallel planes; the discharge, according to the view enunciated above, goes first across the stria next the negative electrode, where the rise in potential is  $K$ , and then across a number of other striæ, the rise of potential across each stria being  $w$ ; thus if  $n$  be the number of such striæ,  $V$  the difference of potential between the plates when the spark passes,

$$V = K + nw.$$

If  $l$  is the distance between the plates,  $\lambda_0$  the length of the stria next the kathode,  $\lambda$  the length of the other striæ, then

$$n = \frac{l - \lambda_0}{\lambda}$$

$$V = \left( K - \frac{\lambda_0}{\lambda} w \right) + \frac{l}{\lambda} w. \quad . \quad . \quad . \quad (1)$$

This may be written

$$V = K' + \alpha l.$$

On this view the curve representing the relation between difference of potential and spark-length is a straight line not



passing through the origin. The curve given by Paschen (Wied. *Ann.* xxxvii. p. 69) for the relation between spark-length and potential when the electrodes were spheres 1 centim. in radius is very nearly straight, and would correspond to the above formula if  $K'$  were between 600 and 700 volts.

If  $R$  is the electromotive intensity required to produce a spark of length  $l$ , we see from the above since  $R = V/l$  that

$$R = \frac{K'}{l} + \alpha.$$

Thus the electromotive intensity required to produce a spark increases as the spark-length diminishes; in other words, the electric strength of a thin layer is greater than that of a thick one.

The curve on this hypothesis representing the relation between the electromotive intensity and the spark-length is a rectangular hyperbola; the curves given by Dr. Liebig (*Phil. Mag.* [5] xxiv. p. 106) for air, hydrogen, carbonic acid, and coal-gas seem to approximate to hyperbolas.

The distance between the striæ is proportional to the time taken by the atoms in the Grotthus chain to recombine; this time will be greater the greater the distance between the atoms; if we assume that it is proportional to the distance travelled by an atom between two collisions, the distance between the striæ will be proportional to the mean free path, and therefore inversely proportional to the density: thus we may write in equation (1)  $\lambda = \beta/\rho$ , where  $\rho$  is the density of the gas. With this substitution equation (1) becomes

$$V = K' + \frac{l\rho w}{\beta}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Paschen's observations on the electric strength of air, hydrogen, and carbonic acid at various pressures seem fairly accordant with this formula; they show, however, that  $K'$  is not quite independent of the density but increases slowly with it. If we are dealing with sparks so long that the second term on the right-hand side of equation (2) is large compared with the first, then the spark-potential for the same gas depends only upon the product  $l\rho$ . Paschen's experiments seem to show that this law holds with great accuracy; it would, however, be interesting to have experiments with smaller values for  $l\rho$  than those used by him.

In the preceding equations we have supposed the field to be uniform and the striæ of the same length; if the field is

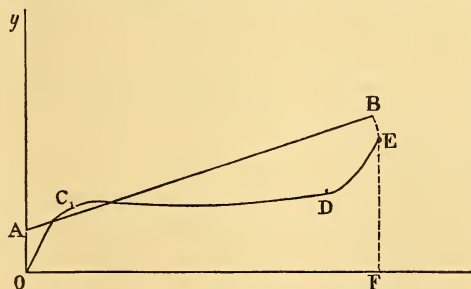
variable the striæ may be of slightly different lengths, and (2) will only be approximately true; the accurate equation will be

$$V = K + w \int_{\lambda_0}^l \frac{dl}{\lambda}.$$

According to this view the discharge takes place when the value of the potential difference has the value given by either (1) or (2) and not when the maximum electromotive intensity has a certain value. Dr. Schuster's reduction of Baille's and Paschen's experiments shows that the maximum electromotive intensity when the spark passes is by no means constant.

If by the combination of the atoms at the end of a stria sufficient heat is produced to dissociate the adjacent gas without the aid of the electric field, the gas dissociated will, as the experiments I described in the *Philosophical Magazine* for April and May 1890 prove, be able to conduct the electricity, even though the potential difference is very small. We should then have a region in the gas where the potential charges are small compared with those in other parts of the gas: the dark space between the negative glow and the positive column seems to be such a region, and it is situated near to the negative glow, the hottest part of the field.

When the dimensions of the electrodes are not large compared with the sparking-distance, the connexion between the sparking-distance and the difference of potential is not linear. The experiments of De La Rue, Hugo Müller, and Freiberg have shown that with pointed electrodes, or small spheres, the sparking-distance for the same difference of potential is greater than with larger electrodes. This is what we should expect from the preceding considerations, for according to them when the spark passes from the negative electrode the



distribution of potential must be represented by the straight line AB, where the abscissæ represent the distance from the

electrode, and the ordinates the excess of potential over that of the negative electrode.

A spark will pass when the curve representing the potential before discharge cuts the curve AB. When the field is uniform the potential curve before discharge is a straight line passing through the origin, and if OF represent the distance between the electrodes OB will be the position of the potential curve before discharge when it first intersects AB; in this case FB is the potential necessary for discharge, and the relation between it and the sparking-distance is represented by equation (2). When, however, the electrodes are small the electric field is very far from uniform; there are great changes in the value of the potential near the electrodes, but at some distance from them the potential changes very slowly. The potential curve before discharge in this case will be somewhat of the form OCDE, and we see from the figure that this may intersect the line AB (when a spark will pass) when the difference of potential between the electrodes FE is less than FB, the difference when the field is uniform. We see in this way that the sparking-distance will be greater for small electrodes than for large ones, and will increase more rapidly with the difference of potential. We notice, too, that in this case the maximum electromotive intensity is greater than in a uniform field.

XIII. *On the Diurnal Variation of the Magnet at Kew.* By W. G. ROBSON and S. W. J. SMITH, of the Normal School of Science and Royal School of Mines\*.

THE multiplication of magnetic observatories makes it extremely desirable that the methods of reducing the observations should be as similar as possible. It is, however, practically impossible that all observatories should determine the diurnal variations of the elements by the elaborate method in use at Greenwich, which, in the case of any one element, necessitates the measurement of the hourly ordinates of the curves at 24 points on all but a very few days of the year under discussion.

Dr. Wild (Rep. Brit. Assoc. 1885, p. 78) advocates the determination of the mean diurnal range from measurements on the comparatively small number of days of very small disturbance, and points out that the inclusion of disturbed

\* Communicated by the Physical Society: read June 6, 1890.

days will affect the form of the curve of diurnal range unless the disturbances themselves occur indifferently at all hours of the day and night.

Mr. Whipple, the Superintendent of the Kew Observatory, made a comparison of the methods of Wild and Sabine, and that in use at Greenwich for the years 1870-71-72 (Rep. Brit. Assoc. 1886, p. 71).

His general conclusion was that the difference between the Kew results, as treated by the two methods of Sabine and Wild, was less than the difference between the Greenwich and Kew results in either case.

The range of the differences is given below :—

Mean of three years 1870-72.

	Range of Differences.
Kew (Sabine and Wild) .....	-0'3 to +0'4
Greenwich and Kew (Sabine)...	-0'6 to +0'6
Greenwich and Kew (Wild) ...	-0'9 to +0'7

It would have been interesting if similar comparisons could have been carried out for more recent years ; but the fact that the Kew magnetic year has not been identical with that used at Greenwich has made such a comparison impossible. The Kew magnetic year has hitherto been from October to October, to admit of the observations being included in the Annual Report made by the Committee to the Royal Society. We understand that in future the civil year will be adopted.

Besides this, some of the Kew results have been obtained not by measuring the hourly ordinates, but by drawing free-hand a mean curve among the superposed traces of "quiet day" curves.

It was therefore determined to make some further comparison of the different methods of reduction, and at the request of Professor Rücker we have determined the diurnal variation of the declination at Kew for three recent civil years.

The years selected were 1883, a year of maximum sun-spots, 1886, and 1887. The mean diurnal range for each year was found by Wild's method—the hourly ordinates for about five quiet days in each month being measured.

The results we obtained have been compared with the



TABLE I.

Year.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	Noon.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	Mid.
1883.	-1.42	-1.34	-1.42	-1.58	-1.88	-2.18	-2.69	-3.01	-2.51	-0.68	+1.93	+4.29	+5.52	+5.38	+4.15	+2.57	+1.32	+0.32	-0.29	-0.75	-1.24	-1.39	-1.55	-1.53
	-0.72	-0.77	-0.98	-1.26	-1.80	-2.29	-3.11	-3.77	-3.32	-1.28	+1.50	+3.89	+5.24	+5.06	+3.61	+2.17	+0.90	+0.29	-0.09	-0.35	-0.53	-0.69	-0.92	-0.82
1886.	-1.61	-1.46	-1.42	-1.33	-1.57	-1.79	-2.02	-2.07	-1.52	-0.03	+2.17	+4.26	+5.21	+4.92	+3.79	+2.39	+1.14	+0.12	-0.64	-1.18	-1.60	-1.93	-1.99	-1.86
	-1.29	-1.17	-1.24	-1.57	-1.95	-2.23	-2.59	-2.71	-2.18	-0.47	+1.86	+3.84	+4.37	+4.43	+3.20	+1.91	+0.91	+0.23	-0.04	-0.38	-0.68	-0.81	-0.97	-1.13
1887.	-1.47	-1.18	-1.05	-1.15	-1.42	-1.62	-1.88	-1.96	-1.35	+0.20	+2.33	+4.09	+4.91	+4.45	+3.17	+1.83	+0.74	-0.05	-0.71	-1.07	-1.47	-1.85	-1.84	-1.74
	-1.00	-0.94	-1.04	-1.25	-1.60	-2.06	-2.47	-2.76	-2.01	-0.25	+1.95	+3.93	+4.66	+4.20	+2.69	+1.39	+0.57	-0.04	-0.34	-0.48	-0.57	-0.80	-0.96	-0.84

TABLE II.

Year.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	Noon.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	Mid.
1870 ...	-0.9	-0.8	-0.7	-0.2	+0.2	+0.2	+0.5	+0.4	+0.6	+0.6	+0.4	+0.1	+0.5	+0.5	+0.4	+0.6	+0.6	+0.2	0.0	-0.1	-0.4	-0.8	-1.1	-1.0
1871 ...	-0.8	-0.6	-0.6	-0.4	+0.2	+0.7	+0.9	+0.7	+0.7	+0.7	+0.2	+0.5	+0.5	+0.7	+0.8	+0.6	+0.3	+0.1	-0.1	-0.2	-0.9	-0.7	-1.1	-0.9
1872 ...	-0.9	-0.7	-0.6	-0.5	-0.1	+0.3	+0.5	+0.8	+0.8	+1.0	+0.6	+0.5	+0.7	+0.6	+0.8	+0.5	+0.5	+0.1	-0.1	-0.7	-0.7	-0.9	-1.1	-0.8
1883 ...	-0.7	-0.6	-0.4	-0.3	-0.1	+0.1	+0.4	+0.8	+0.8	+0.6	+0.4	+0.4	+0.3	+0.3	+0.5	+0.4	+0.4	0.0	-0.2	-0.4	-0.7	-0.7	-0.6	-0.7
1886 ...	-0.3	-0.3	-0.2	+0.2	+0.4	+0.4	+0.6	+0.6	+0.7	+0.4	+0.3	+0.4	+0.3	+0.5	+0.6	+0.5	+0.2	-0.1	-0.6	-0.8	-0.9	-1.1	-1.0	-0.7
1887 ...	-0.5	-0.2	0.0	+0.1	+0.2	+0.4	+0.6	+0.8	+0.7	+0.5	+0.4	+0.2	+0.3	+0.3	+0.5	+0.4	+0.2	0.0	-0.4	-0.6	-0.9	-1.1	-0.9	-0.9
Mean...	-0.7	-0.5	-0.4	-0.2	+0.1	+0.4	+0.6	+0.7	+0.7	+0.6	+0.4	+0.4	+0.4	+0.5	+0.6	+0.5	+0.4	+0.1	-0.2	-0.5	-0.8	-0.9	-1.0	-0.8

Greenwich  
and Kew  
(Whipple)  
Greenwich  
and Kew  
(R. and S.)

corresponding Greenwich results, as published by the Royal Observatory (see Table I.). Thus for the total range for each year at Kew and Greenwich we have the following:—

Total Ranges.

Year.	Kew.	Greenwic h.
1883 .....	9'0	8'5
1886 .....	7'6	7'3
1887 .....	7'4	6'9

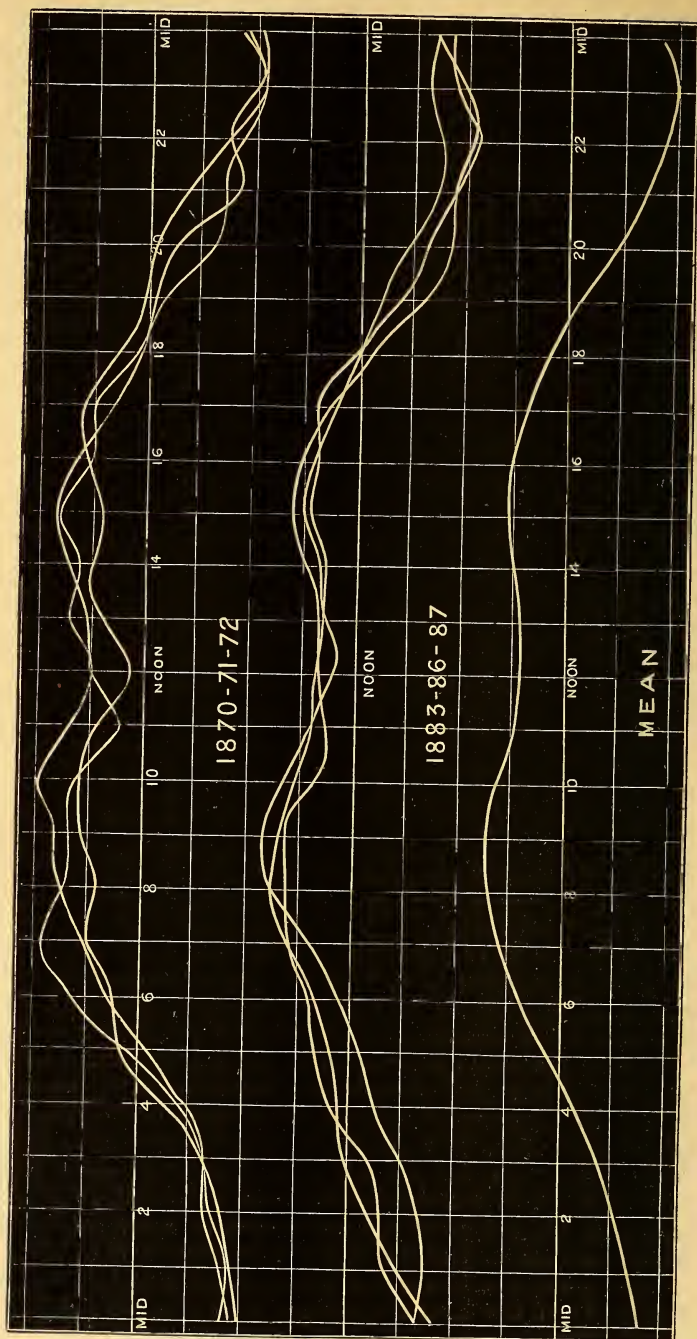
It is noteworthy that the total range at Kew determined from quiet days is greater than that at Greenwich determined from all days except those of great disturbance. If we may argue from so small a comparison this indicates that storms on the whole diminish instead of increasing the diurnal excursions of the needle. The total range is also apparently decreasing yearly.

The range of differences of the corresponding mean hourly values is:—

	Range of Differences.	Year.
Greenwich and Kew ...	−0'7 to +0'8	1883
„ „	−1'1 to +0'7	1886
„ „	−1'1 to +0'8	1887

There is thus in 1883 a difference of 1'5 in a range of 9'—the percentage being 16'7. For 1886 the difference is 1'8 in a range of 7'6—or 23'7 per cent.; while for 1887 the difference is 1'9 in a range of 7'4, or 25'7 per cent.

Table II. shows the differences of the hourly readings for the three years just determined, together with the differences for the years 1870, 1871, and 1872, as determined by Mr. Whipple (Rep. Brit. Assoc. *loc. cit.*). The mean of these hourly differences for the six years has been taken (see Table II.). It is noticeable that there is considerable uniformity in the nature of the differences between the mean hourly readings for Greenwich and Kew respectively. Thus, for each year, the Greenwich mean curve falls below that obtained from the Kew magnetograph at about 7 P.M., and



remains below it until about 4 A.M., from which hour it is above the Kew curve until it crosses it at about 7 P.M. The minimum ordinate for each curve for each year occurs at about 8 A.M., and the maximum at 1 P.M. The declination has its mean value between 10 A.M. and 11 A.M., and again at between 6 P.M. and 7 P.M. Precisely the same features are to be noticed in the tables given by Mr. Whipple for the years 1870, 1871, and 1872 (Rep. Brit. Assoc. 1886, p. 74); so that it may fairly be assumed that the general nature of the difference between the Greenwich and Kew mean curves from 1870 to 1887 is the same.

The general similarity of the differences is shown clearly by the accompanying curves—the abscissæ of which represent hours, while the ordinates give the mean differences between the Greenwich and Kew readings at these hours. The first set are plotted from the data given in Mr. Whipple's paper. The second set are from the data which we have obtained for the years 1883, 1886, and 1887. The lowest represents the mean of the six curves.

The individual readings do not differ from the corresponding mean to an extent greater than 0'4. It would therefore seem possible, knowing one set of values for any particular year—Greenwich or Kew—to determine the other set, correct to within four tenths of a minute. As the Kew results are published earlier than the Greenwich ones, it would be possible to calculate approximately the latter from the former.

XIV. *The Effect of Change of Temperature on the Villari Critical Point of Iron*\*. By HERBERT TOMLINSON, F.R.S.†

[Plates III. & IV.]

THIS paper must be regarded as a continuation of one previously communicated to the Physical Society‡ on the Villari Critical Points of Nickel and Iron. As before, only the temporary magnetization was studied, and the mode of conducting the observations was also the same with the addition that the effect of loading was tested not only at the temperature of the room but also at various temperatures extending to 285° C. The temperature was ascertained from the resistance of a coil of platinum wire wound double and embracing the same part of the iron wire as the secondary

\* The author expresses his thanks to the Elizabeth Thompson Science Fund for aid in this research.

† Communicated by the Physical Society: read June 6, 1890.

‡ Phil Mag. [5] xxix. p. 394.

*Phil. Mag.* S. 5. Vol. 30. No. 183. August 1890. L



coil; the temperature-coefficients of the platinum coil had previously been very carefully determined\*. The iron wire used was 1 millim. in diameter; it had been thoroughly annealed, and the loads employed were not sufficient, even at the highest temperature, to produce any very sensible permanent extension. As a preliminary the wire was heated to  $300^{\circ}\text{C.}$ , tested with all the loads and magnetizing forces to be presently mentioned, and again tested when cooled to the temperature of the room. This treatment was repeated several times until constant results were obtained at both temperatures; the observations recorded in figs. I.–VI. were then made. In these figures the abscissæ represent the number of kilogrammes in the load and the ordinates the percentage alteration of permeability at the temperature indicated on each curve, + signifying increase and – decrease of permeability. The Villari critical point is the value of the magnetizing force for which loading does not affect the permeability and may be ascertained by noting the point at which each curve cuts the line of loads; it varies with the value of the load and with the temperature. In some instances the curves cut the line of loads *twice*, and there are consequently *two* loads which for the magnetizing forces pertaining to the curves have no effect on the temporary magnetization. In the following table is given the load (or loads if there are two) which for each particular magnetizing force and temperature is without effect on the permeability.

TABLE I.

Magnetizing force in C.G.S. units.	Load for which the permeability is the same as for the unloaded wire. Temp. $12^{\circ}\text{C.}$	Ditto. Temp. $76^{\circ}\text{C.}$	Ditto. Temp. $167^{\circ}\text{C.}$	Ditto. Temp. $244^{\circ}\text{C.}$	Ditto. Temp. $285^{\circ}\text{C.}$
2.84	4.6	4.8	5.1 and 12.0	5.8 and 10.1	
3.70	2.5	3.2	3.6	4.2 and 11.5	4.7 and 9.9
4.83	1.8	2.5	2.7	not tested.	3.1 and 12.3

\* For further information concerning the platinum coil and the primary and secondary coils, see Phil. Mag. [5] xxv. p. 372.

It will be seen from Table I. and from figs. I.-IV. that the magnetizing forces 2·84, 3·70, 4·83, and of course all intermediate forces, are Villari critical values. If we regard only the *first point* where each curve cuts the line of loads, we see that at all temperatures the Villari value *increases* as the load *decreases* and, for a given load, increases with the temperature. If, on the contrary, we consider the *second point* of cutting the line of load, we find the critical value *increases both with the load and with the temperature*\*.

It will be seen from fig. I. that as the temperature rises the two points of cutting the load-line creep nearer and nearer together until for a temperature a little below 285° C. they coincide, and the curve osculates the load-line; whilst for 285° C. and for higher temperatures the magnetizing force 2·84 ceases to be a Villari point for any load. When the magnetizing force reaches the value 7·69 (fig. IV.) both points of cutting the load-line vanish, at any rate when the loading is not carried beyond 12 kilos†, and for magnetizing forces beyond 7·69 (figs. V.-VI.) Villari critical values become impossible.

In all cases rise of temperature increases the alteration of the permeability in the positive direction and diminishes it in the negative direction; but the diminution in the latter case is greater than the increment in the former, so that the summits of the two bends in the curves become more and more nearly on the same level.

The percentage alteration of permeability was calculated as follows:—

If  $P_0$  and  $P_n$  represent the permeability with no load and a load of  $n$  kilogrammes respectively, the percentage alteration is

$$\frac{100 (P_n - P_0)}{P_0} \text{ or } \frac{100 (P_0 - P_n)}{P_0},$$

according as the loading produces increase or decrease of permeability. Table II. gives the values of  $P_0$  for the various magnetizing forces.

\* The effect of change of temperature on the critical value is therefore in the same direction for both points of cutting the line of loads, *i. e.* in both cases the Villari value is increased by rise of temperature.

† The second point could, however, be probably reached by taking the load to higher values.

TABLE II.

Magnetizing force in C.G.S. units.	Temporary permeability in C.G.S. units of the unloaded wire at 12° C.	Ditto at 76° C.	Ditto at 167° C.	Ditto at 244° C.	Ditto at 285° C.
2.84	301	306	338	353	385
3.70	325	340	383	385	405
4.83	347	366	413	.....	461
7.69	478	483	548	.....	557
10.40	528	573	638	.....	675
15.32	522	.....	.....	.....	617

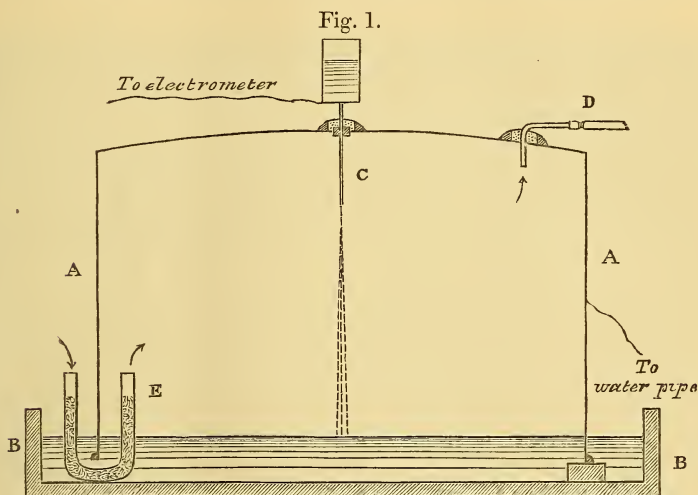
XV. *Electrification of Air by Water-Jet.* By MAGNUS MACLEAN, M.A., F.R.S.E., and MAKITA GOTO (Japan)\*.

SIR WILLIAM THOMSON, experimenting in the rooms of the Old College, Glasgow, found that electrified air could pass through narrow passages, and he suggested to us to try whether electrified air can pass through a metal tube from one room to another. For this purpose a small room adjoining the Natural Philosophy Class-room of Glasgow University was used. In this room a Thomson quadrant electrometer, whose sensibility was 95 divisions of the scale, per 1 volt difference of potential, and a spirit-lamp supported on an insulating stand and connected to the electrometer, were fitted up. Through the handle-hole of the door separating the small room from the class-room, a metal tube 60 centim. long and 1 centim. in diameter and connected to a gas-pipe by a wire was passed. In the fireplace of the small room a small fire was kept burning to produce draught from the class-room to this room. The class-room was electrified by a spirit-lamp connected to one of the conductors of a large 24-plates electrical machine of Wimshurst type. By this arrangement we could observe any variation of electrification in the small room due to the passage of electricity from the class-room to it. We believe electrified air passed through the tube, but the effect was masked by the draughts

\* Communicated by the Authors.

through the chinks, though we took care to close all chinks in the door by cotton-wool. Also, if the electrifying lamp connected to the electrical machine were placed nearer than 3 feet from the door between the two rooms, inductive effect was felt in the small room.

We therefore adopted an arrangement shown in fig. 1. AA is a large sheet-iron vat 123 centim. in diameter and 70



centim. in height inverted on a large tray BB. By filling the tray with water the air is confined in the vat. The jet-tube of a water-dropper C passes through the centre of the top of the vat. The water-dropper was fixed in its position by a piece of ebonite and melted paraffin poured round it, so that it is insulated from the vat, which is always kept connected to water-pipe for earth. By connecting the tube D to an aspirator the air inside the vat could be replaced by the air of the room through the tube E, which is a metallic tube or a glass tube coated with paraffin both inside and outside of the tube, and filled with cotton-wool. By this arrangement we could easily make electrified air pass through the metal tube, but with the cotton-wool tube the results were discordant, therefore we are not yet in a position to say anything definite.

While these experiments were proceeding we came unexpectedly on an interesting result. It was found that the potential inside the vat, as shown by the water-dropper on the top of the vat, and connected to the electrometer, was always about  $\frac{1}{2}$  volt positive at the beginning, and gradually changed towards negative till 5 volts negative was reached in about half



an hour. To make it sure we made more than 15 observations under different conditions, but always with the same result, and we came to the conclusion that the water rushing through the air electrifies it negatively, at least it does so electrify common air full of dust. This result is in accordance with the well-known change of atmospheric electricity to negative during rainy weather.

The following are the results which prove our conclusion :—

(1) After negatively electrifying the air inside the vat by making water drop through it for some time, if it is replaced by the air outside of the vat, the electrometer-reading comes down towards zero.

(2) Simultaneous observations of the electrification of the air inside the vat by the same means and of the air in the room were made. After about 13 minutes the former exceeded the latter, though at that time the air of the room was being electrified negatively by the paraffin lamp used in reading the scale.

(3) After starting the water-dropper and taking the electrometer-readings for some time, say 10 minutes, if it is stopped say for 10 minutes and again started, the initial reading is the same as that just before the interval of stopping, and it again continues to go up.

(4) Whether the water-dropper was insulated or connected to water-pipe by a wire, by connecting it to the electrometer for taking the reading it shows that the negative electrification of the air inside the vat goes on increasing for about half an hour.

(5) No difference in the result was found after painting the inside of the vat. Before painting it presented the surface of rusted iron.

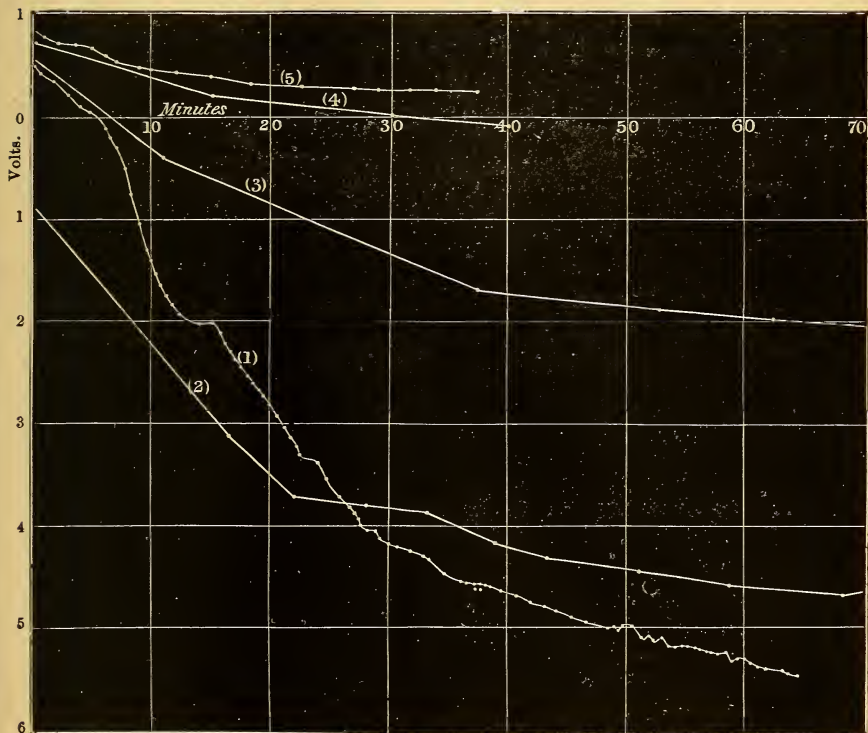
(6) Whether the vat is filled with air electrified positively or negatively before the observation, the electrometer-reading equally goes towards the negative side.

(7) The maximum potential obtained was  $5\frac{1}{2}$  volts negative, but the more the air became free of dust the less became the maximum reached. This is shown by the curves in fig. 2. The curve No. 1 was obtained by observation after filling the vat with the air of the room. The curve No. 5 was obtained after continuous running of the aspirator for about 25 hours. Intermediate curves correspond to the intermediate state of the air as to its purity. In the curve No. 2 the water-dropper was running for some time before beginning the observation.

(8) After putting water into the water-dropper and wait-

ing as usual till the water-dropper comes to equilibrium, the initial reading is always about  $\frac{1}{2}$  volt positive. This we are inclined to regard as due to the electrification of water itself and not to the potential due to the internal arrangement. This initial reading also increases little by little as the air becomes more purified.

Fig. 2.



In the course of these experiments we have observed the following phenomena, which may be of some interest :—

(1) If the air of the room is very highly electrified, continuous sparks can be drawn from any insulated conductors by presenting finger.

(2) Electrified flame is attracted or repulsed as any other electrified body. Flame electrified by the large electrical machine before mentioned takes different shapes according to the position with respect to other conducting bodies either

electrified or connected to the earth. Small spirit-lamp made of metal and put on the positive conductor of the electrical machine is extinguished by the repulsion, but not so easily when it is put on the negative conductor.

# XVI. *An Electromagnetic Theory of Quartz.*

*By A. B. BASSET, M.A., F.R.S.\**

1. **T**HE rotation of the plane of polarization of light by a magnetic field, although presenting several features in common with the rotation of the plane of polarization by syrup or quartz, is a phenomenon of a totally distinct character, which depends upon the existence of an external magnetic force, and disappears as soon as the magnetic force is removed. A theory of magnetic rotation is given by Maxwell †, and some extensions have been made by Fitzgerald ‡; but it is, I think, pretty obvious that Maxwell's theory will not apply to syrup or quartz; for the additional terms consist of the products of the magnetic force and the differential coefficients of the displacements, and are therefore terms of the second order when the magnetic force is produced by optical and not by external causes.

On the other hand, rotations produced by syrup and quartz appear to be phenomena of an essentially similar character, and therefore a theory which explains one ought to explain the other; and the object of the present paper is to endeavour to show how the electromagnetic theory may be extended so as to account for these phenomena.

2. Let us conceive a medium which possesses three rectangular planes of symmetry, and which produces rotatory polarization when a plane wave of polarized light travels through the medium parallel to any one of the axes of symmetry, and elliptic polarization when the wave travels through in any other direction, the values of the rotation per unit of length being different for each of the three axes. The physical properties of the medium, so far as rotatory polarization is concerned, will be specified by three constants,  $p_1$ ,  $p_2$ ,  $p_3$ , which depend upon the amount of rotation produced when the direction of propagation is parallel to any of the three axes. In an isotropic medium the three  $p$ 's will be equal, since the rotation is independent of the direction of the wave; whilst in quartz two of the  $p$ 's must be zero, since no rotation will

\* Communicated by the Author.

† Electricity and Magnetism, vol. ii. chap. xxi.

‡ Phil. Trans. part ii. 1880, p. 691.

be produced when the direction of propagation is perpendicular to the axis. Now in the ordinary theory of double refraction, as developed by Maxwell, the electromotive force is connected with the electric displacement by the three equations

$$P=4\pi f/K_1, \quad Q=4\pi g/K_2, \quad R=4\pi h/K_3,$$

where  $K_1, K_2, K_3$  are the three principal specific inductive capacities. We shall now show that in a crystalline medium, such as has been described above, rotatory polarization may be accounted for by assuming that

$$\left. \begin{aligned} P &= 4\pi f/K_1 + p_3 \dot{g} - p_2 \dot{h}, \\ Q &= 4\pi g/K_2 + p_1 \dot{h} - p_3 \dot{f}, \\ R &= 4\pi h/K_3 + p_2 \dot{f} - p_1 \dot{g}, \end{aligned} \right\} \dots \dots \dots (1)$$

where  $p_1, p_2, p_3$  are constants.

This assumption supposes that when electromotive force acts upon the medium, it produces electric displacement in a direction perpendicular to itself; and that the force depends not only upon the actual displacement, but also upon the rate at which it is taking place.

The equations of electromotive force in terms of the electromagnetic momentum are

$$\left. \begin{aligned} P &= -\dot{F} - d\psi/dx, \\ Q &= -\dot{G} - d\psi/dy, \\ R &= -\dot{H} - d\psi/dz, \end{aligned} \right\} \dots \dots \dots (2)$$

whence

$$\left. \begin{aligned} -\frac{da}{dt} &= \frac{dR}{dy} - \frac{dQ}{dz}, \\ -\frac{db}{dt} &= \frac{dP}{dz} - \frac{dR}{dx}, \\ -\frac{dc}{dt} &= \frac{dQ}{dx} - \frac{dP}{dy}. \end{aligned} \right\} \dots \dots \dots (3)$$

But if we assume that the magnetic permeability of the medium is the same in all directions, we have

$$4\pi\mu\ddot{f} = 4\pi\mu\ddot{u} = -\frac{d}{dt} \left( \frac{db}{dz} - \frac{dc}{dy} \right), \quad \dots \dots \dots (4)$$

$$= \nabla^2 P - \frac{d}{dx} \left( \frac{dP}{dx} + \frac{dQ}{dy} + \frac{dR}{dz} \right), \quad \dots \dots (5)$$

with two similar equations.



Let us now suppose that the relation between electromotive force and electric displacement is given by (1); then if we substitute in (5) and put

$$\mu K_1 = A^{-2}, \quad \mu K_2 = B^{-2}, \quad \mu K_3 = C^{-2}, \quad . \quad . \quad . \quad (6)$$

$$\Omega = A^2 \frac{df}{dx} + B^2 \frac{dg}{dy} + C^2 \frac{dh}{dz}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\frac{d}{d\omega} = p_1 \frac{d}{dx} + p_2 \frac{d}{dy} + p_3 \frac{d}{dz}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and recollect that

$$\frac{df}{dx} + \frac{dg}{dy} + \frac{dh}{dz} = 0, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

(5) will become

$$\left. \begin{aligned} \frac{d^2 f}{dt^2} &= A^2 \nabla^2 f - \frac{d\Omega}{dx} + \frac{d}{d\omega} \left( \frac{dg}{dz} - \frac{dh}{dy} \right), \\ \frac{d^2 g}{dt^2} &= B^2 \nabla^2 g - \frac{d\Omega}{dy} + \frac{d}{d\omega} \left( \frac{dh}{dz} - \frac{df}{dx} \right), \\ \frac{d^2 h}{dt^2} &= C^2 \nabla^2 h - \frac{d\Omega}{dz} + \frac{d}{d\omega} \left( \frac{df}{dy} - \frac{dg}{dx} \right). \end{aligned} \right\} \quad . \quad . \quad (10)$$

Equations (10) are the equations of electric displacement in a doubly refracting medium which exhibits rotatory polarization. The first two terms on the right-hand side produce double refraction, and the last terms produce rotatory polarization. These last terms are quantities in the nature of angular velocities, and are analogous to the components of molecular rotation in Hydrodynamics; one of the results of our hypothesis therefore is, that something in the nature of vortex motion takes place in a medium which exhibits rotatory polarization.

3. In order to obtain the equations of magnetic induction, differentiate (3) with respect to  $t$ , and we shall obtain

$$\begin{aligned} \frac{d^2 a}{dt^2} &= \frac{d\dot{Q}}{dz} - \frac{d\dot{R}}{dy} \\ &= C^2 \frac{d}{dy} \left( \frac{da}{dy} - \frac{db}{dx} \right) - B^2 \frac{d}{dz} \left( \frac{dc}{dx} - \frac{da}{dz} \right) - \frac{d\dot{f}}{d\omega} \end{aligned}$$

by (1). The last term is equal to

$$\frac{1}{4\pi\mu} \frac{d}{d\omega} \left( \frac{db}{dz} - \frac{dc}{dy} \right)$$

by (4); whence the equations of magnetic induction are

$$\left. \begin{aligned} \frac{d^2 a}{dt^2} &= C^2 \frac{d}{dy} \left( \frac{da}{dy} - \frac{db}{dx} \right) - B^2 \frac{d}{dz} \left( \frac{dc}{dx} - \frac{da}{dz} \right) + \frac{1}{4\pi\mu} \frac{d}{d\omega} \left( \frac{d\dot{b}}{dz} - \frac{d\dot{c}}{dy} \right), \\ \frac{d^2 b}{dt^2} &= A^2 \frac{d}{dz} \left( \frac{db}{dz} - \frac{dc}{dy} \right) - C^2 \frac{d}{dx} \left( \frac{da}{dy} - \frac{db}{dx} \right) + \frac{1}{4\pi\mu} \frac{d}{d\omega} \left( \frac{d\dot{c}}{dx} - \frac{d\dot{a}}{dz} \right), \\ \frac{d^2 c}{dt^2} &= B^2 \frac{d}{dx} \left( \frac{dc}{dx} - \frac{da}{dz} \right) - A^2 \frac{d}{dy} \left( \frac{db}{dz} - \frac{dc}{dy} \right) + \frac{1}{4\pi\mu} \frac{d}{d\omega} \left( \frac{d\dot{a}}{dy} - \frac{d\dot{b}}{dx} \right). \end{aligned} \right\} \quad (11)$$

4. We shall now briefly consider the propagation of light in an isotropic medium. In this case  $p_1 = p_2 = p_3$ ,  $A = B = C$ . If therefore the axis of  $z$  is the direction of propagation,  $h = 0$ , and  $f$  and  $g$  are functions of  $z$  and  $t$  alone; whence (10) become

$$\left. \begin{aligned} \frac{d^2 f}{dt^2} &= A^2 \frac{d^2 f}{dz^2} + p \frac{d^3 g}{dz^2 dt}, \\ \frac{d^2 g}{dt^2} &= A^2 \frac{d^2 g}{dz^2} - p \frac{d^3 f}{dz^2 dt}. \end{aligned} \right\} \quad \dots \dots (12)$$

To solve these equations, assume

$$f = L \epsilon^{\frac{2i\pi}{\tau} \left( \frac{z}{V} - t \right)}, \quad g = M \epsilon^{\frac{2i\pi}{\tau} \left( \frac{z}{V} - t \right)}; \quad \dots \dots (13)$$

where  $L$  and  $M$  are complex constants,  $\tau$  is the period of the particular light considered, and  $V$  is the velocity of propagation in the medium.

Substituting in (12), we obtain

$$(V^2 - A^2)L + 2i\pi p M / \tau = 0,$$

$$(V^2 - A^2)M - 2i\pi p L / \tau = 0;$$

whence

$$M = \pm iL,$$

$$V^2 = A^2 \pm 2\pi p / \tau. \quad \dots \dots (14)$$

If the incident light is represented by

$$f = L \cos 2\pi t / \tau, \quad g = 0;$$

and if  $V_1, V_2$  denote the greater and lesser values of  $V$ , we shall obtain in real quantities,

$$f = \frac{1}{2} L \cos \frac{2\pi}{\tau} \left( \frac{z}{V_1} - t \right) + \frac{1}{2} L \cos \frac{2\pi}{\tau} \left( \frac{z}{V_2} - t \right),$$

$$g = -\frac{1}{2} L \sin \frac{2\pi}{\tau} \left( \frac{z}{V_1} - t \right) + \frac{1}{2} L \sin \frac{2\pi}{\tau} \left( \frac{z}{V_2} - t \right);$$

accordingly

$$f = L \cos \frac{2\pi}{\tau} \left\{ \frac{1}{2} z \left( \frac{1}{V_1} + \frac{1}{V_2} \right) - t \right\} \cos \frac{\pi z}{\tau} \left( \frac{1}{V_2} - \frac{1}{V_1} \right),$$

$$g = L \cos \frac{2\pi}{\tau} \left\{ \frac{1}{2} z \left( \frac{1}{V_1} + \frac{1}{V_2} \right) - t \right\} \sin \frac{\pi z}{\tau} \left( \frac{1}{V_2} - \frac{1}{V_1} \right);$$

whence, if  $\psi$  be the angle through which the plane of polarization is rotated after the wave has passed through a length  $z$  of the medium,

$$\psi = \frac{\pi z}{\tau} \left( \frac{1}{V_2} - \frac{1}{V_1} \right).$$

Substituting the values of  $V_1, V_2$  from (14), we obtain

$$\begin{aligned} \psi &= \frac{\pi z}{\tau} \{ (A^2 - 2\pi p/\tau)^{-\frac{1}{2}} - (A^2 + 2\pi p/\tau)^{-\frac{1}{2}} \} \\ &= \frac{2\pi^2 p z}{A^3 \tau^2} = \frac{2\pi^2 p z}{A \lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15) \end{aligned}$$

to a first approximation, where  $\lambda$  is the wave-length in the medium.

This result is in accordance with the law which was experimentally deduced by Biot, viz. *that the rotation is directly proportional to the thickness of the length of the medium traversed by the wave, and inversely proportional to the wave-length of the particular light employed.*

5. We must now consider the theory of quartz. Taking the axis of the quartz as the axis of  $z$ , we must put  $A=B$ ,  $p_1=p_2=0$ , whence writing  $p$  for  $p_3$ , (10) become

$$\left. \begin{aligned} \frac{d^2 f}{dt^2} &= A^2 \nabla^2 f - \frac{d\Omega}{dx} + p \frac{d}{dz} \left( \frac{dg}{dz} - \frac{dh}{dy} \right) \\ \frac{d^2 g}{dt^2} &= A^2 \nabla^2 g - \frac{d\Omega}{dy} + p \frac{d}{dz} \left( \frac{dh}{dx} - \frac{df}{dz} \right) \\ \frac{d^2 h}{dt^2} &= C^2 \nabla^2 h - \frac{d\Omega}{dz} + p \frac{d}{dz} \left( \frac{df}{dy} - \frac{dg}{dx} \right) \end{aligned} \right\} \quad . \quad . \quad (16)$$

We have already pointed out that if a plane wave be travelling perpendicularly to the axis, no rotation is produced. Now if the wave is travelling parallel to the axis of  $x$ , we must have  $f=0$ , whilst  $g$  and  $h$  are functions of  $x$  and  $t$  alone; when this is the case we see from (16) that the rotatory terms vanish, as ought to be the case. Similarly we see that the rotatory terms vanish when the wave is

travelling parallel to the axis of  $y$ . Our equations thus far represent observed facts.

Since everything is symmetrical about the axis, we may without loss of generality assume that the axis of  $y$  is parallel to the wave-front, and we may therefore put

$$f = S\lambda, \quad g = S\mu, \quad h = S\nu,$$

$$S = \epsilon^{\frac{2i\pi}{V\tau}(lx+nz-Vt)};$$

where  $l, n$  are the direction-cosines of the wave-front,  $\lambda, \mu, \nu$  are those of the direction of displacement, and  $\tau$  is the period.

Substituting in (16) we obtain

$$(V^2 - A^2 n^2)\lambda + C^2 l n \nu + (2i\pi p/\tau) n^2 \mu = 0,$$

$$(V^2 - A^2)\mu - (2i\pi p/\tau)\lambda = 0,$$

$$(V^2 - C^2 l^2)\nu + A^2 l n \lambda - (2i\pi p'/\tau) l n \mu = 0;$$

whence eliminating  $\lambda, \mu, \nu$  and putting  $\theta$  for the angle which the normal to the wave-front makes with the axis, we obtain

$$(V^2 - A^2)(V^2 - A^2 \cos^2 \theta - C^2 \sin^2 \theta) = (4\pi^2 p^2/\tau^2) \cos^2 \theta, \quad (17)$$

which determines the velocity of propagation of waves of period  $\tau$ . Putting  $\theta = 0$ , we get

$$V^2 = A^2 \pm 2\pi p/\tau \quad . \quad . \quad . \quad . \quad . \quad (18)$$

which gives the values of  $V$  when the wave is travelling in the direction of the axis. In this case equations (16) reduce to (12), so that the rotation of the plane of polarization is given by (15).

6. The elastic solid theory of double refraction which was proposed by Green is, I believe, universally admitted at the present time to be unsatisfactory; and accordingly during recent years numerous theories have been proposed, which attempt to explain optical phenomena by a quasi-elastic solid theory, based upon assumptions respecting the mutual reaction of æther and matter; and it will therefore be instructive to ascertain whether the terms by which we have endeavoured to explain rotatory polarization on the electromagnetic theory, will also explain this phenomenon on the quasi-elastic solid theory.

The fundamental idea of all such theories is, that the statical properties of the æther in transparent media are the same as *in vacuo*, but that the motion of the æther is modified by the presence of ponderable matter, the effect of which may be represented by forces  $X, Y, Z$ ; and phenomena such as double refraction, rotatory polarization and the like, are



explained by making certain assumptions regarding the form of these forces.

The particular theory of this kind which I shall now consider, and which on the whole is perhaps the most satisfactory, is the theory of Lord Rayleigh\* as modified by Sir W. Thomson†, and which consists in supposing that double refraction may be explained by assuming that  $X, Y, Z$  are equal to  $-\rho_1\ddot{u}$ ,  $-\rho_2\ddot{v}$ ,  $-\rho_3\ddot{w}$ , and that the velocity of propagation of the pressural wave is so small that it may be treated as zero without sensible error. This theory, so far as double refraction is concerned, has been fully worked out by Glazebrook‡, and has been applied by him§, and also by myself|| to investigate the intensities of the reflected and refracted waves, when the reflecting medium is a doubly-refracting crystal. In order to deduce a theory of doubly-refracting media which exhibit rotatory polarization, we shall assume that the effect of the peculiar molecular structure of such media is to introduce into the expressions for the forces the additional terms which are given by the last three terms of (10); so that our equations of motion are:—

$$\left. \begin{aligned} (\rho + \rho_1) \frac{d^2 u}{dt^2} &= -n' \frac{d\delta}{dx} + n \nabla^2 u + \frac{d}{d\omega} \left( \frac{d\dot{v}}{dz} - \frac{d\dot{w}}{dy} \right), \\ (\rho + \rho_2) \frac{d^2 v}{dt^2} &= -n' \frac{d\delta}{dy} + n \nabla^2 v + \frac{d}{d\omega} \left( \frac{d\dot{w}}{dx} - \frac{d\dot{u}}{dz} \right), \\ (\rho + \rho_3) \frac{d^2 w}{dt^2} &= -n' \frac{d\delta}{dz} + n \nabla^2 w + \frac{d}{d\omega} \left( \frac{d\dot{u}}{dy} - \frac{d\dot{v}}{dx} \right), \end{aligned} \right\} \quad . \quad (19)$$

where  $u, v, w$  are the displacements, and  $\rho$  and  $n$  are the density and rigidity of the æther *in vacuo*.

When the medium is isotropic,  $\rho_1 = \rho_2 = \rho_3$ ;  $p_1 = p_2 = p_3$ ; if therefore the axis of  $z$  is taken as the direction of propagation,  $u$  and  $v$  will be functions of  $z$  and  $t$  alone, and  $w$  will be zero, and (19) reduce to

$$\begin{aligned} (\rho + \rho_1) \frac{d^2 u}{dt^2} &= n' \frac{d^2 u}{dz^2} + p \frac{d^3 v}{dz^2 dt} \\ (\rho + \rho_1) \frac{d^2 v}{dt^2} &= n' \frac{d^2 v}{dz^2} - p \frac{d^3 u}{dz^2 dt}, \end{aligned}$$

which are of the same form as (12).

\* Hon. J. W. Strutt, Phil. Mag. June 1871.

† Phil. Mag. Nov. 1888, p. 114.

‡ Ibid. Dec. 1888, p. 521.

§ Ibid. August 1889, p. 110.

|| Proc. Lond. Math. Soc. vol. xx. p. 351.

In the case of quartz,  $\rho_1 = \rho_2$ ;  $p_1 = p_2 = 0$ , the axis of the quartz being the axis of  $z$ . If therefore we put

$$n'/(\rho + \rho_1) = a^2, \quad n'/(\rho + \rho_3) = c^2, \quad q = p/n',$$

(19) become

$$\left. \begin{aligned} \frac{d^2 u}{dt^2} &= a^2 \left( \nabla^2 u - \frac{d\delta}{dx} \right) + qa^2 \frac{d}{dz} \left( \frac{d\dot{v}}{dz} - \frac{d\dot{v}}{dy} \right), \\ \frac{d^2 v}{dt^2} &= a^2 \left( \nabla^2 v - \frac{d\delta}{dy} \right) + qa^2 \frac{d}{dz} \left( \frac{d\dot{v}}{dx} - \frac{d\dot{u}}{dz} \right), \\ \frac{d^2 w}{dt^2} &= c^2 \left( \nabla^2 w - \frac{d\delta}{dz} \right) + qc^2 \frac{d}{dz} \left( \frac{d\dot{u}}{dy} - \frac{d\dot{v}}{dx} \right). \end{aligned} \right\} \quad (20)$$

Solving these equations in exactly the same way as we solved (16), we shall obtain

$$\left. \begin{aligned} (V^2 - a^2 n^2) \lambda + a^2 l n v + (2i\pi q/\tau) a^2 n^2 \mu &= 0, \\ (V^2 - a^2) \mu + (2i\pi q/\tau) a^2 n (l v - n \lambda) &= 0, \\ (V^2 - c^2 l^2) v + c^2 l n \lambda - (2i\pi q/\tau) c^2 l n \mu &= 0. \end{aligned} \right\} \quad (21)$$

Multiplying the first and third by  $l/a^2$ ,  $n/c^2$  respectively and adding, we obtain

$$V^2 \left( \frac{l\lambda}{a^2} + \frac{nv}{c^2} \right) = 0,$$

which requires either that

$$V = 0, \text{ or } l\lambda/a^2 + nv/c^2 = 0.$$

The first equation corresponds to the pressural wave, whilst the second determines the direction of vibration in the optical wave.

Eliminating  $\lambda$ ,  $\mu$ ,  $v$  from (21) we shall obtain

$$(V^2 - a^2)(V^2 - a^2 n^2 - c^2 l^2) = \frac{4\pi^2 q^2}{\tau^2} (a^2 n^2 + c^2 l^2) a^2 n^2, \quad (22)$$

which determines the velocity of propagation of the two waves.

The right-hand side of this equation is not quite the same as (17), but the difference is not very large, since  $a^2 - c^2$  is a small quantity. It might, however, be possible to determine experimentally which formula is the more exact representative of the facts.

7. Boussinesq\* has proposed to explain rotatory polarization by the introduction of the terms

$$p_3 \frac{d\ddot{v}}{dz} - p_2 \frac{d\ddot{w}}{dy}, \quad p_1 \frac{d\ddot{w}}{dx} - p_3 \frac{d\ddot{u}}{dz}, \quad p_2 \frac{d\ddot{u}}{dy} - p_1 \frac{d\ddot{v}}{dx}. \quad (23)$$

\* *Liouville*, deuxième série, vol. xiii. p. 313.

Now the right-hand sides of (5) may be written

$$\begin{aligned} & \frac{d}{dz} \left( \frac{dP}{dz} - \frac{dR}{dx} \right) - \frac{d}{dy} \left( \frac{dQ}{dx} - \frac{dP}{dy} \right) \\ & \frac{d}{dx} \left( \frac{dQ}{dx} - \frac{dP}{dy} \right) - \frac{d}{dz} \left( \frac{dR}{dy} - \frac{dQ}{dz} \right) \\ & \frac{d}{dy} \left( \frac{dR}{dy} - \frac{dQ}{dz} \right) - \frac{d}{dx} \left( \frac{dP}{dz} - \frac{dR}{dx} \right). \end{aligned}$$

Comparing these equations with (23), it appears that Boussinesq's terms could not be deduced by means of any assumption respecting the relation between electromotive force and electric displacement.

In order to apply Boussinesq's theory of quartz to the theory of double refraction of Lord Rayleigh and Sir W. Thomson, we must put  $p_1 = p_2 = 0$  in (23); and the last terms on the right-hand side of (20) will become

$$p \frac{d^3 v}{dz dt^2}, - p \frac{d^3 u}{dz dt^2}, \quad 0.$$

Solving the resulting equations in the same manner as before, we shall obtain

$$(V^2 - a^2)(V^2 - a^2 n^2 - c^2 l^2) = \frac{4\pi^2 q^2 a^4 n^2}{\tau^2} (V^2 - c^2 l^2), \quad (24)$$

the right-hand side of which is different from either of our two former results.

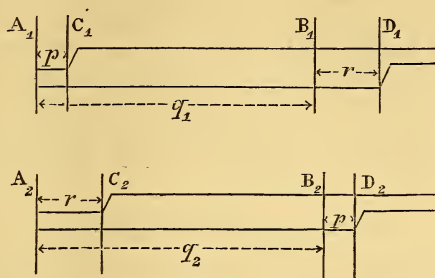
XVII. *On a Method of Eliminating the Effects of Latency of Electromagnetic Styli, in Chronographic Measurements.* By FREDERICK J. SMITH, *Trinity College, Oxford*.\*

WHILE working with the chronograph, a description of which appeared in the *Philosophical Magazine* for May, I have introduced a method of taking time-traces, by which instrumental error is greatly reduced, when styli are used which differ in their "latencies." It is as follows:—Two

\* Communicated by the Author.

traces are made, but the order in which the styli are used is reversed by a pole-changer in the second trace ; by means of this interchange of styli the latencies are cut out.

In the diagram, suppose the real beginnings and endings of



two events to be on the lines A<sub>1</sub> and A<sub>2</sub>, B<sub>1</sub> and B<sub>2</sub> respectively ; let these lengths be called q<sub>1</sub> and q<sub>2</sub>. Suppose C<sub>1</sub> and D<sub>1</sub>, C<sub>2</sub> and D<sub>2</sub> to be the markings of the styli in the two traces, and let r and p be the latencies of the two styli ; then in the first experiment the observed period is

$$q_1 - p + r,$$

in the second one it is

$$q_2 - r + p ;$$

by addition and division by 2,

$\frac{q_1 + q_2}{2}$  is the mean value of the two readings, the quantities r and p being cut out.

It is assumed that the latencies of the styli remain constant during the operations. Repeated experiment on this point shows that constancy of the styli may be fully relied on when a suitable battery, such as the gravity Daniell, is used.

I wish to take this opportunity of correcting an error in the Plate belonging to a paper of mine (p. 377, vol. xxix.). The scribing-point of the tuning-fork should be vertically under or over the points of the styli ; the error was introduced by the faulty arrangement of the instruments when they were photographed.



XVIII. *Notes on Secondary Batteries.* By J. H. GLADSTONE, *Ph.D.*, F.R.S., and W. HIBBERT, F.I.C.\*

**E**IGHT years ago, one of us, in conjunction with the late Mr. Tribe, published a series of papers on the Chemistry of Secondary Batteries†. Since that time accumulators have undergone many improvements in detail, but they still present some unsolved problems of a more or less subtle character. In this paper we give an account of some experiments undertaken to test points which have arisen in the last few years.

*Action of Sodium Sulphate.*

In May 1889 Mr. Preece delivered a lecture at the Society of Arts dealing generally with his experience of Secondary Batteries. Among the topics treated was the influence of the composition of the electrolyte on the working of the cell, and it was stated that the addition of sodium sulphate to the acid solution was of very considerable advantage. Mr. Preece determined the proportions of acid and sulphate which gave the best result in a year's working, and found that a comparatively small quantity of the salt was sufficient to produce the effect.

We have determined the percentage composition of the liquid from a sample kindly furnished by Mr. Preece, and find it to be as follows:—

Sodium sulphate ( $\text{Na}_2\text{SO}_4$ )	. . .	0·81
Sulphuric acid ( $\text{H}_2\text{SO}_4$ )	. . .	29·39
Water	. . . . .	69·80
		<hr/>
		100·00

The specific gravity at ordinary temperatures is about 1·23‡.

When used in secondary batteries instead of the usual acid, it is stated that there is less buckling of the plates and little or no scaling. The chief benefit, however, is stated to be that the sodium salt diminishes the chance of objectionable sulphating in the cell, and where such sulphating occurs, enables it

\* Communicated by the Physical Society: read June 20, 1890.

† *Nature*, 1882 and 1883, vols. xxv. and xxvi.; afterwards published by Macmillan.

‡ In making this liquid, it would be best to add together 68 parts (by weight) of water, 30 of strong sulphuric acid, and 2 parts of crystallized sodium sulphate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ).

to be removed by a charging current much more readily than when sulphuric acid alone is employed.

Mr. Preece did not explain the beneficial action of the sodium sulphate, but in the discussion following the lecture Sir F. Abel threw out the idea that it was "probable that a double salt of sulphate of lead and sodium was formed which was soluble, whereas the sulphate of lead was comparatively insoluble."

We have made some experiments to test the value of this suggestion. It may be well, however, to note that lead sulphate is so nearly insoluble in dilute sulphuric acid that comparatively large errors are easily possible.

We took advantage of the greater solubility of lead sulphate in strong acid. Measured volumes of this were added to water, the precipitate formed allowed to settle, and the lead salt remaining in solution determined by precipitation as sulphide.

The mean results are :—1 part of lead sulphate dissolves in 105,000 parts of the acid mixed with water, in 90,000 parts of a similarly diluted acid containing 5 per cent. sodium sulphate, and in 107,000 parts of Mr. Preece's solution.

As these numbers deal with such minute quantities we lay no stress on their absolute value. Their relative values are more useful, and evidently the addition of the sodium salt has not materially increased the solubility of lead sulphate.

This conclusion was confirmed by experiments of another type. To equal quantities of a dilute acid and a similar acid containing sodium sulphate we added a few drops of strong acid saturated with lead sulphate. Precipitates were formed in both cases, but it was possible so to adjust the number of drops that the precipitate did not appear for an appreciable time. We could therefore see in which it appeared first. In many experiments and many variations of procedure, we nearly always obtained earlier precipitation in liquids containing sodium or magnesium sulphates than in those consisting simply of dilute acid. We judge therefore that lead sulphate is not more soluble in these liquids, and that the explanation of the action of sodium sulphate must be sought in some other direction.

Mr. Swinburne has suggested that, as lead sulphate is dissolved by sodium hydrate, the action may be due to that hydrate being produced by electrolysis of the sodium sulphate. Experiment showed that in a simple solution of neutral sulphate of soda, a paste made of equal parts of red lead and sulphate of lead was more readily reduced than in dilute sulphuric acid. It was also easy to detect sodium hydrate on the cathode by red litmus-paper. But this last result was no

longer obtained when the sodium-sulphate solution contained sulphuric acid in the proportion of 1 volume to 10. The acid present interferes with such a simple test, and we sought for information on the point by determining the ratio of acid to sulphate of soda in the pores of the spongy lead, and comparing it with the ratio of the same substances in the body of the liquid. Preliminary experiments indicated the following as the best course to pursue.

A strip of spongy lead was used as cathode in a liquid somewhat similar to that analysed above. The ratio was  $\frac{H_2SO_4}{Na_2SO_4} = 30$ . A current was passed for three hours, falling slowly from about 2 amperes to 1.5. The strip was then taken out and placed in 120 cubic centim. of distilled water and allowed to diffuse for 40 minutes. It was then placed in fresh distilled water for 18 hours. The forty minutes' diffusate gave a ratio of  $\frac{H_2SO_4}{Na_2SO_4} = 25$ , only a little lower than that shown by the original liquid. The 18 hours diffusate gave a ratio  $\frac{H_2SO_4}{Na_2SO_4} = 11.8$ . Evidently, then, the portions of the liquid which diffused last were much richer in sodium salt than the earlier ones.

This would show that a large proportion of sulphate of sodium is formed in close contact with the lead sulphate, and we have already seen that this is favourable to the reduction of that body.

But there is another consideration. It is well known that the spongy lead formed on one of the plates in a secondary battery is to some extent acted on by the liquid.

It occurred to us that this direct chemical action between lead and sulphuric acid might be influenced by sodium sulphate. We therefore placed a quantity of red lead on a sheet of lead and reduced it electrolytically. The sheet was then cut into small pieces and divided into two equal quantities of about 20 grammes each. One half was put into a flask containing 1 volume of acid to 6 of water; the other half was put into a similar acid with the addition of 5 per cent. of sodium sulphate. Hydrogen gas was evolved from both flasks at the ordinary temperature. The following Table shows the results:—

Time, in days.	Hydrogen collected, in cubic centimetres.			
	From Acid.		From Acid containing $\text{Na}_2\text{SO}_4$ .	
	Per diem.	Total.	Per diem.	Total.
1	160	160	116	116
2	125	285	91	207
3	120	405	87	294
7	75	695	54	512

It is evident that the sodium sulphate exercised a protecting influence on the lead.

In another experiment with a solution containing as small a proportion of sodium sulphate as that used by Mr. Preece, the protective influence was still observable, though much less marked.

These results support the idea that part of the effect produced by sodium sulphate lies in its power to diminish the local actions arising between the acid and the different parts of the plates.

It is not unlikely that this chemical action has something to do with the difficulty experienced in electrolytically reducing pure lead sulphate when that substance unmixed with other compounds is simply immersed in dilute acid; for at the moment of incipient decomposition the lead must be very finely divided, with its affinities in their most active state.

### *Sub-sulphate of Lead.*

In a paper read before the Royal Society\*, Dr. Frankland doubts whether the lead sulphate formed and decomposed in the cell is the ordinary white sulphate known to chemists, and has studied the action of dilute acid on litharge and on minium. From litharge he obtained a buff-coloured compound, for the composition of which he gives the formula  $(\text{SO}_3)_3(\text{PbO})_5$ . From red lead he obtained a brownish-red compound,  $\text{S}_2\text{Pb}_3\text{O}_{10}$ . Dr. Frankland thinks it highly probable that one or other of these salts takes part in the electrolytic processes of the storage battery. He remarks, however, very truly that the working conditions in a battery are very different from those of his experiments.

\* Proc. Roy. Soc. 1888.



With reference to these results we have made some observations.

*Buff-coloured body from Litharge.*—The formula  $(\text{SO}_3)_3(\text{PbO})_5$  can be written  $2\text{PbO} + 3\text{PbSO}_4$ . In other words, the substance may either be a true sub-sulphate, or a mixture of the ordinary sulphate and oxide of lead. When attempting to prepare some of this compound, preliminary results suggested the following experiment.

Known quantities of litharge and sulphuric acid were digested together in a flask. From time to time the flasks were shaken vigorously and a small quantity of the clear liquid subtracted. The strength of the acid was carefully determined; and from this, together with the known volume of acid, it was easy to find how much acid had combined with the lead oxide. The curves given below, which are drawn through the actual points of observation, show the course of the action for 28 days, the ordinates giving the acid absorbed, and the abscissæ the time.

In Exp. I., 33.41 grams of litharge and 150 cubic centim. of 1 to 5 acid were used. This liquid contained 43.38 grams of sulphuric acid.

In Exp. II., 39.73 grams of litharge and 150 cubic centim. of 1 to 6 acid = 36.37 grams  $\text{H}_2\text{SO}_4$  were used.

In Exp. III., 39.92 grams of litharge and 150 cubic centim. of 1 to 10 acid = 25 grams  $\text{H}_2\text{SO}_4$  were used.

The acid required for total conversion of the litharge into sulphate would be,

In Exp. I. = 14.7 grams.

In Exp. II. = 17.45 „

In Exp. III. = 17.54 „

Of course only three fifths of these quantities would have been required to form the compound  $(\text{SO}_3)_3(\text{PbO})_5$ .

The salt gradually became white in colour. It is evident that in each case the action was slow and progressive, without any sudden change of rate to mark the formation of a sub-salt.

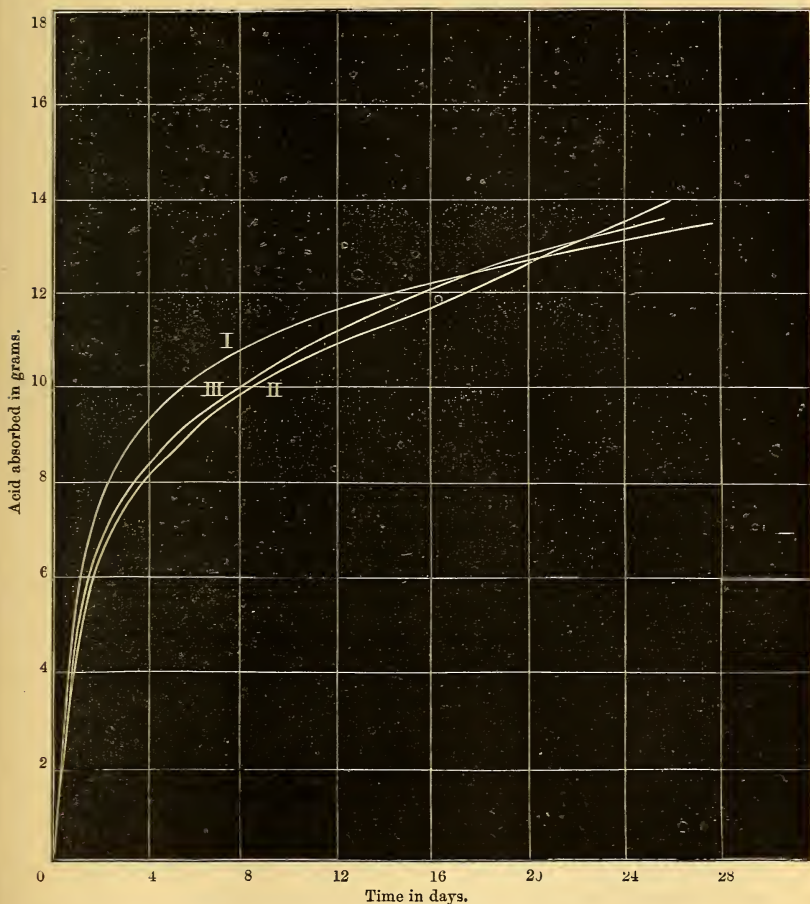
At a later date we stopped the experiments and analysed the substances produced in Exps. I. and II.

In I. we found 31.26 per cent. of  $\text{SO}_4$ , which indicates the presence of 98.6 per cent.  $\text{PbSO}_4$  and 1.4 per cent. of  $\text{PbO}$ .

In II. we found 31.67 per cent. of  $\text{SO}_4$ , which indicates 99.5 per cent.  $\text{PbSO}_4$  and 0.5 per cent. of  $\text{PbO}$ .

The general outcome is clearly in favour of the idea that the

action is a continuous one, which will only finish when the whole of the litharge is converted into sulphate. As the experiment proceeds there is an increasing proportion of insoluble sulphate present, which no doubts acts as a protective coat for the unchanged litharge, and thus renders the transformation less rapid. We found in fact that the action was greatly hastened if we continually broke up the substance in a mortar.



We see therefore no reason to doubt the view put forth as far back as January 1882, that the substance produced in the voltaic reaction is ordinary sulphate of lead, a substance which is

easily oxidated by means of the current, and is reduced without serious difficulty, especially when broken up by better conducting bodies.

*High Initial Electromotive Force.*

During the prosecution of the experiments described in the preceding pages our attention was again drawn to the high electromotive force which, as is well known, is found in a secondary battery for a short time after the charging current has been stopped. So far as we know, the explanations of this curious phenomenon which have been hitherto given are not looked upon as satisfactory. These explanations depend on the presence and action of electrolytic gases, which are either supposed to be occluded by the electrodes, or else to form secondary products differing from the ordinary elements in much the same way as ozone differs from oxygen.

We thought it probable that the chief cause of the high E.M.F. might be found in the great inequalities in the strength of acid produced by the charging current. There is no doubt that the acid becomes much stronger in the immediate vicinity of the peroxide plate. The strong and weak acid thus produced at the positive and negative plates respectively, being contained in spongy masses of material, require some time to diffuse, and the normal E.M.F. of 2 volts cannot be attained until diffusion has produced uniformity in the strength of the acid. We put this idea to experimental test.

Most of the observations were made on a small experimental cell in which were:—

- (1) a negative plate consisting of a strip of lead (1 inch  $\times$  3) covered with spongy lead ;
- (2) a positive plate made of similar lead covered with peroxide ;
- (3) an electrolyte of dilute acid containing 18.5 per cent.  $\text{H}_2\text{SO}_4$  (= 1 volume of acid to about 9 of water).

We also provided a small porous earthenware jar filled with stronger acid, into which we could introduce the peroxide plate when desired.

In the first series of experiments the plates were charged in the uniform electrolyte by a current of nearly half an ampere, and after breaking the battery-circuit, observations were taken of the E.M.F. by the condenser method.

Time, after stopping the charging current.	Electromotive force, in volts.			
	Exp. I.	Exp. II.	Exp. III.	Exp. IV.
At once .....	2.58	.....	.....	2.58
5 seconds .....	.....	.....	.....	2.28
1 minute .....	2.16	2.18	2.17	2.14
2 minutes .....	2.13	2.17	2.16	2.12
5 " .....	2.06	2.10	2.10	2.06
10 " .....	2.01	2.04	2.02	2.05
15 " .....	2.00	2.01	2.01	

Peroxide plate now put into the jar of stronger acid.				
Time after change of acid round peroxide.	Acid 34 per cent.*	Acid 34 per cent.*	Acid 34 per cent.*	Acid 58 per cent.*
$\frac{1}{2}$ minute .....	2.05 volts.	2.06 volts.	2.05 volts.	2.16 volts.
1 " .....	2.07 "	2.09 "	2.09 "	2.20 "
2 " .....	2.07 "	2.12 "	2.12 "	2.21 "
4 " .....	2.09 "	.....	.....	2.24 "
5 " .....	2.10 "	2.13 "	2.13 "	

From this Table it is evident that the rate of fall in the various experiments is fairly uniform, and also that an increase in the strength of the acid round the positive plate (peroxide) is able to give a large increase in the E.M.F. of the cell. We further see that the greater portion of the fall in E.M.F. takes place in the first few seconds after stopping the charging current. This we should expect if the action depends on differences of density in acid, for these differences will be greatest and diffusion most marked in the early stages. In the following set of experiments the spongy lead stood in 18.5 per cent. acid, while the porous jar containing the peroxide plate was filled with acid whose strength in Exps. I. and II. was 34 per cent., and in Exp. III. 58 per cent. The

Time, after stopping the charging current.	Electromotive force, in volts.		
	Exp. I.	Exp. II.	Exp. III.
At once .....	2.61	.....	2.61
5 seconds .....	.....	.....	2.44
1 minute .....	2.22	2.24	2.33
2 minutes .....	2.21	2.23	2.31
5 " .....	2.18	2.21	2.28
10 " .....	2.17	2.20	2.28
15 " .....	2.14	2.16	2.27
25 " .....	.....	.....	2.27
30 " .....	.....	.....	2.25

\* These strengths refer to the acid in the porous jar. That in the general body of the cell remained as before—18.5 per cent.



cell thus arranged was charged as before, and after stopping the charging current observations were taken of the E.M.F.

From this Table it appears that the rate of fall is very much slower than before. This is especially marked in Exp. III., where the strength of the acid in the jar is nearer the possible maximum producible in the interstices of the spongy materials.

It may be worth notice, that the value of the E.M.F. to which the cells finally *rise* in Exps. I., II., and III. of the first series is very nearly the same as that to which they *fall* in the first two experiments of the second series. If the rise is due, as we think, to the diffusion inwards of the stronger acid, some such agreement might be expected.

We therefore regard the abnormal E.M.F. as due to the inequality of acid strength, and its gradual disappearance as due to equalization of strength produced by diffusion.

XIX. *On Dropping-Mercury Electrodes.* By J. BROWN\*.

IN Prof. Ostwald's Reply † he is scarcely correct in describing my paper ‡ as a "supposed disproof of v. Helmholtz's theory." It was perhaps unnecessary to disprove what had not been proved. V. Helmholtz put forward an explanation based on several unproved hypotheses. I offered what appeared to me a simpler and more probable theory. Prof. Ostwald, however, goes further; and there arises the question whether many of the supporters of v. Helmholtz's theory would accept Prof. Ostwald's exposition of it, or the predictions which he founds so easily upon it. He is, however, so sure of his ground as to go the length of prophesying in his fourth paragraph (p. 480) what will happen if I try a certain experiment. Well, that experiment I had of course already repeatedly tried before I made any assertion as to the result; and now, to make sure, I have repeatedly tried it again, and so far from the current being "much weaker" than in the previous case, as Prof. Ostwald implies that it obviously must be, I am unable to detect a mean difference of one half per cent. between them. Any subsequent decrease of the current by polarization of the resting mercury is explained equally by either his hypothesis or that which I advocate, as is also the current referred to in the last paragraph of his reply.

It is after all possible that the initial equality of these currents (however this may affect Prof. Ostwald's view) might, by the adoption of some further not impossible hypotheses, be made to agree provisionally with the view of v. Helmholtz.

\* Communicated by the Author.

† Phil. Mag. June 1890.

‡ Ibid. May 1889.

It may suffice, therefore, that attention has been called to a theory alternative to that of v. Helmholtz, and which seems, to me at least, much simpler and more probably true.

An undoubted knowledge of even the sign of the potential of mercury in contact with an electrolyte would go a great way towards settling the question at issue. According to my view, it is probably negative. V. Helmholtz's theory is founded on the assumption that it is positive; but, notwithstanding the rather decided way in which this assumption is at first stated\*, no real proof is given; and the subsequent remark ("wäre z. B. das Queksilber positiv"†) indicates the recognized provisional character of the assumption. It lies with those who would give to the provisional theory of v. Helmholtz the character of an ascertained law of Nature to provide a knowledge of the true value of the hypotheses on which it is based before it can carry the weight they propose to attach to it, or serve as a reliable support for the further researches already dependent on it.

XX. *Problems in Probabilities: No. 2, Competitive Examinations.* By Professor F. Y. EDGEWORTH, D.C.L.‡

THE following study is related to the first number of the series§ as being another instance of the Probability-calculus applied to a practical interest. In a paper on "The Statistics of Examinations," which was published in the September number of the Journal of the Royal Statistical Society for 1888, and in a sequel to that paper which will shortly be published in the same Journal, I have made an estimate of the extent to which the results of competitive examinations depend upon the accident of one examiner rather than another equally competent being appointed to mark the work of the candidates. Referring to those papers for a fuller exposition of the statistical data and the practical conclusions, I propose here to abstract the mathematical reasoning.

The fundamental axiom is the proposition, evidenced by analogy and specific experience, that the marks given by different examiners to the same piece of work are apt to be arranged according to some law of error or facility-curve which is constant for the same class of examiners and work examined. The analogy between errors of observation and discrepancies in marking is evident. But, as the transition is

\* *Wissenschaftliche Abhandlungen*, i. p. 934.

† *Ibid.* p. 936.

‡ Communicated by the Author.

§ See *Philosophical Magazine*, October 1886.

rather abrupt from objective quantities observed by the senses to degrees of intellectual quality estimated by the judgment, I have confirmed the analogy by trying an experiment in an intermediate case, where the quantity to be determined is objective, but the operation by which it is determined is an estimate rather than a simple observation. Of this sort are the answers which I have obtained by asking a number of persons separately: "What is my weight?" Having collected 96 estimates made in reply to this question, I find that they are constant to a definite law of frequency. That law is exhibited in the annexed table or scheme; in which the ordinary numerals denote pounds above nine stone (thus 25 means 10 st. 11 lb.), and the Roman numerals *above* denote the number of estimates which are entered in each of the spaces bounded by the ordinary numerals (thus there were four estimates below 9 st. 10 lb., and nineteen between that figure and 10 st. 6 lb.)\*. The verification of our axiom is

IV.	XIX.	XXIV.	XXVI.	XIX.	IV.
10.	20.	25.	30.	40.	
II.	XIV.	X.	XV.	VI.	I.
† I.	VII.	XIII.	XII.	XII.	III.

shown by the *lower* rows of Roman numerals which respectively designate the distribution of the first 48 answers which I received, and of the second batch. I add the following verifications. Regarding as an error the deviation of any estimate from the average of all ‡, namely 25, I find that the average of the errors in defect is 7·2; the average of the errors in excess is 6·8. Now split up the forty-seven errors in defect into two batches as nearly as may be; the average of the first twenty-four—first in the order of arrival—is 7·5; of the remaining twenty-three, is 6·8. So the average of the first twenty-five errors in excess is 5·6, of the remaining twenty-four 8.

Even the batches of sixteen show considerable steadiness. The following table exhibits this constancy. The first column designates the position of each batch of sixteen in the accidental order in which it was received and entered. Thus

\* Where a number of estimates coincided at one of the boundaries, *e. g.* 20, I gave half to one compartment, *e. g.* IV.-XIX., half to the other, XIX.-XXIV. Where the number was odd I gave the benefit to the compartment nearer to the centre.

† The apparent anomaly that the whole of certain compartments contains more or less than the sum of the parts is explained by the preceding note.

‡ *Average* in this paper stands for Arithmetic Mean.

1. designates the first sixteen estimates which I received. The second column contains the average of each batch, expressed in pounds above nine stone. The third column gives the average of the sixteen errors measured without regard to *sign* from the average of each batch, and multiplied by the constant  $1\cdot25 \left( = \sqrt{\frac{\pi}{2}} \text{ nearly} \right)$  for the sake of comparison with the entries in the fourth column, each of which is the *Mean* of similarly reckoned errors, in the Gaussian sense of *Mean Error*: that is, the square root of the sum of squares of errors divided by the number thereof less by one, that is here 15.

Order of entry.	Average.	Average error $\times 1\cdot25$ .	Mean error.
I.	24·5	8·2	8·1
II.	23	7·6	7·8
III.	22·5	8	8·6
IV.	22	10	9·8
V.	29	6·6	6
VI.	29	9	9·6
Means ...	25	8·2	8·3

It will be observed that these estimates obey not only *a* law, but *the* law of error; according to which the Mean Error ought to be equal to the Average Error  $\times \sqrt{\frac{\pi}{2}}$ . For further

verification of this incident I may refer to the scheme on page 172, where it appears that the probable error, as deduced from the distribution of the observations, is 5. Now, according to the Tables compiled for the Error-function, the number of observations outside a distance on either side from the centre of three times the probable error ought to be 4·3 per cent. That is exactly what occurs. It is true that the average and mean error do not perfectly fit the probable error. But the imperfection is hardly greater than might be expected in dealing with a number of observations so limited as 96. Nor would I contend for a perfect fulfilment of the law of error—more perfect than in the case of human statures and other



natural groups\*. Indeed I am not concerned to show that the law of error is fulfilled; except so far as this incident may afford some guarantee of greater stability. It is on this account only, if at all, that I am concerned with another striking incident, namely that the Mean of all the estimates†, the apparent weight, 9 st. + 25 lb., coincides with the real weight, which is exactly, or oscillates about, 10 st. 11 lb.

A less perfect, but still I think sufficient, verification of our axiom is afforded by another series of 96 estimates which I obtained by asking the additional question: "What is my

XIX.	XXXII.	XXVI.	XIX.
	75	9	10
XIII.	XVI.	XI.	VIII.
VI.	XV.	XVI.	XI.

height"? The grouping of the series is as before exhibited by the first two rows of figures in the annexed scheme. The correspondence of the parts with the whole and with each other is shown by the third and fourth rows, referring respectively to the first and second batches of forty-eight estimates. The average of the thirty-five errors in defect—measured from the average of the ninety-six observations, namely 8.6—is 1.73. The average of the first eighteen errors in defect is 1.55. The average of the remaining seventeen errors in defect is 1.9. Again, the average of the sixty-one errors in excess is .98. The average of the first thirty-one of those errors is 1; the average of the remaining thirty is .96.

As in the case of the weights, the apparent ‡ and true measures coincide. But there does not exist that guarantee of stability which may be afforded by conformity to a Probability-curve. That hypothesis is negatived by the protuberance of the lower limb which has just now been evidenced. It may be added that, whereas the lower quartile is distant from the Median by less than 1.5, there occur (in so small a set) three observations distant respectively from the Median 5, 7, 8. This occasional darting out of the lower limb is unfavourable to that steadiness in the average of small batches which we noticed in the case of the weights. The Medians of component batches are sufficiently steady§.

\* The aggregation of observations at round numbers is one of the vitiating causes in both cases.

† The Arithmetic Mean and Median coincide.

‡ Taking as the apparent weight  $8\frac{3}{4}$ , intermediate between the *average* which is  $8\frac{1}{2}$  nearly and the *median* which is 9 nearly.

§ For further details see the companion paper.

A still less perfect verification is presented by a series of

X.	X.	XX.	XX.	X.	X
8.5	14	50	100		225
<hr/>					
V.	V.	X.	X.	V.	V.
7	17.5	55	122.5	225	
<hr/>					
V.	V.	X.	X.	V.	
10	12.5	30	87.5	300	

eighty answers which I have obtained to the question : "How many five-pound notes are equal in weight to a sovereign?" The grouping of these estimates is represented in the first of the annexed schemes\*; the grouping of two component batches by the second and third scheme. It will be seen that there is a general resemblance between the two parts and the whole. The displacement of the Median seems not inconsistent with the hypothesis of a constant facility-curve. I thus conclude, partly from a rough application of the formula which I have cited from Laplace in the predecessor to this paper for the error of the Median of any facility-curve†, partly by a still rougher reasoning as to the divergency that might be expected, if we were dealing with a genuine Probability-curve.

But it must be admitted that the upper extremity of the curve defies law. The maximum of the first batch of 40 is 1500; the maximum of the second batch of 40 is 20,000‡. These fluctuations are so violent that we could not expect to determine their law of frequency without statistics more copious than I have attained for examination marks. It should be considered, however, that at examinations the maximum and minimum are usually fixed, so that enormous vibrations of the extremities are impossible. In so far as the abnormal or incalculable element in the fluctuation of the maximum or minimum may make itself felt, it should be held that my estimates of the extent to which chance affects examinations are underrated.

These experiments in an intermediate case seem to warrant our applying with caution the Theory of Errors to the more specific experience which I shall now adduce. It consists of

\* Cf. p. 172.

† Phil. Mag. October 1886, p. 375.

‡ The true figure is 6!

two kinds : marks given by two examiners to several papers, and marks given to the same paper by several examiners. The former kind of statistics are more copious ; and in some respects more valuable. For they admit of being freed from a constant difference, of the nature of a "personal equation," between the marking of two examiners ; which equally affecting all the competitors does not disturb their *order* ; and therefore perhaps ought not to be reckoned\*.

My method of dealing with these data may be described by taking as an example the most perfect specimen which I obtained, namely the marks given by two examiners to 400 pieces of English composition. First I took the difference between the two marks given to each paper ; then squared those differences, found the Arithmetical Mean of those squares, and took the square root of that Mean Square as the *Mean Deviation* in a sense analogous to Gauss's use of *Mean Error*. The peculiar propriety of this coefficient as a measure of discrepancy is that it not only represents, as well as other sorts of average error, the deviation between marks in any particular subject ; but also leads to the coefficient of the Probability-curve which measures the deviation between *sums* of marks. Thus the Mean Deviation for the 400 pairs of marks in English composition proved to be 67, which coefficient not only gives a general idea of the discrepancy to be expected between any two marks, but also yields a precise system of measures for the discrepancy between the sum of several marks assigned by two examiners to the same pieces of work *in pari materiâ*. That discrepancy would fluctuate according to a Probability-curve whose *modulus* is  $\sqrt{2} \times 10 \times 67$ , or whose *probable error* is  $\cdot 674 \dots \times \sqrt{10} \times 67$ .

For our purpose it is generally convenient to express the Mean Deviation as a percentage of the mean mark for a whole set of papers. Thus in the case before us the average of the 800 marks was 227 ; and accordingly the Mean Deviation per cent. in round numbers 30.

This result requires to be corrected for a certain "personal equation." The constant difference between the two sets of marks is about 20, nearly ten per cent. of the average mark. The square of this constant difference is to be subtracted from the uncorrected Mean Square ; of which 67 was the square root. The corrected Mean Deviation is 64 ; expressed as a percentage of the average mark, 28 nearly.

The worth of this result may be appreciated from the state-

\* See on this point the companion paper in the 'Journal of the Statistical Society' for 1890.

ment that, whereas the (uncorrected) Mean Deviation for the whole set of 400 pairs is 67, the corresponding determinations for the first, second, and third batches of 133 papers were respectively 63, 67, 72. I have similarly verified other results obtained by the same or a similar method. Thus the Mean Deviation for marks given by two examiners to fifteen papers in Greek Prose is 25 per cent.; for marks given by the same pair of examiners to thirty pieces of Latin Prose, 26 per cent. For sixty pieces of Greek and Latin Prose and Verse composition (including some of the Latin Prose but not any of the Greek Verse before mentioned) I obtained,—by a more summary, but in the particular instance at least sufficiently safe, method\*—again 25 per cent.

When the statistics are in the form of marks given by several examiners to the same piece of work, I have extracted the Mean *Error* according to the usual rules; and then multiplied the coefficient by  $\sqrt{2}$  in order to obtain the Mean *Deviation* as above defined. In the only case in which I have been able to compare the two methods of determination the results yielded are fairly consilient. I refer to Latin Prose Composition, for which, according to the first method, I extracted from thirty pairs of marks given to as many pieces of prose the Mean Deviation 26 per cent. By the second method I obtained from twenty-eight marks given to the same piece of prose by as many highly competent examiners the Mean Deviation 20 per cent.—of the average of the twenty-eight marks; which, being four fifths of the maximum, is not exactly comparable with the *general* average referred to in the first method.

I annex a summary statement of the results obtained by one or other of those methods†:—

\* Using the formula: Mean Deviation (in the sense above defined)  

$$= \sqrt{\frac{\pi}{2}} \text{ Average Deviation; which relation had held good for a great}$$
 number of marks given by the same examiners in a variety of Classical subjects including Composition.

† These computations derive some confirmation from an experiment which Mrs. Bryant, D.Sc., of the North London Collegiate School, has communicated to me. Having examined forty Geometry papers, she re-examined them after some weeks. The discrepancy between the two sets of marks (corrected for a certain difference of *scale*) proves to be only 12 per cent. For further remarks on the Table see the companion paper.



Designation.	Number of Marks on which the Computation is based.	Mean Discrepancy per cent. of mean mark.
High School, Geometry and History ...	160	15
Cambridge Honours in Classics, Trans- lation, History, Composition (mixed)	480	18
India Civil Service, Latin Prose Com- position.....	28	20
Oxford Honours in Literæ Huma- niores, Philosophy (alone) .....	480	21
Cambridge Honours in Classics, Com- position (alone) .....	150	25
English Composition .....	800	28

These data are adapted to certain problems which are of practical interest.

I. The first problem is, What is the probability that any particular candidate who has come out successful at an examination would have been successful (or *vice versâ*) if the candidate's work and that of his competitors had been appraised by a different though equally competent examiner (or examiners)? This general problem may be variously subdivided. First (A) success may be defined by the attainment of a predetermined number of marks, a fixed Honour Line. Or (B) the number of prizes, say  $n$ , may be predetermined; and the first  $n$  candidates, without respect to the absolute number of their marks, may obtain prizes. Other distinctions turn on the presence or absence of an attribute which is particularly favourable to the calculation of probability: namely, a certain plurality which renders applicable the laws of large numbers; the attribute in virtue of which the movement of multitudinous atoms is more tractable than the problem of three bodies. We may inquire whether a candidate would be displaced, if ( $x$ ) the mark assigned to each paper in each subject had been what may be called the *true mark*—namely the mean of the marks given by an indefinite number of equally competent examiners; or ( $\bar{x}$ ), if the marks in each subject had been given by a single examiner (or a few) different from the one (or two) who acted on the given occasion. Again ( $y$ ) the number of competing candidates may be large, or ( $\bar{y}$ ) not so. Lastly ( $z$ ) there may be

several subjects, the candidate's place being determined by the sum of his marks in each ; or ( $\bar{z}$ ) there may be only one or two subjects.

Of the immense number of cases formed by the combinations of these attributes I shall discuss only the most interesting. First in the order of simplicity is *Axz.* In this case there is a fixed Honour-line, say  $H$  ; the comparison is between the place actually obtained by the candidate and the place which he would have obtained if in each subject the marks had been determined by a numerous jury of competent examiners ; the number of competitors may be either many or few ; the number of subjects is large, say  $S$ . Since the number of subjects is large and the marking in each subject fluctuates with the change of examiners according to a *definite* law of frequency, it follows that sums of  $S$  marks fluctuate according to the law of error, the Probability Curve. Let  $C$  be the Mean Deviation for the marking in each subject ; in the sense above defined, that is  $\sqrt{2} \times$  the Gaussian Mean Error. Then the Probability-curve, according to which the compound mark determined by any set of  $S$  examiners will fluctuate, has for its Modulus the coefficient  $C$  ; which is ascertainable by observation. Now suppose the candidate has obtained the mark  $H + l$ . The problem may be likened to the familiar one: If the average of  $S$  observations of given precision be  $H + l$ , what is the probability that the true value is less than  $H$ . By received reasoning the probability in question is

$$\frac{1}{\sqrt{\pi}C} \int_0^{\infty} e^{-\frac{x^2}{C^2}} dx ;$$

which may be calculated from the usual tables.

*Axz.* This case differs from the preceding in that the comparison of the actual compound mark is not with the true mark, but with the mark which any other set of  $S$  competent examiners might have assigned. It is as if, in the parallel problem, we sought the probability, not that the true value is less than  $H$ , but that any second measurement made under similar conditions should fall below  $H$ . According to a well-known theory the solution is obtained by substituting  $\sqrt{2} \times C$  for  $C$  in the solution of the preceding problem.

*Bxyz.* This is the case in which a fixed large number, say  $n$ , prizes are assigned to the  $n$  candidates who come out first (irrespective of the absolute number of their marks) ; and the inquiry is whether any particular candidate would have his status changed from successful to unsuccessful, or *vice*

*versâ*, if each of the marks in each subject had been determined by a jury; the number of candidates, say  $m$ , and the number of subjects,  $S$ , being large. The number of candidates and prizes being large, we may assume that the mark of the  $n$ th candidate in a descending order of merit, that is the Honour line, will be constant for any particular set of examiners; for much the same reason that, if two large batches of similar objects, *e. g.* statures of the same nation, be taken at random, the quartiles, octiles, deciles, &c. remain constant. Thus the problem is reduced to  $Axyz$  which—as one case of  $Axz$ —has been solved.

$\bar{B}xyz$ . This problem is related to the preceding  $Bxyz$ , as  $A\bar{x}z$  to  $Axz$ .

$Bxyz$ . This case differs from  $Bxyz$  in that the number of the competitors (and prizes) is small. First, let there be only two competitors, and one prize. The problem is: What is the probability that the verdict of any particular set of  $S$  examiners would be reversed, if the two papers in each of the  $S$  subjects had been marked by a jury. Let the (compound) marks of the two candidates differ by  $l$ . The probability of reversal is identical with the probability that the difference between the candidates in a particular direction, or with its *sign*, according to the actual set of examiners, should differ by as much as  $l$  from the difference in the same direction under the jury-system. If, as before,  $C$  is the Mean Deviation in each subject, then, upon principles to which allusion has been made, the required probability is

$$\int_l^{\infty} \frac{1}{\sqrt{\pi^2 SC}} e^{-\frac{x^2}{2SC^2}} dx.$$

Next, let there be three candidates; and, to fix the ideas, let there be two prizes, and let the question be, What is the probability that the second prize-man would fail to obtain a prize, if the work were marked by other examiners? In order that the original second should become third, it is evident that he must come out below the original third. Thus,  $l$  being the distance between the original second and third, the solution would be the same as for the simple case, if the original first were not liable to move relative to the original second. But, in virtue of this liability, a certain proportion of cases in which the original second comes out below the original third are not failures for the original second. Thus  $l$ , the distance from the first of the unsuccessful, or Honour-line as it may be called, being the same, the probability of failure decreases with the increased number of candidates. The limiting case



where, the candidates and prizes being indefinitely numerous, the Honour-line may be regarded as fixed, our  $Bxyz$ . It will be observed that the measure of discrepancy for  $Bxyz$  is less than the corresponding measure for the extreme case of  $Bx\bar{y}z$  in the ratio  $1 : \sqrt{2}$ . We have thus a rough measure of the inaccuracy which we commit in treating intermediate cases according to the rule proper to either extreme.

$Bx\bar{y}z$ . This relation of this case to the preceding is like the relation of  $Bxyz$  to  $B\bar{x}yz$ ; which has already been considered. The coefficient of discrepancy which is proper to  $Bx\bar{y}z$  should be multiplied by  $\sqrt{2}$  for  $B\bar{x}yz$ .

$Bx\bar{y}\bar{z}$ . This case differs from the preceding in that the number of the papers is small. At this stage therefore the Probability-curve which has hitherto illumined our course disappears. A certain twilight may, however, be derived from that source of illumination. Take the extreme case of two candidates examined in one subject for a prize. What is the probability that the award of one examiner would be reversed by an equally competent examiner? As we saw under a preceding head, the answer turns upon the variation with the change of examiners in the difference between the marks of the two candidates. Such a difference between differences of marks will in general fluctuate according to the same law as a sum of *four* marks taken at random from under the facility-curve, according to which by our postulate the marks of different examiners fluctuate. But a sum of four observations taken from under any facility-curve will in general fluctuate according to a law which is getting on for a Probability-curve, unless indeed the given facility-curve be exceedingly abnormal. But so far is the facility-curve with which we have to deal from being exceedingly abnormal, that it is presumably getting on for a Probability-curve. Accordingly the rule for  $Bx\bar{y}z$  may pretty safely be extended to  $Bx\bar{y}\bar{z}$ ; especially where we have specific experience that the facility-curve in question does not violently rebel against the normal law of error—experience which I have obtained with respect to several subjects. For example, let a prize be given to the one of two candidates who obtains the higher mark for a piece of Latin Prose, of about the same calibre as the Composition at the India Civil Service or Cambridge Classical Tripos Examinations. Even if the successful candidate exceeds his rival by *fifty* per cent. (of the mean between the two marks), there is some probability, say one in a hundred, that the verdict would be reversed by another equally competent examiner.



II. The answers which have been given to the first problem are required for the solution of the second problem: At any examination of which the circumstances are given, how many of the candidates are *uncertain* in this sense, that there is an appreciable chance of any assigned one of them who is now successful coming out unsuccessful, and *vice versa*; if the work were marked by different but equally competent examiners? If we confine ourselves to the general case of several candidates and several subjects (*yz*), we have only to measure from the Honour-line in both directions a distance such that the probability of any candidate at this distance being displaced is very small, say less than one in a hundred. This *improbable* error, or discrepancy as it may be called, is found by multiplying the *probable* error, or discrepancy, proper to the case by 3.5. The candidates above that limit may be described as "safe."

The reader who applies this formula to statistics of examinations, such as those which are given in the Reports of the Civil Service Commissioners, may be surprised to find that the number of the uncertain unsuccessful is greater than that of the uncertain successful; although, in the case of a determinate number of prizes (B), every instance of a successful candidate being in the wrong box involves an instance of an unsuccessful candidate being misplaced. The explanation of this anomaly is that, in applying the received formula, we have made the common assumption that the *à priori probability* of the candidate's real mark, so to speak, being one figure rather than another is constant. The nature of that assumption and the caution with which it must be made\* are well illustrated by these problems. In the present case the *à priori* probabilities are not constant. In general the marks of candidates at an examination are not distributed equably between the positions of the senior and the man at the bottom; but are heaped up in the form of a Probability-curve†. Now the scene of our operations is the upper extremity of this Probability-curve; whence it follows that the *à priori* probability (for each point or degree) diminishes as we ascend

\* See my paper "On *A priori* Probabilities" in the *Philosophical Magazine* for September 1884; also 'Metretike' (London, Temple Co., 1887).

† With respect to this statement and others which may seem to require proof the reader is again referred to companion papers in the *Journal of the Statistical Society*, Sept. 1888 and Sept. 1890. I have sometimes in those papers used the term "true mark" for the mean of the marks given by an indefinite number of examiners—a conception which is not absolutely essential to the  $\bar{x}$  variety of our problems.

from below towards the Honour-line and above it. The effect of this consideration is that we have somewhat underrated the probability of displacement for positions above the Honour-line, and somewhat overrated it for positions below. It may be assumed, I think, that these errors will compensate each other when we determine the total number of the uncertain in the manner which I have indicated.

III. I have made a similar assumption in solving the following *third* problem. At any examination of which the circumstances are given, what number of candidates is *most probably* displaced? I proceed as follows. Having ascertained the coefficient of the probability-curve which governs the case, I determine numbers corresponding to equal increments of that coefficient above and below the Honour-point. In each of the degrees so constituted I find how many candidates are comprehended; and I assign to the candidates in each degree the probability of displacement which is found by Problem I. (with the aid of the proper tables) to appertain to the centre of the degree. The product of the number of candidates and the probability of their displacement gives for each degree the number most probably displaced; which numbers being added give the total number most probably displaced. It is assumed that the underrating of the probability above the line will fairly well be compensated by the overrating below.

An example will make my meaning clear. With reference to an examination for 50 clerkships of the second class, of which the statistics are given in the Twentieth Report of the Civil Service Commissioners\*, how many would most probably be displaced if the work has been marked by another set of equally competent examiners. The problem is of the species *B̄xyz*, the candidates being numerous and the papers about ten in number. The Honour-line is at 1720, and the *probable error* for the regulating Probability-curve (what I have elsewhere called the *probable discrepancy*) is taken as 50; upon the assumption that the *Mean Error* for each of the ten papers is 15 per cent., that is the lowest coefficient which I have actually observed. Accordingly the intervals 1720–1730 &c. correspond each to a fifth of the *Probable error* †. The computation is shown in the annexed Table.

\* Parliamentary Papers, 1876, xxii. p. 180.

† Here called *probable error* with reference to the tables in the books; elsewhere in connexion with the subject-matter *probable discrepancy*; being  $\sqrt{2} \times$  *probable divergence* of a mark from the “true mark.”



In this Table the first column denotes degrees of probable error corresponding to intervals of marks designated in columns 2 and 4. Columns 3 and 5 give the number of candidates successful and unsuccessful whose marks fall in those intervals; column 6 the total of those numbers. Column 7 contains the values of half of the integral  $\frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx$  for  $x = \text{Probable Error}^* \times .1, .2, \&c. - 1.8, 2.2$  respectively (values obtained from the fourth table appended to DeMorgan's 'Calculus of Probabilities'). Column 8 gives the difference between .5 and each of these values, the corresponding integral between limits  $\infty$  and  $x$ ; which represents the probability of displacement for candidates in the corresponding compartment. Column 9, the product of column 6 and column 8, gives the most probable of number of those who would be displaced, for each degree or interval. The sum of these numbers is the most probable number displaced, out of all the candidates. I take the half of this number as the most probable number of successful candidates who would be displaced on re-examination.

In conclusion I submit a Table containing answers to Problems 2 and 3 for certain cases which seem to me fairly typical of the various statistics which I have inspected.

In this Table the *first* column designates a service to which appointment is made by competitive examination. The *second* column contains references to the Reports of the Civil Service Commissioners, in which are published the marks given at public examinations. The Reports referred to are in the 22nd volume of the Parliamentary papers for 1875 and for 1876. The *third* column gives the number of candidates at each of the examinations referred to in this table. The *fourth* column gives the corresponding numbers of successful candidates. The *fifth* column contains the mark of the lowest successful candidate at each of the examinations, or of the highest unsuccessful, or some intermediate number (figures differing from each other by quantities which may be neglected). The *sixth* column contains the aggregate marks which occupy the halfway position in the order of merit at each examination. Thus at the second examination (referred to in the second row of the table) there being 171 candidates, the aggregate mark which is 86th in the order of merit is 1601; in round numbers 1600. At the first examination, the number of candidates being even, viz. 150, the Median is intermediate between the 75th mark, which is (in the descending order of merit) 1601, and the

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\* See footnote, p. 183.



1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
Designation.	Reference to Report of Civil Service Commission.	Total number of candidates.	Number of successful.	Honour line.	Median.	Probable discrepancy.	Improbable discrepancy.	Limits of uncertainty.	Number of the uncertain.	Proportion of the successful quite safe.	Most probable number of displacements.	Proportion of the successful most probably displaced.
								Upper. Lower.	Suc- Unsuc- cessful. cessful.			
Clerks No. 2.	XX. p. 168.	150	24	1850	1600	48	168	2018 1682	19 25	.2	5	.2
Clerks No. 2.	XX. p. 180.	171	50	1720	1600	48	168	1888 1552	33 49	.34	7	1.4
India } Civil Service. }	XIX. p. 522.	206	38	1055	674	27	95	1150 960	15 14	.60	3	.08
India } Civil Service. }	XX. p. 431.	198	37	1076	740	30	105	1181 971	13 16	.65	3	.08
Cavalry and } Infantry. }	XIX. p. 328.	329	152	2872	2737	82	287	3159 2585	32 25	.8	4.5	.03
Cavalry and } Infantry. }	XX. p. 245.	351	110	3301	2560	77	269	3570 3032	29 23	.74	4	.04

76th which is 1597; in round numbers 1600. In the *seventh* column, each entry is the discrepancy which is as likely as not to occur between the sum of ten marks given to any candidate's papers at the examination referred to and the sum of the marks which might have been given to the same work by any other set of equally competent examiners. This figure is calculated from the formula: Mean Discrepancy = Mean Error  $\times \sqrt{2} \times .477$  (or Mean Error  $\times .67 \dots$ )  $\div \sqrt{10}$ . Here 10 is the number (or greater than the number) of the papers answered by a candidate. The other figures are explained in the books on Probabilities. The Mean Error is a coefficient determined by observation in the manner described in this paper (above 176). For most of the examinations the lowest figure actually observed, viz. 15, has been taken for the Mean Error. For the India Civil Service the higher coefficient 18 has been used; partly because that figure actually has been observed for that examination; and partly because the examination includes more advanced and speculative subjects than the Examinations for which the coefficient 15 was observed. The *eighth* column gives the discrepancy which in each case is very unlikely to occur, against the occurrence of which the odds are about 100:1. The improbable discrepancy is by the Theory of Errors equal to the probable discrepancy multiplied by 3.5 nearly. In the *ninth* column each upper limit is formed by adding the improbable discrepancy to the Honour-Line, the lower limit by subtracting the same figure from the same. In the *tenth* column the number of the successful who are uncertain is ascertained by counting the number of candidates whose marks are between the honour-line and the upper limit of uncertainty; the number of the unsuccessful who are uncertain is found by counting the number of candidates between the honour-line and the lower limit of uncertainty. To form the *eleventh* column subtract the number of the uncertain successful from the total successful; the remainder is the number of those who are "safe" in this sense that for any assigned one of them the odds against his being displaced upon a reexamination of his work are about 100 to 1. The number of the safe divided by the number of the successful at each examination is entered in the eleventh column. The laborious formation of the *twelfth* column is described above at page 185. To form the *thirteenth* column divide each entry in the twelfth column by the corresponding entry in the fourth. The average of the figures in the thirteenth column relating to the same class of examination gives the proportion of the successful candidates which would most probably be displaced upon a reexamination of their work—most probably in the same sense as we may say that the average death-rate represents the proportion of the population who will most probably die in any proximate year. Thus in the case of the India Civil Service we may say—or rather might have said at the period to which the statistics relate, twelve years ago—that the most probable proportion of displacement—the

degree of failure of justice which may be expected—amounts to 8 per cent. of the successful; or rather  $8 \div \sqrt{2}$ , say 6, per cent., if we define the just verdict as that which would be found by taking the average of the results obtained by a variety of competent examiners.

XXI. *Some Electrical Properties of Flames.* By MAGNUS MACLEAN, M.A., F.R.S.E., and MAKITA GOTO (*Japan*)\*.

[Plate V.]

IN connexion with our experiments on the “Electrification of Air by Combustion,” we were led to make some experiments on the electricity of different parts of the flame itself. A Bunsen burner was used, and the potentials at different points, both inside and outside of the flame, were examined. In fig. 1, Plate V., is shown the arrangement for examining the inside of the flame. AA and BB are platinum wires insulated from the burner and projecting into the flame 5 millim. above the upper end of the burner. These wires can be adjusted by bending so as to lie in various positions from the middle line of the flame to its boundary. In our experiments one of them was left insulated (with its end free in air), while the other was connected to a terminal of a Thomson Quadrant Electrometer. Or, again, one wire was connected to one terminal of the electrometer, and the other to the other terminal. The Bunsen burner itself was always connected to earth. The sensitiveness of the electrometer was generally such that a difference of potential of  $\frac{1}{200}$  volt between the terminals could be observed.

In fig. 2 is shown the arrangement for examining the outside of the flame. C is a platinum wire fused into a glass tube which covers the wire except a very small portion of its end. D is the scale for measuring the distance of the point of the platinum wire from the boundary of the flame. E is the index.

By these arrangements it was found that the flame is negatively electrified, while the film of air surrounding the flame is positively electrified. These results were already obtained by Elster and Geitel. Our results agree with what they found, though our method of examining the different parts of the flame is different from their method. (See an abstract of their experiments by S. P. Thompson in ‘Nature,’

\* Communicated by the Authors.

vol. xxvi. No. 666.) In fig. 3 is shown the curve of potential obtained after several observations. It will be observed that the potential at the middle line of the flame is nearly zero, and the surface of maximum negative potential lies just inside of the flame, while the surface of maximum positive potential lies at a distance of 2 millim. from the boundary of the flame. The maximum difference of potential between these two surfaces was found to be between  $2\frac{1}{2}$  and 3 volts.

Similar results were obtained with other flames; but in the case of glowing charcoal the point of the platinum wire had to be brought very close to it in order to obtain the indication of positive potential of the film of air surrounding it.

Having thus made quantitative measurements of the potentials of different parts of a flame, it was expected that the magnitude of the electrification of the air would depend on the part of the flame that was earthed; that is, that maximum positive electrification would be obtained when the most negative part of the flame was earthed and *vice versa*. This expectation was verified by placing the Bunsen burner 3 feet below the nozzle of a water-dropper connected in the usual manner to a quadrant-electrometer.

The flame of the Bunsen burner was next surrounded by a wire-gauze cage, which was made to lie on the surface of the flame. The burner and wire gauze were connected to a gas-pipe for earth. Under this arrangement the effect of the flame was just like that of glowing charcoal, the electrometer connected to the water-dropper showing 6 volts positive.

Another cage open at the top, and connected to earth, was made to lie on the surface of maximum positive potential surrounding the flame. This was difficult to do, and only a part of the cage fulfilled the condition. In this case the air was electrified to  $2\frac{1}{2}$  volts negative, while the burner without the cage electrified the air to less than one volt.

These experiments help to explain why glowing charcoal electrifies air positively, for it acts like a solidified flame connected to earth. For a similar reason spongy platinum, when it glows in hydrogen or coal-gas, is negatively electrified like glowing charcoal.

In these experiments it was desirable to know the maximum electrifying effect of the flame, and this was done by the following method:—The flame to be tested is placed on a stand insulated or uninsulated about 3 feet below the nozzle of the water-dropper, which is connected to the electrometer. The room is electrified, say negatively, to a certain potential which is indicated by the electrometer, by turning



an electrical machine in the further end of the room. The flame to be tested is then lighted, and the change of deflexion of the electrometer, if any, is noted. If the change of the deflexion is towards negative, the flame is put out and the room is further electrified negatively by turning the machine; but if the change of the deflexion is towards positive we wait for some time till the electrification of the room decreases by some scale-divisions, and the flame is again tried to see the effect. This process is continued till no change is observed on lighting the flame. The reading at that time is taken as the maximum effect of the flame. The following observation on a spirit-lamp connected to a gas-pipe may be taken as a specimen :—

Deflexion before lighting.	Deflexion after lighting.	Direction and amount of change.
30	20	+ 10
15	13	+ 2
$13\frac{1}{2}$	12	+ $1\frac{1}{2}$
12	11	+ 1
6	$8\frac{1}{2}$	- $2\frac{1}{2}$
$8\frac{1}{2}$	$8\frac{1}{2}$	0

The maximum effect is therefore  $8\frac{1}{2}$  divisions, equal to 0·6 volt negative, 14 divisions of the scale corresponding to one volt.

When this same lamp was put on an insulating stand and connected to the negative pole of one Daniell's cell, the other pole being connected to gas-pipe, the maximum deflexion was 40 scale-divisions (= 3 volts), and when two Daniell's cells were used in the same way the maximum deflexion was 60 scale-divisions (=  $4\frac{2}{7}$  volts).

Experiments the arrangements for which are shown diagrammatically in fig. 4, were also tried. A, B are metal plates supported about 2 millim. apart by the insulating material C, and joined by wires to the terminals of the electrometer. A spirit-lamp is placed about a foot below, so that the hot air from the flame passes between the two metals. Differences of potential produced by this arrangement are given in the following table :—

Metal positive relative to other metal.	Metal negative relative to other metal.	Deflexion.	Difference of potential in volts.
Polished Zinc B.	Polished Zinc A.	2.0	.04
Unpolished.	Polished Zinc.	17.0	.32
Unpolished Copper.	Polished Copper.	1.6	.03
Polished Copper.	Polished Zinc.	41.6	.78
Platinum.	Polished Zinc.	43.6	.82
Platinum.	Polished Copper.	9.0	.17

Hot air from the flame seems to have a different property from ordinary hot air, because the hot air from a large red-hot soldering bolt, put in the place of the spirit-lamp, had no effect; nor had breathing upon the plates, nor the vapour from hot water any effect.

## XXII. Notices respecting New Books.

*The Theory of Determinants in the Historical Order of its Development.*

—Part I. *Determinants in general*, Leibnitz (1693) to Cayley (1841). By THOMAS MUIR, LL.D. (Macmillan, 1890. Pp. xii + 278.)

DR. MUIR is most favourably known to English mathematicians by his previous work in the region of Determinants, both in original directions and in the way of gathering together and putting into compendious shape the results obtained by his predecessors. By the way, we are glad to see that a “greatly enlarged” edition of his “treatise” is in course of preparation. It was fitting and natural that he should be inspired to write some such work as the present, if only he could secure the leisure for doing so. He himself remarks that whilst writing his “treatise,” “it was repeatedly forced on my attention that the history of the subject had been very imperfectly looked into. Not only, as it appeared, had injustice been done by the attribution of isolated theorems and demonstrations to authors other than the first discoverers, but the labours of the great founders of the theory had been disproportionately represented, and a considerable amount of valuable work had actually been lost sight of altogether.” He accounts for this naturally enough. The outcome of his discovery was the forming of a resolution “to set about collecting the whole literature of the subject, in order that, as a first step on the way to a history, a *biblio-*

*graphy* might be compiled." A first instalment of his labours took the form of a "List of Writings," which occupied 41 pages of the 'Quarterly Journal of Mathematics' (vol. xviii. pp. 110-149): this, as an offprint, was very liberally dispersed and resulted in a supplemental list, of 22 pages, which was printed in the same journal (vol. xxi. pp. 299-320). It is of interest to our readers to note that a by-result was the note on Schweins, entitled "An overlooked discoverer in the Theory of Determinants," which was printed in our Journal [Phil. Mag. vol. xviii. pp. 416-427 (1884)].

Dr. Muir's object is twofold. To provide a work of reference to all that has been written on the subject, and "which should be so indexed that any one engaged in research might easily ascertain exactly what had been done on any particular topic, how it had been done, and what possible developments it foreshadowed." To show clearly to whom every step in advance had been due, furnishing the student with the actual data on which the author's conclusions were based. These two matters have been kept well in view, and the result is a work well worthy of taking rank with the recent historical writings of Todhunter and others on mathematical subjects.

The first 100 pages consider what had been done by mathematicians in the period 1693-1812. The prime contributors are Bézout, Vandermonde, Laplace, Lagrange, Monge, Binet, and Cauchy. Were the contributions of these worthies left out, "there would be exceedingly little left to anyone else, and even that little would be of minor interest." A glance at these names shows that the writings of French mathematicians were the most important in this period. Accompanying the retrospect (pp. 131-2) here given is an admirable Table, which enables the reader to run down any particular result, which marks this epoch, to its discoverer.

The second period analysed in this volume ranges from 1813-1841. The period of "pioneering" extended to 120 years, this to only 30 years or thereabouts. In the longer period we have 20 papers by 13 writers, in the period before us we have 35 papers by 18 writers; and these have representatives from the following nationalities:—English, Italian, and Polish, in addition to the previous French and German. Some of the English contributions saw the light first in our pages: viz. Drinkwater (on Simple Elimination, vol. x. 1831); Sylvester (on Derivation of Coexistence, vol. xvi. 1839); the same (A method of determining by mere inspection the derivatives from two equations of any degree, vol. xvi. 1820).

Dr. Muir has done his work very thoroughly, and has supplied all necessary aid to the student for the easy reading of a vast mass of results; and we heartily wish him equal success in the completion of what will possibly be the more difficult, because more crowded with authors and results, period which yet lies before him. It would have added to the utility of the work if the date and author's name of the memoir analysed could have been furnished at the top of each page.

XXIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 124.]

April 16, 1890.—J. W. Hulke, Esq., F.R.S., Vice-President,  
in the Chair.

THE following communications were read :—

1. "On the disturbed Rocks of North-western Germany." By  
Prof. A. von Könen, For. Corr. G.S.

After referring to the disturbances of Palæozoic times, the author commented upon the Miocene dislocations of the Harz, Rhineland, Westphalia, and Nassau, which have a N.W.-S.E. strike, varying to N.-S. or E.-W., and which are similar to postglacial dislocations.

He briefly discussed the origin of these dislocations, and noticed their peculiarities, and proceeded to consider the relationship of the intruded basalts to the disturbances, supposing that during the process of faulting the earth's crust was pressed downward along synclinal lines and that the basaltic magma escaped upwards through the inverted funnel-shaped synclinal fissure.

Comparison was made between these Tertiary basalts and the products of modern volcanic eruptions, and it does not appear to the author to be unlikely that the cause of the outflow of many of the lavas in the latter was similar to that which produced the extension of the Tertiary basaltic rocks.

2. "On the Origin of the Basins of the Great Lakes of America." By Prof. J. W. Spencer, M.A., Ph.D., F.G.S., State Geologist of Georgia.

From the study of the hydrography of the American lakes, from the discovery of buried channels revealed by borings, from the inspection of the glaciation of the lake-region, the consideration of the late high continental elevation, and the investigation of the deformation of old water-levels, as recorded in the high-level beaches, the explanation of the Origin of the Basins of the Great Lakes becomes possible.

The original Erie valley drained into the extreme western end of Lake Ontario—the Niagara river being modern—by a channel now partly buried beneath drift. Lake Huron, by way of Georgian Bay, was a valley continuous with that of Lake Ontario; but between these two bodies of water, for a distance of about 95 miles, it is now buried beneath hundreds of feet of drift. The old channel of this buried valley entered the Ontario basin about twenty miles east of Toronto. The northern part of Lake-Michigan basin was drained into the Huron basin, as at present; whilst the southern basin of that lake emptied by a now deeply drift-filled channel into the south-western part of Huron. The buried fragments of a great ancient valley and river, and its tributaries, are connected with submerged channels in Lake Huron and Lake Ontario, thus forming the course of



the ancient St. Lawrence (Laurentian) river, with a great tributary from the Erie basin and another across the southern part of the State of Michigan. This valley is of high antiquity, and was formed during times of high continental elevation, culminating not long before the Pleistocene period. The glaciation of the region is nowhere parallel with the escarpments, forming the sides of, or crossing the lakes or less prominent features. During the Pleistocene period, and especially at the close of the episode of the upper Till, the continent was greatly depressed, and extensive beaches and shore-lines were made, which are now preserved at high elevations. With the re-elevation of the continent these old water-levels have been deformed, owing to their unequal elevations. This deformation is sufficient to account for the rocky barriers at the outlets of the lakes. Some of the lakes have been formed, in part, by drift obstructing the old valley. The origin of the basins of the Great Lakes may be stated as the valley (of erosion) of the ancient St. Lawrence River and its tributaries, obstructed during, and particularly at the close of, the Pleistocene period, by terrestrial movements, warping the earth's crust into barriers, thus producing lake-basins, some of which had just been formed in part by drift deposited in the ancient valley.

3. "On Ornithosaurian Remains from the Oxford Clay of Northampton." By R. Lydekker, Esq., B.A., F.G.S.

4. "Notes on a 'Wash-out' found in the Pleasley and Teversall Collieries, Derbyshire and Nottinghamshire." By J. C. B. Hendy, Esq.

Sections were given of the "Wash" showing the thickening of the coal as it approaches the same, and the splitting of the "Wash" itself into two branches. Various measurements were noted, and certain disturbances recorded. In every section examined, the sides of the "Wash" are more or less slickensided, and in some few cases the coal is distorted next to the "Wash;" but the author is of opinion that these are due to lateral pressure and movement subsequent to the denudation of the coal and deposition of the sandstone, and he remarks on the difficulty of reconciling the regularity of the underclay with the theory of the formation of "Washes" by disturbance.

He considers that they are due, in Durham and elsewhere, to currents flowing at a high rate of speed in one direction, carrying away the denuded material, and, as in the case of the Derbyshire "Wash," to a series of inundations, each inrush denuding a certain amount, and on subsiding redepositing part of the material at a higher level, while the remainder was carried away in suspension.

In conclusion, notice was taken of "washes" occurring in other localities.

April 30.—Dr. A. Geikie, F.R.S., President, in the Chair.

The following communications were read:—

1. "On certain Physical Peculiarities exhibited by the so-called 'Raised Beaches' of Hope's Nose and the Thatcher Rock, Devon." By D. Pidgeon, Esq., F.G.S.

The author described the peculiarities of these so-called beaches,

including the absence of stratification, the presence of splinters of rock like that of the overlying limestone cliffs, the scarcity of rounded pebbles, and the great abundance of sharply fractured shells associated with unbroken rock-dwelling shells.

He enumerated the fossils collected from these deposits by Mr. A. R. Hunt, which include *Trophon truncatus* and *Pleurotoma turricula*, and calling attention to the observations of Messrs. Feilden and De Rance, and of Dr. Moss upon the ice-foot of Arctic regions, and the accumulation of material in the trenches found therein concluded that the deposits under consideration were formed at a time when a small bay existed between Hope's Nose and the Thatcher Rock, which has since been destroyed by denudation of the intervening sandstone, in which bay an ice-foot once existed; and further, that the two deposits form the surviving relics of the mingled mass of chips, shells, shell-fragments, Crustacea, &c., which must have filled the trench in the ice-foot demanded in such a position. This would place the time of formation of the deposits at the close of the Glacial period.

2. "The Devonian Rocks of South Devon." By W. A. E. Ussher, Esq., F.G.S., of H.M. Geological Survey.

This paper is the result of work done in continuation of the labours of the late Mr. Champenowne, and refers particularly to the area north of the Dart and east of Dartmoor.

Owing to the complicated stratigraphy of the region, we have to fall back upon such information as can be procured for the general types of Upper, Middle, and Lower Devonian faunas; for though the lithological constituents of these three divisions are broadly distinguishable, there are no definite lithological boundaries between them.

The Lower Devonian is mainly distinguished by the occurrence of sandstone and grit, but the upper beds are shales passing into the Middle Devonian slates.

The Middle Devonian consists of limestones, and shaly limestones upon slates, the latter representing the Calceolen-Schiefer, and containing *Spinifer speciosus*. *Stringocephalus* is found here and there in the middle Devonian Limestones. The upper part of the middle Devonian Limestones (with Lummaton fauna) passes into the *cuboides*-beds of the Upper Devonian. The Upper Devonian contains thin-bedded limestones, often concretionary, with chocolate-red and pale greenish slates and mudstones. These beds correspond to the Goniaticen-Schichten, Kramenzelstein and Knollenkalk of Germany, and to the Cypridinen-Schiefer.

In the Upper and Middle Devonian rocks we find a local prevalence of schalstein and tuffs, breaking up the limestones. The slate and sandstone type of Upper Devonian in North Devon appears to give place southward to a purely slate type, possibly accompanied by overlap of the Culm measures. The author groups the South Devon rocks under the following heads:—

- |                                     |   |  |
|-------------------------------------|---|--|
| Upper.                              | { | 1. Cypridinen-Schiefer.                  |
| 2. Goniatite-limestones and slates. |   |  |
| 3. Massive Limestones.              |   |  |
| Middle.                             | { | 4. Ashprington Volcanic Series.          |
|                                     |   | 4. Middle Devonian Limestones.           |
|                                     |   | 5. Eifelian slates and shaly limestone.  |
| Lower.                              | { | 6. Slates and sandstones, generally red. |
|                                     |   | 7. Slates with hard grits.               |

After discussing the relationship of the Lincombe and Warberry beds and the New Cut Homalonotus-beds, the author notes the discovery of *Pleurodictyum* by Mr. Whidborne in the Railway Cutting at Saltern Cove. He proves the Lower Devonian age of the Cockington beds and their correlation with the Torquay Lower Devonian by the discovery of fossils. He considers it probable, though not certain, that the main mass of Meadfoot beds is below the Lincombe, Warberry, and Cockington sandstones.

The distribution of the Middle Devonian Limestones is described. *Stringocephalus* is found in limestones containing *Rhynchonella cuboides*. The upper parts of the limestone-masses (East Oghwell, Kingskerswell, Barton, Ilsham, &c.) may be Upper Devonian. The massive limestones may terminate abruptly or pass laterally into shales, and the whole mass of the limestones seems to be replaced by slates between the Yealmpton and Totnes areas.

The commencement of the phase of volcanic activity which caused the accumulation of the Ashprington series is shown to coincide with the latest stage of Eifelian deposition, and the Ashprington series may represent continuous or intermittent vulcanicity up to a late stage in the Upper Devonian. North of Stoke Gabriel a mass of limestone seems to have been formed contemporaneously with the volcanic material on the immediate borders of which it occurs. Elsewhere the limestones are interrupted by local influxes of volcanic material. The occurrence of other local developments of Middle and Upper Devonian volcanic rocks is described.

The relationship of the Middle and Upper Devonian deposits varies. In some cases Upper Devonian shales may have been deposited against Middle Devonian limestones; in others there is a continuous development of limestone, the Middle Devonian limestones being succeeded by *Cuboides*-beds, *Goniatite*-limestones, and Knollenkalk. The local variations of these are described, and fossil-lists given. The Knollenkalk is shown to pass under *Entomis*-bearing beds ("Cypridinen-Schiefer"), which are described, though a detailed account of their relationship to the Culm-measures is reserved for a future occasion.

May 14.—Dr. A. Geikie, F.R.S., President, in the Chair.

The following communications were read:—

1. "The so-called Upper-Lias Clay of Down Cliffs." By S. S. Buckman, Esq., F.G.S.

The blue clay of Down Cliff, Dorset, which has been referred to



the Upper Lias, has yielded Ammonites of the genus *Dumortieria* to the author, notably *D. radians*. This blue clay is *below* the Yeovil Sands; but the position of *D. radians* in the Cotteswolds is in the limestone *above* the Cotteswold Sands, which has been placed in the Inferior-Oolite series.

The author, by combining the Down-Cliffs and Chideock-Hill sections, obtains a sequence of beds from the Middle Lias to the top beds of the Inferior Oolite, including the zones of *spinatum*, *commune* and *falciferum*, *jurense*, *opalinum*, *Murchisonae*, *concavum*, and *Parkinsoni*.

The genus *Dumortieria* binds the *opalinum*- and *jurense*-zones together; while at Symondsburry Hill the author has found *Ludwigia Murchisonae* and *Lioceras opalinum* in the same bed, which renders it difficult to draw a line of demarcation between Lias and Oolite at the top of the *opalinum*-zone.

The facts adduced in the paper furnish additional evidence of the unreliability of a grouping which depends upon lithological appearances, and it was because no satisfactory line could be drawn between Lias and Oolite that the author, in a previous paper, supported the continental plan of grouping Upper Lias and part of the Inferior Oolite under the term Toarcian upon palæontological grounds. In the present paper he furnishes further statements in support of this view.

2. "On some new Mammals from the Red and Norwich Craggs." By E. T. Newton, Esq., F.G.S.

3. "On Burrows and Tracks of Invertebrate Animals in Palæozoic Rocks, and other Markings." By Sir J. William Dawson, LL.D., F.R.S., F.G.S.

4. "Contact-alteration at New Galloway." By Miss M. I. Gardiner.

A description is given of an alternating series of grits and shales occurring at the eastern end of the northern edge of the Cairnsmore of Fleet granite-mass. The rocks here are generally more altered than around other parts of the granite margin. The author describes a transverse section about half a mile from the granite, and traces the changes which occur in the rocks when passing towards the granite. She notices (1) the extreme variation in the amount of alteration in different places, but at the same distance from the granite; (2) the entire recrystallization, in one locality, of the shales for about 2 feet and of the grits for about 100 yards from the granite margin; (3) that material seems to have travelled through the rock, so that the most altered grit largely consists of crystals, here of one mineral, there of another, as though material had been conveyed from one part of the rock to another to form small nests; (4) the apparent order of succession of the minerals, garnets rarely containing anything but colouring-matter and quartz, chialite containing garnets, and bands of mica sweeping round both; (5) evidence which appears to the author to indicate dynamic metamorphism, as furnished by the sigmoidal folding of knots in the



shales and by the appearance of phenomena suggesting thrust-planes.

The author considers, however, that the main metamorphism is due to the intrusion of the granite, and that the variation in the amount of alteration at the same distances, the mode of alteration of the grits, and the transference of material might be accounted for by the passage of highly heated water. Other evidence points to the changes having been brought about slowly.

Among the minerals produced in the contact-zone are secondary quartz, felspar, brown and white micas, chialstolite, sillimanite, and garnet, their modes of occurrence being described in detail, in rocks of various degrees of alteration up to those in an abnormally high state of alteration near the granite, which resemble rocks of doubtful origin in other localities.

May 21.—Dr. A. Geikie, F.R.S., President, in the Chair.

The following communications were read:—

1. "On some Devonian and Silurian Ostracoda from North America, France, and the Bosphorus." By Prof. T. Rupert Jones, F.R.S., F.G.S.

2. "On the Age, Composition, and Structure of the Plateau-gravels of East Berkshire and West Surrey." By the Rev. A. Irving, B.A., D.Sc., F.G.S.

The author refers to the view propounded by him somewhat tentatively seven years ago, and since confirmed by the researches of Prof. Prestwich, as to the Preglacial age (probably Pliocene) of these deposits, pointing out the inconclusive nature of the evidence of Glacial age furnished by the presence in them of angular "sarsens." He regards the absence of Miocene marine deposits in this part of North-western Europe as supporting the published view of Zittel and other continental writers that the Miocene period was, in South-eastern England, one of elevation and subaerial waste and degradation of the Weald to the south, and of East-Mercian England to the north-west, this period of waste of the Cretaceous rocks having furnished much of the materials which, in Pliocene times, were carried across a sloping plateau by fluvial agencies.

The composition and structure of the plateau-gravels are next described, reference being made to previous writings of Prof. Rupert Jones and to the recent papers of Prof. Prestwich. Reference is also made to the explanation suggested by the author seven years ago of the anomalous contrast presented by the lithological conditions of the flint-pebbles and the subangular flint-fragments which are intermingled in these gravels. The great masses of unstratified and unrolled flint-débris on the Aldershot Hills are compared with the Preglacial "Schotte" of the lower Alpine valleys. The plateau-gravels are described as occupying altitudes ranging from nearly 600' (O.D.) at Aldershot and on the north side of Netley Heath, down to 280' (O.D.) at Bearwood and Farley Hill. A list of 22 localities (with altitudes) is given where actual sections of the plateau-gravels can be studied.

Evidence of glacial action at lower levels (210' to 240', O.D.) is then given, sections being described at Nine-mile Ride (Old Windsor Forest), Wokingham, and Sunninghill, and apparent evidence of glaciation at Bracknell, Warfield, and Finchampstead. Photographs of some of these sections are given, and the levels of the plateau-gravels and the glaciated sections correlated by a sectional diagram.

The author concludes, from the evidence given in the paper, that:—

1. The Plateau-gravels are of fluvial origin, their materials having been transported from the Weald-region to the south.

2. They mark roughly the ancient lines of Pliocene drainage of an old elevated Tertiary region, the present valley-system having been mainly determined by their absence.

3. That the modern Lower Thames Valley was initiated in Pliocene times, the main line of drainage having been somewhat further north than at present.

4. That attention to altitudes reveals the fact that the present valley-system was outlined and the major part of it actually excavated in an interval that intervened between the age of the Plateau-gravels and the Glacial Epoch.

5. That the deposition of the Plateau-gravels probably covers most of the geologic time represented by the Pliocene.

A note is added on the probable progressive elevation of the Weald from west to east.

3. "Further Note on the Existence of Triassic Rocks in the English Channel off the Coast of Cornwall." By R. N. Worth, Esq., F.G.S.

A specimen of Triassic conglomerate trawled seven miles south of the Deadman headland, and several miles east of the previously recorded Lizard outlier is described, and reasons given for its occurrence *in situ*. It contains pebbles of slate, grits, vein-quartz, quartz-felsite, and andesitic rock.

4. "On a new Species of *Coccodus* (*C. Lindstromi*, Davis)." By J. W. Davis, Esq., F.G.S.

June 4.—Dr. A. Geikie, F.R.S., President, in the Chair.

The PRESIDENT referred to the sad loss which the Society had sustained through the death of Mr. Dallas, and read the following resolution, which had been passed by the Council and ordered to be entered upon its Minutes:—

"The Council desires to record on its Minutes an expression of its deep regret at the death of the Assistant-Secretary, Mr. Dallas, which took place on the 29th ultimo, and of its sense of the loss inflicted on the Council and Society by the removal of one who, for the long period of twenty-two years, had done them invaluable service, and who, by his courtesy, kindness, and helpfulness had endeared himself as a personal friend to the Fellows."

The following communications were read :—

1. "As to certain 'Changes of Level' along the Shores on the Western side of Italy." By R. Mackley Browne, Esq., F.G.S.

After noticing the prevailing opinion that such changes as he treats of were caused by earth-movements of elevation and depression, the author suggests that the altered levels were due to altered conditions of the Mediterranean. He brings forward objections to the prevailing theory, and remarks on the possibility of periodical oscillating alterations in the tidal depth of the ocean.

After noticing the special characteristics of the Mediterranean, he infers that submergence and emergence on the Bay of Baiæ would follow equivalent alteration in the level of the Atlantic waters, such as would be probably developed by changed conditions of astronomical forces ; and after discussing the possible dates and periods of the changes at Pozzuoli, makes the suggestion that within a period of two thousand years alterations may have taken place in the astronomical combinations, out of which a change in the surface-level of the oceans generally may have become developed, and wherefrom consequently a synchronous change in the Mediterranean would also occur, and observes that the amount of actual tidal effects has never been ascertained.

2. "North-Italian Bryozoa." By A. W. Waters, Esq., F.G.S.

3. "Notes on the Discovery, Mode of Occurrence, and Distribution of the Nickel-Iron Alloy 'Awaruite' and the Rocks of the District on the West Coast of the South Island of New Zealand in which it is found." By Professor G. H. F. Ulrich, F.G.S.

In an introduction the author describes the original discovery, determination, and naming of the mineral in 1885 by Mr. W. Skey, and clears up a misunderstanding by which he himself had been credited with the discovery ; he furthermore gives a historical sketch of the further investigations and publications referring to the mineral.

The geology of the Awaruite-bearing district is described. The rocks consist of peridotites and serpentines, breaking through metamorphic schists with occasional massive intrusions of acid rock. The petrographical characters of the peridotites of the hill-complex, including the Olivine and Red-Hill Ranges, and serpentines are considered in detail, and the mode of occurrence of the Awaruite in them and in the sands derived from their denudation is discussed. The author submits a sketch-map of the localities where the mineral has been discovered in sand, including not only Gorge River, but also Silver Creek, Red Hill, and other localities, and quotes Mr. Paulin's belief that it occurs diffused through the whole extent of peridotite and serpentine rocks, and inferentially in the drifts derived therefrom.



XXIV. *Intelligence and Miscellaneous Articles.*

## NOTE ON DIAMAGNETISM AND CARNOT'S PRINCIPLE.

BY OLIVER J. LODGE.

IN the May 1889 number of the Philosophical Magazine Mr. J. Parker states a series of propositions which are equivalent to the invention of an ingenious perpetual-motion machine, consisting of a wheel with a diamagnetic rim spinning near a permanent magnet, so that one side of the wheel approaches and the other side recedes from a strong magnetic field. So long as the wheel spins slowly, nothing happens; but as soon as it spins so fast that the diamagnetism excited lags behind the magnetic force producing it, the side receding from the intense region will be repelled more powerfully than the side approaching from the weak region, and hence there will be perpetual motion.

There are several ways of getting over this, and one of these Mr. Parker suggests, viz. that diamagnetism may be a thing excited instantaneously; though naturally he is not much impressed with the likelihood of his suggestion. He rather takes refuge in an appeal against the second law of thermodynamics, as possibly in-

applicable to magnetic substances, cycle  $\int \frac{dQ}{T}$  being perhaps negative for paramagnetic, and positive for diamagnetic, bodies.

Returning to the subject in the last number of the Philosophical Magazine (July 1890), he emerges from this position to make the still wilder suggestion that diamagnetism does not really exist; that Faraday was deceived throughout his long and acute investigation by the obviously disturbing and constantly guarded-against paramagnetism of the air!

Would it not, however, be possible that the spinning of a bismuth wheel should exert a demagnetizing effect on a magnet, while the spinning of an iron wheel should exert a strengthening effect? When one comes to think of it, the ordinary act of magnetization consists in bringing on a magnet in a weak position and drawing it off in a strong; moreover the hypothetical induced molecular currents of Weber, which would certainly lag behind their cause by reason of self-induction, would get themselves strengthened and weakened as the hypothesis requires. In such case the energy of spin would be obtained at the expense of the magnetic field.

The diamagnetism of known non-conductors is so disappointingly feeble, and the rapidity of its excitation so exceedingly great (judging from the magneto-optic effect), that it is perhaps not worth while actually to try if a disk of heavy glass delicately suspended and rapidly spun between the poles of a strong magnet *in vacuo* could maintain its motion.

University College, Liverpool,  
July 6, 1890.

*Phil. Mag.* S. 5. Vol. 30. No. 183. August 1890. P



## A METHOD OF DETECTING CHEMICAL UNION OF METALS.

BY DR. G. GORE, F.R.S.

It is well known that evolution of heat during the mixing of two substances is a sign of chemical union; that considerable heat is evolved during the melting together of certain metals, for instance zinc and platinum; and M. J. Regnault has shown that whilst zinc, during its amalgamation by mercury, absorbs heat and becomes more electropositive, cadmium by amalgamation evolves heat and becomes less electropositive (*Comptes Rendus Acad. Sci.* June 10, 1878; *Chemical News*, vol. xxxviii. p. 33).

Having already found in a large number of instances that the chemical union of two soluble substances, such as halogens, acids, salts, &c., might be detected by the depression of voltaic energy which occurs when the two dissolved substances are in the proportions of their ordinary chemical equivalents (see *Proc. Roy. Soc.* vol. xlv. p. 265; "Examples of Solution-compounds," *Proc. Birm. Phil. Soc.* vol. vii. p. 33; *Chemical News*, 1890, vol. lxi. p. 172), I have adopted a similar method in this case, and have made a series of experiments to ascertain the relative amounts of voltaic energy in a one-per-cent. aqueous solution of common salt, of a series of amalgams composed of different proportions of cadmium and mercury, and observed whether there was a distinct depression of that energy indicating chemical union, when the particular amalgam composed of equivalent weights of the two metals was employed.

As I had previously found that the amalgam changed in electromotive force spontaneously, in order to balance this influence, I employed, instead of a voltaic couple composed of platinum and one bar of a series of bars of different composition, a couple composed of a bar of fixed composition formed of the two metals in the proportions of their equivalent weights, and one bar of a series of bars of different composition. The two bars in each experiment were connected with an ordinary torsion-galvanometer of 50 ohms resistance, and the amount of permanent deflexion of the needles after about half a minute was recorded. This method was found sufficiently sensitive for the purpose. The composition of the bars of varied composition is shown below by the chemical formulæ.

After some preliminary experiments, the results of which agreed with those given, the following series was made:—

Voltaic couple.		Deflexion.
Cd Hg with Cd		+5
" "	Cd <sub>17</sub> Hg <sub>10</sub>	3.3
" "	Cd <sub>15</sub> Hg <sub>10</sub>	3
" "	Cd <sub>13</sub> Hg <sub>10</sub>	1
" "	Cd <sub>12</sub> Hg <sub>10</sub>	1
" "	Cd <sub>10</sub> Hg <sub>10</sub>	0
" "	Cd <sub>10</sub> Hg <sub>12</sub>	+4
" "	Cd <sub>10</sub> Hg <sub>13</sub>	-2
" "	Cd <sub>10</sub> Hg <sub>15</sub>	-9
" "	Cd <sub>10</sub> Hg <sub>17</sub>	-4
" "	Hg	-5 to 6

As the amounts of deflexion varied with different parts of the surface of the same bar, the surfaces of the bars were scraped quite clean and the experiments with the amalgams  $\text{Cd}_{12}\text{Hg}_{10}$ ,  $\text{Cd}_{10}\text{Hg}_{10}$ , and  $\text{Cd}_{10}\text{Hg}_{12}$  repeated; the same numbers as given above were obtained.

The numbers obtained in each case show a distinct depression of strength of current with the amalgam composed of equivalent weights of the two metals, similar to that obtained with halogens, acids, and salts, and indicate that the two metals chemically unite together in the proportions of their ordinary chemical equivalents. The method may therefore probably be employed for the purpose of detecting the chemical union of metals.

#### ON THE SPECTRA OF THE ALKALIES.

BY PROF. H. KAYSER AND PROF. C. RUNGE.

The investigation of the spectra of the alkalies has led us to results which we present in the following short abstract.

The spectra of the alkalies are formed in an entirely analogous manner, which is especially manifest if, instead of the wave-lengths, we consider the reciprocals—that is, the numbers of vibrations. Each spectra is seen to be made up of several series of lines, each of which may be represented with great accuracy by the formula

$$\frac{1}{\lambda} = A - \frac{B}{n^2} - \frac{C}{n^4};$$

where  $\lambda$  is the wave-length, A, B, and C are three constants, and  $n$  stands for the series of whole numbers from  $n=3$  upwards. For  $n=2$  the formulæ give in all cases negative—that is, impossible numbers of vibrations;  $n=3$  represents the fundamental vibrations.

The lines of the various series of each element behave very differently as regards visibility, widening out with increase of vapour-density. In each element we find one chief series which contains the strongest lines, those which appear most easily, and those which are most easily reversible; it extends in all cases from the red end of the spectrum to the extreme ultra-violet. The members of the principal series, with the exception of lithium, are with all alkalies pairs, whose distance is less as the wave-length increases; we have found that the difference of the numbers of vibrations for the two lines of each pair is inversely proportional to the number of this pair, that is of the value  $n$ , which, when inserted in the formula, gives the pair.

Besides the chief series, all alkalies have accessory series which essentially appear in the visible part of the spectrum. In lithium there are two secondary series, and in sodium four, each two of

which, however, are congruent. Potassium is similar, while rubidium and cæsium again have only two secondary series, which are congruent. The congruence, which in the formula of the series expresses itself by identity of the second and third constants for the two series, has the effect that two such congruent series appear as a series of pairs, but in which the difference of vibration of both lines of the pairs is constant for each series, in opposition to the deportment of the chief series.

The result comes out that this difference of vibration of the pairs of the secondary series is identical for each element with the difference of vibration of the first pair of the principal series  $n=3$ . It has further come out that the magnitude of this difference of vibration is connected with the atomic weight; *the difference of vibration is very nearly proportional to the square of the atomic weight*. With lithium no pairs are visible; this law extended to lithium enables us to calculate from its atomic weight that the difference of possible pairs would be so small that we should probably see the lines double.

If we compare the spectra of the alkalis with each other, it is most distinctly evident that both the chief series as well as the secondary series extend towards the red side of the spectrum. This is of course just as apparent in the constants A, B, C, which change, in a manner obviously expressed by a law, from one element to another. It is worthy of mention that the constant B changes very little, and is the same, not only for the alkalis, but, as seems to be the case, for other elements also.

We consider it premature to try to discover the law according to which the constants vary from one element to another before we have investigated other elements. We hope before long to lay before the Academy our results in reference to the alkaline earths.

As a further result of our investigations we must mention that, in contradiction to the statements of Lockyer, who considered that he had found the lines of all pair alkalis among those of Fraunhofer, only sodium is represented in the Sun, and probably also only its chief series.—*Sitzungsberichte der Berliner Akademie*, June 5, 1890.

#### ON THE ELECTRICAL SERIES FOR FRICTIONAL ELECTRICITY.

BY J. SCHIFF.

The author gives the following series for frictional electricity:—hair skins, smooth glass, wool, ground glass, silk, resins, collodium, steatite.—*Beiblätter der Physik*, vol. xiv. p. 525.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

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SEPTEMBER 1890.

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XXV. *Contributions to the Molecular Theory of Induced Magnetism.* By J. A. EWING, F.R.S., *Professor of Engineering in University College, Dundee* \*.

AS the facts of induced magnetism become better known, increasing interest attaches to molecular theories and increasing difficulty attends the theories that are current. Weber's fundamental conception that the molecules of iron or nickel or cobalt are always magnets, and that the process of magnetizing consists in turning them from many directions towards one direction, has been strongly confirmed by the now well-established fact that there is a true saturation value, a finite limit to the intensity of magnetism, which may be reached or very closely approached by using a strong magnetic force†. Without going further back, to enquire (with Ampère) how the molecules come to be magnets, we may take this conception as the natural starting-point of a theory. But when we go on to examine the conditions of constraint on the part of the rotatable molecules which have been suggested to make the theory square with what is known about permeability, about residual magnetism and other effects of magnetic hysteresis, about the effects of stress, of temperature, of mechanical vibration, and so forth, we find a mass of arbitrary assumptions which still leave the subject

\* Communicated by the Author, having been read before the Royal Society, June 19, 1890.

† Ewing and Low, *Phil. Trans.*, 1889, A, p. 221; see also H. E. J. G. du Bois, *Phil. Mag.* April 1890.



bristling with difficulties. Many of the phenomena suggest, for instance, the idea that there is a quasi-frictional resistance which opposes the turning of the molecular magnets; this notion lends itself well to account for the most obvious effects of magnetic hysteresis and the reduction of hysteresis by vibration. On the other hand, it conflicts with the fact that even the feeblest magnetic force induces some magnetism. My object in this paper is to refer to another (and not at all arbitrary) condition of constraint which not only suffices to explain all the phenomena of hysteresis without any notion of friction, but seems to have in it abundant capability to account for every complexity of magnetic quality.

In describing Weber's theory, Maxwell points out that, if each molecular magnet were perfectly free to turn, the slightest magnetic force would suffice to bring the molecules into complete parallelism, and thus to produce magnetic saturation. He continues:—"This, however, is not the case. The molecules do not turn with their axes parallel to the force, and this is either because each molecule is acted on by a force tending to preserve it in its original direction, or because an equivalent effect is produced by the mutual action of the entire system of molecules. Weber adopts the former of these suppositions as the simplest,"\*

Weber supposes a directing force to act in the original direction of the molecule's axis which continues to act as a restoring force in that direction after the molecule is disturbed. This assumed constraint is quite arbitrary; moreover, if it were the only constraint, there would be no residual magnetism when the deflecting force was withdrawn. Accordingly, Maxwell modifies Weber's theory by introducing the further assumption that when the angle of deflexion exceeds a certain limit the molecule begins to take permanent set. The development of this, however, does not agree well with the facts.

The alternative which is offered in the sentence I have quoted from Maxwell was not followed up by him, and seems to have been very generally overlooked, notwithstanding its obvious freedom from arbitrary assumption. Several writers, notably Wiedemann† and Hughes‡, have recognized the inter-molecular magnetic forces by suggesting that the molecules, when unacted on by any magnetizing force from outside, may form closed rings, or chains, "so as to satisfy their

\* Maxwell, *Electricity and Magnetism*, vol. ii. § 443.

† Wiedemann, *Galvanismus*, 2nd ed. vol. ii. (1), p. 373.

‡ Hughes, *Roy. Soc. Proc.* May 10, 1883.

mutual attraction by the shortest path.”\* But Wiedemann expressly postulates a frictional resistance to rotation, which will prevent this arrangement from being more than approximately attained, and which may be more or less overcome by vibration†.

I lately commented on the fact that soft iron and other magnetic metals (notably nickel under particular conditions of strain‡) show a remarkably close approach to instability at certain stages in the magnetizing or demagnetizing process§. When the magnetic force reaches a particular value, the rate of change of magnetism with respect to change of force may become enormous. Referring to this in a paper which has just been published||, Mr. A. E. Kennelly has reverted to the idea of chains of magnetic molecules held together by the inter-molecular magnetic forces, and contends that when such a chain is ruptured by applying a sufficiently strong external magnetic force it will fall to pieces throughout, and the molecular magnets which compose the chain will take their alignment suddenly. He accordingly sketches what he calls a “chain-theory” of magnetization and an adaptation of the theory of Hughes, in which, however, he postulates an elastic resistance to the rotation of the molecules in addition to the constraint afforded by their mutual magnetic forces. Mr. Kennelly’s remarks are highly interesting and suggestive; but I do not think (for reasons which will appear immediately) that the notion of closed magnetic chains can be maintained as a general account of the molecular structure of unmagnetized iron.

I have experimented on the subject by making a model molecular structure consisting of a large number of short steel bar-magnets, strongly magnetized, each pivoted like a compass-needle upon a sharp vertical centre and balanced to swing horizontally. We cannot readily imitate in a model the two degrees of rotational freedom possessed by the axes of actual molecular magnets, but a group of magnets swinging in one plane gives a sufficiently good general idea of the nature of the equilibrium which is brought about by inter-molecular forces, and the manner in which that equilibrium is disturbed

\* Hughes, *loc. cit.*

† Wiedemann, *Phil. Mag.* July 1886, p. 52; *Elektricität*, vol. iii. §§ 784–785.

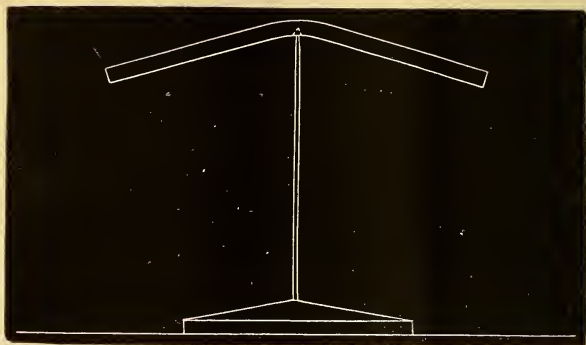
‡ See a paper by H. Nagaoka, *Journal of the Science College of the University of Tokio*, vol. ii. (1888) p. 304.

§ *Journal of the Institution of Electrical Engineers*, No. 84 (1890) pp. 38–40.

|| *The Electrician*, June 7 and 13, 1890.

when an external force is applied. The model is very easily made. Each magnet is a piece of steel wire about one tenth of an inch in diameter and two inches long (fig. 1), bent in

Fig. 1.



the middle to bring the centre of gravity below the point of support. The hole, or rather recess, for the pivot is made by a centre punch: the pivot itself is a sewing-needle fixed upright in a small base-plate which is punched out of a sheet of lead. The bars swing with but little friction, and their pole-strength is sufficient to make the mutual forces quite mask the earth's directive force when they are set moderately near one another. The group is arranged on a board on which lines are drawn to facilitate regularity in grouping when that is wanted, and the board slips into a large frame or open-sided flat box wound round the top, bottom, and two sides, with a coil through which an adjustable current may be passed to expose the group to a nearly homogeneous external magnetic force. The coil is wound in a single very open layer, through which a sufficiently good view of the group inside is obtained\*. A liquid rheostat with a sliding terminal is used to secure continuity in varying the magnetic force. It is scarcely necessary to add that the magnetic force which is applied to the group is too weak to have any material effect on the magnetism of individual bars. It alters their alignment only, just as a magnetic force alters the alignment of Weber's molecular magnets.

When a number of these magnets are grouped either in a regular pattern or at random, and are left after disturbance

\* In showing the experiments, the board with the magnets on it may, of course, be placed in clear view above the coil; the coil is then made larger, or a stronger current is used.

to come to rest free from external magnetic force, they of course assume a form which has no resultant magnetic moment, provided the number be sufficiently great; but it is apparent that they do not arrange themselves in closed chains. Any such configuration would in general be unstable. Many stable configurations admit of being formed, and if the magnets are again disturbed and left to settle, the chances are much against any one configuration immediately repeating itself. One general characteristic of these configurations is that they contain *lines* consisting of two, three, or more magnets, each member of a line being strongly controlled by its next neighbours in that line, but little influenced by neighbours which lie off the line on either side. Thus, if there are two magnets simply, they form (as might be anticipated) a highly stable pair, thus:—

→ →

With three magnets, two form a line along one side of the triangle joining the fixed centres, and the third lies parallel, or nearly so, facing oppositely. Four magnets will usually form two lines with directions which lie nearly along two sides of the quadrilateral; but diagonally opposite magnets may pair, leaving the others unattached. Suppose them set at the corners of a rectangle with unequal sides, they may lie in any of these forms



if the inequality in distance be not too great. All these configurations are stable, and the condition of least energy, while making the first of them the most probable, does not prevent the occasional formation of the others. In a long line, the same condition leads in general to this formation:—

→ → → → → → → →

but it is by no means uncommon to find a line broken into two or more sections, thus:—

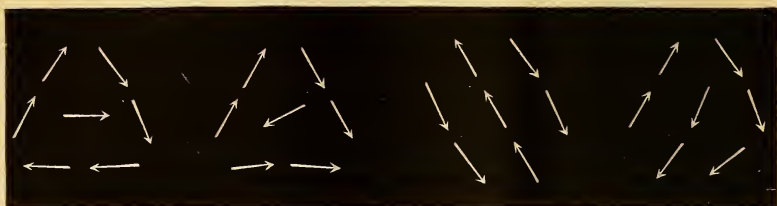
→ → → → ↗ ← ← ←

Seven magnets grouped so that the centres of six form a



regular hexagon, with one in the middle, have a great variety of possible stable configurations, of which these are examples:—

Fig. 2.



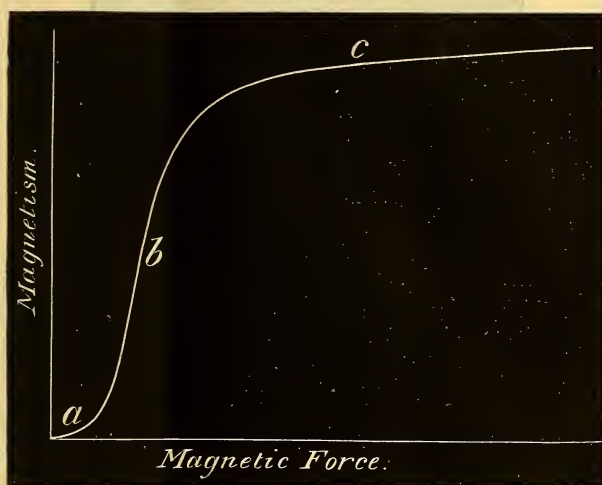
Experimental study of the forms which may be assumed by groups, and of the vibrations which may be transmitted through groups, is interesting, but to pursue it would be beside my present purpose. In all cases, the configuration assumed by a group is such that there is stability for small displacements, but different positions of the group may be stable in different degrees, and if members of the group be turned through a sufficiently great angle, they become unstable, and fall into a new position of stability, bringing about a partial reconstruction of the lines that characterize the group. Special interest attaches to square patterns, from the fact that iron and nickel (probably cobalt also) crystallize in the cubic system. In a square pattern of many members, we find, in general, lines running parallel with all sides of the square when the group settles without directive force after a disturbance.

Let the group, or collection of groups, be subjected to an external magnetic force,  $\mathfrak{H}$ , gradually increasing from zero. The first effect is to produce a *stable* deflexion of all members except those which lie exactly along or opposite to the direction of  $\mathfrak{H}$ . This results in giving a small resultant moment to the group (assuming that there was none to begin with), which increases at a uniform or very nearly uniform rate as  $\mathfrak{H}$  increases. This corresponds to the first stage in the magnetization of iron or other magnetic metal (*a*, fig. 3). The initial susceptibility is a small finite quantity, and it is sensibly uniform for very small values of  $\mathfrak{H}$ .

Suppose that, without going beyond this stage, we remove  $\mathfrak{H}$ ; the molecular magnets, not having been deflected beyond the limit of stability, simply return to their initial places, and there is no residual magnetism. This, again, agrees with the fact that no residual magnetism is produced by very feeble magnetizing forces. Up to this point there has been no magnetic hysteresis. But let the value of  $\mathfrak{H}$  be increased until any

part of the group becomes unstable, and hysteresis immediately comes into play. At the same time, there begins to be a marked augmentation of susceptibility—that is to say, a marked increase in the rate at which resultant moment is acquired. It is not difficult to arrange groups in which the state of instability is reached with one and the same value of  $\mathfrak{H}$  throughout the group. But, in general, we shall have different elementary magnets, or different lines of them, reaching instability with different values of  $\mathfrak{H}$ . The range of  $\mathfrak{H}$ , however, which suffices to bring about instability throughout the whole, or nearly the whole, of the members in most groups is not large; we, therefore, find in the action of the model a close analogy to the second stage (*b*, fig. 3) of the process of magnetization, in which the magnetism rises more or less suddenly, as well as to the first stage (*a*).

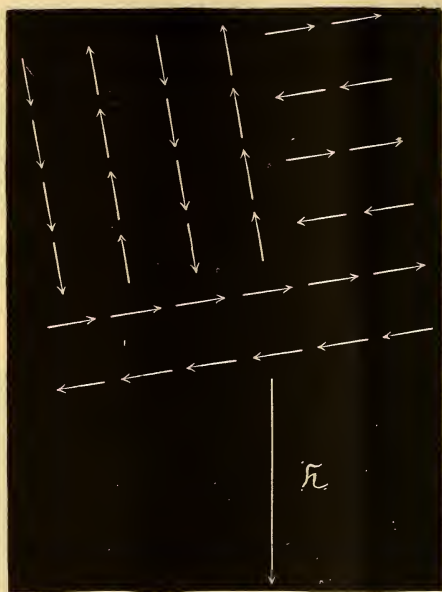
Fig. 3.



During the second stage (*b*), the magnetic elements fall for the most part into lines which agree more or less exactly with the direction of  $\mathfrak{H}$ . If, at the end of this stage, we remove  $\mathfrak{H}$ , we find that a very large proportion of the moment which the group has acquired remains; in other words, there is a great deal of residual magnetism. To take an instance, suppose we have a group lying initially as in fig. 4, and apply a magnetic force,  $\mathfrak{H}$ , in the direction sketched, the first stage (*a*) deflects all the molecular magnets slightly, without making any of them become unstable; the second

stage (b) brings the molecules into the general direction shown in fig. 5, or rather that is the direction they assume

Fig. 4.

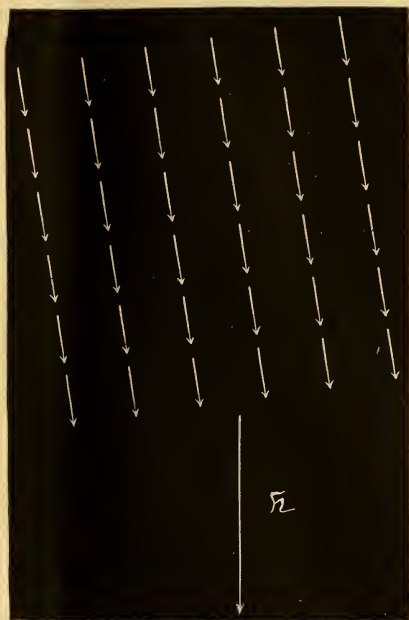


when  $\mathfrak{H}$  is removed, and the residual magnetism contributed by the group is then the sum of their moments resolved along  $\mathfrak{H}$ . When  $\mathfrak{H}$  is acting, the components along  $\mathfrak{H}$  are slightly greater, for the molecules are then (stably) deflected through a small angle towards the line of  $\mathfrak{H}$ .

Let  $\mathfrak{H}$  be further increased—we now have the third stage (c) (fig. 3), which consists in the closer approach to saturation that is caused by the molecules being more nearly pulled into exact line with  $\mathfrak{H}$  (fig. 6). Whether there will be instability during the deflexion of them from the lines of fig. 5 will depend on the closeness of the poles, and on the inclination of the lines of fig. 5 to the direction of  $\mathfrak{H}$  (see below). In some groups saturation will be complete with a finite value of  $\mathfrak{H}$ ; in others, it will only be closely approximated to. In magnetizing any actual specimen of iron, we have, of course, to deal with a multitude of groups the lines to which lie at very various inclinations to  $\mathfrak{H}$ . If we remove the force  $\mathfrak{H}$  at a point in stage c, we find very little, if any, more residual magnetism than was found at the end of stage b. The

ratio of residual to induced magnetism is a maximum about the end of stage *b*, and diminishes as stage *c* proceeds. This, again, agrees completely with the observed facts.

Fig. 5.



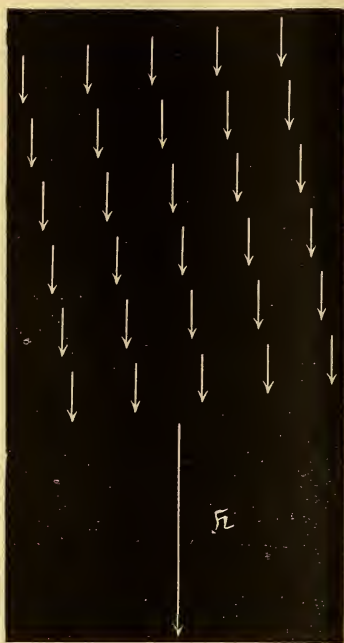
There is *some* hysteresis during the removal (whether complete or partial) and reapplication of magnetic force, because (provided we have enough groups to deal with) there will be some lines of elements which pass to and fro through a condition of instability during the removal and reapplication of the force. For certain inclinations of the line, the movements are not reversible.

Suppose, next, that having applied and removed a strong force  $\mathfrak{H}$ , leaving strong residual polarity, we begin slowly to reverse  $\mathfrak{H}$ . At first, the effects are slight; presently, however, instability begins, and, as the force is increased within a narrow range, we find the molecules all upset. This is followed by a stage of nearly elastic deflexion as saturation is approached. Thus, the well-known general characteristics of cyclic processes are all reproduced in the model (see fig. 8 below).



Again, a small repeated cyclic change of  $\mathfrak{H}$  superposed upon a constant value of  $\mathfrak{H}$  produces small changes of aggregate polarity, which are reversible if the change of  $\mathfrak{H}$  is very

Fig. 6.



small. This, as Lord Rayleigh has shown\*, is what happens in a magnetic metal, and the susceptibility with respect to small cyclic changes is small in the model, just as it is in the actual solid.

The chief facts of permeability and retentiveness, and hysteresis generally, are therefore at once explicable by supposing that Weber's molecular magnets are constrained by no other forces than those due to their own mutual magnetic attractions and repulsions. No arbitrary constraining forces are required. In the model the centres of rotation are fixed; in regard to the actual solid we may make an equivalent supposition, namely, that the distances between the molecular centres do not change (except in so far as they may be changed by strain).

Hysteresis, then, is not the result of any quasi-frictional

\* Phil. Mag. March 1887.

resistance to molecular rotations; it occurs whenever a molecule turns from one stable position of rest to another through an unstable condition. When it is forced to return, it again passes through a condition of instability. This process, considered mechanically, is not reversible; the forces are different for the same displacement, going and coming, and there is dissipation of energy. In the model the energy thus expended sets the little bars swinging, and their swings take some time to subside. In the actual solid the energy which the molecular magnet loses as it swings through unstable positions generates eddy currents in surrounding matter. Let the magnets of the model be furnished with air-vanes to damp their swings, and the correspondence is complete.

A regular group of elementary magnets, especially when furnished with air-vanes, gives a good illustration of what has been called magnetic viscosity. When the imposed force  $\mathcal{H}$  reaches a critical value one of the outer members of the group becomes unstable, and swings slowly round; its next neighbours, finding their stability weakened, follow suit, and the disturbance spreads through the group in a way eminently suggestive of those phenomena of time-lag in magnetization which I have described in a former paper\*.

The model shows equally well other magnetic phenomena which presumably depend on the inertia of the molecules, such as the fact that a given force causes more magnetic induction when suddenly applied than when gradually applied, and leaves less residual magnetism when suddenly removed than when gradually removed.

The well-known effects of mechanical vibration in augmenting magnetic susceptibility and reducing retentiveness are readily explicable when we consider that vibration will cause periodic changes in the distances between molecular centres. This has not only a direct influence in making the molecular magnets respond more easily to changes of magnetic force by reducing their stability during the intervals when they recede from each other, but tends indirectly towards the same result by setting them swinging.

The effects of temperature which are common to the three magnetic metals may be stated thus:—Let any moderate magnetizing force be applied, not strong enough to produce anything like an approach to magnetic saturation, and let the temperature be raised. Then the permeability *increases* until the temperature reaches a certain (high) critical value, at which, almost suddenly, there is an almost complete disappearance of magnetic equality. As regards the first effect,

\* Roy. Soc. Proc., June 1889.

it is clear that an increase of permeability is to be expected from the theory; expansion with rise of temperature involves a separation of the molecular centres, and therefore a reduction of stability. As regards the almost sudden loss of susceptibility which occurs at a high temperature, it may do no harm to hazard a rather wild conjecture. We may suppose the molecular magnets to be swinging more or less, the violence of the swings increasing as the temperature rises, until finally it develops into *rotation*. Should this happen, all trace of polarity would of course disappear. The conjecture that the molecular magnets oscillate more and more as the temperature rises, is at least supported by the fact (carefully investigated by Hopkinson \* in iron and nickel; data for cobalt also have lately been supplied by du Bois †) that under *strong* magnetic forces rise of temperature reduces magnetism; for with strong forces the molecular magnets are already ranged so that their mean direction is nearly parallel to  $\mathfrak{H}$ : hence the earlier effect of heat (to diminish stability and facilitate alignment) does not tell, and the increased swinging simply results in reducing the mean value for each molecule of its moment resolved parallel to the magnetizing force.

Before referring to effects of stress we may consider shortly the stability of a pair or line of magnets, treating each as a pair of poles subject to the law of inverse squares. Take first a single pair of equal magnets with centres at C and C' (fig. 7). The poles P P' would lie in the line CC', but for the imposed force  $\mathfrak{H}$ , which produces a deflexion CC'P' or C'CP =  $\theta$ .

Let  $\alpha$  be the angle which  $\mathfrak{H}$  makes with the line of centres,  $m$  the pole-strength, and  $r$  the half length of the magnetic axis of each magnet. The deflecting moment is

$$2\mathfrak{H}mr \sin (\alpha - \theta),$$

and the restoring moment is

$$\frac{m^2 \overline{CN}}{\overline{PP'}^2},$$

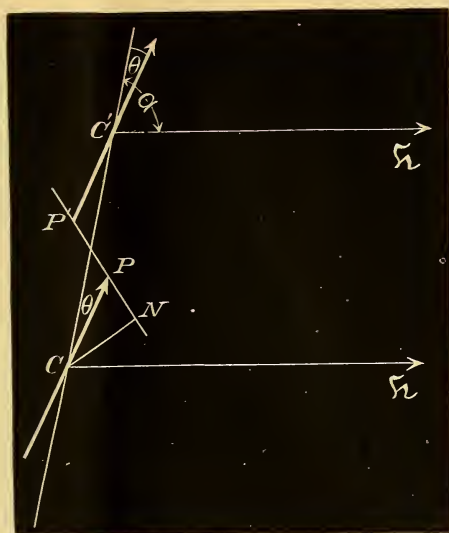
CN being drawn normal to PP'. The restoring moment at first increases with  $\theta$ , but passes a maximum at a value of  $\theta$  which depends on the relation of  $r$  to the distance between the centres. The condition of equilibrium is

$$2\mathfrak{H}mr \sin (\alpha - \theta) = \frac{m^2 \overline{CN}}{\overline{PP'}^2};$$

\* Phil. Trans. 1889, A, p. 443; Roy. Soc. Proc., June 1888.

† Phil. Mag. April 1890.

Fig. 7.



and as  $\mathfrak{H}$  and  $\theta$  are increased the equilibrium becomes neutral, that is to say, the condition of instability is reached, when

$$\frac{d}{d\theta} \{2\mathfrak{H}mr \sin(\alpha - \theta)\} = \frac{d}{d\theta} \frac{m^2 \overline{CN}}{\overline{PP}^2}.$$

These two equations serve to determine the value of  $\mathfrak{H}$  and of  $\theta$  at which instability occurs. If we have to deal with a long line of magnets instead of a single pair, we have to write  $2m^2$  instead of  $m^2$  in the restoring moment.

A considerable amount of stable deflexion is possible when the distance between the poles is not small compared with  $r$ . When the direction of  $\mathfrak{H}$  is not much inclined to  $CC'$  (that is, when  $\alpha$  has a value approaching 0) there is no instability. In rows with various inclinations to  $\mathfrak{H}$ , the first to become unstable as  $\mathfrak{H}$  is increased will be that for which  $\alpha - \theta$  is equal to  $\frac{1}{2}\pi$ .

If  $a$ , the half distance between the poles in the undeflected position, be small compared with  $r$ , there is but little deflexion before instability occurs, and in that case, provided  $\alpha$  be not small, nor nearly equal to  $\pi$ , the occurrence of instability is defined by the condition

$$\frac{d}{d\theta} \frac{\overline{CN}}{\overline{PP}^2} = 0,$$



which is satisfied when  $\tan \phi = \frac{1}{\sqrt{2}}$ ;  $\phi$  being the inclination of PP' to the line of centres. Hence, with the same proviso ( $\alpha$  not nearly equal to 0 or to  $\pi$ , and  $a$  small compared with  $r$ ), the value of  $\mathfrak{H}$  which causes the instability is

$$\mathfrak{H} = \frac{m}{12\sqrt{3} \cdot a^2 \sin \alpha}$$

for a single pair of magnets, and twice this quantity for the middle members of a long row. This is of course least for magnets which lie normal to  $\mathfrak{H}$ .

In the special case when  $\alpha = \pi$ , instability occurs when

$$\mathfrak{H} = \frac{m}{8a^2}$$

with the single pair, or  $m/4a^2$  with the row.

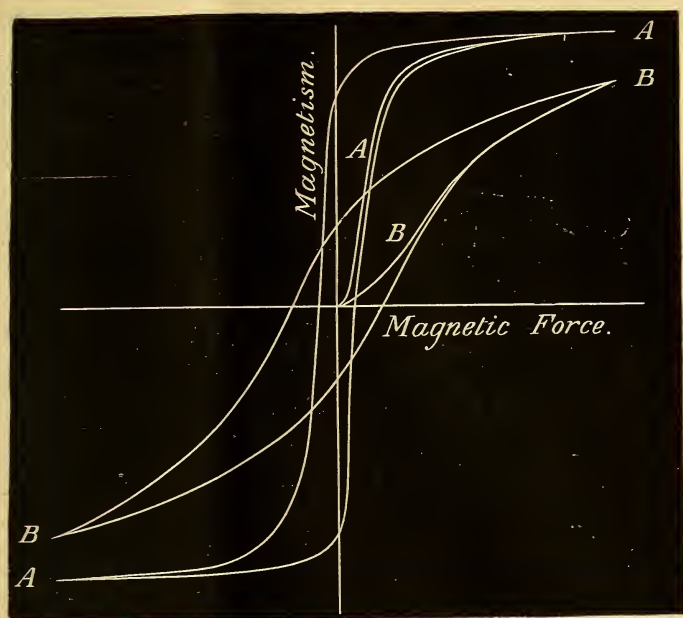
Applied to the case of a group of rows, uniform in distance between the centres, but various as regards their direction with respect to  $\mathfrak{H}$ , these considerations show that after  $\mathfrak{H}$  has reached a value sufficient to make the most susceptible members unstable, no very great increase is required to bring about instability in by far the greater number of the other rows. One general effect of increasing the distance between all the centres is to reduce the range of variation of  $\mathfrak{H}$  within which most of the different rows become unstable as the force is progressively increased.

In annealed metal, where we may expect considerable general homogeneity, as regards distance between the centres of the molecular magnets, we find that practically the whole of the abrupt stage in the process of magnetization is included within narrow limits of magnetizing force. We accordingly obtain curves like A A (fig. 8).

When the metal is strained sufficiently to receive permanent set the curves take more rounded outlines (such as B B), showing less susceptibility throughout, less residual magnetism, and more coercive force. The most natural explanation of this, on the basis of the molecular theory, appears to be that set produces on the whole a shortening of the distances between molecular centres, hence greater stability and more coercive force; but this is associated with heterogeneity, that is variety in the distances, hence the rounded outlines of the curves. We know that set tends to develop, or at least to emphasize, heterogeneity; for instance, a bar of iron or steel pulled in the testing-machine stretches irregularly after the elastic limit is passed.

The effects of stress and consequent elastic strain on magnetic quality are so complex and so various in iron, nickel,

Fig. 8.



and cobalt, that it would be premature to attempt any full discussion of them from the point of view of the theory now sketched. Only a few general features need be referred to at present. Some of these can be traced experimentally in the model by setting the supports of the magnets upon a sheet of thin india-rubber, which may be stretched or distorted to imitate the conditions of longitudinal or torsional strain.

When pulling stress is applied, those rows of molecular magnets which lie more or less along the direction of the stress have their stability reduced by the lengthening of the lines of centres; similarly, rows which lie more or less normal to the stress have their stability increased. The resulting effect on the general susceptibility of the material will depend on which of these conflicting influences preponderates. Let pull be applied before magnetization begins, while the metal is still in a neutral state. The stretching of longitudinal lines and the contraction of transverse lines will not only alter the stability of those molecules which continue to lie in their original rows, but will tend to make the members of those

rows which are much lengthened swing round and form transverse lines in which they will be more stable than before. We may therefore reasonably expect that the permeability with regard to strong fields will be reduced by pull, as it actually is both in iron and in nickel, though with regard to weak fields the permeability may be increased, as it is in iron.

Again, the theory explains well why the effects of stress are by no means the same (1) when the stress is applied first and the magnetic force after, and (2) when the magnetic force is applied first and the stress after.

Let a moderate magnetizing force be applied and then begin to apply stress. The first effects are in general large, for the strain precipitates into instability those molecular magnets which were already on the verge of instability. This is beautifully apparent in iron (see *Phil. Trans.* 1885, part ii., plates 63 and 64); and the theory shows why the first effects are not reversible, why they do not disappear when the stress is removed, and why it is only in subsequent applications and removals of the stress that the magnetic changes become cyclic.

The same remark evidently applies to the first effects of stress on residual magnetism; also to the first effects of temperature-change either on induced or residual magnetism. Again, the theory shows that when a cyclic change of stress is repeated, there will be hysteresis in the corresponding changes of magnetism, whether induced or residual, unless either the cyclic range is very small or the magnetism approaches saturation. During each application of the stress some molecular magnets will swing through unstable positions; during the removal of stress they will swing back, but not at the same values of stress. And it will be characteristic of this hysteresis that the variation in magnetism will begin slowly when the change from applying to removing stress, or from removing to applying stress, begins. All this agrees with the facts.

Moreover, the theory shows that even in the absence of any resultant magnetization a cycle of stress makes the molecular configuration pass through a series of changes which will at first not be cyclic, but will become cyclic when the stress-cycle is repeated, and in which any intermediate value of the stress will be associated with different configurations during the going and coming parts of the process. In other words, we see that there will be hysteresis in the relation of molecular configuration to stress when a cycle of stress is repeated. Hence certain rather obscure effects which have been observed in magnetic experiments; for instance, where an iron wire is



loaded and partially unloaded down to a given load before being magnetized, its permeability is not the same as when the wire is completely unloaded and reloaded up to the same load. Experimental results of this kind led me in 1884 to write:—"If we apply and remove stress in a wire whose magnetic state is entirely neutral, *we cause some kind of molecular displacement in the relation of which to the applied stress there is hysteresis.*"\* The theory now offered shows how this happens. Hence also the remarkable hysteresis which the thermoelectric quality of iron exhibits with regard to cyclic changes of stress, discovered by Cohn, and more fully described in *Phil. Trans.* 1886, p. 361. The hysteresis of molecular configuration with respect to stress has been proved to be removable or reducible by vibration.

From this theoretical explanation of hysteresis in the effects of stress, it at once follows that a cyclic change of stress (provided it be not very small) involves some dissipation of energy in a magnetic metal, whether the piece be magnetized or not. We may expect this dissipation to be most considerable under conditions which make the magnetic hysteresis large. But it will occur even when there is no external trace of magnetism.

This of course implies that, in a cyclic process of loading and unloading, work must be spent. There is no perfect elasticity in a magnetic metal, however slowly the process of straining be performed. Under any load there is less strain during application than during removal. This is borne out by experiments on the extension of iron wires (*Brit. Assoc. Report*, 1889, p. 502).

The same action occurs to a marked degree in torsional strains. In a twisted specimen there will be a tendency on the part of the molecular magnets to range themselves along lines agreeing more or less with the direction of maximum contraction. Alternate twisting to opposite sides should therefore cause much molecular swinging through unstable positions, with consequent dissipation of energy, even in a piece which is not magnetized.

Without going at present into details, it may be added that the phenomena of molecular "accommodation" studied by Wiedemann and by H. Tomlinson accord with the theory, and that it seems to lend itself well to explain the very remarkable results which have been obtained by Nagaoka†

\* *Phil. Trans.* 1885, part ii. p. 614.

† *Journal of the College of Science of the University of Tokio*, vol. ii. 1888.



in experiments with nickel wire under twist or under a combination of pull and twist. It also agrees with what little is known as to the influence that previous magnetization in one direction has upon subsequent magnetization in another direction.

To sum up, I have endeavoured to show:—

(1) That in considering the magnetization of iron and other magnetic metals to be caused by the turning of permanent molecular magnets, we may look simply to the magnetic forces which the molecular magnets exert on one another as the cause of their directional stability. There is no need to suppose the existence of any quasi-elastic directing force or of any quasi-frictional resistance to rotation.

(2) That the intermolecular magnetic forces are sufficient to account for all the general characteristics of the process of magnetization, including the variations of susceptibility which occur as the magnetizing force is increased.

(3) That the intermolecular magnetic forces are equally competent to account for the known facts of retentiveness and coercive force and the characteristics of cyclic magnetic processes.

(4) That magnetic hysteresis and the dissipation of energy which hysteresis involves are due to molecular instability resulting from intermolecular magnetic actions, and are not due to anything in the nature of frictional resistance to the rotation of the molecular magnets.

(5) That this theory is wide enough to admit explanation of the differences in magnetic quality which are shown by different substances or by the same substance in different states.

(6) That it accounts in a general way for the known effects of vibration, of temperature, and of stress upon magnetic quality.

(7) That in particular it accounts for the known fact that there is hysteresis in the relation of magnetism to stress.

(8) That it further explains why there is, in magnetic metals, hysteresis in physical quality generally with respect to stress, apart from the existence of magnetization.

(9) That, in consequence, any (not very small) cycle of stress occurring in a magnetic metal involves dissipation of energy.

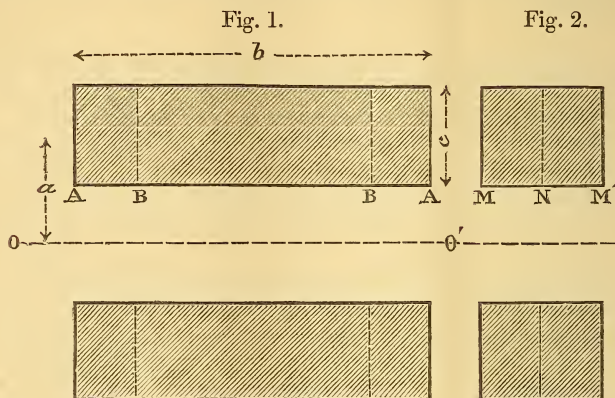
XXVI. *A Formula for Calculating approximately the Self-induction of a Coil.* By PROFESSOR JOHN PERRY, D.Sc., F.R.S.\*

**A**N easy empirical formula for enabling the coefficient of self-induction (*the inductance*) of any coil to be calculated with approximate correctness is very much wanted. I have been led to take up the matter through having to design an instrument with various cylindric coils whose inductances should bear certain relations to one another, and it was necessary for me to see at a glance with some exactness the effect of altering their dimensions. It is to be observed that for practical purposes extreme accuracy of calculation is of no importance, because the mechanical inaccuracies in constructing coils are considerable. It will be seen that my method of arriving at what may almost be called a rational formula has been suggested by Prof. James Thomson's ingenious method of considering the flow of water over a rectangular gauge-notch.

I consider only hollow cylindric coils. Thus fig. 1 shows the section of a coil whose dimensions are  $c$  centimetres measured radially,  $b$  parallel to the axis, mean radius of coil  $a$ ,  $oo'$  being the axis. The supposition I make is that all the coils considered are so long ( $b$  so great) that,  $\frac{c}{a}$  being the same in all, the field near the ends is the same in all. Without much straining of the meaning of words, we may say that the inductance of a coil is the total induction when unit current passes in the coil; and if there is only one convolution, it is proportional to the reciprocal of what may be called the magnetic resistance. My supposition comes to this: that if the dimension  $b$  is great enough, increase of the magnetic resistance produced by increasing  $b$  is proportional to the increase of  $b$ . Let  $MNM'$  (fig. 2) show the limiting length beyond which increase of resistance will be proportional to increase of length. Evidently  $MM'$  must be a function of  $c$  and  $a$ , and if written in the shape  $2sc$  it may be expected that  $s$  will be constant for small values of  $\frac{c}{a}$ . The magnetic resistance due, then, to the end parts,  $AB$ , of the coil (fig. 1) will be the same as that of the coil, fig. 2. Now the magnetic resistances of all similar coils are inversely proportional to their dimensions, and for all coils similar to that shown in fig. 2 for any

\* Communicated by the Physical Society: read June 20, 1890.

value of  $a$  or  $c$  but for the same values of  $\frac{c}{a}$ , the magnetic resistance is inversely proportional to  $a$ , say that it is  $\frac{p}{a}$ ,



$p$  being a function of  $\frac{c}{a}$ . Now the remaining part of the coil (fig. 1) may be considered made up of coils of square section  $c \times c$  and of mean radius  $a$ ; and the additional magnetic resistance introduced by each of these is inversely proportional to  $a$  if  $\frac{c}{a}$  is constant. There are  $\frac{b-2sc}{c}$  of them, and the total magnetic resistance, irrespective of the ends, is proportional to  $\frac{b-2sc}{ca}$  if  $\frac{c}{a}$  remains constant. Say that it is  $(b-2sc) \frac{q}{a^2}$ , where  $q$  is a function of  $\frac{c}{a}$ . The whole magnetic resistance is then

$$\frac{p}{a} + \frac{q}{a^2} (b-2sc).$$

And the inductance  $L$  for one winding is the reciprocal of this. If there are  $n$  windings,

$$L = \frac{n^2 a^2}{pa + qb - 2sqc} \quad \dots \quad (1)$$

As  $sc$  is comparable with the axial distance inside a coil from the end, at which the lines of force are no longer perceptibly curved,  $s$  may be supposed to be a proper fraction. In finding the values of  $p$ ,  $q$ , and  $s$ ,  $p$  and  $q$  being functions of  $\frac{c}{a}$ , and  $s$  being nearly constant, it is evident that if we, experimentally or by calculation, find  $L$  for various values of

$a$ ,  $b$ , and  $c$ , it is enough if one of these remain constant. Mr. C. E. Holland has worked out for me the following values of  $\frac{L}{4\pi n^2}$  in C.G.S. units, keeping  $c=1$  centimetre, from the series published as Appendix III., page 321, vol. ii. of the second edition of Maxwell's 'Electricity and Magnetism.' Unfortunately, unless the ratios of  $\frac{c}{a}$  and  $\frac{b}{a}$  are small, this series does not enable  $L$  to be calculated. I propose later to amend the formula when I have, either by calculation or experiment, found  $L$  for values of  $\frac{c}{a}$  and  $\frac{b}{a}$  greater than  $\frac{1}{2}$ ; and I regret that the difficulty of obtaining values of  $L$  in these cases is so great as it is. Calling Mr. Holland's calculated  $\frac{L}{4\pi n^2}$  by the letter  $l$ , the following Table shows the results of his calculations:—

$a.$	$b.$	$c.$	$l.$
4	1	1	9.060
4	2	1	7.303
4	3	1	5.993
2	1	1	3.094
2	2	1	1.985
2	3	1	1.034
4	1	2	7.460
3	1	1	5.914
3	2	1	4.510
3	3	1	3.420
6	1	1	16.0436
6	2	1	13.527
6	3	1	11.704
10	1	1	31.8655
10	2	1	27.763
10	3	1	24.834

Now it is evident that if of any coil the dimensions are  $a$ ,  $b$ , and  $c$ , then  $L$  for this coil is  $c$  times the  $L$  for a coil whose dimensions are  $\frac{a}{c}$ ,  $\frac{b}{c}$ , 1. Hence Mr. Holland's numbers enable us to study the general case, so long as  $\frac{c}{a}$  and  $\frac{b}{a}$  are less than  $\frac{1}{2}$ . I find that with more than enough accuracy



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for practical purposes we may take, when  $c=1$  centim.,

$$\frac{L}{4\pi n^2} \text{ or } l = \frac{a^2}{\cdot 2317a + \cdot 39 + \cdot 44b} \cdot \cdot \cdot \quad (2)$$

Hence generally, from the law as to similar coils,  $l$  is

$$\frac{c \frac{a^2}{c^2}}{\cdot 2317 \frac{c}{a} + \cdot 39 + \cdot 44 \frac{b}{c}} \text{ or } \frac{a^2}{\cdot 2317a + \cdot 39c + \cdot 44b}.$$

So that generally

$$L \text{ in centimetres} = \frac{4\pi n^2 a^2}{\cdot 2317a + \cdot 39c + \cdot 44b} \cdot \cdot \quad (3)$$

I give it in this form to enable its accuracy to be tested. And it is obvious that  $q$  of (1) is a constant, whereas  $p$  is a linear function of  $\frac{c}{a}$  including a constant.

$$L \text{ in centimetres} = \frac{n^2 a^2}{\cdot 01844a + \cdot 031c + \cdot 035b} \cdot \cdot \quad (4)$$

Or taking the ohm as  $10^9$  centimetres per second,

$$L \text{ in secohms} = \frac{n^2 a^2 \div 10^7}{1\cdot 844a + 3\cdot 1c + 3\cdot 5b} \cdot \cdot \quad (5)$$

If  $\alpha$  is the cross sectional area pertaining to one winding, whether made up partly of insulation or not,

$$n = \frac{bc}{\alpha};$$

and if  $R$  is the resistance of the coil in ohms, as  $R = \frac{2\pi a p b c}{\alpha^2}$ ,

$$\frac{L}{R} = \frac{V \div 10^9 \pi \rho}{\cdot 2317a + \cdot 39c + \cdot 44b}; \cdot \cdot \cdot \quad (6)$$

where  $V$  is the volume of the coil in cubic centimetres,  $\rho$  = resistance in ohms of a copper wire 1 centim. long, of smaller section than 1 centim., just as much smaller as the actual wire is than the covered wire.

Let  $\rho_0$  = specific resistance of copper in ohms.

Taking it that if there is no insulation,  $\rho = \rho_0 = 1\cdot 62 \times 10^{-6}$ .

Let  $W_1$  = weight of copper in the coil (disregarding the weight of the insulating material, this is the weight of coil),

$W_2$  = weight of volume of the coil of copper,

$$\frac{W_2}{W_1} = \frac{\alpha}{\text{section of copper}} = \frac{\rho}{\rho_0}.$$

It is evident that if for any coil whatever we calculate  $\frac{L}{R}$  on the assumption that there is no space occupied by insulation, we have only to multiply this by  $\frac{W_1}{W_2}$  to obtain  $\frac{L}{R}$ , taking taking insulation into account. Another way of putting our result is

$$\frac{L}{R} = \frac{V' \div 1000}{\cdot 728a + 1\cdot 33c + 1\cdot 5b}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

where  $V'$  is the volume, in centimetres, of *copper* in the coil. For a coil of given volume wound with given wire, to diminish the ratio of  $\frac{L}{R}$ , increasing  $c$  is nearly of the same importance as increasing  $b$ ; whereas these are about twice as important as increasing  $a$ . In fact  $\frac{L}{R}$  is nearly proportional to  $\frac{abc}{a + 2(b + c)}$ ; and of course it is less as the wire is finer, because the volume of the insulation is relatively greater.

It may be noted that the empirical formula given in this paper, although seemingly truer when  $\frac{b}{a}$  and  $\frac{c}{a}$  are smaller, is not true when  $\frac{b}{a}$  and  $\frac{c}{a}$  are zero. The inductance of one spire of wire whose section is infinitely small is infinite; and it would have been possible to get an empirical formula, fairly correct for ordinary values of  $a$ ,  $b$ , and  $c$ , which would give an infinite value for  $L$  when  $\frac{b}{a}$  and  $\frac{c}{a}$  are zero, based on the expression given by Maxwell,

$$\frac{L}{L\pi n^2} = a \left( \log \frac{8a}{R} - 2 \right),$$

where  $R$  is a function of  $b$  and  $c$ . Such a formula would, however, be much less useful for ordinary purposes than the one I have given.

XXVII. *The Changes of Property of Amalgams by Repeated Fusion.* By Dr. G. GORE, F.R.S.\*

IT is well known that various alloys undergo a change of properties by repeated melting and cooling. Having found during some experiments made for examining the changes of volta-electromotive force of alloys during fusion, that an amalgam composed of 1 part by weight of cadmium and 4 of mercury gave different results after each successive melting, notwithstanding that the chemical composition of the substance remained unaltered, I took a freshly made bar of the substance and a strip of sheet platinum and formed a voltaic couple with them in a solution composed of 1 part by weight of common salt and 100 of distilled water, and ascertained the fixed amounts of deflexion it produced of the needles of an ordinary torsion-galvanometer of 50 ohms resistance after different numbers of fusions of the amalgam; they were as follows:—

Number of Fusions.	Deflexions.
1 . . . . .	29
4 . . . . .	24
8 . . . . .	11
12 . . . . .	12

The differences of strength of current were manifestly due to the fusions, and not to any loss of mercury or oxidation of the cadmium. The amalgam melted at  $98^{\circ}$  C., and was not on any occasion heated above  $130^{\circ}$  C. There was no visible fume or sublimate caused by volatilization of the mercury, and it was found in a separate experiment that a diminution of as much as 20 per cent. in the proportion of mercury, produced only about one degree difference of deflexion of the needles.

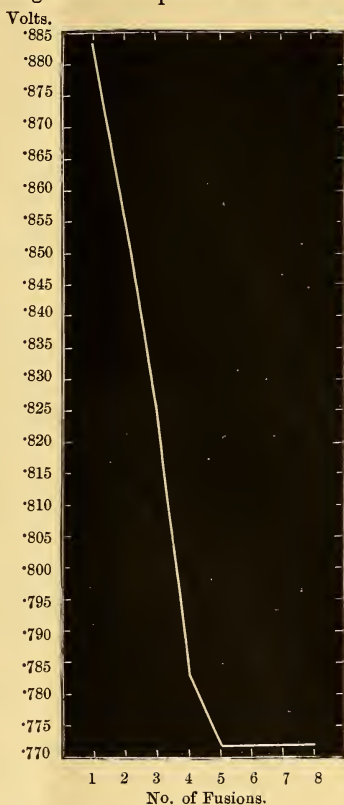
I took a second freshly made bar of the same substance, and measured the electromotive force of the couple in the same electrolyte at  $17^{\circ}\cdot5$  C. after each fusion and cooling, by the method of balance, with a suitable thermoelectric pile (see Proc. Birm. Phil. Soc. vol. iv. p. 130; 'The Electrician,' vol. xii. March 15, 1884, p. 414), and obtained the following results:—

Number of Fusions.	Volts.	Number of Fusions.	Volts.
1 . . . .	·8809	5 . . . .	·7724
2 . . . .	·8553	6 . . . .	"
3 . . . .	·8267	7 . . . .	"
4 . . . .	·7838	8 . . . .	"

\* Communicated by the Author.

The annexed diagram shows the curve of the change.

Curve showing Effect of repeated Fusions on Cd Amalgam.



In order to ascertain whether the alloy changed in property spontaneously, a third freshly prepared bar was kept in a horizontal position and examined daily with the help of the same electrolyte and galvanometer. The following permanent deflexions were obtained :—

Number of Days.	Deflexions.	Number of Days.	Deflexions.
1 . . .	18	6 . . .	7.5
2 . . .	10	7 . . .	6.5
3 . . .	10	8 . . .	7.5
4 . . .	7.25	9 . . .	7.0
5 . . .	8.0	10 . . .	6.0

At the first moment of immersion of the couple each day the amount of temporary deflexion was about 30 degrees, and



the above numbers are the amounts of permanent deflexion produced at the end of three minutes. The bar was wiped dry after each experiment, and no error was produced by oxidation; and as a large bulk of the liquid was employed, the diminution of amount of fixed deflexion was not due to exhaustion of the solution. The diminished electromotive force indicated a spontaneous molecular change going on in the amalgam during the first few days.

In order to find whether the amalgam altered in volume by repeated fusion, the specific gravity of a freshly made piece was taken after the 1st and 6th fusion. The substance was melted under water, and no loss of weight, or oxidation occurred during the process.

After the 1st fusion the spec. grav. was = 12.5438 at 14°·5 C.  
 " 6th " " " = 12.6190 "

From the various results obtained in this research and from other considerations, I conclude that this amalgam, by the act of fusion and subsequent cooling, and by spontaneous change, suffers a loss of molecular motion, potential heat, chemical activity, voltaic energy, diminishes in volume, and becomes less corrodible in a solution of chloride of sodium. The changes appear to be permanent.

It is evident that the method employed, viz. measurement of volta-electromotive force, may be used for detecting and measuring physical changes produced in alloys by repeated melting, lapse of time, &c.

XXVIII. *On the Electrostatic Force between Conductors conveying Steady or Transient Currents.* By Dr. OLIVER LODGE\*.

AT the last meeting of the Physical Society this session Mr. Boys described some attempts he had made to detect mechanical force between a pair of Hertz resonators delicately suspended and immersed in a region of electromagnetic waves.

The attempt so far had not been successful; but Mr. Boys, by attending to the energy manifested by Mr. Gregory's method and by another method of his own, showed good reason why the force, if any, was just too small to be observed even with his extremely delicate appliances, and conjectured that a moderate increase in sensitiveness would be necessary in order to detect the effect. Everyone must have full confidence that if any such mechanical effect exists Mr. Boys will show it us

\* Communicated by the Author.

before long; but, in common with Prof. Fitzgerald, I feel provisionally and tentatively doubtful whether any mechanical effect really exists between electric pulses travelling along wires with the velocity of light. In a wire subject to electric stationary waves there are obvious electrostatic pulses at either end and electrokinetic pulses in the middle: but Mr. Boys had allowed for all that, and arranged that the opposing effects of ends and middle should conspire to assist each other in causing rotation. What I felt doubtful about was whether even in infinite wires, wherein all complication by reflexion and stationary waves was avoided, a pair of pulses travelling side by side, like a pair of humps (or a hump and a hollow) on a pair of parallel cords, would exert any force on each other. It is known that two charged bodies flying side by side with the velocity of light will exert no such effect (Mr. Heaviside has shown that this is equivalent to saying that two elements in the same wave-front exert no mechanical force on each other); but whether the same thing is true of two wire-conducted pulses has not, so far as I know, been examined by mathematicians.

If it should turn out that pulses at full speed have no effect, then two straight oscillators in similar phases should repel each other, by the electrostatic effect of the slackening and stationary pulses which are being reflected at the ends.

Such an action seems optically rather interesting. Maxwell predicted that a reflector or absorber would be repelled by light; though, as we know, the complication of the more vigorous molecular action of material surroundings prevented Mr. Crookes from detecting this precise effect. We know, however, that it must exist; and the repulsive effects between alternating magnets and copper disks, detected by Faraday and recently made much of in an interesting manner by Prof. Elihu Thomson, are examples of this very thing. We can even say what the stress caused by full sunshine ought to be, viz. about 50 microbarads\*; that is, the weight of half a milligramme per square metre: but it has not yet been experimentally observed. If Mr. Boys finds his effect, at least if he finds it in the form I suggest, as an overbalancing static repulsion, it will represent an action between two sources of light or between two similarly illuminated bodies.

On the afternoon of the meeting of the Physical Society,

\* Langley's recent estimate, that a square centimetre fully exposed to sunshine receives 2.84 C.G.S. thermal units per minute, is equivalent to an energy of 67 ergs per cubic metre of sunshine, or 67 microbarads. (A "barad" means an erg per cubic centimetre, or a dyne per square centimetre.)

by Mr. Boys' kindness, I made in a back room a hasty experiment on the pulses of a Leyden-jar discharge, which was passed either in the same or in opposite directions through a pair of flexible parallel strips of aluminium-foil, looked at through a microscope.

A fairly distinct effect was observed, its sign being, so far as one could tell, the sign of the electrokinetic effect; *i. e.* attraction between currents in the same direction, repulsion (more easily observed, because, as it was arranged, nearly four times as strong) between opposing currents. Hence it would seem, so far as this crude observation goes, that pulses in wires do exert their electrodynamic effect. I expected, however, that, by suitably arranging matters, the electrostatic effect of the pulses could be made able to overpower their electromagnetic effect. It is perhaps rather a barbarous plan to consider the two things separately; but until some one attacks the problem in a powerful manner I have been interested in groping at it, and accordingly make this communication.

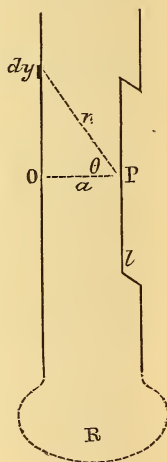
First, consider the action of currents in general on each other, and find the ratio between their electrostatic and electrokinetic forces. So far as I know, the electrostatic force between two steady currents is usually overlooked.

No advantage in generality is gained by treating two separate circuits, a movable portion arranged near a fixed portion of one and the same circuit is sufficient.

Arrange a short length,  $l$ , at a distance,  $a$ , from a long parallel conductor; with a resistance,  $R$ , intervening between  $O$  and  $P$ , the middle opposite points of each; and through the whole send a current,  $C$ , up one and down the other.

Then the difference of potential between the two points is  $RC$ , or, with alternating currents,  $PC$ , where  $P$  is the impedance of the wire  $R$ ; and if the capacity per unit length of the two conductors is called  $S_1$ , the linear density of charge on each is on the average  $\lambda = S_1 RC$ ; a little more above  $O$  and a little less below it; but unless the distribution of potential differs greatly from a linear distribution, as when  $l$  is comparable to a wave-length, the mean value will serve.

The electrostatic attraction between the two conductors is



$$F = \int_0^l \int_{-\infty}^{+\infty} \frac{\lambda dy \cdot \lambda' dy' \cdot \cos \theta}{K r^2} = \int_0^l \int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi} \frac{\lambda dy \cdot \lambda' \cos \theta d\theta}{K a} \\ = \frac{2\lambda\lambda' l}{K a} = \frac{2l}{K a} (S_1 R C)^2. \quad (1)$$

Unless one of the conductors is very long there is another term, which, however, it is unnecessary to write.

The electrokinetic repulsion between the same conductors is similarly

$$F' = \iint \frac{\mu C dy C' dy' \cos \theta}{r^2} = \frac{2\mu l}{a} \cdot C^2. \quad (2)$$

### Steady Currents.

Hence with steady currents the ratio of the static attraction to the magnetic repulsion is

$$\frac{F}{F'} = \frac{S_1^2 R^2}{\mu K}, \quad (3)$$

which on every possible system of units is a pure number.

To get a notion of its value, suppose the wires to be round and of radius  $\rho$ ; then

$$S_1 = K / 4 \log \frac{a}{\rho};$$

so, remembering that

$$\frac{1}{\mu K} = (\text{the velocity of light})^2 = \left( \frac{30 \text{ ohms}}{\mu} \right)^2,$$

we see that the above numerical ratio is

$$\frac{F}{F'} = \left\{ \frac{\text{number of ohms in the wire } R}{120 \log \frac{a}{\rho}} \right\}^2. \quad (3')$$

Suppose, for instance, the wires were 50 diameters apart, or  $4 \log a/\rho = 18.4$ , the two forces would be equal, and just balance each other, if  $R$  was 552 ohms.

With any resistance greater than this the electrostatic force would have the advantage, and two opposite currents in the given wires would *attract*.

### Alternating Currents.

If the current used is an alternating one, impedance must be inserted in (1) and (3) instead of resistance: no other change is necessary. Hence an impedance-meter suggests itself. Send a current alternating with given frequency through the pair of conductors joined by the impedance to be



measured, and either adjust  $S_1$  until the electrostatic and electrodynamic forces balance, or estimate the outstanding force by a torsion arrangement. Supposing a balance could be got, the impedance of the intervening conductor, for the particular frequency applied, is

$$P = \frac{1}{S_1''v} = 60 \log \frac{a^2}{\rho \rho'} \text{ ohms.}$$

*Leyden-Jar Discharge.*

Next proceed to consider the transient current of a Leyden-jar discharge round the same circuit.

Let a jar of capacity  $S$  charged to potential  $V_0$  be discharged round a circuit whose total resistance and inductance are  $R_0$  and  $L_0$  respectively. Then the current at any instant after the discharge has begun is

$$C = \frac{V_0}{pL_0} e^{-mt} \sin pt; \text{ where } m = \frac{R_0}{2L_0}, \text{ and } m^2 + p^2 = \frac{1}{SL_0}.$$

The electrodynamic repulsion between the two wires previously considered, when the discharge occurs, is therefore, applying (2), an impulse:—

$$\begin{aligned} \phi' &= \frac{2\mu l}{a} \cdot \left( \frac{V_0}{pL_0} \right)^2 \int_0^\infty e^{-2mt} \sin^2 pt \cdot dt \\ &= \frac{2\mu l}{a} \cdot \frac{\frac{1}{2}SV_0^2}{R_0} \cdot \dots \dots \dots (4) \end{aligned}$$

To investigate the electrostatic attraction completely we should have to take into account the sinuous distribution of potential in space over the circuit; but, unless the waves are much shorter than usual, the ultimate effect on a short length will be very little different from the effect of a uniform potential alternating sinuously in time, the difference of potential at any instant between the fixed and movable wire being

$$V = PC,$$

where  $P$  is the impedance of the intervening portion of the circuit.

Hence the electrostatic impulse is, by (1),

$$\begin{aligned} \phi &= \frac{2l}{Ka} S_1^2 P^2 \int_0^\infty C^2 dt \\ &= \frac{2l}{Ka} \cdot \frac{\frac{1}{2}SV_0^2}{R_0} \cdot S_1^2 P^2 \dots \dots \dots (5) \end{aligned}$$

And the ratio of the two impulses is

$$\frac{\phi}{\phi'} = \frac{S_1^2 P^2}{\mu K} \dots \dots \dots (6)$$

Now  $P^2 = p^2 L^2 + R^2$ , where  $p^2 = \frac{1}{SL_0} - \left(\frac{R_0}{2L_0}\right)^2$ .

So, noticing that  $R/R_0 = L/L_0$  as nearly as we please,

$$P^2 = \frac{L}{L_0} \left( \frac{L}{S} + \frac{3}{4} R_0^2 \right).$$

The second term is frequently negligible, though there is no difficulty in taking it into account if it is not ; so the ratio of the impulses, at its least, is

$$\frac{\phi}{\phi'} = \frac{S_1^2}{K^2} \cdot \frac{L}{L_0} \cdot \frac{L/\mu}{S/K} \dots \dots \dots (6')$$

The first of these three numerical factors depends merely on the shape of the acting conductors and their distance apart. The second is a proper fraction which may be made as near unity as we choose. The third involves a comparison between the electromagnetic measure of inductance of the wire included in the circuit, and the electrostatic measure of capacity of the discharged Leyden jar.

Taking as an example the same round wire conductor as before, with

$$S_1 = \frac{K}{4 \log \frac{a}{\rho}}, \quad = \frac{K}{18.4} \text{ say,}$$

and considering  $\frac{L}{L_0}$  as  $\left(\frac{18.4}{20}\right)^2$  for instance, we perceive that the two impulses will be equal and just balance each other if the length representing  $L$  on the magnetic system of units be 400 times as great as the length representing  $S$  on the electrostatic system. Any wire longer than this gives attraction the advantage ; any wire shorter than this favours repulsion.

Or, with different jars discharging round a given circuit, small jars will exhibit the electrostatic impulse, big ones the electrokinetic.

Illustrating numerically still further : a length of 30 metres of No. 16 copper wire opened out into a single large loop has a self-induction of 500 "metres" or 50 micro-secohms. Using this as the wire  $R$  between the two suspended conductors, the critical-sized Leyden jar which should excite no force

when discharged through them is about  $1\frac{1}{4}$  "metres" or .00014 microfarad; *i. e.* smaller than the ordinary "pint" size.

With the help of an adjustable condenser, an instrument for measuring the *L* of well-insulated coils free from iron suggests itself here.

#### *Ribbon Conductors.*

If strips are used instead of round wires for the movable conductor, the electrostatic effect has an artificial advantage given it: for take a pair of similar strips, of length  $l$ , breadth  $b$ , and distance apart  $a$ , the force caused by a current  $C$  flowing through them with uniform intensity everywhere is easily calculated to be

$$\frac{4C^2l\mu}{a} \left( \frac{a}{\tan \alpha} + \frac{\log \cos \alpha}{\tan^2 \alpha} \right),$$

where  $\alpha$  is an angle whose tangent is  $b/a$ .

The quantity in brackets has a maximum value  $\frac{1}{2}$  when  $\alpha=0$ , *i. e.* when the plates are far apart enough for their shape to be immaterial; and its value decreases steadily towards zero, viz.  $\frac{1}{2}\pi \cot \alpha$ , as  $\alpha$  approaches  $90^\circ$ ; the whole becoming ultimately  $2\pi\mu C_1 \cdot Cl$ .

As for the electrostatic force between strips, I do not know how far we are justified in assuming uniform distribution of density, even if given uniform distribution of current; but at least when the plates are close together the force will not be very different from

$$2\pi \cdot \frac{SV}{KA} \cdot SV = \frac{2\pi l}{Kb} \cdot (S_1 PC)^2;$$

the value of  $S_1$  being  $\frac{Kb}{4\pi a}$ .

So the ratio of the forces for large close plates is

$$\frac{K}{\mu} \cdot \left( \frac{Pb}{4\pi a} \right)^2 = \left( \frac{\text{no. of ohms in impedance of wire}}{120 \pi a/b} \right)^2.$$

Hence with strips six times as broad as their distance apart the forces will balance for a steady current when the interposed wire is only 60 ohms resistance.

#### *Measure of "v."*

In applying an experimental observation of this kind to a determination of the product of the æther constants  $\mu$ ,  $K$ , (and it just strikes me that it is after all only a modification of the method by which Maxwell himself made one of the early deter-

minations), it will be better to use round wires rather than strips, because linear dimensions then come in only under a logarithm, and moreover are such as can be measured with considerable accuracy without difficulty. Some of Mr. Boys' quartz-fibre and aluminium-tube devices ought to permit the zero of force to be sharply got, and thus a good measure of "v" to be made.

We should have to observe very exactly the neutralization of all force between the suspended and fixed conductors while a steady current was passing through them, with an interposed wire of known resistance, and then use the relation (3) or (3') in the form

$$\mu K = S_1^2 R^2,$$

or

$$"v" = \frac{S_1}{K} \cdot \frac{R}{\mu} = \frac{\text{resistance of wire expressed as a velocity}}{4 \log \frac{a}{\rho}}. \quad (7)$$

If the acting conductors are set very near each other,  $a$  being still the distance between their centres, the denominator alters itself a little, becoming

$$2 \log \frac{a^2 - 2\rho^2 + a\sqrt{(a^2 - 4\rho^2)}}{2\rho^2},$$

with an easy additional complication if it is convenient to make the sectional radii unequal\*.

By filling the vessel containing the acting conductors with other insulating media, it is possible that the "v" for them could be directly measured.

#### *Action of Moving Charges and Pulses.*

So far I have not taken into account the sinuosity of distribution of Leyden-jar discharges in space, nor the possibility of pulses passing the two portions of the circuit between which the force is being observed at different times or in different phases. It would seem as if a small assemblage of short-waved pulses sent round a long circuit might be prevented from exerting any mechanical action on each other if the adjacent parts of the circuit in which their action was to be observed were purposely separated by an intervening length of wire of many wave-lengths unsymmetrically introduced into the circuit. But before committing myself I should like to make a few experiments. Nevertheless I am tempted to go on a little further.

If instead of considering pulses rushing along stationary wires, we consider charged wires moving along endways with

\* See Foster and Lodge, *Phil. Mag.* June 1875, p. 456.



the speed of light, Mr. Heaviside has attacked the general problem in the *Philosophical Magazine* for April 1889. He there shows that between two planes perpendicular to a wire thus moving and moving with it at a distance apart equal to the length of the wire, the electrostatic intensity is

$$E = \frac{2\lambda}{Kr},$$

and the magnetic intensity is

$$H = \frac{2\lambda v}{r},$$

where  $\lambda$ , the linear density, may be distributed anyhow on the wire. Outside these two planes the force is zero.

If the two intensities were to act, one on a stationary charge of any number of electrostatic units, the other on a stationary magnetic pole of the same number of magnetic units, the two forces would be equal. If they act on a wire conveying a steady current, and charged up to a certain linear density, the forces will be equal when the statical measure of density is equal to the magnetic measure of current, *i. e.* when  $C = v\lambda$ ; for then

$$E\lambda = H\mu C.$$

Lastly, if the two forces due to one bit of charged wire, moving in its own line with the speed of light, act on another similarly moving piece, the current equivalent to the second wire will be  $v\lambda'$ ; and again there will be an equality between electrostatic and electrokinetic forces;

$$\frac{2\lambda}{Kr} \cdot \lambda' = \frac{2\lambda v}{r} \cdot \mu\lambda'v.$$

Not by any different  $\lambda$ , or by any rearrangement of  $\lambda$ , can the balance be disturbed: only by a different  $v$ . If either wire moves with velocity less than that of light, the electrostatic force overpowers the other, but, so long as the full velocity is maintained, the density on either wire may have any value positive or negative without disturbing the balance; and this is natural enough, when, as here,  $\lambda$  and  $C$  vary together; for if  $\lambda$  be zero or negative anywhere,  $C$  is also zero and negative, and the balance persists.

Now proceed to the case of alternating pulses travelling along parallel stationary wires. Their speed of travel is the speed of light, and though the distribution of both density and current is sinuous there is nothing in that disturbing to a balance; moreover, so long as the waves are freely progressive,  $\lambda$  and  $C$  still accompany each other exactly, and nothing but a balance will be observed in a closed circuit, however the phases operating in the acting portions be altered, if the right

proportion holds between the current and the potential, as already calculated.

But if by reflexion at distant unjoined ends of an open circuit the pulses be turned from progressive into stationary waves, then localities can be found on the wires at which attraction or repulsion permanently occurs; for  $\lambda$  and  $C$  are no longer companions, the sinuous distribution of current lags a quarter period behind the sinuous distribution of charge. Hence at a given instant there will be places where the current force is a maximum and the static force zero; while at a quarter wave-length on either side the current force is zero and the static force a maximum. Halfway between these places only will the two forces be equal, but with alternate agreement and disagreement of sign. A readjustment of phase between the conductors will now make all the difference; a shift of a quarter wave-length changing from maximum to zero, and a shift of half a wave-length bringing about reversal of sign.

According to all this therefore (if it be correct) it follows that the simple ideas on which Mr. Boys set to work are right after all, and that he will detect the forces in the way he expects.

#### *Variation with Distance.*

A few words as to the magnitude of the effect to be expected. Hertz has shown (see 'Nature,' vol. xxxix. p. 404) that at a reasonable distance from a rectilinear oscillator, one or two wave-lengths being practically sufficient, the electric force (or electromotive intensity) is perpendicular to the radius vector from middle of oscillator, and is of magnitude

$$E = \frac{Ql q^2}{K\rho} \cdot \sin(q\rho - pt) \cdot \sin\theta; \dots (8)$$

where  $\rho$  and  $\theta$  are the polar coordinates of the place, and  $q = 2\pi/\lambda$ .

Calling the length of the oscillator the axis, and the normal plane through its middle the equator, this means that the electric force is a maximum at the equator, diminishes towards the poles, and varies along any radius with the inverse distance from the centre.

At smaller distances the law is not so simple, but at any distance in the equatorial plane the electric oscillation is parallel to the oscillator, and of amplitude

$$\frac{Ql}{Kr^3} \sqrt{(q^4 r^4 - q^2 r^2 + 1)},$$

showing that close to the oscillator the electric force varies as the inverse cube of the distance, at intermediate distances

more slowly, while at a very few wave-lengths (practically one is sufficient) the first term under the root overpowers the others, and the ordinary law of the inverse distance holds good.

To get an idea of the magnitude of this intensity at any considerable distance from the axis, write  $Q = SV$ , where  $V_0$  is measured by the length of spark employed at the oscillator, and write for  $q^2$  its value  $\frac{\mu K}{LS}$ ; then the amplitude of the electric force is

$$E = \frac{SVl \cdot \mu K \cdot \sin \theta}{K\rho \cdot LS};$$

or, as  $L = 2l\mu \left( \log \frac{4l}{d} - 1 \right) = 2\mu l c$ , say,

$$E = \frac{V \sin^2 \theta}{2rc} \dots \dots \dots (9)$$

Take as a numerical example any convenient oscillator, say, to avoid unnecessary repetition of specification, the small oscillator drawn to scale on page 54 of the *Philosophical Magazine* for July 1889, which emits waves 1 metre long: let its constant  $c = 4\frac{1}{2}$ , and its spark be, as there quoted, 8 millimetres, so that  $V_0$  is about 26,000 volts. Then the initial electric intensity at a distance of a couple of wave-lengths in the equator is

$$E_0 = \frac{26000 \text{ volts}}{18 \text{ metres}} \\ = 14.4 \text{ volts per centimetre.}$$

Putting therefore at this distance of 2 metres a parallel wire half a wave-length long as receiver, it utilizes 50 centimetres of the above electromotive force, and gives a maximum sparking potential of 720 volts, which corresponds to a spark-gap of about a tenth of a millimetre between flat surfaces. This is an upper estimate, because time for a quarter-period's dissipation should be allowed, the result being multiplied by a dissipation-factor  $\exp. \left( -\frac{\frac{1}{4}\lambda}{vSR} \right)$ ; where R is to be found as follows.

#### *Energy of Radiation.*

The mean energy of the radiation per unit volume is, as is well known (Maxwell, art. 793),  $\frac{KE^2}{8\pi}$ ; which in the present case, abbreviating the characteristic factor,  $\left( \log \frac{4l}{d} - 1 \right)$  or its equivalent, to  $c$ , is

$$\frac{K}{8\pi} \cdot \frac{V^2 \sin^2 \theta}{4\rho^2 c^2} \dots \dots \dots (10)$$

The energy sent per second through the sphere of radius  $\rho$  with velocity " $v$ ," is

$$\begin{aligned} & \int_0^\pi 2\pi\rho \sin \theta \cdot \rho d\theta \cdot \frac{KV^2 \sin^2 \theta}{32\pi\rho^2 c^2} \cdot v \\ &= \frac{4}{3} \cdot \frac{KV^2}{16c^2} \\ &= \frac{V^2}{12\mu v c^2} \cdot \dots \dots \dots (11) \end{aligned}$$

And this is the rate at which the oscillator radiates energy during its activity. Comparing (11) with (10) we see that the equatorial radiation exceeds the mean radiation in the proportion of 3:2.

The difference of potential  $V$  is not constant, but decreases logarithmically according to the law

$$V = V_0 e^{-\frac{t}{SR}};$$

where  $R$  is a dissipation-coefficient of the dimension of resistance, and of value easily found, thus:—

Total energy radiated for every spark of the oscillator is

$$\int_0^\infty \frac{V_0^2 e^{-\frac{2t}{SR}}}{12\mu v c^2} \cdot dt = \frac{\frac{1}{2}SV_0^2 \cdot R}{12\mu v c^2},$$

which must also equal  $\frac{1}{2}SV_0^2$ , the initial energy; hence

$$R = 12\mu v c^2 = 360c^2 \text{ ohms.}$$

Taking as a numerical example the same oscillator as above, with  $c = 4\frac{1}{2}$  and  $V = 88$  electrostatic units, all these values are easily estimated. For instance the mean energy of the radiation per unit volume at any considerable distance  $r$ , say 2 metres, in the equator, is

$$\begin{aligned} \frac{KV^2}{32\pi c^2 r^2} &= \frac{88 \times 88}{25 \times 81 r^2} = \frac{3 \cdot 8}{r^2} = \frac{3 \cdot 8}{4 \times 10^4} \text{ barads} \\ &= 95 \text{ microbarads, at a distance of two metres.} \end{aligned}$$

This will cause a momentary pressure on a metallic surface normally exposed to it, of 95 microdynes per square centimetre, or a milligram weight per square metre; and is nearly twice as strong as full sunshine while it lasts.

At 1 metre distance, I need hardly say, the energy and the pressure are 4 times as great.

The area of energy absorbed by a fine wire linear receiver may be estimated roughly by finding the closeness of a grid



of parallel wires which would just not let any radiation pass through it. Suppose, for instance, that a grid with wires 10 centimetres apart satisfies this condition; then each wire mops up energy for a breadth of 5 centimetres on either side of itself. The heat generated in such a wire at each spark is

$$\frac{3}{2} \cdot \frac{bl}{4\pi r^2} \cdot \frac{1}{2} SV_0^2.$$

This, in the numerical case already taken, with  $\frac{S}{K} = 1.4$  centim. and  $KV_0^2 = (88)^2$  dynes, gives, at a distance of 1 metre,

$$\frac{3 \times 500}{25 \times (100)^2} \times .7 \times (88)^2 = 32.5 \text{ ergs per spark};$$

which, repeated 100 times a second by a suitable contact-breaker, would yield 3250 ergs per second, or 1 ordinary thermal unit every  $3\frac{1}{2}$  hours.

The dissipation-factor, mentioned at the end of last section, is  $e^{-\frac{100}{1.4 \times 12 \times 81}}$ .

*Attempt at further detail.*

To work out more completely what happens when one oscillator is used to excite another arranged parallel to it at an equatorial distance  $r$ , not near enough to re-act, I suppose we may consider the receiver as subjected to an impressed E.M.F. given by (8), and write down the equation to its current  $x$  at any instant,

$$\ddot{x} + 2\kappa\dot{x} + n'^2x = \frac{l'V_0}{2rc} e^{-mt} \sin(qr - pt), \quad \dots (12)$$

the solution of which is given (for instance) in Lord Rayleigh's 'Sound,' vol. i. p. 62.

The heating of the receiver at each spark will be  $\int_0^\infty R'\dot{x}^2 dt$ .

If there be two such receivers, far enough off each other not to encroach on each other's field, the current attraction between them will be proportional to  $\dot{x}_1\dot{x}_2$ , and the static repulsion to  $x_1x_2$ .

Calling the right-hand side of the above equation  $U$ , and writing  $n'^2 - \kappa^2 = n^2$ , the complete solution is

$$x = \frac{1}{n} \int_0^t e^{-\kappa(t-t')} \sin n(t-t') \cdot U' dt' + \frac{x_0}{\cos \gamma} \cdot e^{-\kappa t} \cos(nt - \gamma); \quad \dots (13)$$

where  $U'$  is the same function of  $t'$  that  $U$  is of  $t$ , and where

$$\tan \gamma = \frac{\dot{x}_0}{nv_0} + \frac{\kappa}{n}.$$

The second term in the above, which expresses free vibrations in the receiver, may be made zero, because it contains the initial disturbance of the receiver as a factor; and the first term, which expresses forced vibrations, simplifies down to

$$x + C = \frac{l'V_0}{4nrc} \cdot e^{-mt} \left( \frac{\sin \alpha}{p-n} \cos (qr-pt+\alpha) - \frac{\sin \beta}{p+n} \cos (qr-pt+\beta) \right), \quad (14)$$

where  $\tan \alpha = \frac{p-n}{\kappa-m}$ , and  $\tan \beta = \frac{p+n}{\kappa-m}$ .

If there is anything like agreement between the natural periods of vibrator and resonator, the first of these two terms overpowers the other.

Another way of writing the solution is

$$x + C = \frac{l'V_0}{4rcn} \cdot \frac{\sin (\beta-\alpha)}{\kappa-m} e^{-mt} \cdot \sin (qr-pt+\alpha+\beta). \quad (15)$$

### Appendix.

It is in accordance with theory to assert that the action of two given magnets on each other varies inversely with the permeability of the medium; that the action of two currents on each other varies directly as the permeability of the medium; and that the action of a current on a given magnet is independent of the properties of the medium.

To avoid misunderstanding, it must be perceived that the statement refers to a given magnet, not to a magnet of numerically specified strength, because about that there would be some ambiguity according to the medium in which it was measured.

Similarly, the static action between two charges is inversely as the dielectric constant of the medium; the action between a given charge moving at the approximate light-speed and a given magnet is independent of the medium, except in so far as its properties affect the velocity of light; while the dynamic action between two given charges moving together at the light-speed is proportional to the permeability.

It may be as well to have direct experimental verification for some of these things.

XXIX. *The Interactions of Circular and Longitudinal Magnetizations.* (Preliminary Note.) By Prof. C. G. KNOTT, D.Sc.\*

IN the course of an extended series of investigations into the relations of magnetism and stress, part of which is already published in the *Trans. Roy. Soc. Edinb.* (vol. xxxv.), I was led to consider the effect of a current passing along a wire upon its longitudinal magnetic intensity. Wiedemann, Buff, and Villari† have discussed this problem in some of its aspects. It does not seem possible, however, to deduce from their results completely satisfactory conclusions as to the effect of the current upon the apparent longitudinal permeability. The question as it presented itself to my mind was not so much as to the effect of a varying current along the wire upon the apparent longitudinal moment, but rather as to the behaviour of the wire in various longitudinal fields according as it was carrying a current or not. It was to be expected, in accordance with the results of previous investigators, that a diminution of longitudinal intensity would be an evident accompaniment of a steadily sustained circular magnetization. In other words, the susceptibility to a longitudinal magnetizing force would, in all probability, be smaller when a current was passing along the wire. This has been fully established in the experiments, of which this forms a short preliminary note. Other effects, however, have been observed, which are (so far as I know) novel, and which may lead to clearer views regarding the internal structure of magnets and magnetized matter.

In the experimental work I have been assisted by Mr. Tsuruta, a graduating student of physics in the Imperial University.

The wire to be experimented with was carefully annealed and then inserted as the core of a solenoid of copper wire of 138 coils per centimetre length. The wire and solenoid lay magnetically east and west, and at a suitable distance from the one end a delicately suspended mirror with small magnets attached to its back served in the usual way as the magnetometer. The deflexions were measured by the familiar reflected-beam method, the spot of light moving over a scale at a distance of 1·7 metre from the magnetometer-mirror. Before the wire was inserted, the electromagnetic action of the coil on the magnetometer was corrected by a small adjustable coil

\* Communicated by the Author, having been read before the Royal Society of Edinburgh, July 21, 1890.

† For references, see Wiedemann's *Die Lehre von der Elektrizität*, vol. iii. pp. 456-462; for theoretical discussion see p. 476.

in circuit with the solenoid and set close to the magnetometer. The wire was then inserted, and subjected to cyclic variations of magnetic force. The magnetizing current was changed continuously from a given positive value to an equal negative value, and back again to the original positive value. The variation was effected in a gradual manner by means of a liquid rheostat, consisting of a column of dilute sulphate of zinc with zinc electrodes, through which a steady current from a battery of Daniell cells was constantly flowing. By means of a sliding zinc electrode, the necessary current was shunted through the solenoid circuit. The tangent-galvanometer included in this circuit was of course far removed from the solenoid, and was so placed that the operator, in adjusting the rheostat, could easily read the galvanometer-deflexion.

In the earlier experiments careful attention was paid to the first effects, as well as to the permanent cyclic condition which soon becomes established after a few cyclic changes of the magnetizing current have been gone through. At suitable stages in the variation of the current, the current was kept steady until the corresponding deflexion of the magnetometer-needle was observed and noted. These remarks will suffice at present to indicate the general method adopted in studying the cyclic changes, which have been so fully investigated by Warburg and Ewing.

One of my objects was to study the modification produced on this cycle and on whatever else may be associated with it, when a current is passed along the magnetized wire. This linear current (as we shall call it) was derived from one or more Bunsen cells. It entered the iron wire at the end furthest removed from the magnetometer and returned along two copper wires stretched parallel to the iron wire and very close to it.

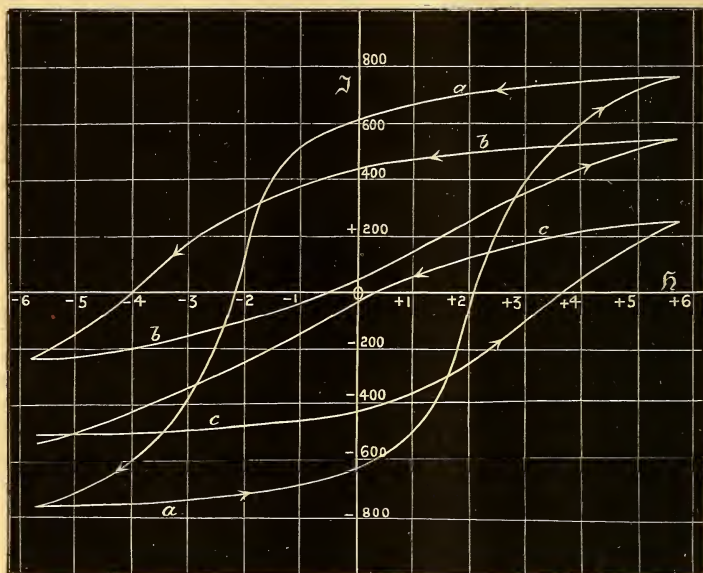
A complete set of experiments consisted in :—

- (1) Taking a permanent magnetic cycle when no linear current was flowing along the wire.
- (2) Observing the initial effect when the linear current was made to flow in one direction along the wire, and taking the permanent magnetic cycle with this current kept steady.
- (3) Observing the initial effect when the linear current was broken, and taking again the permanent magnetic cycle as in (1).
- (4) Observing the initial effect of the linear current put on in the other direction, and taking the permanent magnetic cycle with this current steady.
- (5) Operating as in (3).



It was soon found that in good experiments the permanent magnetic cycles in (1), (3), and (5) were practically identical; so that in later experiments (3) was omitted. It was also established by direct experiment that the permanent magnetic cycle in (2) was quite independent of the magnetic condition of the wire when the linear current was put on.

Some of the features of the case are shown in the curves given. This is chosen as an average type, the departures from which, when the relative magnitudes of linear current and field are altered, will be briefly indicated below. In these curves magnetic force ( $\mathfrak{H}$ ) is measured horizontally, magnetic intensity ( $\mathfrak{I}$ ) measured vertically. The magnetic force is



given in electromagnetic C.G.S. units; and the magnetic intensity (very roughly) in the same.

Curve *a* corresponds to the permanent magnetic cycles (1), (3), (5); curves *b* and *c* give the cycles when the linear current is flowing first in the one and then in the other direction. The current used in this experiment was about two amperes.

A glance at these curves is sufficient to teach us that the linear current modifies the properties of iron in relation to the magnetic after-effect in three well marked ways.

First, the total range of magnetic intensity produced by a given cyclic variation of magnetic force is markedly dimi-

nished when the current is flowing along the wire. This means a diminution in susceptibility. Here also may be mentioned the fact that the first effect of putting on the current when the wire is strongly magnetized is a diminution of longitudinal magnetic intensity.

Secondly, when the linear current is flowing, the average magnetic intensity over a whole cycle no longer corresponds to the condition of zero polarity, as in the normal case when no linear current is flowing. For the one current, the magnetic intensity oscillates, so to speak, about a large positive polarity; and for the current in the reverse direction it oscillates about a nearly equal negative polarity. If we reckon polarity in the usual way as a directed quantity measured from the south pole to the north, then the direction of the linear current is in the same direction as the average polarity which it sustains, when the wire is subjected to an absolutely symmetrical cycle of magnetizing force on each side of zero.

Thirdly, the curves *b* and *c* are no longer symmetrical on the side of the zero-line of magnetic force. The closed curve *b* is more pointed at its positive end than at its negative end; the curve *c*, on the other hand, is more pointed at its negative end than at its positive. If we turn the figure upside down, the general appearance remains the same as before. Thus the effect of the linear current is such as very distinctly to modify the form of the ascending and descending branches. The descending branch of *b* is very similar to the ascending branch of *c*; and the ascending branch of *b* is very similar to the descending branch of *c*. We may connect this peculiarity with the peculiarities already described in these words:—

A current passing along an iron wire, which is being magnetized, diminishes the apparent susceptibility of the wire; but this effect is more pronounced when the wire is acquiring a longitudinal polarity in the opposite direction to that in which the linear current is flowing. Hence, during any cyclic operation, the wire tends to acquire an average polarity in the same direction as that in which the current flows.

These effects are more pronounced the stronger the linear current is as compared with the magnetizing field. In a moderate cyclic field the effect of the linear current may be so strong as to prevent the wire ever acquiring other than one kind of polarity. For example, this effect was produced in a field  $\pm 4$  with a current of nearly 2 amperes. For the linear current in one direction the *b* curve never dipped below the zero-intensity line, and for the current in the other direction the curve *c* never rose above it.

On the other hand, in stronger magnetizing fields, from 10

and upwards, the *b* and *c* curves for the same linear current of 2 amperes tend to *terminal* coincidence, but diverge at the intermediate stages. It is proposed to study more fully these relations, and to extend the investigations to nickel and cobalt.

In the course of these experiments an effect was noticed which demonstrates the extraordinary complexity of magnetic distribution in a magnetized wire. If, before the wire has been magnetized at all, a current is passed along it no appreciable longitudinal polarity is produced, as measured by a magnetometer-needle placed as in the above experiments. Suppose, however, that the wire has been pretty strongly magnetized; and that, in the manner discovered by Auerbach, and used almost universally now, the wire is demagnetized by reversals of gradually diminishing magnetizing currents until the magnetometer-needle stands almost exactly at zero. It is of course generally recognized that the wire so demagnetized cannot be regarded as being in anything like the same condition as it was in its originally unmagnetized state, although it appears to have lost polarity. That this view is correct may be at once demonstrated by simply passing a pretty strong current along the wire, when a very pronounced polarity will be evidenced by a comparatively large deflexion of the magnetometer-needle. Reversing the current will reverse this polarity. Heating to a red heat can alone truly demagnetize an iron wire.

Imperial University, Tokyo,  
May 30, 1890.

XXX. *Notes on Photographs of Rapidly Moving Objects, and on the Oscillating Electric Spark.* By C. V. BOYS, A.R.S.M., F.R.S., Assistant Professor of Physics at the Normal School of Science and the Royal School of Mines, South Kensington\*.

[Plate VI.]

1. I HAD occasion last Christmas to show to a juvenile audience a modification by the late Dr. Guthrie of one of Plateau's experiments, which beautifully illustrates the effect of the surface-tension of a liquid during the growth and formation of a drop. Under ordinary circumstances a drop of water is so small that the formation of the neck and separation of the drop are too rapid for it to be possible to follow the process by the eye. If the drops were larger the process would be slower, but a larger drop, owing to the weight of water, cannot be formed in air. Dr. Guthrie caused the drop

\* Communicated by the Physical Society: read May 2, 1890.



to grow at the end of a pipe half an inch or so in diameter dipped below the surface of paraffin. By this means the effective weight of the drop is very much reduced, and the surface tension is reduced, so that a large drop can be formed, and the process is made comparatively slow. I have found that the development of the drop can be made still more gradual, and that still larger drops may be formed by adding bisulphide of carbon to the paraffin so as further to reduce the effective weight of the drop.

While trying to devise some way of representing this experiment on paper, I saw at the Royal Institution an apparatus exhibited by Mr. Friese Greene, with which photographs at the rate of ten a second could be taken upon a travelling film moved on between and stopped during each exposure.

Examination of the growing drop through a small window in a card disk made to rotate ten times a second, showed that even this rate applied to large and slowly forming drops was not sufficient to give anything like a continuous representation of the forms assumed. However, I found no difficulty in obtaining twenty photographs a second; and, had I required them, I could certainly have obtained fifty sharp and fully exposed photographs in this time, by the following method:—An electric arc was focused by a pair of seven-inch lenses upon the lens of an ordinary half-plate camera. A box with a glass front and back, containing the liquids and the growing drop, was placed immediately in front of the large lenses, and the drops were focused by the lens of the camera upon the ground-glass screen at the end of a slide forty-two inches long. This could be charged with four  $10 \times 4$  plates (two  $10 \times 8$  plates cut longitudinally), and then be drawn by hand from one end to the other of a seven-foot slide which protected the plates from light everywhere except at one place where a window  $4 \times 1$  inches had been cut. Through this window the image of the falling drops was cast upon the moving plate. Just in front of the camera-lens a disk of card with an aperture near the edge was made to rotate at any desired speed by one of Cuttriss's P. 1 motors. Everything was then started, and the speed of the motor and rate of dropping adjusted until the really intermittent but apparently continuous view of the phenomenon upon the ground plate was as desired. The slide was then rapidly drawn from end to end by hand, the speed being such as to obtain rather more than one complete cycle during the motion of the slide. In the photograph, of a portion of which Plate VI. fig. 1 is an exact copy, the exposures were at the rate of fourteen a second, and lasted about one five hundred and sixtieth of a second each. The



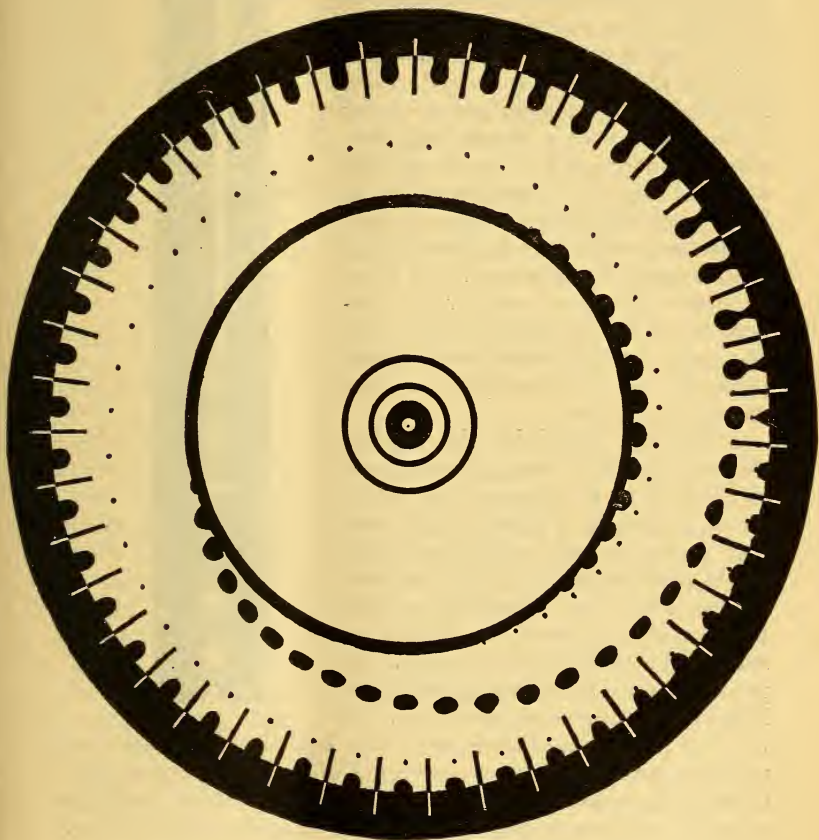
exposure was more than enough to make a perfectly black and white negative, and the outlines were clear and sharp. Another series taken at the rate of twenty a second with an exposure of one eight hundredth of a second each, in which forty-three separate views were taken in the complete cycle, was cut up into strips and mounted on a large disk of cardboard with forty-three equidistant and narrow slits near the edge. When the cardboard is made to rotate in front of a looking-glass, after the fashion of the thaumatrope, the original experiment is again perfectly presented, and all the features are evident without the necessity for using these objectionable liquids. The drop is seen to slowly enlarge until it is too heavy to be supported by the surface-tension, the form becomes unstable, a neck begins to develop, which gradually gets narrower until the drop separates. The free drop being suddenly released from the one-sided pull, vibrates as it falls, not in the manner figured in the text-books, between a prolate and oblate spheroid, but rather in a triangular fashion, with the base and vertex alternately uppermost, as recently described by Ph. Lenard\*. The falling drop reaches the water at the bottom of the box, where it vanishes for a time only, for it has not mixed with this water, and so it presently bounces out, as shown in fig. 1, after which it again falls into the water. Meanwhile the end of the neck from which the drop broke away has gathered itself together into the little drop or spherule so ably described by Plateau, which has an upward velocity imparted to it, since it separated from the upper or pendant drop after the falling drop had broken away. Moreover, just as the falling drop vibrates after it is released, so the pendant drop vibrates also and grows as it vibrates, coming into collision with the upward moving spherule, which it drives away by a blow. Fig. 2 is a reduced copy of the thaumatrope. The method described could be made more perfect by using films on rollers driven by the same motor that makes the card rotate, so that the separate photographs should neither overlap nor leave space unoccupied; but I did not make use of this refinement, as my object was simply to get the true outline in a particular experiment, and not to construct a piece of mechanism. The apparatus described was simply extemporized out of the materials at hand, and it answered my purpose perfectly.

2. As I wished in the lectures referred to above to show that exactly the same process goes on even when the finest jet of water breaks up into beads, though of course the process is hundreds or thousands of times more rapid, I was

\* *Annalen der Physik und Chemie*, vol. xxx. 1887.

anxious to obtain photographs of these forms which should be as sharp and as clear as the photographs already described.

Fig. 2.



Mr. Chichester Bell described to me in a letter a method which he had used successfully for this purpose, which is more especially interesting now, as Lord Rayleigh has recently exhibited photographs taken by a very similar method. Mr. Chichester Bell simply makes a small spark with one or two Leyden jars several feet away from the plate. The jet of water is allowed to fall between the spark and the plate, but as close to the plate as possible. The shadow cast under these conditions is perfectly sharp and will stand considerable magnification, and the light is quite sufficient to blacken the plate except when the water-drop protects it. Fig. 3 is an

enlargement of one of these photographs. The water was broken up regularly by simply blowing into a key which whistled a note of 2730 complete vibrations a second, so that each drop moved to the position occupied by the next in the  $\frac{1}{2730}$  of a second. Lord Rayleigh photographed jets of water by the spark with a camera and lens, using in addition a large condensing and field lens, so as to obtain sufficient light; but it appears that the glass of the lenses is not of much advantage, if any, because, as he himself has since suggested, it absorbs so large a proportion of the ultra-violet rays that the gain by concentration is about balanced by the absorption of the most actinic rays.

3. Having found by the shadow method that there was an abundance of light from a comparatively feeble spark, I thought it possible that each half period of an oscillating spark might produce sufficient light to leave a clear record on a rapidly moving photographic plate of the shadow of small and rapidly moving objects. To put this to the test of experiment, the following arrangement was made. In the first place an oscillating spark was formed between a pair of polished brass knobs about one tenth of an inch apart, by discharging a condenser of large capacity through one or two coils of gutta-percha-covered copper wire to give self-induction. Details of the electrical arrangements will be given at the end of these notes; but I may state here that the separate flashes of light in the spark followed one another at the rate of about 4500 a second. A "half plate" was held in a recess in a disk of wood screwed to a whirling-table, so that it could be made to rotate in its own plane at a high speed. A card-screen with a narrow slit was placed just in front of the plate, so that the light from the spark could fall on the plate through the slit. The jet of water was then formed just in front of the slit, and when the plate was rapidly revolving the spark was formed. The plate, on being developed, was found to have impressed upon it a picture like an open fan with the water-

Fig. 3.





drops arranged in spiral lines. This method was not so convenient as a modification in which, instead of a glass plate spinning in its own plane, a flexible film was employed, wrapped round and held by two india-rubber bands upon a brass cylinder  $1\frac{1}{2}$  inches in diameter. This could be made to rotate at a very high speed by means of a light band from a whirling-table. Pl. VI. fig. 4 is a copy of a photograph obtained in this way. Here it will be seen that the intermittent light is automatically produced, and the period of the intermittence is constant for any particular apparatus. However, as carried out, the value of this method of observing the movements of rapidly moving bodies loses its practical value because the spark is alight during a large proportion of the time of each oscillation, so that it is by no means an instantaneous phenomenon.

4. In order to show the oscillating spark and to examine it by photography, I wished to have some more convenient means than the rotating mirror employed by Dr. Lodge. With this the observer is taken by surprise whenever a spark passes, for he does not know exactly in what direction to look, and therefore he finds it more difficult to recognize the peculiarities of the drawn-out spark than he would if he were certain that he would see the spark in the exact direction in which he was looking. Besides this it is not easy, when photographing the spark, to ensure that the whole phenomenon from the birth to the dying flickers of every spark shall be impressed upon the plate.

The method which I am about to describe appears to me to attain these ends more perfectly than any other with which I am acquainted, and it does not introduce any difficulties of its own.

A brass disk (Pl. VI. fig. 5) has six achromatic opera-glass lenses of about seven inches focus screwed into it, but not at the same distance from the axis. One pair, 1, 1, on opposite sides of a diameter are placed equidistant from the axis; the next pair 2, 2 are placed one tenth of an inch nearer the axis; the third pair 3, 3 one tenth of an inch nearer still. The wheel is mounted on an axle, carrying a grooved pulley-wheel, and is accurately balanced. It may then be made to rotate, if necessary, at the very high speed of over a hundred turns a second. The spark is formed on one side of the plate, and a screen or photographic plate is held on the opposite side; and the two are so adjusted that the spark is focused upon the screen or plate. Now, when the disk is made to rotate, the image of the spark is drawn out into a beaded band; but as it is possible to turn the disk so fast that it has moved through



an angle of nearly one hundred and eighty degrees during the existence of a spark, while to turn it through a right angle is perfectly easy, each lens will project a beaded arc of a circle perhaps nearly half a turn in extent. If the separate lenses were all at the same distance from the axis, these six semicircular arcs would be projected on the top of one another and confusion would result; but as they are displaced by an amount which is about the same as the length of a convenient spark, the separate arcs are just made to clear one another. Therefore, if the plate is large enough to take an arc of the length of sixty degrees, the whole record of the spark will afterwards be found upon it. By this means it is possible to make use of the high speed which is necessary to widely separate the several constituents of the oscillating spark without at the same time causing the record to be spoiled by the overlapping of the image formed by one lens by that produced by the next. A single pair of lenses, instead of six, would prevent the overlapping, but then to certainly obtain the whole record it would be necessary to make the plate receive an arc of one hundred and eighty degrees, which, on optical grounds, would be objectionable. If the sparks are to be shown on a screen it is best to make the spark in the axis of rotation, and show the complete circle or a large part of it; but if the image is to be photographed, it is best to place the spark exactly opposite one lens and use such a size of plate that when the disk is turned one image just begins to leave the plate on one side when the next is coming in on the other.

In order to make the most of a plate, it is convenient to expose it in a common camera-slide held in the hand or in a groove behind a card screen, with a curved aperture of such a size that the image from all three lenses can fall upon the plate. The plate can then be moved on by hand one stage after every spark, and five or six groups taken on one half plate. Specimens of portions of a few of the photographs obtained are arranged together in Pl. VI. fig. 6.

Dr. Lodge has lately photographed oscillatory sparks, and has observed their peculiarities; I shall therefore do no more than merely mention the most striking features. The spark is obviously alight nearly all the time that it lasts, the intervals of darkness are short. The oscillatory spark proper is, I believe, always determined by what may be called a pilot-spark, due to the discharge of the knobs and wires outside the self-induction.

The pilot-spark is well seen at *p* in A, fig. 6, which is a photograph taken with a very high speed and considerable

magnification. That this pilot-spark is due to the discharge of the knobs is certain, because in the first place it is a quarter period behind the centre of the first spark of the oscillation proper, and in the second place because in a photograph taken under similar conditions, but after a small Leyden-jar had been directly connected to the terminals, the pilot-spark was far brighter than before and was even brighter than any of the succeeding alternating elements, while it occupied the same place, namely one quarter period before the centre of the first spark of the oscillation proper. The very exact analogy between the motion of the electricity in an oscillating spark and of the bob of a common pendulum may be worth tracing:—

The electric displacement gradually increases as the machine is worked until the electromotive force is sufficient to break the air-gap which held the electricity on one side.

The steady oscillation of the electricity then begins, and in a quarter period the electric velocity is at its greatest value, the current is strongest, or the spark is brightest; the current then gradually gets less until for a moment it ceases and the spark goes out.

The electric displacement is now nearly the same in amount as at first, but in the opposite direction, it therefore starts back again, and so swings backwards and forwards as the knobs become alternately + and - (as is indicated in some of the photographs by the brighter glow alternately at each end of the spark), but getting less at every swing, owing partly to electrical resistance wastefully producing heat and partly to electromagnetic radiation which will give rise to oscillating currents in neighbouring conductors, especially if they have the same period, until at last the whole store of energy has been wasted and the electricity is at rest.

The displacement of the bob gradually increases as the thread which draws it to one side is pulled until the force is sufficient to break the thread which held the bob on one side.

The steady oscillation of the pendulum then begins, and in a quarter period the velocity is at its greatest value; the velocity then gradually gets less until for a moment the bob is at rest.

The displacement of the bob is now nearly the same as at first, but in the opposite direction; it therefore starts back again and so swings backwards and forwards, resting alternately on one side and on the other, but getting less at every swing, owing partly to resistance wastefully producing heat and partly to wave-motion transmitted through the supporting wall which will cause other pendulums to start swinging, especially if they have the same period, until at last the whole store of energy has been wasted and the bob is at rest.

In order to increase the total number of oscillations, I have introduced what I call a trap, which consists of a second air-gap in the circuit kept open by a prop while a strong spring tends to close it. The spark-gap is then made very short, but the potential can be raised up to any degree that the con-

denser will safely stand. A string tied to the prop is then pulled, and the spring completes the second gap so quickly that not more than one or two oscillations can take place after the spark begins and before the filling of the air-gap at the trap. Thus a higher potential can be obtained than would be possible if the short working spark-gap alone determined the potential, while the resistance in circuit is less than before owing to the shortness of the spark.

Two sparks taken with the trap are shown in B, fig. 6. Two longer sparks taken without a trap are reproduced in C, fig. 6. The gain in number of oscillations is not very great, as the measures by Messrs. Robson and Smith at the end of this paper show; but there is a gain, especially as compared with a short spark taken without a trap. The trap, however, is practically useful in another way, it enables one to fix the instant at which the spark shall occur, which, besides being convenient, is important if for any reason the highest possible speed of rotation is required. While the lenses will run continuously at so low a speed comparatively as fifty or seventy revolutions a second, it would not be well to run them at high speeds for more than a few seconds together. By the use of the trap this is possible, whereas, if the high speed had to be kept up during the long time that it takes to charge a condenser of so great a capacity to the sparking-point, there would be great risk to the bearings of the wheel of lenses. For instance, to obtain a spark about one tenth of an inch long from the condenser used in these experiments, from twenty to thirty turns of the handle of a large eight-plate Wimshurst machine had to be made.

Anomalous variations of brilliancy are not unusual, as may be seen in A, but a curious example is indicated by the letter *p* in D. This represents the latter or dying portion of a spark taken on the same negative and under the same general conditions as A. In this case it will be seen that the light instead of going out at the end of an oscillation travelled slowly across the gap to the other terminal, forming apparently a kind of ball-discharge.

One series of photographs I may here refer to, though the effect sought for is not so evident as I had expected. In this series a short vertical spark was formed, with its length parallel to the direction of the motion of the lens which at any time might be opposite to it. A magnetic field was produced in the line joining the spark and the lens. Then it was hoped that the current oscillating backwards and forwards would be largely deflected laterally alternately on either side so as to produce a zigzag impression. The arrangements



were very imperfect, but there is a very slight lateral shift which I believe to be real, but it will be necessary to try the experiment again under more perfect conditions.

I must express my obligation to our lecture-assistant, Mr. R. Chapman, who has performed the whole of the purely photographic part of the experiments, and whose experience in this direction has been of very great service.

The following are the particulars of the apparatus that has been used. The electrical constants were determined by Messrs. W. G. Robson and S. W. J. Smith.

### *Condenser.*

A wooden tray was made, as shown in fig. 7,  $28\frac{1}{4}$  inches long and  $16\frac{1}{4}$  inches wide inside, but with the base projecting on each side so as to form a 22-inch square. A sheet of varnished glass of this size was laid upon the base, and then twenty-six pieces of thin window-glass  $28 \times 16$  inches were piled on one another in the tray. The window-glass had been well washed, dried, and varnished while hot on each side all round the edge for a width of two inches. Pieces of tinfoil  $24 \times 12$  inches were laid on each of the oblong pieces of glass, except the top one, and long tongues of tinfoil 3 inches wide were brought out alternately on the two sides. On one side all these tongues were brought out in the middle and bent down so as to rest on the square glass plate below; on the other side they were brought out in four sets of three each with a space of two inches between each set. These were separately bent down to lie on the square glass plate below. By this means the capacity can be made variable in the proportions of 1, 2, 3, and 4 by simply connecting the wire to 1, 2, 3 or 4 of these electrodes. A strip of tinfoil lying over all the ends and held in contact by weights keeps them all connected except when a smaller capacity is required.

Total capacity 0.0979 microfarad.

Total capacity of battery of ten large jars 0.0451 microfarad.

Total capacity of small jar used to connect knobs (p. 355) .0026 microfarad.

### *Self-Induction.*

Two coils, containing 330 yards each of No. 16 copper wire covered with gutta-percha to No. 7, were made use of in the form in which they arrived from the makers. The two coils are marked C and U. The following are the dimensions in inches approximately:—



	Outside diam.	Inside diam.	Depth.
C . . .	12	$8\frac{1}{4}$	6
U . . .	$11\frac{1}{2}$	$7\frac{1}{2}$	6

The resistances of the coils are:—

	B.A. units.	Ohms.
C . . . .	2.423	2.391
U . . . .	2.514	2.481

The self-inductions determined by Sumpner's method (Journal of the Soc. of Telegraph Engineers, 1887, fig. 5) were found to be

C . . .	$26.89 \times 10^6$	C.G.S. units.
U . . .	$26.31 \times 10^6$	„ „

In comparing the number of oscillations measured with those calculated from the electric constants given, experience showed that the photographs, such as those in fig. 6, were not so suitable as one taken with the spark in the line of the axis of the wheel of lenses, because, though the definition along a radius was not so good in the latter arrangement, it was for the purpose of determining the intervals of darkness just as good, moreover it gave a much larger arc on one plate which made it possible to obtain the centre on the plate, and therefore the angle between two points on the arc, with greater accuracy. If the lenses were screwed into the face of a flat cone so that the axes of each should meet in the axis of rotation at the place of the spark, then definition would be equally perfect in all parts of the circle. I did at first intend to place the lenses in such a cone, but for various reasons the plate seemed preferable.

The comparison of the calculated number of oscillations with the number found is complicated by the relations between true ohms and B.A. units, as follows:—

If the condenser is standardized with reference to the B.A. unit of resistance, then, since the B.A. unit is 1.33 per cent. too small, the number expressing the resistance is too large and therefore the number expressing the capacity is too small, since one varies inversely as the other, and so the number expressing the capacity of such a condenser must be multiplied by 1.0133 to obtain the true capacity.

The self-induction determined by comparison with capacity and resistance is found from the expression

$$L = \text{a number} \times r_1 \times r_2 \times C.$$

If the resistances  $r_1$   $r_2$  are given in true ohms, then, as the

number expressing C is too small by 1·33 per cent., therefore the number expressing L is also too small by 1·33 per cent., and the nominal value of L must be multiplied by 1·0133. But if  $r_1$  and  $r_2$  are given in B.A. units, then, since these numbers are each too large by 1·33 per cent., therefore the number expressing L is also too large by this amount, since one of the resistances and the capacity will balance, and therefore the number expressing L must be divided by 1·0133.

Now, the decrement being small, the numbers of oscillations in a second  $n = \frac{1}{2\pi\sqrt{LC}}$ ; therefore, if L and C have each to be multiplied by 1·0133,  $n$  should be divided by 1·0133; but, on the other hand, if one has to be multiplied and the other divided by 1·0133, then these corrections balance and  $n$  requires no correction.

Messrs. Robson and Smith determined from the photographs the actual number of oscillations per second, and they determined also, assuming the microfarad to be correct, the number that ought to have been produced. The following are their results :—

Observed number . . .	2293	3170	3264	2115	1806											
Calculated number . . .	2210	3126	3126	2210	1826											
Number of elementary sparks in complete spark . . . . .	<table> <tr> <td rowspan="2">}</td><td>16</td><td>23</td><td>20</td><td>15</td><td>14</td></tr> <tr> <td></td><td></td><td></td><td></td><td></td></tr> </table>					}	16	23	20	15	14					
}	16	23	20	15	14											

These were all taken on half plates and were subject to the difficulty of centering. One spark was taken on a large plate, so that all six lenses produced images of the same spark. In this case the observed number was 1852, and the calculated number 1826. Now, if this number is corrected by dividing it by 1·0133, the calculated number becomes 1802, showing the actual number to be about 2·7 per cent. too great. As window-glass was used for the condenser, which, owing to soakage, gives smaller capacities as the time of discharge is made smaller, it is probable that part of the discrepancy may be due to this; but in the measurement of the capacity of the condenser the effect of soakage was made as small as possible by making, as far as such a thing could be done by hand, the contact of discharge instantaneous. The self-induction, too, as measured, may have been slightly different to the self-induction for oscillations at the rate of 1852 a second.

Mr. Smith has calculated the self-induction, using Prof. Perry's formula, given at the last meeting of the Physical Society, but the irregular form of the coils would not permit

of an accurate number being obtained in this way. The figure obtained is about  $51 \times 10^6$ , a value which agrees with the observations better than that found by experiment.

I should add that I do not attach any importance to the discrepancies referred to. The experiments were made mainly with the view of showing the oscillating spark to an audience more clearly than is possible by the method of Dr. Lodge. For the purpose of measurement a window-glass condenser is not suitable at all, and I do not think the rotating lenses are so suitable as the method employed by Dr. Lodge, in which the plate itself is made to rotate in its own plane, for then the centre can be determined with the greatest accuracy.

The actual gain in number of sparks produced by the trap was found by making three experiments, in which all the conditions were the same except those specified.

A. No trap . .	$\frac{1}{10}$ inch spark	32 elementary sparks.
B. No trap . .	$\frac{1}{20}$ inch spark	29                   "
C. Trap giving } potential of A.	$\frac{1}{20}$ inch spark	37                   "

I should in conclusion state that the measurements given at the end of these notes were made after the meeting of the Physical Society at which the paper was read, and that some other additions have been made to the fourth part of these notes.

XXXI. *On the Cheapest Form of Light, from studies at the Allegheny Observatory.* By S. P. LANGLEY and F. W. VERY\*.

THE object of this memoir is to show, by the study of the radiation of the fire-fly, that it is possible to produce light without heat other than that in the light itself; that this is actually effected now by nature's processes; and that these are cheaper than our industrial ones in a degree hitherto unrealized. By "cheapest" is here meant the most economical in energy, which for our purpose is nearly synonymous with heat; but as a given amount of heat is producible by a known expenditure of fuel at a known cost, the word

\* Communicated by the Authors, to whom we are likewise indebted for the *clichés*.

“cheapest” may also here be taken with little error in its ordinary economic application.

We recall that in all industrial methods of producing light there is involved an enormous waste, greatest in sources of low temperature, like the candle, lamp, or even gas-illumination, where, as I have already shown, it ordinarily exceeds 99 parts in the 100; and least in sources of high temperature, like the incandescent light and electric arc, where yet it is still immense, and amounts, even under the most favourable conditions, to very much the larger part.

It has elsewhere\* been stated that for a given expense at least one hundred times the light should in theory be obtainable that we actually get by the present most widely used methods of illumination. This, it will be observed, is given as a minimum value, and it is the object of the present research to demonstrate that not only this possible increase, but one still greater, is actually obtained now in certain natural processes, which we know of nothing to prevent our successfully imitating.

It is now universally admitted that wherever there is light, there has been expenditure of heat in the production of radiation existing in and as the luminosity itself, since both are but forms of the same energy; but this visible radiant heat which is inevitably necessary, is not to be considered as waste. The waste comes from the present necessity of expending a great deal of heat in invisible forms before reaching even the slightest visible result, while each increase of the light represents not only the small amount of heat directly concerned in the making of the light itself, but a new indirect expenditure in the production of invisible calorific rays. Our eyes recognize heat mainly as it is conveyed in certain rapid æthereal vibrations associated with high temperatures, while we have no usual way of reaching these high temperatures without passing through the intermediate low ones; so that if the vocal production of a short atmospheric vibration were subject to analogous conditions, a high note could never be produced until we had passed through the whole gamut, from discontinuous sounds below the lowest bass, up successively through every lower note of the scale till the desired alto was attained.

There are certain phenomena, long investigated, yet little

\* See results of an investigation by S. P. Langley, read before the National Academy in 1883, and given in ‘Science’ for June 1, 1883, where it is shown that in the ordinary Argand-burner gas-flame indefinitely over 99 per cent. of the radiant energy is (for illumination purposes) waste.



understood, and grouped under the general name of "phosphorescent" which form an apparent exception to this rule, especially where nature employs them in the living organism, for it seems very difficult to believe that the light of a fire-fly, for instance, is accompanied by a temperature of 2000° Fahr., or more, which is what we should have to produce to gain it by our usual processes. That it is, however, not necessarily impossible, we may infer from the fact that we can by a known physical process produce a still more brilliant light without sensible heat where we are yet sure that the temperature exceeds this. No sensible heat accompanies the fire-fly's light any more than need accompany that of the Geissler tube; but this might be the case in either instance, even though heat were there, owing to its minute quantity, which seems to defy direct investigation. It is usually *assumed*, with apparent reason, that the insect's light is produced without the invisible heat that accompanies our ordinary processes; and this view is strengthened by study of the fire-fly's spectrum, which has been frequently observed to diminish more rapidly toward the red than that of ordinary flames.

Nevertheless, this, though a highly probable and reasonable assumption, remains assumption rather than proof, until we can measure with a sufficiently delicate apparatus the heat which accompanies the light, and learn not only its quantity, but, what is more important, its quality. Apart from the scientific interest of such a demonstration is its economic value, which may be inferred from what has already been said. I have therefore thought it desirable to make the light of the fire-fly the subject of a new research, in which it is endeavoured to make the bolometer supplement the very incomplete evidence obtainable from the visible spectrum.

As we may learn from elementary treatises, phenomena of phosphorescence are common to insects, fishes, mollusks, vegetables, and organic and mineral matter. Among luminous insects, the fire-fly of our fields is a familiar example, though others of the species attain greater size, and perhaps greater intrinsic brilliancy, especially the *Pyrophorus noctilucus*, Linn., found in Cuba and elsewhere. Its length is about 37 millim., width 11 millim., and it has, like other *Pyrophori*, three light-reservoirs—two in the thorax and one in the abdomen. To procure this Cuban fire-fly, I invoked the aid of the Smithsonian Institution, and through the kindness of Professor Felipe Poey, of Havana, and Señor Albert Bonzon, of Santiago de Cuba, in the Island of Cuba, living specimens of the *P. noctilucus* were received here during the summer of 1889. I have also to acknowledge my obligations to Professor C. V.

Riley, and to Professor L. A. Howard, to whose knowledge and kind care I am doubly indebted.

After a preliminary spectral examination in Washington, I found it more convenient to continue the research at the Allegheny Observatory by means of the very special apparatus supplied by the liberality of the late William Thaw, of Pittsburgh, for researches in the lunar heat-spectrum\*. Photometric measurements throughout the spectrum of the insect's light were also made.

I have indicated the steps of the investigation; but the experiments have been so largely and so intelligently made by Mr. F. W. Very, that it is just to consider him as an associate rather than an assistant in the researches. I shall accordingly in what follows not discriminate between what each has contributed.

#### HISTORICAL NOTES.

We make no attempt to give any bibliography of the subject, and these notes are confined to what seems important in the history of the physical side of it.

*Nathaniel Hulme*†.—*Exp.* 6. A dead shining glow-worm was put upon water contained in a wide-mouthed phial, at the temperature of 58°. The phial was then sunk in boiling-hot water; and as the heat communicated itself to the contents of the phial, the light of the glow-worm became much more vivid.

*Exp.* 7. Another lucid dead glow-worm was put into warm water at 114°, to see if that degree of heat would extinguish the light; but, on the contrary, its glowing property was augmented. All the water was then poured off, yet the insect continued to shine for some length of time.

*Exp.* 8. Two living glow-worms were put into a one-ounce phial, with a glass stopple; and though they were perfectly dark at the time, yet if the phial were briskly rubbed with a silken or linen handkerchief till it became pretty warm, it seldom failed to make them display their light very finely. This experiment was very frequently repeated. It had the same illuminating effect upon the light of a dead glow-worm.

*Exp.* 9. The complete influence of 212 degrees of heat was now applied to the light of a glow-worm by pouring upon one when dead, but in a luminous state, some boiling water.

\* Described in the *Memoirs of the National Academy*, vol. iv. part 2, p. 112.

† *Phil. Trans. Roy. Soc. Lond.* vol. xc. pp. 180-181 (1800).

Its light was instantly extinguished thereby, and did not revive. The experiment was repeated, and with the same result.

*Macaire* \* (quoted by Becquerel) found that the luminous matter taken from the body of a glow-worm and heated, increased in brilliancy up to a temperature of about  $41^{\circ}\text{C}.$ , after which the light diminished, became reddish, and ceased at  $52^{\circ}\text{C}.$  An electric current increased the luminosity in both the living insect and in the luminous part separated from the remainder of the body, but ceased to have any effect in a vacuum. Oxygen and carbon monoxide increased the light of the living insect and of the luminous matter taken from its body; but the light ceased in a vacuum, in hydrogen, in carbon dioxide, in sulphurous anhydride, and in sulphuretted hydrogen.

*Carus* † observed that the luminous matter taken from the body of the glow-worm ceases to shine when dried, but glows again when moistened.

*Matteucci* ‡ found that the phosphorescent substance of the Italian glow-worm (*Lampyrus italica*) soon ceased to glow in hydrogen or in carbon dioxide, but shone decidedly brighter in oxygen than in air, the oxygen being consumed and carbon dioxide appearing. He drew the conclusion that the production of light in this insect is entirely due to the combination of oxygen with carbon, which is one of the elements of the phosphorescent matter. The greatest brilliancy occurred at a temperature of  $37^{\circ}$  or  $38^{\circ}\text{Cent.}$ , but all phosphorescence ceased above  $50^{\circ}$  or below  $-6^{\circ}\text{Cent.}$

*Robert* § found that a glow-worm cut in halves continued to glow for half an hour, when the light ceased, but commenced again on the near approach of a candle, and continued as bright as ever for thirty-six hours, after which it was impossible to renew it.

*Pasteur* || has examined the spectra of our *Pyrophorus* without finding any appearance of bright or dark lines. He states that M. Gernez has made a similar observation on the spectrum of the glow-worm.

*Becquerel* ¶ gives a good summary of the results of previous observers. Since phosphorescent solids give banded spectra,

\* *Bibliothèque Universelle de Genève*, 1821.

† *Analekten zur Natur- und Heilkunde*, Leipzig, 1829; see also *Comptes Rendus*, lix. p. 607 (1864).

‡ *Ann. de Chim. et de Phys.* [3] ix. p. 71 (1843); also in *Comptes Rendus*, xvii. p. 309.

§ *Comptes Rendus*, xvii. p. 627 (1843).

|| *Ibid.* lix. p. 509 (1843).

¶ *La Lumière*, 1867.



and thus differ from ignited solids and liquids, which have continuous spectra, M. Becquerel concludes, from the apparent continuity of the spectrum of the light from phosphorescent animals, that their light approaches nearer to that of ordinary incandescence—a deduction which the following result renders unnecessary.

C. A. Young\* states that the “common” fire-fly gives a continuous spectrum, extending from a little above Fraunhofer’s line C in the scarlet to about F in the blue, gradually fading out at the extremities. He observes that it is noticeable that precisely this portion of the spectrum is composed of rays which, while they more powerfully than any others affect the organs of vision, produce hardly any thermal or actinic effect. In other words, very little of the energy expended in the flash of the fire-fly is wasted.

(This is a most important and interesting inference ; but it will be observed that this is necessarily rather assumed as highly probable than actually demonstrated, since the method did not permit the dealing with the invisible rays except by inference.)

It is quite different with our artificial methods of illumination. In the case of an ordinary gas-light, experiments show that at most one per cent. of the radiant energy consists of *visible* rays, the rest being invisible heat ; that is to say, over ninety-nine per cent. of the gas is wasted in producing rays that do not help in making objects visible†.

Secchi‡ at first thought that the spectrum of the glow-worm was monochromatic, but, with an improved spectroscope, recognized that other colours were present, though feebly, and decided that the spectrum was sensibly continuous.

Quatrefages§, in connexion with the paper of Secchi, remarks that the previous observations of Spallanzani and Macaire, repeated with much care by Matteucci and Becquerel, show beyond doubt that the light of glow-worms and elaters is due to slow combustion. Thus the light is extinguished in a vacuum and in irrespirable gases, it reappears in contact with the air, it is perceptibly increased by the presence of pure oxygen, it persists after the death of the creature, and finally it is accompanied by the generation of carbon dioxide. Nevertheless he points out that there is a distinct kind of phosphorescence in the marine *Noctilucidæ*, due to the con-

\* The American Naturalist, Salem, 1870, vol. iii. p. 615.

† S. P. Langley has shown that the waste is in fact even greater than this ; see ‘Science,’ vol. i. No. 17, p. 482 (1883).

‡ *Comptes Rendus*, lxxv. p. 321 (1872). § *Ibid.* p. 322 (1872).



traction of muscular fibre, the shining tissue being seen through the translucent body-wall. This species of phosphorescence is increased by irritants, but is independent of the presence of oxygen, and is not extinguished or in any way modified by hydrogen or by carbon dioxide.

*Robin and Laboulbène*\* find the luminous organs of *P. noctilucus* composed of irregularly polyhedral cells, 0.04 to 0.06 millim. thick, between which pass very numerous fine tracheæ and nerves. The inner face of the organ is composed of adipose tissue, and the outer of a transparent modification of the ordinary chitinous covering of the insect. The authors conclude that the light is due to chemical decomposition of a nitrogenous body with formation of crystalline urates.

*Jousset de Bellesme*† finds that although the phosphorescent cells, when separated from the body of the insect, continue to glow for several hours, yet if crushed they instantly lose their illuminating power, which indicates that for the production of the light the living cells must retain their integrity, and that they are not mere reservoirs of a phosphorescent substance, but continuous generators of it. He surmises that the light-giving substance may be phosphuretted hydrogen.

*Meldola*‡ is quoted by *Spiller*§ as having examined the glow-worm spectrum and determined its approximate limits.

*Conroy*|| finds the glow-worm's light green, and in a small direct-vision spectroscope, showing a continuous spectrum from C to b, appearing like a broad band of green light extending from 0<sup>μ</sup>.518 to 0<sup>μ</sup>.587, with a faint continuous spectrum into the red to 0<sup>μ</sup>.656.

*R. DuBois*¶.—Perhaps the most important of previous memoirs on phosphorescent insects is by this writer. It contains an account of photometric measures in wave-length scale, and also of heat-measures with the thermopile. The latter represent the only attempt even, in this direction, I know of, and seem to be judiciously made, but to be insufficient (on account of the limitations of such apparatus) to establish the author's conclusion that the light is accompanied by no sensible heat. This conclusion, we repeat, though very probably correct, does not seem to rest on the evidence of an apparatus of at all the necessary sensitiveness. This memoir, however, appears to be in general an excellent one, and well worthy the student's attention.

\* *Comptes Rendus*, lxxvii. p. 511 (1873).

† *Ibid.* xc. p. 318 (1880).

‡ *Proc. Entomol. Soc.* p. iii. (1880).

§ *Nature*, vol. xxvi. p. 345.

|| *Nature*, vol. xxvi. p. 319 (1882).

¶ *Bulletin de la Société Zoologique de France*, parts 1, 2, and 3, 1886.

From all these statements it is abundantly clear that not only physicists and chemists, but naturalists, have been led to conclude that this light is not associated indissolubly with any so-called vital principle or vital process, but that it is a result of certain chemical combinations, and that nothing forbids us to suppose it may be one day produced by some process of the laboratory or manufactory. With this conclusion in mind, we now proceed to observations meant to demonstrate the fact that this process (presumably discoverable but still unknown) gives light without invisible heat.

These observations are :—1. Photometric. 2. Thermal.

#### PART I.—PHOTOMETRIC OBSERVATIONS.

The first impression on viewing the light of the *Pyrophorus noctilucus* through a spectroscope is that it consists essentially of a broad band in the green and yellow, while with precaution we see this extending into and beyond the borders of the blue and orange, but not very greatly farther, and these have been taken by previous observers as its absolute limits. No one appears to have experimentally and distinctly answered the question, “Would the light not extend farther were it bright enough to be seen?”; nor has it been proven as clearly as might be desired that the result depends on the quality rather than the quantity of the light, or given conclusive evidence, that if the light of the insect were as bright as that of the sun it would not extend equally far on either side of the spectrum.

It is impossible to increase the intrinsic brilliancy by any optical device, but if it be impossible to make the light of the insect as bright as that of the sun, it is on the other hand quite possible to make the light of the sun no brighter than that of the insect; and this would appear to be the first step in obtaining a definite proof that the apparently narrow limits of the insect's spectrum are due to the intrinsic quality of the light and not to its feeble intensity. The only conclusive method of determining this would appear to be to balance the light from the insect with that of a definite portion of sunlight by any ordinary photometric device; and having taken this sunlight as nearly equal as possible to that of the insect, though certainly not greater, to let this determined quantity fall on the slit of a spectroscope at the same time with the light from the insect, two spectra being formed one over the other in the same field and at the same time.

The actual doing this is not so easy as it might appear, owing to experimental difficulties connected with the insect,

a part of which arises from the fact that its light is not only fitful but unequal, being of very varying intensities when not wholly intermittent.

The simplest way in which the experiment can be performed is perhaps the following :—

The insect is placed immediately in front of the slit of a spectroscope so that the light of its thoracic or abdominal portion falls upon the slit. This forms a narrow spectrum which should be brought into the lower or upper half of the field, the insect being attached to the spectroscopic apparatus in a position as nearly fixed as possible. The spectroscope is now placed with the axis of its collimator in the line of a ray of sunlight cast from a heliostat without. In the path of this ray is a screen with a circular diaphragm covered with ground glass ; a lens in front of the slit casts on one portion of it an image of the white circle formed by the ground glass, which image is the same size as the illuminating organ of the insect, and forms a spectrum of the same height in the reserved portion of the field. A suitable disposition of lenses placed between the glass screen and the siderostat enables any degree of illumination to be given to the former, from full sunlight to nearly absolute darkness. If the normal spectrum be studied, a grating is selected of such open ruling that the entire visible spectrum of the first order can be seen in the field, but the grating is first so placed that what is seen is not the spectra but the reflected image of the slit, the grating thus acting (at first) the part of a mirror ; so that the observer first sees the two circles of light of approximately equal size and brilliancy, one formed by the insect, the other by the sunlight, and the light of this latter, by the arrangement of lenses between the screen and the siderostat, is then adjusted so that while remaining of the size of the insect, it is judged to have the same intrinsic brilliancy, or at any rate not a superior one.

The essential thing is that a photometric comparison shall be made of the two lights before the spectra are formed, and that under these conditions the sunlight is equal but not superior to that of the insect.

The necessary condition of equality of the two lights from which the spectra are to be formed having thus been secured, the grating is moved until the two spectra are brought into the field. The result of this direct test is that the solar spectrum when intrinsically of the same brightness, or even when clearly of less brightness than that of the insect, extends somewhat further toward the red and distinctly further toward the violet, the insect light being more intense than that of the



sun for equal lights in the green, but ending more abruptly on the violet side.

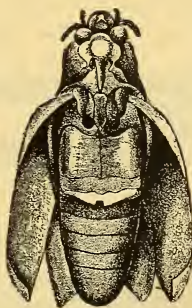
It may be added that when the insect's light grew brighter, the increment appeared to be more in the blue end, or as if the average wave-length diminished with the intensity, but there was not opportunity to put this beyond doubt.

Photometric observations in the prismatic spectrum were made previously to the adoption of the arrangement above detailed, the first being on July 1, 1889, using thoracic light. The insect was mounted on an adjustable stand to which it was attached loosely, so as to give it such freedom of motion as is needed to ensure its emitting the light. It was consequently necessary to re-adjust its position incessantly, and this necessity constitutes a very obvious difficulty. The thoracic light-spots are two ovals, each about 2 millim. by 1.5 millim. (see fig. 1). Their light is not so bright as the abdominal light, but much steadier, and, like that, of a decidedly greenish hue. One of these oval spots was placed over the centre of a slit, open just enough to receive the light, or about 1.5 millim. This slit was in the focus of a glass lens of 8 centim. aperture and 82 centim. focus, which acted as a collimator. The prism was a very large one of flint (faces 11.5 centim. high, 10.5 centim. wide), whose mounting included an automatic minimum-deviation attachment. The observing lens was similar to the collimator, with a low-power eye-piece in whose field was a pair of heavy vertical

Fig. 1.



Fig. 2.



*Pyrophorus noctilucus.*

parallel wires. The whole was mounted on the spectrometer, primarily designed for bolometric measures and fully described

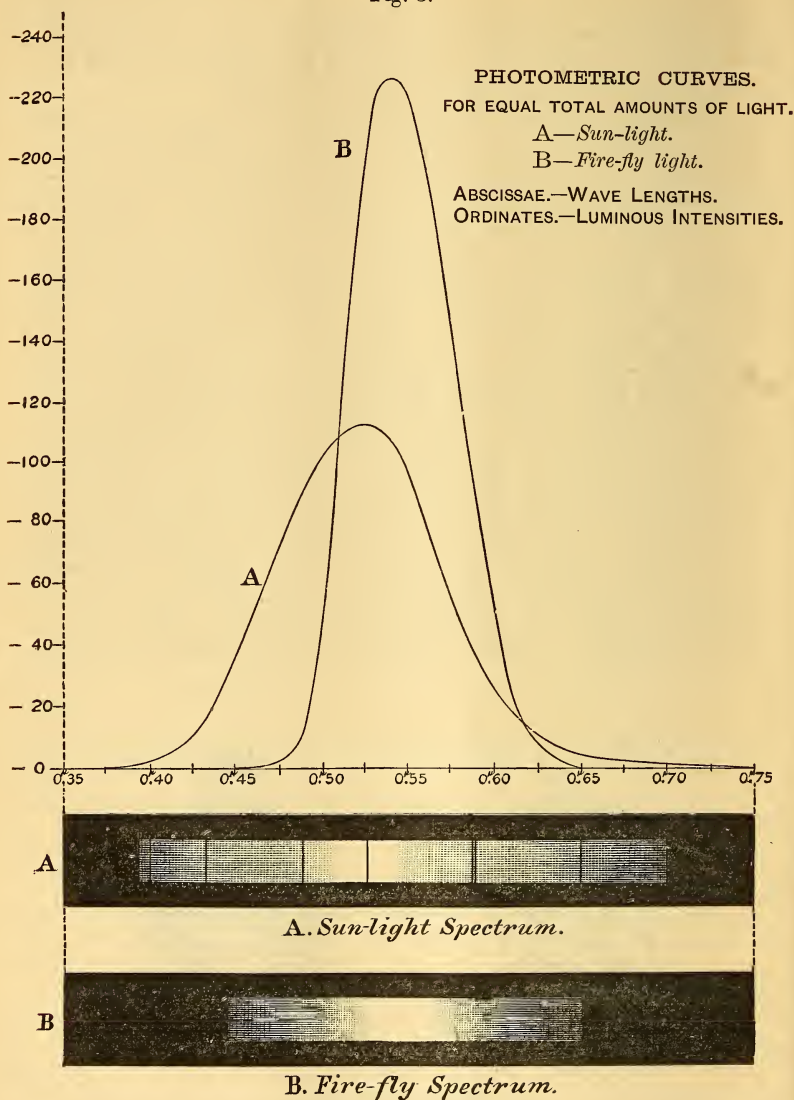
*Phil. Mag. S. 5. Vol. 30. No. 184. Sept. 1890.*

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elsewhere\*. The insect turned so as to show the abdominal light is depicted in fig. 2.

Fig. 3.



The observer waited for some time in a wholly darkened room, and to the eye, thus rendered sensitive, the visible spectrum, before magnification, was about 2 millim. high and

\* See this Journal, March 1883, p. 173.

20 millim. long, the parallel wires being distinctly visible in the indigo at a setting of  $45^{\circ} 25'$ , corresponding to a wave-length of  $0^{\mu}468$ , and in the red at  $43^{\circ} 53'$ , corresponding to  $0^{\mu}640$ . The spectrum then was visible from a little beyond F to near C, or through a range of  $0^{\mu}172$ . As might have been anticipated from the greenish colour of the light, the maximum brilliancy was in the green near E, or near wave-length  $0^{\mu}53^*$ . From this point the light fell away on both sides more rapidly than in the solar spectrum. (See fig. 3, A, B.)

July 2.—A comparison of the spectra of the thoracic and of the abdominal light gave the latter upon the average about double the intrinsic brightness of the former. This was only a crude estimate, but more exact methods under the limited time for experiment would have been useless, owing to the very fluctuating character of the light. In continuation of the photometric measurements of the preceding day on the thoracic light, this was compared with that from the flame of an ordinary Bunsen burner at its greatest luminosity, whose area was limited by a diaphragm to that of the size of the thoracic light. The light from the base of this luminous flame (height of flame about 3.5 centim., air shut off at base of burner) gave a continuous spectrum, which in these first comparisons was alternated with that of the insect. The spectra were judged to be equal in the blue and the red, but that of the insect was much brighter in the green. Again, a spectrum being formed from light taken midway between the base and point of the flame was found to be everywhere too bright, but especially so in the red.

July 3.—Continuation of photometric measures but with abdominal light.

Wires seen in indigo....	4	529	$0^{\mu}463$	Abdominal light.
" " red .....	43	47	$0^{\mu}663$	Range $0^{\mu}200$ .
" " indigo....	46	56	$0^{\mu}390$	Range $0^{\mu}382$ .
" " red .....	43	21	$0^{\mu}772$	Bunsen burner.

(Luminous flame 4 centim. high, at point one third down from top, just within inner and slightly darker cone, seen through hole 2.5 millim. in diameter). Under these circumstances the spectrum of the insect's light was in the green a fair match for that of the burner, elsewhere the latter was brighter but not very greatly so. Since the insect's spectrum was followed through  $0^{\mu}18$  with the thoracic light, while with that of the same character but double the brightness it was followed only through a very little more, or  $0^{\mu}20$ , and

\* In the normal heat-spectrum the maximum has a wave-length  $0^{\mu}57$ .

while at the same time that of a but slightly brighter artificial flame was followed through nearly double or  $0^{\mu}38$ , it seems probable that the insect's light actually ceases near the given limits, and does not merely disappear from the inability of the eye to follow a diminishing light. While we observe from these first photometric measures that the insect's spectrum has undoubtedly a decided maximum in the green, we are led to infer that this spectrum is very probably of the nature of a broad band stretching from beyond F to near C *where it terminates*, and this very important inference we shall see confirmed later by other and more exact measures.

August 5.—Comparison of relative brightness in different parts of spectrum of abdominal light with that from a student's lamp.

A spectrometer supplied with means\* for bringing into the same field the spectra of two different lights, formed by a Rutherford grating of 17296 lines to the inch (instead of the prism) was employed for this purpose. The upper half of the slit received the insect's light, the lower half a beam from the brightest part of the Argand flame, which had passed through two Nicol's prisms, one of which was attached to a divided circle. The two spectra were then seen in the same field with their edges in exact juxtaposition. In the field of the observing telescope was a slit 1 millim. wide, subtending not quite  $9.5$  (minutes of arc), which allowed light having a range of wave-length of about  $0^{\mu}01$  to pass. The spectrum of the lamp-light was brighter in every part of the field though in unequal degrees till it was diminished by turning the Nicol's prism. The angle through which the prism was turned to produce equality having been noted, the values deduced from the ordinary formula (transmitted light  $= l \cos^2 \alpha$ , the angle  $\alpha$  being  $90^\circ$  when the light is diminished as much as possible by crossing the planes of the Nicols at right angles) are as follows, where the fractions are those by which the brightness of the lamp spectrum at the various points is to be multiplied to produce equality with the insect spectrum.

Part of spectrum corresponding to centre of slit at focus of observing telescope.	Blue-green very near F.	Green near b.	Green near E.	Yellow green.	Citron.	Yellow.	Orange-yellow near D.	Orange.
Wave-length.....	$0^{\mu}49$	$0^{\mu}51$	$0^{\mu}53$	$0^{\mu}54$	$0^{\mu}56$	$0^{\mu}58$	$0^{\mu}59$	$0^{\mu}60$
Brightness .....	0.02	0.21	0.34	0.37	0.24	0.19	0.17	0.09

\* Alluded to but not fully described in the Am. Journ. Sci., August 1877.

Owing to the motion of the insect and the varying brilliancy of the light emitted, these figures (each of which is the result of the mean of several trials including at least two measures) still leave much to be desired. The supply of the insects, which had been procured and maintained alive with difficulty, however, did not allow of the experiments being further prolonged, nor of the securing a direct comparison with the solar spectrum. The value of each part of the lamp spectrum having, however, been independently determined with all possible exactness in terms of the solar spectrum, we are enabled to exhibit a comparison of the latter with the insect spectrum so as to show them together (fig. 3, A and B). It is assumed that the same amount of luminous intensity (*i. e.* energy in terms of vision as determined by purely photometric methods) is taken whether from the sun or the insect. The subjoined curves (fig. 3, A) show the solar and the insect luminosity throughout the visible spectrum on the preceding assumption of the intrinsic equality, a result which, however, might be liable to a slight correction of the relative places of the maxima if a direct comparison with sunlight were obtained. The important fact, however, seems to be brought out almost beyond question, that when spectra are formed from two *equal* lights, one from the sun the other from the insect, the latter's spectrum terminates both at an upper and a lower limit at which the solar light is still conspicuous. The conclusion follows that the insect spectrum is lacking in the rays of red luminosity and presumably in the infra-red rays, usually of relatively great heat; or that it seems probable that we have here *light without heat*, other than that heat which the luminosity itself comprises and which is but another name for the same energy.

Any other supposition would apparently involve the hypothesis that the spectrum, which we have seen end at the red, has a renewal in the invisible infra-red where the main portion of the solar heat and that of all ordinary illuminants is known to exist. Although this last hypothesis cannot be considered to have much weight, and though we are led to agree with previous observers that it may be assumed with much probability that the ordinary invisible heat would, if we had means to observe it, be found unassociated with the fire-fly's light, yet this assumption is itself far from being proof, and in view of the great importance of the conclusions in question, we shall now try whether it be possible to settle the point by thermal measures with the bolometer.



## PART II.—THERMAL OBSERVATIONS.

To give an idea of the amount of heat at our disposition for experiment, and of the actual minuteness of the radiation which proceeds from even the most luminous tropical insect, we may say that if that rate of radiation from a lampblack surface 1 square centim. in area, which represents the amount of heat necessary to raise 1 grm. of water  $1^{\circ}$  C. in 1 minute (*i. e.* one small calorie), be taken as unity, then the luminous radiation of the fire-fly's heat per square centim. of exposed luminous surface, as we have found, is about 0.0004 calorie in 10 seconds, and the total luminous radiation from the most powerfully illuminating light-spot of the insect (the abdominal one) will not exceed 0.00007 calorie in the same time. But a small portion of this could fall upon the bolometer, and that which actually reached it during the time (10 seconds) required for each observation was sufficient only to affect an ordinary mercurial thermometer having a bulb 1 centim. in diameter by rather less than  $0^{\circ}0000023$ , or by less than  $\frac{1}{400000}$  of one degree Centigrade.

We have just mentioned that the total amount of heat-radiation upon which we have to make our investigation represents less than  $\frac{7}{100000}$  calorie, while that portion of this which falls upon the apparatus would, in the time of one operation, only raise the temperature of an ordinary mercurial thermometer by less than  $\frac{1}{400000}$  degree; and we have first to notice the difficulty that in case invisible heat exists in company with the light (and it certainly does exist in ordinary emanations from the surface of any living creature independent of phosphorescence), we have in this minute radiation heat of two different kinds, both invisible, and which it is yet indispensable for us to discriminate.

We are helped to do this by the consideration that while the insect, like any non-luminous one, must emit "animal heat" from all its surface, its general surface-temperature is certainly low, since it feels cold to the hand, whose greater warmth excites it to shine. This heat, then, corresponds to a temperature much below  $50^{\circ}$  C.; and such temperatures must, as we have shown in other memoirs, be accompanied by the emission of waves whose length relegates them to quite another spectral region to that in which the invisible heat associated with light mainly appears. We can then discriminate the rays of this invisible "animal" heat without the formation of a heat-spectrum, by their inability to pass through a glass which transmits with comparative freedom radiant heat whose wave-length is less than  $3\mu$ , the latter including the region

where, if there be invisible heat radiated with the light, it must mainly lie.

The heat in the spectral region of the infra-red we are considering we know in advance must be, if it bear any sort of relation to the light, almost immeasurably small; and, in fact, it defied at first all attempts to obtain not merely a quantitative measurement, but even any certain experimental evidence of its existence. At last, upon July 24, with the arrival of a new stock of over two dozen insects, and with the aid of experience derived from previous failures, these heat-measures were resumed. For the first described, the thoracic light is taken.

The insect was placed 125 centim. from the mirror of 25.4 centim. aperture and 73.4 centim. focus, so that its image was formed at 178 centim. and enlarged about 1.42 diameter, when a small portion of it filled an aperture equal to the bolometer employed, which was selected from the most sensitive of those used in previous researches in lunar heat, and had an aperture of 19 square millim. By the preceding arrangement of the mirror an image of one of the thoracic bright spots, with enough of the surrounding body to represent an area of about 13 square millim., was enlarged to nearly the surface of the bolometer.

Employing all the precautions taught by a multiplied experience, we obtained by a series of exposures of the bolometer to the insect-radiation a series of small but real galvanometer-deflexions which represent the excess of total heat-radiations from the insect over those from a metal plate of a temperature of about 25° C. forming the background. These heat-radiations come jointly from the luminous spot (area 3 to 4 square millim.), and about 9 square millim. of the surrounding body. To determine their characters, we interposed a sheet of glass\* which cut off all the observed heat. The heat from the luminous spectrum and from a spectral region below it extending to about 3" (30,000 tenth-meters) was known to be capable of passing through this glass. The evidence, then, is that there is no heat in the spectrum below this feeble radiation from the luminous thoracic region sufficient to be capable of affecting the apparatus, though this was so sensitive as to promptly respond to the feeble body-radiation from the somewhat larger section of the luminous and non-luminous surface.

#### *Continuation on Abdominal Heat.*

The insect's light, then, is unaccompanied (in the specimen

\* Described in the memoir "On the Temperature of the Surface of the Moon," Mem. Nat. Acad. of Sciences, vol. iii., as "B."

subject to this experiment) by any measurable heat ; but to make it still more evident that this is due to the absence of heat below the red (body-heat not being in question), we now proceed to take an artificial flame, occupying the same area as the radiating luminous part of the insect, and to see whether heat is observed in it. If the flame be no brighter than the insect, and the heat be nevertheless observed in it when in the insect heat is lacking, it is obvious that in the latter case none is observed, because (sensibly) none is emitted ; and this conclusion is reached, *à fortiori*, when the flame-light is less than that of the insect.

July 27.—Through a circular aperture 2·5 millim. in diameter there were passed alternately the total radiant heat and that transmitted by glass from a nearly non-luminous Bunsen-flame whose luminosity was very much *fainter* than that from the insects. On this day there seemed to be an exceedingly minute deflexion averging  $\frac{1}{4}$  of one division of the galvanometer-scale from the total radiation of an equal portion of the abdominal light-spot of the insect, while from the flame there was a mean deflexion of 177·5 divisions, showing that the total heat-radiation from an equal area of a less luminous flame was many hundred times that from the luminous area of the insect.

Glass being interposed, the heat due to this flame-radiation fell to 14·5 divisions, or about 8 per cent. of the original radiation, showing that of the quality of Bunsen-flame heat immediately in question (that above 3" transmissible by glass) there was still something like 60 times that of the combined body and luminous radiation of the insect in the far less luminous flame. Subsequently, by the use of a lens giving greater concentration, measurable indications of insect-radiation above 3", and therefore distinct from any possible body-heat, were obtained through glass, showing the flame-radiation of this quality from an equal area of the same intrinsic brilliancy, *i. e. invisible* heat and of long wave-length, but shorter than 3", to be about 400 times that of the insect.

These experiments were repeated with different luminous flames and with different insects on succeeding days. In some of them especially luminous insect specimens were secured, which, with favourable conditions of the galvanometer, gave very measurable deflexions on the latter. By a similar use of the glass to that described, it appeared that flames whose intrinsic brilliancy is nearly comparable to that of a point below the middle of the candle-flame, and whose total brilliancy is as exactly as possible comparable to that of the insect, give several hundred times the heat of the latter, even if we consider only that quality of heat which is found above 3",



while if we compare the total radiations (*i. e.* those directly observed without the use of the glass) the contrast is still stronger.

It follows that the insect-light is accompanied by approximately one four-hundredth part of the heat which is ordinarily associated with the radiation of flames of the luminous quality of those which were the subject of experiment. This value is confirmed by other methods which we do not give here. It will conduce to a clearer comprehension of this if we exhibit in a series of curves derived from our observations the spectral distribution of one unit of energy in the gas-flame spectrum (diagram 4, fig. 1); of the electric-arc spectrum (fig. 2); of the sun (fig. 3); and of the insect (fig. 4). In all these the abscissæ are the same, the portion between  $0^{\mu}4$  and  $0^{\mu}7$  (violet to red) showing the part of the energy utilized in light, while that from  $0^{\mu}7$  to  $3^{\mu}$  shows the part wasted as invisible heat. The energy in each case being the same, the areas are the same, except that owing to the relative importance of the light heat-curve (fig. 4), only about  $\frac{1}{20}$  of the latter can be shown in the limits of the plate.

The curves in fig. 3 deal with luminous intensity only, and give no means of drawing those economic conclusions which appear to follow from our experiments, and which the curves in diagram 4 supply. These curves all exhibit the spectrum on the normal scale, from that easily visible, lying between  $0^{\mu}4$  in the violet and  $0^{\mu}7$  in the red, then to  $3^{\mu}$  near the limit of the glass-transmission. In the case of the first three, representing spectra of the gas-flame, the electric arc, and the sun, nearly all the energy lies above  $3^{\mu}$ ; in that of the gas-flame a considerable portion lies below  $3^{\mu}$  (and still more in that of the candle-flame, if that were shown, where most of the energy would lie below  $3^{\mu}$  or outside the limits of the drawing). The curves then, we repeat, represent equal amounts of energy (which without sensible error we may assume to be all exhibited as *heat*) and enclose equal areas.

The total area represents in each case the expenditure of a unit of cost in thermal energy, the area between  $0^{\mu}4$  and  $0^{\mu}7$ , the proportion of this utilized as *light*; though, as we have just stated, in the case of fig. 4, the representative of the fire-fly spectrum, only a fraction of this can be shown (owing to the limits of the drawing).

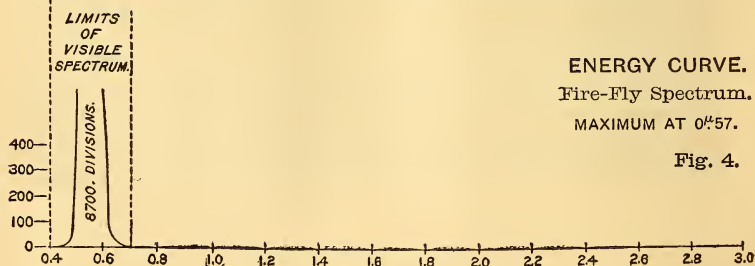
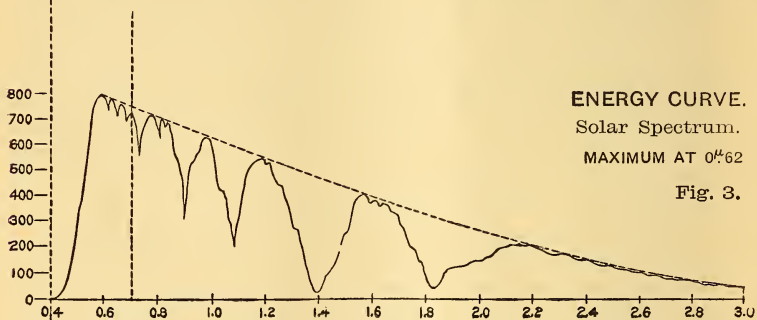
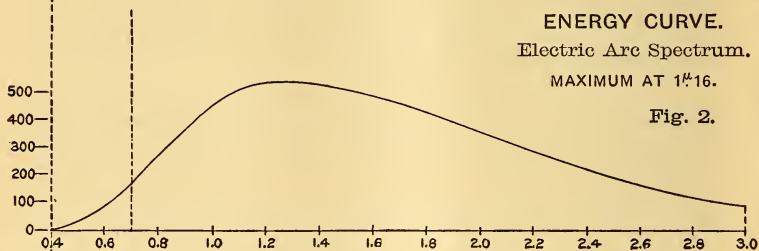
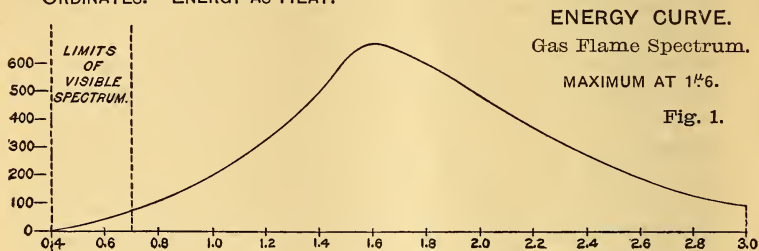
Resuming, then, what we have said, we repeat that nature produces this cheapest light at about one four-hundredth part of the cost of the energy which is expended in the candle-flame, and at but an insignificant fraction of the cost of the electric light or the most economic light which has yet been



## Diagram 4.

Four Curves of Equal Areas, showing one unit of heat displayed successively in heat spectrum of Gas, Electric Arc, Sun and Fire-Fly.

ABSCISSAE. — WAVE LENGTHS.  
ORDINATES. — ENERGY AS HEAT.



devised ; and that, finally, there seems to be no reason why we are forbidden to hope that we may yet discover a method (since such a one certainly exists and is in use on the small scale) of obtaining an enormously greater result than we now do from our present ordinary means for producing light.

# APPENDIX.

*Determination, in Calories, of the Heat in the Luminous (Abdominal) Radiation of Pyrophorus noctilucus.*

The determination is reached by two steps :—(1) The calibration of the galvanometer, so as to give the value of its division in calories ; and (2) the inference from the observed deflexion in divisions of the total of calories radiated.

(1) The bolometer, whose face occupied 0.19 square centim. (*a*), gave a deflexion of 342 divisions (*b*), at a distance of 25 centim. (*r*) from a 5 centim. circular aperture filled by a blackened Leslie cube. Seen from the centre of this aperture, the bolometer occupied then  $\frac{a}{2\pi r^2} = 0.0000484$  of the hemisphere, and would have received this fraction of the total radiation, except that, being placed exactly opposite the radiating surface, more than the mean radiation fell on it in a proportion which calculation shows to be about  $\frac{1}{3}$ . The fraction of the total radiation which it actually received, then, was 0.0000645 (*c*).

Accordingly the total radiation would have caused a deflexion  $\frac{b}{c} = 5,300,000$  divisions.

The surface of the cube was at a temperature of 99° C., and was limited by the diaphragm to an area of 19.6 square centim. (*d*). The total radiation from one centimetre, then, would have caused a deflexion of  $\frac{b}{cd} = 270,400$  div. The temperature of the bolometer, which was that of the apartment, was 20° C. According to Dulong and Petit's law, the radiation from such a surface at 99° C. to one at 20° C. would be 1.11 cal. per minute (*e*), which does not greatly differ from our own independent determinations; and for 10 sec. = 0.167 min. (*f*) (the time of the galvanometer-swing) it equals 0.185 cal. (*ef*). Hence  $\frac{b}{cdef} = \frac{270400}{0.185} = 1462000$  div. is the potentiality of work in 1 calorie, to be expressed in the swing of the galvanometer-needle, and 1 div. = 0.000000684 cal.

(2) The galvanometer received the fire-fly radiation through a lens which occupied 0·00655 of a hemisphere, and would have transmitted this fraction of the total heat except for its position, which caused it to transmit  $\frac{1}{3}$  more than the average, which is 0·00873 (*g*). The measured radiation from this fractional part gave 0·84 div. (*h*), and  $\frac{h}{g} = 96\cdot2$  div. is the deflexion which would be given by the total abdominal emission, or

$$96\cdot2 \times 0\cdot000000684 = 0\cdot0000658 \text{ cal.}$$

Since the luminous surface has an area of about  $\frac{1}{6}$  square centim., this corresponds to a radiation of 0·00039 per square centim. of radiating surface in the time of the galvanometer-needle's swing, or to  $\frac{0\cdot0004}{f} = 0\cdot0024$  cal. per square centim. per minute.

(Taking the water-equivalent of the bulb of an ordinary mercurial thermometer 1 centim. in diameter at 0·25 gr., we find

$$\frac{0\cdot84 \times 0\cdot000000684}{0\cdot25} = 0\cdot0000023,$$

showing that if such a thermometer were placed in the position occupied by the bolometer, its rise during the time of the latter's exposure to the radiation of the insect would be between two and three one-millionths of a Centigrade degree.)

## XXXII. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 200.]

June 18, 1890.—Dr. A. Geikie, F.R.S., President,  
in the Chair.

THE following communications were read:—

1. "The Borrowdale Plumbago, its Mode of Occurrence and probable Origin." By J. Postlethwaite, Esq., F.G.S.

After giving details of the mode of occurrence of the plumbago of Borrowdale in veins traversing diabase and diorite, which break through the Volcanic Series of Borrowdale, the author refers to the modes of occurrence of plumbago in other regions, and contrasts these with the surroundings of the Lake-District masses. He points out that many thousand feet of volcanic rock supervened between the Borrowdale plumbago-bearing rocks and the overlying carbonaceous shales of Silurian age. On the other hand, he finds similarities between the containing rocks in Borrowdale and the diamond-

bearing rocks of South Africa, and considers that the conditions under which the plumbago was formed in the Lake District approached much more closely to those which gave rise to the Kimberley diamonds than to those which originated the plumbago deposits in North America, though there is great dissimilarity in the chemical composition of the intrusive rocks in the two cases, especially with regard to the quantity of magnesia present. He suggests that the molten magma in its upward course passed through a deep-seated stratum of highly carbonaceous material, and tore off numerous fragments, the bituminous matter in which became acted upon by heat, a further alteration being subsequently caused by the intrusion of the diorite.

2. "Notes on the Valley-Gravels about Reading, with especial reference to the Palæolithic Implements found therein." By O. A. Shrubsole, Esq., F.G.S.

The following deposits containing implements are described :—

A. *North of the Thames.*

- (i) Gravel at Toot's Farm, Caversham ; 235 feet above sea-level.
- (ii) Clayey gravel by side of Henley Road, Caversham ; 168 feet above sea-level.
- (iii) Subangular gravel at Shiplake ; 200 feet above sea-level.

B. *South of the Thames.*

- (i) Gravel at Elm Lodge Estate, Reading ; 197 feet above sea-level.
- (ii) Gravel on disturbed beds at Redlands ; 157 feet above sea-level.
- (iii) Comminuted flinty gravel at Southern Hill ; 223 feet above sea-level.
- (iv) Gravel at Sonning Hill ; 185 feet above sea-level.
- (v) Gravel at Ruscombe, Twyford ; 165–170 feet above sea-level.

The author concludes that the highest gravels (235–280 feet above sea-level) do not, so far as is known, contain any traces of man, and that a considerable amount of valley-erosion occurred before the deposition of the earliest gravels which have furnished human relics. Further, he considers that the deposits indicate the occurrence of a severe climate at an early stage, and its recurrence at a later one, viz. during the deposition of the gravels found at a height of 197 feet and 144 feet respectively above the sea-level. He believes that many of the implements found in the lower levels at Reading have been derived from gravels of various dates and different levels, which have been swept away by denudation, and that this will account for the mixed character of the types of implements.



XXXIII. *Intelligence and Miscellaneous Articles.*

## ON THE THEORY OF THE OSCILLATORY DISCHARGE.

BY PROF. J. STEFAN.

THE theory of the oscillatory discharge of a Leyden jar has been developed by Sir William Thomson and Kirchhoff. It gives for the intensity of the current of the discharge an equation which agrees with that for the motion of a pendulum in a resisting medium. In developing the theory it was assumed that the discharge-current fills the entire section of the discharging wire with uniform density. With very rapidly succeeding currents this supposition is far from the reality. In such cases the motion of the electricity in metallic conductors is almost entirely restricted to a thin layer on the surface of the conductor.

The theory may be developed by taking into account this unequal division of the current. The result is essentially that an oscillatory discharge is always made up of two motions, one of which is extinguished much earlier than the other. It is the latter which, as the time increases, acquires the character of a pendulum motion. The amplitudes diminish, however, much more rapidly according to the new theory than according to the old one.

In so far as the influence of the resistance on the time of oscillation of this motion is small, the new theory gives a formula for it analogous with the earlier one, excepting that, instead of the coefficient of self-induction of the wire, we have that of the induction on a filament in the surface. In consequence of this the time of vibration is independent of the magnetic condition of the discharging wire, and is therefore almost as large for an iron wire as for a copper one, while according to the older theory it is found to be many times greater for the former.

The interposition of a break in the circuit might cause a still greater deviation from the pendulum motion than that indicated by theory. Such a deviation has the effect that the discharge-circuit on a conductor connected with it also induces electrical movements in another, even when the time of vibration of the latter is quite different from the time of oscillation of the exciting discharge, and when therefore a true resonance is excluded.

This motion experiences also an increase if the induction-impulse is repeated in a favourable time, that is in one corresponding to the special vibrations of the conductor, for instance in consequence of a reflexion at the end of the inducing wire. The observations made by Sarasin and De la Rive may be referred to this.

Electricity in motion shows much more markedly than in other phenomena the property of inertia. This discharge is often compared with the oscillations of a liquid in two communicating tubes. Such a comparison affords only an image of the phenomenon which is difficult of observation. A wider significance may, however, be ascribed to it. The energy which corresponds to the difference in

height of the liquid in the tubes is changed during the equalization into *vis viva* of the liquid. This may again be transformed into energy of the original kind, so that the fresh difference in height has the opposite position to the former. In the convertibility of the two energies into each other is found the reason of the vibratory motion which would otherwise be conceived to be due to inertia. If, owing to friction, part of the energy is transformed into heat, which is not convertible, the amplitudes of the vibrations are continually slower. The motion is as if the liquid had not complete inertia.

To the difference of potentials between the plates of a charged condenser an electrical energy corresponds. If the plates are connected by a wire, part of this energy is converted into heat, owing to resistance; the rest is again changed into another energy, which, as the fact of the oscillating discharge shows, may again be transformed into an electrostatic one, in such a manner that a difference of potential is established in the condenser opposite to the original one. The question is, of what value is this energy? In the special case in which the discharging wire is passed spirally round an iron core, the nature of the greatest part of this energy is known. It is the magnetic energy which is accumulated in the magnetized iron during the equalization of the discharge, and which after the equalization is complete still maintains a current in the same direction, and charges the condenser afresh, but in the opposite direction. It is simplest, even in case there is no magnetic core, to conceive this energy as a magnetic one which has its seat in the magnetization of the medium in which the discharge takes place. This assumption is sufficient also for establishing the laws of electrodynamic induction.—*Wiener Sitzungsberichte*, June 12, 1890.

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#### CALORIMETRICAL OBSERVATIONS ON THE DISENGAGEMENT OF HEAT AND LIGHT IN ELECTRICAL DISCHARGES. BY G. STAUB.

The author determines the ratio  $N$  of the total energy  $E$  emitted by a gas to that which is perceived as light  $L$ . With this view he introduces a Geissler's tube into an ice-calorimeter from the bottom of which the mercury is removed. The ice and water transmit all the rays of light and only absorb those of heat; he then blackens the Geissler tube, and thus retains the visible rays also in the ice-calorimeter. If the quantity of heat in the first case is  $Q$  and in the second  $E$ ,  $L = E - Q$ .

The width of the Geissler tube was altered as well as the pressure in it, and condensers and also breaks were interposed in the circuit. The results of the experiment were as follows.

With the help of electrical discharges in Geissler tubes, light of considerably greater useful effect may be obtained than in the glow-lamp. The maximum for one of Blattner's was 10 per cent., and for a Geissler tube with condensers 32.8 per cent. The useful

effect increases with the density and quantity of electricity which passes through the tube. It decreases as the pressure and diameter of the capillary tube increases. If the Geissler tube is filled with hydrogen, the optical effect is less than in air, other things being equal.

These results agree with the experiments on glow-lamps and flames, in so far that the higher the temperature the higher in general is the useful effect.—*Beiblätter der Physik*, vol. xiv. p. 538.

#### OBSERVATIONS ON ATMOSPHERIC ELECTRICITY IN THE TROPICS.

BY PROF. F. EXNER.

The present paper forms the conclusion of a former one which appeared under the same title (*Phil. Mag.* vol. xxix. p. 520), and gives a complete discussion of the measurements contained in the latter. The connexion between fall of potential and vapour-pressure, which the author found to exist in our regions, is also fully confirmed for the tropics, so that we may now regard the electrical constants of the earth as determined with great certainty. The quantity of electricity which is found in a column of a square centimetre base above the earth's surface is, including the charge of the latter,  $-0.0038$  absolute electrostatic units. The total charge  $Q$  of the earth is,  $Q = -2 \times 10^{18}$  in the same units, and its potential  $V$  referred to a point in space is  $-9 \times 10^9$  volt. A further fact now fully established is that the sign of the normal fall of potential in the tropics is the same as with us, that is positive. Only few observations could be made as to the change of fall of potential with height, yet this showed distinctly an increase as required by theory.

The daily period of atmospheric electricity is decidedly less pronounced in the tropics than with us, which is probably connected with the extraordinary constancy of the weather. On most days maxima could not be observed.—*Wiener Berichte*, July 10, 1890.

#### INVESTIGATION OF ELECTRICAL VIBRATIONS WITH THERMO-ELEMENTS. BY DR. IGNATIUS KLEMENCIC.

The author investigated Hertz's vibrations by the help of a thermoelement soldered between the ends of the secondary inductor. By using two such inductors, one of which served as standard while the other was moved about in the space affected, it was possible to measure the distribution of energy in a ray proceeding from the primary mirror, and at right angles to it. The factor of condensation of a secondary mirror was further measured for two different pairs of primary conductors, and was found to be 7 for a pair made exactly according to Hertz's directions, and equal to 2.7 for a pair twice as long. The mirrors were exactly of the dimensions mentioned by Hertz.—*Wiener Berichte*, July 17, 1890.



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XXXIV. *On the Theory of Surface Forces.*

*By* Lord RAYLEIGH, *Sec. R.S.\**

SINCE the time of Young the tendency of a liquid surface to contract has always been attributed to the mutual attraction of the parts of the liquid, acting through a very small range,—to the same forces in fact as those by which the cohesion of liquids and solids is to be explained. It is sometimes asserted that Laplace was the first to look at the matter from this point of view, and that Young contented himself with calculations of the *consequences* of superficial tension. Such an opinion is entirely mistaken, although the authority of Laplace himself may be quoted in its favour†. In the introduction to his first paper‡, which preceded the work of Laplace, Young writes :—"It will perhaps be more agreeable to the experimental philosopher, although less consistent with the strict course of logical argument, to proceed in the first place to the comparison of this theory [of superficial tension] with the phenomena, and to inquire afterwards for its foundation in the ultimate properties of matter." This he attempts to do in Section VI., which is headed *Physical Foundation of*

\* Communicated by the Author.

† *Méc. Cél. Supplément au X<sup>e</sup> livre*, 1805 :—"Mais il n'a pas tenté, comme Segner, de dériver ces hypothèses, de la loi de l'attraction des molécules, décroissante avec une extrême rapidité; ce qui était indispensable pour les réaliser."

‡ "On the Cohesion of Fluids," *Phil. Trans.* 1805.

*Phil. Mag.* S. 5. Vol. 30. No. 185. Oct. 1890.



*the Law of Superficial Cohesion.* The argument is certainly somewhat obscure ; but as to the character of the "physical foundation" there can be no doubt. "We may suppose the particles of liquids, and probably those of solids also, to possess that power of repulsion, which has been demonstrably shown by Newton to exist in æriform fluids, and which varies in the inverse ratio of the distance of the particles from each other. In air and vapours this force appears to act uncontrolled ; but in liquids it is overcome by a cohesive force, while the particles still retain a power of moving freely in all directions. . . . It is simplest to suppose the force of cohesion nearly or perfectly constant in its magnitude, throughout the minute distance to which it extends, and owing its apparent diversity to the contrary action of the repulsive force which varies with the distance."

Although nearly a century has elapsed, we are still far from a satisfactory theory of these reactions. We know now that the pressure of gases cannot be explained by a repulsive force varying inversely as the distance, but that we must appeal to the impacts of colliding molecules\*. There is every reason to suppose that the molecular movements play an important part in liquids also ; and if we leave them out of account, we can only excuse ourselves on the ground of the difficulty of the subject, and with full recognition that a theory so founded is probably only a first approximation to the truth. On the other hand, the progress of science has tended to confirm the views of Young and Laplace as to the existence of a powerful attraction operative at short distances. Even in the theory of gases it is necessary, as Van der Waals has shown, to appeal to such a force in order to explain their condensation under increasing pressure in excess of that indicated by Boyle's law, and explicable by impacts. Again, it would appear that it is in order to overcome this attraction that so much heat is required in the evaporation of liquids.

If we take a statical view of the matter, and ignore the molecular movements†, we must introduce a repulsive force to compensate the attraction. Upon this point there has been a good deal of confusion, of which even Poisson cannot be acquitted. And yet the case seems simple enough. For consider the equilibrium of a spherical mass of mutually attracting matter, free from external force, and conceive it divided by

\* The argument is clearly set forth in Maxwell's lecture "On the Dynamical Evidence of the Molecular Constitution of Bodies" (Nature, vol. xi. p. 357, 1875).

† Compare Worthington, "On Surface Forces in Fluids," Phil. Mag. xviii. p. 334 (1884).

an ideal plane into hemispheres. Since the hemispheres are at rest, their total action upon one another must be zero, that is, no force is transmitted across the interface. If there be attraction operative across the interface, it must be precisely compensated by repulsion. This view of the matter was from the first familiar to Young, and he afterwards gave calculations, which we shall presently notice, dependent upon the hypothesis that there is a constant attractive force operative over a limited range and balanced by a repulsive force of suitable intensity operative over a different range. In Laplace's theory, upon the other hand, no mention is made of repulsive forces, and it would appear at first as if the attractive forces were left to perform the impossible feat of balancing themselves. But in this theory there is introduced a pressure which is really the representative of the repulsive forces.

It may be objected that if the attraction and repulsion must be supposed to balance one another across any ideal plane of separation, there can be no sense, or advantage, in admitting the existence of either. This would certainly be true if the origin and law of action of the forces were similar, but such is not supposed to be the case. The inconclusiveness of the objection is readily illustrated. Consider the case of the earth, conceived to be at rest. The two halves into which it may be divided by an ideal plane do not upon the whole act upon one another; otherwise there could not be equilibrium. Nevertheless no one hesitates to say that the two halves attract one another under the law of gravitation. The force of the objection is sometimes directed against the pressure, denoted by  $K$ , which Laplace conceives to prevail in the interior of liquids and solids. How, it is asked, can there be a pressure, if the whole force vanishes? The best answer to this question may be found in asking another—Is there a pressure in the interior of the earth?

It must no doubt be admitted that in availing ourselves of the conception of pressure we are stopping short of a complete explanation. The mechanism of the pressure is one of the things that we should like to understand. But Laplace's theory, while ignoring the movements and even the existence of molecules, cannot profess to be complete; and there seems to be no inconsistency in the conception of a continuous, incompressible liquid, whose parts attract one another, but are prevented from undergoing condensation by forces of infinitely small range, into the nature of which we do not further inquire. All that we need to take into account is then covered by the ordinary idea of pressure. However imperfect a theory developed on these lines may be, and indeed must be, it pre-

sents to the mind a good picture of capillary phenomena, and, as it probably contains nothing not needed for the further development of the subject, labour spent upon it can hardly be thrown away.

Upon this view the pressure due to the attraction measures the cohesive force of the substance, that is the tension which must be applied in order to cause rupture. It is the quantity which Laplace denoted by  $K$ , and which is often called the molecular pressure. Inasmuch as Laplace's theory is not a molecular theory at all, this name does not seem very appropriate. Intrinsic pressure is perhaps a better term, and will be employed here. The simplest method of estimating the intrinsic pressure is by the force required to break solids. As to liquids, it is often supposed that the smallest force is adequate to tear them asunder. If this were true, the theory of capillarity now under consideration would be upset from its foundations, but the fact is quite otherwise. Berthelot\* found that water could sustain a tension of about 50 atmospheres applied directly, and the well-known phenomenon of retarded ebullition points in the same direction. For if the cohesive forces which tend to close up a small cavity in the interior of a superheated liquid were less powerful than the steam-pressure, the cavity must expand, that is the liquid must boil. By supposing the cavity infinitely small, we see that ebullition must necessarily set in as soon as the steam† pressure exceeds that intrinsic to the liquid. The same method may be applied to form a conception of the intrinsic pressure of a liquid which is not superheated. The walls of a moderately small cavity certainly tend to collapse with a force measured by the constant surface-tension of the liquid. The pressure in the cavity is at first proportional to the surface-tension and to the curvature of the walls. If this law held without limit, the consideration of an infinitely small cavity shows that the intrinsic pressure would be infinite in all liquids. Of course the law really changes when the dimensions of the cavity are of the same order as the range of the attractive forces, and the pressure in the cavity approaches a limit, which is the intrinsic pressure of the liquid. In this way we are forced to admit the reality of the pressure by the consideration of experimental facts which cannot be disputed.

The first estimate of the intrinsic pressure of water is doubtless that of Young. It is 23,000 atmospheres, and agrees

\* *Ann. de Chimie*, xxx. p. 232 (1850). See also Worthington, Brit. Assoc. Report, 1888, p. 583.

† If there be any more volatile impurity (*e.g.* dissolved gas) ebullition must occur much earlier.



extraordinarily well with modern numbers. I propose to return to this estimate, and to the remarkable argument which Young founded upon it.

The first great advance upon the theory of Young and Laplace was the establishment by Gauss of the principle of surface-energy. He observed that the existence of attractive forces of the kind supposed by his predecessors leads of necessity to a term in the expression of the potential energy proportional to the surface of the liquid, so that a liquid surface tends always to contract, or, what means precisely the same thing, exercises a tension. The argument has been put into a more general form by Boltzmann\*. It is clear that all molecules in the interior of the liquid are in the same condition. Within the superficial layer, considered to be of finite but very small thickness, the condition of all molecules is the same which lie at the same very small distance from the surface. If the liquid be deformed without change in the total area of the surface, the potential energy necessarily remains unaltered; but if there be a change of area the variation of potential energy must be proportional to such change.

A mass of liquid, left to the sole action of cohesive forces, assumes a spherical figure. We may usefully interpret this as a tendency of the surface to contract; but it is important not to lose sight of the idea that the spherical form is the result of the endeavour of the parts to get *as near to one another* as is possible†. A drop is spherical under capillary forces for the same reason that a large gravitating mass of (non-rotating) liquid is spherical.

In the following sketch of Laplace's theory we will commence in the manner adopted by Maxwell‡. If  $f$  be the distance between two particles  $m, m'$ , the cohesive attraction between them is denoted in Laplace's notation by  $m m' \phi(f)$ , where  $\phi(f)$  is a function of  $f$  which is insensible for all sensible values of  $f$ , but which becomes sensible and even enormously great, when  $f$  is exceedingly small.

"If we next introduce a new function of  $f$  and write

$$\int_f^\infty \phi(f) df = \Pi(f), \quad . \quad . \quad . \quad . \quad (1)$$

then  $m m' \Pi(f)$  will represent (1) the work done by the

\* Pogg. *Ann.* cxli. p. 582 (1870). See also Maxwell's 'Theory of Heat,' 1870; and article "Capillarity," *Enc. Brit.*

† See Sir W. Thomson's lecture on Capillary Attraction (Proc. Roy Inst. 1886), reprinted in 'Popular Lectures and Addresses.'

‡ *Enc. Brit.*, "Capillarity."



attractive force on the particle  $m$ , while it is brought from an infinite distance from  $m'$  to the distance  $f$  from  $m'$ ; or (2) the attraction of a particle  $m$  on a narrow straight rod resolved in the direction of the length of the rod, one extremity of the rod being at a distance  $f$  from  $m$ , and the other at an infinite distance, the mass of unit of length of the rod being  $m'$ . The function  $\Pi(f)$  is also insensible for sensible values of  $f$ , but for insensible values of  $f$  it may become sensible and even very great."

"If we next write

$$\int_z^\infty \Pi(f) f df = \psi(z), \quad . . . . . (2)$$

then  $2\pi m\sigma\psi(z)$  will represent (1) the work done by the attractive force while a particle  $m$  is brought from an infinite distance to a distance  $z$  from an infinitely thin stratum of the substance whose mass per unit of area is  $\sigma$ ; (2) the attraction of a particle  $m$  placed at a distance  $z$  from the plane surface of an infinite solid whose density is  $\sigma$ ."

The intrinsic pressure can now be found immediately by calculating the mutual attraction of the parts of a large mass which lie on opposite sides of an imaginary plane interface. If the density be  $\sigma$ , the attraction between the whole of one side and a layer upon the other distant  $z$  from the plane and of thickness  $dz$  is  $2\pi\sigma^2\psi(z)dz$ , reckoned per unit of area. The expression for the intrinsic pressure is thus simply

$$K = 2\pi\sigma^2 \int_0^\infty \psi(z) dz. \quad . . . . . (3)$$

In Laplace's investigation  $\sigma$  is supposed to be unity. We may call the value which (3) then assumes  $K_0$ , so that

$$K_0 = 2\pi \int_0^\infty \psi(z) dz. \quad . . . . . (4)$$

The expression for the superficial tension is most readily found with the aid of the idea of superficial energy, introduced into the subject by Gauss. Since the tension is constant, the work that must be done to extend the surface by one unit of area measures the tension, and the work required for the generation of any surface is the product of the tension and the area. From this consideration we may derive Laplace's expression, as has been done by Dupré\* and Thomson†. For imagine a small cavity to be formed in the interior of the

\* *Théorie Mécanique de la Chaleur* (Paris, 1869).

† "Capillary Attraction," *Proc. Roy. Inst.* Jan. 1886. Reprinted, 'Popular Lectures and Addresses,' 1889.

mass and to be gradually expanded in such a shape that the walls consist almost entirely of two parallel planes. The distance between the planes is supposed to be very small compared with their ultimate diameters, but at the same time large enough to exceed the range of the attractive forces. The work required to produce this crevasse is twice the product of the tension and the area of one of the faces. If we now suppose the crevasse produced by direct separation of its walls, the work necessary must be the same as before, the initial and final configurations being identical; and we recognize that the tension may be measured by half the work that must be done per unit of area against the mutual attraction in order to separate the two portions which lie upon opposite sides of an ideal plane to a distance from one another which is outside the range of the forces. It only remains to calculate this work.

If  $\sigma_1, \sigma_2$  represent the densities of the two infinite solids, their mutual attraction at distance  $z$  is per unit of area

$$2\pi\sigma_1\sigma_2\int_z^\infty \psi(z) dz, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or  $2\pi\sigma_1\sigma_2\theta(z)$ , if we write

$$\int_z^\infty \psi(z) dz = \theta(z). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The work required to produce the separation in question is thus

$$2\pi\sigma_1\sigma_2\int_0^\infty \theta(z) dz; \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and for the tension of a liquid of density  $\sigma$  we have

$$T = \pi\sigma^2\int_0^\infty \theta(z) dz. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The form of this expression may be modified by integration by parts. For

$$\int \theta(z) dz = \theta(z) \cdot z - \int z \frac{d\theta(z)}{dz} dz = \theta(z) \cdot z + \int z \psi(z) dz.$$

Since  $\theta(0)$  is finite, proportional to  $K$ , the integrated term vanishes at both limits, and we have simply

$$\int_0^\infty \theta(z) dz = \int_0^\infty z \psi(z) dz, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$T = \pi\sigma^2\int_0^\infty z \psi(z) dz. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In Laplace's notation the second member of (9), multiplied by  $2\pi$ , is represented by  $H$ .

As Laplace has shown, the values for  $K$  and  $T$  may also be expressed in terms of the function  $\phi$ , with which we started. Integrating by parts, we get by means of (1) and (2),

$$\int \psi(z) dz = z\psi(z) + \frac{1}{3}z^3\Pi(z) + \frac{1}{3}\int z^3\phi(z) dz,$$

$$\int z\psi(z) dz = \frac{1}{3}z^3\psi(z) + \frac{1}{3}z^4\Pi(z) + \frac{1}{8}\int z^4\phi(z) dz.$$

In all cases to which it is necessary to have regard the integrated terms vanish at both limits, and we may write

$$\int_0^\infty \psi(z) dz = \frac{1}{3}\int_0^\infty z^3\phi(z) dz, \quad \int_0^\infty z\psi(z) dz = \frac{1}{8}\int_0^\infty z^4\phi(z) dz; \quad (11)$$

so that

$$K_0 = \frac{2\pi}{3}\int_0^\infty z^3\phi(z) dz, \quad T_0 = \frac{\pi}{8}\int_0^\infty z^4\phi(z) dz. \quad (12)$$

A few examples of these formulæ will promote an intelligent comprehension of the subject. One of the simplest suppositions open to us is that

$$\phi(f) = e^{-\beta f}. \quad \dots \dots \dots (13)$$

From this we obtain

$$\Pi(z) = \beta^{-1}e^{-\beta z}, \quad \psi(z) = \beta^{-3}(\beta z + 1)e^{-\beta z}, \quad \dots (14)$$

$$K_0 = 4\pi\beta^{-4}, \quad T_0 = 3\pi\beta^{-5}. \quad \dots \dots \dots (15)$$

The range of the attractive force is mathematically infinite, but practically of the order  $\beta^{-1}$ , and we see that  $T$  is of higher order in this small quantity than  $K$ . That  $K$  is in all cases of the fourth order and  $T$  of the fifth order in the range of the forces is obvious from (12) without integration.

An apparently simple example would be to suppose  $\phi(z) = z^n$ . From (1), (2), (4) we get

$$\Pi(z) = -\frac{z^{n+1}}{n+1}, \quad \psi(z) = \frac{z^{n+3}}{n+3 \cdot n+1},$$

$$K_0 = \frac{2\pi z^{n+4}}{n+4 \cdot n+3 \cdot n+1} \Big|_0^\infty \dots \dots \dots (16)$$

The intrinsic pressure will thus be infinite whatever  $n$  may be. If  $n+4$  be positive, the attraction of infinitely distant parts contributes to the result; while if  $n+4$  be negative, the parts in immediate contiguity act with infinite power. For the transition case, discussed by Sutherland\*, of  $n+4=0$ ,

\* Phil. Mag. xxiv. p. 113 (1887).

$K_0$  is also infinite. It seems therefore that nothing satisfactory can be arrived at under this head.

As a third example we will take the law proposed by Young, viz.

$$\left. \begin{aligned} \phi(z) &= 1 \text{ from } z=0 \text{ to } z=a, \\ \phi(z) &= 0 \text{ from } z=a \text{ to } z=\infty; \end{aligned} \right\} \quad . \quad . \quad . \quad (17)$$

and corresponding therewith,

$$\left. \begin{aligned} \Pi(z) &= a-z \text{ from } z=0 \text{ to } z=a, \\ \Pi(z) &= 0 \text{ from } z=a \text{ to } z=\infty, \end{aligned} \right\} \quad . \quad . \quad (18)$$

$$\left. \begin{aligned} \psi(z) &= \frac{1}{2}a(a^2 - z^2) - \frac{1}{3}(a^3 - z^3) \\ &\quad \text{from } z=0 \text{ to } z=a, \\ \psi(z) &= 0 \text{ from } z=a \text{ to } z=\infty. \end{aligned} \right\} \quad . \quad . \quad (19)$$

Equations (12) now give

$$K_0 = \frac{2\pi}{3} \int_0^\infty z^3 dz = \frac{\pi a^4}{6}, \quad . \quad . \quad . \quad (20)$$

$$T_0 = \frac{\pi}{8} \int_0^a z^4 dz = \frac{\pi a^5}{40}. \quad . \quad . \quad . \quad (21)$$

The numerical results differ from those of Young\*, who finds that “the contractile force is one-third of the whole cohesive force of a stratum of particles, equal in thickness to the interval to which the primitive equable cohesion extends,” viz.  $T = \frac{1}{3}aK$ ; whereas according to the above calculation  $T = \frac{1}{20}aK$ . The discrepancy seems to depend upon Young having treated the attractive force as operative in one direction only.

In his Elementary Illustrations of the Celestial Mechanics of Laplace†, Young expresses views not in all respects consistent with those of his earlier papers. In order to balance the attractive force he introduces a repulsive force, following the same law as the attractive except as to the magnitude of the range. The attraction is supposed to be of constant intensity  $C$  over a range  $c$ , while the repulsion is of intensity  $R$ , and is operative over a range  $r$ . The calculation above given is still applicable, and we find that

$$\left. \begin{aligned} K &= \frac{\pi}{6} (c^4 C - r^4 R), \\ T &= \frac{\pi}{40} (c^5 C - r^5 R). \end{aligned} \right\} \quad . \quad . \quad . \quad (22)$$

\* *Enc. Brit.*; Collected Works, vol. i. p. 461.

† 1821. Collected Works, vol. i. p. 485.



In these equations, however, we are to treat  $K$  as vanishing, the specification of the forces operative across a plane being supposed to be complete. Hence, as Young finds, we must take

$$c^4C = r^4R; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and accordingly

$$T = \frac{\pi c^4 C (c - r)}{40}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

At this point I am not able to follow Young's argument, for he asserts (p. 490) that "the existence of such a cohesive tension proves that the mean sphere of action of the repulsive force is more extended than that of the cohesive: a conclusion which, though contrary to the tendency of some other modes of viewing the subject, shows the absolute insufficiency of all theories built upon the examination of one kind of corpuscular force alone." According to (24) we should infer, on the contrary, that if superficial tension is to be explained in this way, we must suppose that  $c > r$ .

My own impression is that we do not gain anything by this attempt to advance beyond the position of Laplace. So long as we are content to treat fluids as incompressible there is no objection to the conception of intrinsic pressure. The repulsive forces which constitute the machinery of this pressure are probably intimately associated with actual compression, and cannot advantageously be treated without enlarging the foundations of the theory. Indeed it seems that the view of the subject represented by (23), (24), with  $c$  greater than  $r$ , cannot consistently be maintained. For consider the equilibrium of a layer of liquid at a free surface  $A$  of thickness  $AB$  equal to  $r$ . If the void space beyond  $A$  were filled up with liquid, the attractions and repulsions across  $B$  would balance one another; and since the action of the additional liquid upon the parts below  $B$  is wholly attractive, it is clear that in the actual state of things there is a finite repulsive action across  $B$ , and a consequent failure of equilibrium.

I now propose to exhibit another method of calculation, which not only leads more directly to the results of Laplace, but allows us to make a not unimportant extension of the formulæ to meet the case where the radius of a spherical cavity is neither very large nor very small in comparison with the range of the forces.

The density of the fluid being taken as unity, let  $V$  be the potential of the attraction, so that

$$V = \iiint \Pi(f) \, dx \, dy \, dz, \quad . \quad . \quad . \quad . \quad (25)$$

$f$  denoting the distance of the element of the fluid  $dx dy dz$  from the point at which the potential is to be reckoned. The hydrostatic equation of pressure is then simply

$$dp = dV ;$$

or, if A and B be any two points,

$$p_B - p_A = V_B - V_A. \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Suppose, for example, that A is in the interior, and B upon a plane surface of the liquid. The potential at B is then exactly one half of that at A, or  $V_B = \frac{1}{2} V_A$ ; so that

$$\begin{aligned} p_A - p_B = \frac{1}{2} V_A &= 2\pi \int_0^{\frac{1}{2}\pi} \int_0^\infty \Pi(f) f^2 df \sin \theta d\theta \\ &= 2\pi \int_0^\infty \Pi(f) f^2 df. \end{aligned}$$

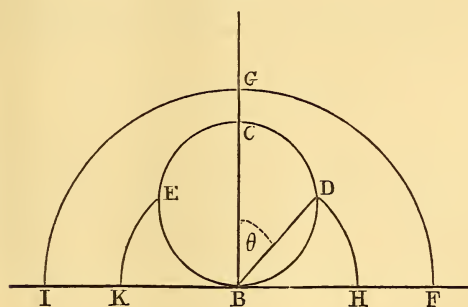
Now  $p_A - p_B$  is the intrinsic pressure  $K_0$ ; and thus

$$K_0 = 2\pi \int_0^\infty \Pi(f) f^2 df = \frac{2\pi}{3} \int_0^\infty \phi(f) f^3 df,$$

as before.

Again, let us suppose that the fluid is bounded by concentric spherical surfaces, the interior one of radius  $r$  being either large or small, but the exterior one so large that its curvature may be neglected. We may suppose that there is no external pressure, and that the tendency of the cavity to collapse is balanced by contained gas. Our object is to estimate the necessary internal pressure.

Fig. 1.



In the figure B D C E represents the cavity, and the pressure required is the same as that of the fluid at such a point as B. Since  $p_A = 0$ ,  $p_B = V_B - V_A$ . Now  $V_A$  is equal to that part of  $V_B$  which is due to the infinite mass lying below the plane B F. Accordingly the pressure required ( $p_B$ ) is the

potential at B due to the fluid which lies above the plane B F.  
Thus

$$p_B = \iiint \Pi(f) dx dy dz,$$

where the integrations are to be extended through the region above the plane B F which is external to the sphere B D C E. On the introduction of polar coordinates the integral divides itself into two parts. In the first from  $f=0$  to  $f=2r$  the spherical shells (*e. g.* D H) are incomplete hemispheres, while in the second part from  $f=2r$  to  $f=\infty$  the whole hemisphere (*e. g.* I G F) is operative. The spherical area D H, divided by  $f^2$ ,

$$= 2\pi \int_0^{\frac{1}{2}\pi} \sin \theta d\theta = 2\pi \cos \theta = \pi f/r.$$

The area GF =  $2\pi f^2$ .

Thus, dropping the suffix B, we get the unexpectedly simple expression

$$p = \frac{\pi}{r} \int_0^{2r} \Pi(f) f^3 df + 2\pi \int_{2r}^{\infty} \Pi(f) f^2 df. \quad (27)$$

If  $2r$  exceed the range of the force, the second integral vanishes and the first may be supposed to extend to infinity. Accordingly

$$p = \frac{\pi}{r} \int_0^{\infty} \Pi(f) f^3 df = \frac{2}{r} \times \frac{\pi}{8} \int_0^{\infty} f^4 \phi(f) df, \quad (28)$$

in accordance with the value (12) already given for  $T_0$ . We see then that, if the curvature be not too great, the pressure in the cavity can be calculated as if it were due to a constant tension tending to contract the surface. In the other extreme case where  $r$  tends to vanish, we have ultimately

$$p = 2\pi \int_0^{\infty} \Pi(f) f^2 df = K_0.$$

In these extreme cases the results are of course well known; but we may apply (27) to calculate the pressure in the cavity when its diameter is of the order of the range. To illustrate this we may take a case already suggested, in which  $\phi(f) = e^{-\beta f}$ ,  $\Pi(f) = \beta^{-1} e^{-\beta f}$ . Using these, we obtain on reduction,

$$p = 2\pi \beta^{-4} \left\{ \frac{3}{\beta r} - e^{-2\beta r} \left( 2\beta r + 4 + \frac{3}{\beta r} \right) \right\}. \quad (29)$$

From (29) we may fall back upon particular cases already considered. Thus, if  $r$  be very great,

$$p = \frac{2}{r} \times 3\pi \beta^{-5};$$

and if  $r$  be very small,

$$p = 4\pi\beta^{-4},$$

in agreement with (15).

In a recent memoir\* Fuchs investigates a second approximation to the tension of curved surfaces, according to which the pressure in a cavity would consist of two terms; the first (as usual) directly as the curvature, the second subtractive, and proportional to the cube of the curvature. This conclusion does not appear to harmonize with (27), (29), which moreover claim to be exact expressions. It may be remarked that when the tension depends upon the curvature, it can no longer be identified with the work required to generate a unit surface. Indeed the conception of surface-tension appears to be appropriate only when the range is negligible in comparison with the radius of curvature.

The work required to generate a spherical cavity of radius  $r$  is of course readily found in any particular case. It is expressed by the integral

$$\int_0^r p \cdot 4\pi r^2 \cdot dr. \quad . \quad . \quad . \quad . \quad (30)$$

As a second example we may consider Young's supposition, viz. that the force is unity from 0 to  $a$ , and then altogether ceases. In this case by (18),  $\Pi(f)$  absolutely vanishes, if  $f > a$ ; so that if the diameter of the cavity at all exceed  $a$ , the internal pressure is given rigorously by

$$p = \frac{2}{r} \times \frac{\pi}{8} \int_0^a f^4 \phi(f) df = \frac{2}{r} \times \frac{\pi a^5}{40}. \quad . \quad . \quad (31)$$

When, on the other hand,  $2r < a$ , we have

$$\begin{aligned} p &= \frac{\pi}{r} \int_0^{2r} (a-f) f^3 df + 2\pi \int_{2r}^a (a-f) f^2 df \\ &= \pi \left\{ \frac{a^4}{6} - \frac{4}{3} ar^3 + \frac{8}{5} r^4 \right\}, \quad . \quad . \quad . \quad . \quad (32) \end{aligned}$$

coinciding with (31) when  $2r = a$ . If  $r = 0$ , we fall back upon  $K_0 = \pi a^4/6$ .

We will now calculate by (30) the work required to form a cavity of radius equal to  $\frac{1}{2}a$ . We have

$$4\pi \int_0^{\frac{1}{2}a} p \cdot r^2 dr = \frac{\pi^2 a^7}{4} \left( \frac{1}{18} + \frac{1}{35} \right).$$

The work that would be necessary to form the same cavity,

\* *Wien. Ber. Bd. xcvi. Abth. II. a, Mai 1889.*



supposing the pressure to follow the law (31) applicable when  $2r > a$ , is

$$\int_0^{\frac{1}{2}a} \frac{2}{r} \cdot \frac{\pi a^5}{40} \cdot 4\pi r^2 dr = \frac{\pi^2 a^7}{40}.$$

The work required to generate a cavity for which  $2r > a$  is therefore less than if the ultimate law prevailed throughout by the amount

$$\frac{\pi^2 a^7}{4} \left( \frac{1}{10} - \frac{1}{18} - \frac{1}{35} \right) = \frac{\pi^2 a^7}{4 \cdot 9 \cdot 7}. \quad \dots \quad (33)$$

[To be continued.]

### XXXV. On some Problems in the Kinetic Theory of Gases.

By S. H. BURBURY, F.R.S.\*

#### Maxwell's Law of Distribution.

1. **W**HEN a gas or mixture of gases is at rest in the normal state, the distribution of velocities among the molecules may be defined thus:—Take an origin O, and let the vector velocity of each molecule be represented by a line drawn from O. Then the number per unit of volume of molecules of mass M, whose velocities are represented by lines from the origin to points within the element of volume  $dQ$  at P, is

$$N \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} e^{-hM \cdot OP^2} dQ;$$

where N is the number of molecules of mass M in unit of volume, and  $\frac{3}{2h}$  is the mean kinetic energy of a molecule.

2. I shall employ two other variables:—

Let V denote the vector velocity of the common centre of gravity of two molecules whose masses are M and  $m$ . Call this their *common velocity*.

Let R denote the velocity of M,  $r$  that of  $m$ , relative to this common centre of gravity. Then the velocity of M is the resultant of V and R, that of  $m$  is the resultant of V and  $r$ .

The relative velocity of M and  $m$  is  $R+r$ , and shall be denoted by  $\rho$ , so that

$$\frac{R}{r} = \frac{m}{M}, \quad \rho = \frac{M+m}{m} R = \frac{M+m}{M} r.$$

3. The molecules whose velocities are represented by lines

\* Communicated by the Author.

from the origin to points within the element of volume  $dQ$  at  $P$  shall be said to have velocities  $OP$  ( $dQ$ ). Or if we give to  $dQ$  any particular form, as  $\omega^2 d\omega dS$ ,  $\omega$  being  $OP$  and  $dS$  being a small solid angle, we may speak of the velocities  $OP$  ( $\omega^2 d\omega dS$ ). If  $\lambda, \mu, \nu$  be direction-cosines of the axis of a cone containing the elementary solid angle  $dS$ , we may speak of the direction  $\lambda \mu \nu dS$  as comprising all lines drawn from the vertex of that cone and falling within it; and  $\lambda \mu \nu \omega^2 d\omega dS$  as comprising all velocities between  $\omega$  and  $d\omega$  in directions within that cone.

4. In Maxwell's distribution, if we consider all pairs of molecules,  $M$  and  $m$ , having common velocity  $V$ , and relative velocity  $R+r$ , for given  $V$  all directions of  $R$  or  $r$  are equally probable.

Let  $OC = V$ ,  $POp = R+r$ ,

$$\frac{PO}{pO} = \frac{m}{M} = \frac{R}{r}.$$

If  $OC$  be given, the number of the pairs in question for which the angle  $POC$  lies between  $\theta$  and  $\theta + d\theta$  is proportional to

$$e^{-h(M \cdot PC^2 + m \cdot pC^2)} \sin \theta d\theta.$$

Now

$$\begin{aligned} M \cdot PC^2 + m \cdot pC^2 &= MR^2 + mr^2 + \overline{M+m} V^2 \\ &\quad - 2(M \cdot R - m \cdot r) V \cos \theta, \end{aligned}$$

which is independent of  $\theta$  because  $MR - mr = 0$ . The number is therefore proportional to  $\sin \theta d\theta$ , and this proves the proposition.

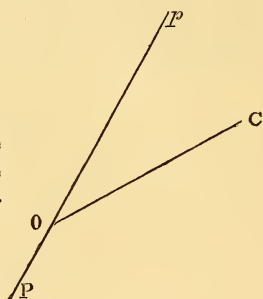
5. If the molecules behave in their mutual encounters as elastic spheres, then for given direction of the relative velocity before encounter, all directions after encounter are equally probable.

I think it unnecessary to give a proof of this proposition.

6. (a) Every distribution of velocities among the molecules which satisfies the condition that for given  $V$  all directions of  $R$  are equally probable, is undisturbed by encounters, or by the mutual action of the molecules, and is therefore, in the absence of external forces, stationary.

(b) No distribution whatever of velocities among the molecules is undisturbed by encounters, or by the mutual action of the molecules, unless it satisfies the condition that for given  $V$  all directions of  $R$  are equally probable.

Of these theorems (a) corresponds to the well-known pro-

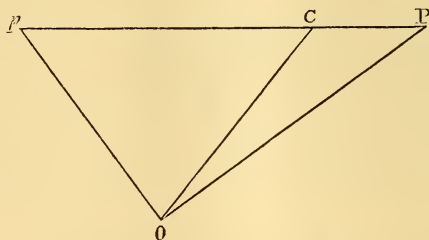


position that Maxwell's distribution is stationary. The converse (b) is founded on Boltzmann's proof (*Sitzungsberichte*, Vienna, 1872), but is much simplified by using  $V$  and  $R$  for variables.

We will prove these theorems, (a) and (b), first on the hypothesis that the molecules are to be treated as elastic spheres. We will suppose two classes of molecules having mass  $M$  and  $m$  respectively. It will be sufficient if we prove our propositions for the encounters of  $M$  with  $m$ .

Let  $\bar{F}(xyz) dx dy dz$ , or  $F dx dy dz$ , be the number per unit of volume of molecules of mass  $M$  whose velocities are represented by lines from the origin to points within the element of volume  $dx dy dz$  at  $xyz$ . Similarly  $f(x'y'z') dx' dy' dz'$ , or  $f dx' dy' dz'$ , is the corresponding number for the  $m$ 's. If  $xyz$  be denoted by  $P$ , and  $x'y'z'$  by  $p$ , we will write  $F_P$  and  $f_p$  for  $F$  and  $f$ .

Let  $C$  be the point  $\xi \eta \zeta$ . Consider all the pairs,  $M$  and  $m$ ,



which have  $OC$  for common velocity. About  $C$  as centre describe two spherical shells, one with radii  $R \dots R + dR$ , the other with radii  $r \dots r + \frac{M}{m} dR$ . Let  $P$  be a point in the first shell. The common velocity being  $OC$ , and the velocity of  $M$  being  $OP$ , the velocity of  $m$  is  $Op$ , where  $p$  is a determinate point in the second shell, namely in  $PC$  produced so that  $\frac{Cp}{CP} = \frac{M}{m}$ . And so  $f_p$  can be expressed as a function of  $\xi \eta \zeta$ , and of  $xyz$ , the coordinates of  $P$ .

The effect of an encounter between  $M$  and  $m$  under these circumstances is, without altering  $V$ , to substitute for  $PCp$  some other common diameter of the spherical shells as the relative velocity. Let it be  $P'Cp'$ . Then all directions of  $P'Cp'$ , given  $PCp$ , are equally probable.

The number of pairs  $M$  and  $m$  per unit of volume and time, having  $OC$  for common velocity, for which the relative velocity is  $PCp(dS)$  before, and  $P'Cp'(dS')$  after, encounter,  $dS$  and

$dS'$  being small solid angles, is

$$\frac{dS'}{4\pi} F_P f_P dS \pi s^2 \rho, \text{ that is } F_P f_P \frac{dS dS'}{4\pi} \pi s^2 \rho,$$

where  $s$  is the sum of the radii of  $M$  and  $m$ .

The number of pairs for which it is  $P'Cp'(dS')$  before, and  $PCp(dS)$  after, encounter is

$$\frac{dS}{4\pi} F_P f_P dS' \pi s^2 \rho, \text{ that is } F_P f_P \frac{dS dS'}{4\pi} \pi s^2 \rho.$$

If, then,  $F_P f_P = F_{P'} f_{P'}$ , the number per unit of volume and time of pairs for which the relative velocity turns, as the result of encounter, from  $PCp$  to  $P'Cp'$  is equal to the number for which it turns from  $P'Cp'$  to  $PCp$ . And if this is true, given  $C$ , for every two directions of  $PCp$ , and for all positions of  $C$ , it follows that the distribution of velocities is not affected by encounters between  $M$  and  $m$ .

Now  $F_P f_P$  represents the chance that, given  $V = OC$ , the relative velocity shall have direction  $PCp$ . And we see that if, given  $OC$ , this chance be the same for all directions through  $C$ , the distribution of velocities is not affected by encounters. So (a) is proved.

If for some two directions of the diameter  $F_P f_P \neq F_{P'} f_{P'}$  we proceed as follows, adapting Boltzmann's proof.

Let

$$H = \iiint dx dy dz F(xyz)(\log F(xyz) - 1) \\ + \iiint dx dy dz f(xyz)(\log f(xyz) - 1),$$

the limits being in each case  $\pm\infty$ , or, as we will write it,

$$H = \iiint dx dy dz \{ F(\log F - 1) + f(\log f - 1) \};$$

then

$$\frac{dH}{dt} = \iiint dx dy dz \left\{ \frac{dF}{dt} \log F + \frac{df}{dt} \log f \right\}.$$

Now  $F$  is supposed to vary only by encounters between the  $M$ 's and the  $m$ 's. Therefore

$$\frac{dF_P}{dt} = T'_P - T_P;$$

where  $T_P$  is the number per unit of time of encounters with the  $m$  molecules which the  $M$  molecules with velocity  $OP$  undergo, and  $T'_P$  is the number per unit of volume and time of encounters between  $M$  and  $m$  from which  $M$  issues with velocity  $OP$ . Now  $P$  being given, and the velocity of  $M$  being  $OP$ ,  $C$  or  $\xi\eta\zeta$  may have any position whatever, and



the position of  $p$  is determined by that of  $C$ . Hence

$$\begin{aligned} T_P &= F_P \iiint d\xi d\eta d\zeta \pi s^2 \rho f_p, \\ &= \iiint d\xi d\eta d\zeta \pi s^2 \rho F_P f_p; \end{aligned}$$

and since all the directions of the relative velocity before encounter are equally probable,

$$T'_P = \iiint d\xi d\eta d\zeta \pi s^2 \rho \frac{1}{4\pi} \iint F_P f_{p'} dS,$$

in which  $\iint dS$  denotes integration for all directions of the diameter,  $P'Cp'$ , of the spheres described about  $C$ , or  $\xi \eta \zeta$ , through  $P$ . Let  $\frac{1}{4\pi} \iint F_P f_{p'} dS$  be denoted by  $\overline{F_P f_{p'}}$ , then, given  $P$ ,

$$\frac{dF_P}{dt} = \iiint d\xi d\eta d\zeta \pi s^2 \rho (\overline{F_P f_{p'}} - F_P f_p),$$

and by symmetry  $\frac{df_p}{dt}$  has the same value. In this equation  $f_{p'}$  and  $f_p$  are supposed to be expressed as functions of  $\xi \eta \zeta$  and the coordinates of  $P$  or  $P'$ .

In order to find  $\frac{dH}{dt}$ , we multiply  $\frac{dF_P}{dt}$  by  $\log F_P$  and  $\frac{df_p}{dt}$  by  $\log f_p$ , and then integrate over all positions of  $P$  in space. If  $P\bar{C}p$  and  $P'Cp'$  be any two diameters of the spherical shells described with radii  $R$  and  $r$  about  $C$ ,  $\frac{dH}{dt}$  will contain the term

$$\pi s^2 \rho (\log F_P + \log f_p) (F_P f_{p'} - F_P f_p);$$

that is

$$\pi s^2 \rho \log (F_P f_p) (F_P f_{p'} - F_P f_p).$$

By symmetry, as  $P'$  is a position which  $P$  will assume in the integration,  $\frac{dH}{dt}$  will also contain the term

$$\pi s^2 \rho \log (F_P f_{p'}) (F_P f_p - F_P f_{p'}).$$

And adding the two terms together,  $\frac{dH}{dt}$  contains the term

$$\pi s^2 \rho \log \frac{F_P f_p}{F_P f_{p'}} (F_P f_{p'} - F_P f_p),$$

and will consist wholly of a series of terms of that form.

Now this expression is necessarily negative unless  $F_P f_{p'} = F_P f_p$ , and is then zero. Therefore  $\frac{dH}{dt}$  is necessarily

negative unless  $F_P f_{p'} = F_P f_p$  for every two directions of the diameter through C; that is unless, for given V, all directions of the relative velocity are equally probable. Now in stationary motion H must be invariable with the time. Therefore the motion is not stationary, or the distribution of velocities is not unaltered by encounters, unless the condition be satisfied. So (b) is proved.

7. We will next assume that the two molecules M and m act on each other with finite forces. Then in the infinitely short time  $dt$  the relative velocity is by their mutual action during encounter turned through some small angle; and generally also altered in magnitude, in such manner as that

$$\frac{1}{2} \frac{Mm}{M+m} \rho^2 + \chi = \text{constant},$$

$\chi$  being the potential of the mutual action.

It is not necessary to restrict the number of  $m$  molecules which may simultaneously be in encounter with, and affect the motion of, a given M. But by the superposition of small motions, we may regard the total time-variation of the velocity of M as the sum, or resultant, of the time-variation due to the action of all the  $m$  molecules separately, each acting for the time  $dt$ . We can then prove that for any given class of M's with any class of  $m$ 's, as the result of their mutual action,  $\frac{dH}{dt}$  is negative unless the condition is satisfied, in which case it is zero.

The mutual action is assumed to depend on the relative positions, not on the velocities, of M and  $m$ .

We assume also the distribution to be uniform in space, so that the number per unit of volume of any given class of molecules is independent of the position.

Let, then, at any instant the distance between M and  $m$  be between  $q$  and  $q+dq$ .

Let the common velocity be  $OC=V$ , and let the velocity of M be  $OP(R^2 dR dS)$ .

The velocity of  $m$  or  $Op$  is then determined by these conditions. In order completely to define the motion we require one other coordinate of position. Let it be  $\theta$ . Consequently the number of pairs M and  $m$  satisfying these conditions at any instant is  $F_P f_p R^2 dR dS dq d\theta$ . Call this the first state.

By mutual action V is not affected. The motion under the influence of the mutual action is determinate, and after time  $at$  the same variables shall be denoted by accented letters. Then  $q', R', S', \theta'$  are functions of  $q, R, S, \theta$ , known if the

law of mutual action is known. Call this the second state. The number of pairs,  $M$  and  $m$ , in the second state, at any instant is  $F_P' f_p' R'^2 dR' dS' dq' d\theta'$ .

Now by a known theorem (Boltzmann, *Sitzungsberichte*, Vienna, 1871; Watson, 'Kinetic Theory of Gases,' Prop. III.),

$$R^2 dR dS dq d\theta = R'^2 dR' dS' dq' d\theta',$$

or, since

$$dq = -\rho dt, \text{ and } dq' = -\rho' dt,$$

$$R^2 dR dS d\theta \rho dt = R'^2 dR' dS' d\theta' \rho' dt.$$

The number of pairs which in unit of volume and time  $dt$  pass by their mutual action from the first to the second state is

$$F_P f_p R^2 dR dS d\theta \rho dt;$$

and the number which so pass from the second state to the first is

$$F_P' f_p' R'^2 dR' dS' d\theta' \rho' dt.$$

If therefore

$$F_P' f_p' = F_P f_p,$$

the number of pairs which pass from the first to the second state is equal to the number which pass from the second to the first in the same time, and this being true for all positions of  $C$  and of  $P$ , the distribution of velocities is unaffected by the mutual action of  $M$  and  $m$ .

If  $F_P' f_p' \neq F_P f_p$ , then we form  $\frac{dH}{dt}$  as before, and it will as before consist of a series of terms, each of the form

$$\log \frac{F_P f_p}{F_P' f_p'} (F_P' f_p' - F_P f_p),$$

and is therefore necessarily negative until for given  $C$ ,  $F_P' f_p'$  becomes equal to  $F_P f_p$  for all directions through  $C$ .

8. The complete expression for  $\frac{dH}{dt}$  in case of elastic spheres is

$$\iiint d\xi d\eta d\zeta \int_0^\infty dR \pi s^2 \rho \cdot R^2 \iint dS \log (Ff) \{ \overline{F'f'} - Ff \},$$

where  $\iint dS$  denotes integration over a spherical shell described with radii  $R \dots R + dR$  about the point  $\xi \eta \zeta$  as centre, and  $\overline{F'f'}$  denotes the mean value of  $Ff$  for all positions of the diameter of that shell.

This may be put in the form

$$\int_0^\infty dV V^2 \int_0^\pi d\alpha 2\pi \sin \alpha \int_0^\infty dR \pi s^2 \rho R^2 \iint dS \log (Ff)(\overline{F'f'} - Ff),$$

where  $\alpha$  is the angle made by OC with a given line—or, changing the order of integration,  $\frac{dH}{dt} =$

$$\int_0^\infty dV V^2 \int_0^\infty dR \pi s^2 \rho R^2 \int_0^\pi d\alpha 2\pi \sin \alpha \iint dS \log (Ff)(\overline{F'f'} - Ff).$$

9. In case of finite forces acting between the molecules, we have no such simple expression as  $\pi s^2 \rho$  to denote the number per unit of time of encounters between two molecules with relative velocity  $\rho$ . We might define an encounter to be a case in which the relative velocity of two molecules is turned by their mutual action through an angle exceeding a certain limit, reckoning from the time when mutual action begins, to a time when it has ceased, to be appreciable. If with that definition we denote by  $\pi s^2 \rho$  the number of encounters per unit of time,  $s$  is generally a function of  $\rho$  or of  $R$ . We might use  $\pi s^2 \rho$  in this sense for any medium in which the coincidence of two or more encounters for the same molecule simultaneously is so rare as to be negligible.

10. The equation

$$F_P f_p = F_{P'} f_{p'}$$

is satisfied by

$$F_P = C e^{-hM \cdot OP^2},$$

$$f_p = C' e^{-hm \cdot Op^2},$$

where  $C, C'$  are constants, because if  $PCp, QCq$  be two diameters of the spherical shells,

$$M \cdot OP^2 + mOp^2 = M \cdot OQ^2 + mOq^2.$$

It is also satisfied by

$$F_P = C e^{-hM(OP^2 + u^2 - 2uOP \cos \beta)},$$

$$f_p = C' e^{-hm(Op^2 + u^2 - 2uOp \cos \beta')},$$

where  $u$  is a constant line measured in any direction, and  $\beta, \beta'$  are the angles made by  $OP$  and  $Op$  with that direction, because  $M \cdot OP \cos \beta + m \cdot Op \cos \beta'$  has the same value for all directions of  $PCp$ . These are the values of  $F_P$  and  $f_p$  when both sets of molecules,  $M$  and  $m$ , have the same velocity,  $u$ , combined with the velocities required by the kinetic theory for a gas at rest.

A motion of this description is called by Professor Tait



"mass motion." I prefer to call it a *motion of simple translation*. Since the equation  $F_P f_p = F_P f_{p'}$  is satisfied by such a motion, the distribution of velocities is unaffected by encounters. As is otherwise also evident, because the motion of translation does not affect the relative velocities, it is not necessary that  $u$  should be small. It may, for instance, be the earth's motion in space. If, however,  $u$  be very small in a motion of this kind, the number per unit of volume of molecules of mass  $M$  whose velocities are between  $\omega$  and  $\omega + d\omega$  in direction  $\lambda \mu \nu dS$  is

$$M \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} e^{-hM\omega^2} \omega^2 d\omega dS (1 + 2\lambda hM\omega u),$$

the direction of  $u$  being taken for axis of  $x$ .

*On Disturbed States of a Gas.*

11. Thus far we have treated only of a gas at rest or in simple translation, in both of which cases  $\frac{dH}{dt} = 0$ . Both may be regarded as normal states. We come now to consider certain disturbances in which, by the action of external causes, the gas is maintained in a state differing from the normal state. We might suppose generally the number per unit of volume of molecules of mass  $M$  having velocities  $\lambda \mu \nu \omega^2 d\omega dS$  to be

$$F(\omega) \omega^2 d\omega dS,$$

and

$$F(\omega) = N \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} e^{-hM\omega^2} \{ 1 + \sum C_i Y_i \},$$

where the  $Y$ 's are any spherical harmonic functions referred to the origin, the  $C$ 's functions of  $\omega$ , and  $\sum C_i Y_i$  is supposed very small compared with unity. In the problems with which we shall deal the harmonics will be of the first and second orders only.

12. In such a system  $H$  differs from the minimum value which it would have were there no external disturbing causes. Encounters between the molecules tend to diminish  $H$ , and so to reduce the system to the normal condition, and the rate of diminution of  $H$  increases with the increase of the disturbance. If there be an external cause always producing the disturbance at a constant rate, a state of steady motion will be reached in which the disturbance is diminished by encounters as fast as it is increased by the operation of external conditions. We shall denote by  $\frac{dH}{dt}$  the time-variation of  $H$

due to encounters, and by  $\frac{\partial H}{\partial t}$  its time-variation due to external causes. In steady motion

$$\frac{dH}{dt} + \frac{\partial H}{\partial t} = 0.$$

In like manner for any other function, as  $F$ ,  $\frac{dF}{dt}$  shall be the time-variation due to encounters,  $\frac{\partial F}{\partial t}$  that due to external causes, and the condition for steady motion is

$$\frac{dF}{dt} + \frac{\partial F}{\partial t} = 0.$$

13. Let us consider the case of two sets of molecules, each subject to a small disturbance.

For the  $M$  set let

$$F(\omega) = N \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} e^{-hM\omega^2} (1 + X).$$

For the  $m$  set let

$$f(\psi) = n \left( \frac{hm}{\pi} \right)^{\frac{3}{2}} e^{-hm\psi^2} (1 + x).$$

Here  $N$  and  $n$  are the numbers of molecules per unit volume of the  $M$  and  $m$  sets respectively, and  $X$  and  $x$  represent the disturbances.

Let us form the spherical shells described about  $C$ , with radii  $R$ ,  $r$  as in (6). Let  $PCp$  be any common diameter, and

$$\omega = OP, \quad \psi = Op.$$

Let  $X_P$ ,  $x_p$  be the values of  $X$  and  $x$  at  $P$  and  $p$  respectively. In that case

$$\begin{aligned} M\omega^2 + m\psi^2 &= (M+m)V^2 + MR^2 + mr^2 \\ &= (M+m)V^2 + \frac{Mm}{M+m}\rho^2 \\ &= (M+m) \left( V^2 + \frac{M}{m}R^2 \right). \end{aligned}$$

and

$$\overline{F'f'} - Ff = Nn \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \left( \frac{hm}{\pi} \right)^{\frac{3}{2}} e^{-h \left( \overline{M+m}V^2 + \frac{Mm}{M+m}\rho^2 \right)} \{ \overline{X+x} - (X_P + x_p) \},$$

where

$$\overline{X+x} = \frac{1}{4\pi} \iint (X_P + x_p) dS,$$

the integral being over the whole spherical surfaces, that is for all directions of  $P'CP'$ .

Also

$$\begin{aligned}\log (Ff) &= \log \{F(OP) \cdot f(OP)\} \\ &= -h \left( \overline{M+m} V^2 + \frac{Mm}{M+m} \rho^2 \right) + X_P + x_p + \log \left( Nn \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \left( \frac{hm}{\pi} \right)^{\frac{3}{2}} \right).\end{aligned}$$

And therefore

$$\begin{aligned}& \int \int dS \log (Ff) (\overline{F'f'} - Ff) \\ &= Nn \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \left( \frac{hm}{\pi} \right)^{\frac{3}{2}} \epsilon^{-h \left( \overline{M+m} V^2 + \frac{Mm}{M+m} \rho^2 \right)} \{ \overline{X+x} \iint (X+x) dS - \iint (X+x)^2 dS \} \\ &= Nn \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \left( \frac{hm}{\pi} \right)^{\frac{3}{2}} \epsilon^{-h \left( \overline{M+m} V^2 + \frac{Mm}{M+m} \rho^2 \right)} 4\pi \{ \overline{X+x}^2 - \overline{(X+x)^2} \},\end{aligned}$$

the last factor being the square of the mean *minus* the mean of the square of  $X_P + x_p$ , for all directions of  $PCP$ .

Hence we can find  $\frac{dH}{dt}$  in the form

$$\begin{aligned}\frac{dH}{dt} &= 4\pi \frac{M+m}{m} Nn \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \left( \frac{hm}{\pi} \right)^{\frac{3}{2}} \int_0^\infty dV \cdot V^2 \int_0^\infty dR \pi s^2 R^3 \times \\ &\quad \times \epsilon^{-h \left( \overline{M+m} V^2 + \frac{Mm}{M+m} \rho^2 \right)} \int_0^\pi d\alpha 2\pi \sin \alpha \{ \overline{X+x}^2 - \overline{(X+x)^2} \},\end{aligned}$$

in which  $\frac{M+m}{m} R$  is written for  $\rho$ .

#### EXAMPLES.

14. *Diffusion*.—Two reservoirs, A and B, are connected by a uniform horizontal tube. In A is a mixture of two gases, gas M and gas m, in certain proportions. In B is a mixture of the same two gases in different proportions. The temperature and pressure of the mixture are the same in either reservoir and at all points in the tube between them. Gas M is of greater density in A than in B.

Then a stream flows through the tube, of M from A to B, of m from B to A. If the proportions in which the gases are mixed in the reservoirs be maintained constant, as if for instance the reservoirs were of infinite extent, the stream becomes steady.

Let  $N$  be the number per unit of volume of molecules of gas  $M$ ,  $n$  the number for gas  $m$ , at any point in the tube. By Avogadro's law  $N + n$  is constant throughout, or taking the axis of the tube for that of  $x$ ,

$$\frac{dN}{dx} = - \frac{dn}{dx}.$$

The stream velocity is assumed to be very small compared with the molecular velocity of mean square. The problem of diffusion is to find the stream velocity.

Take as an element of volume in the tube a cylinder of length  $\delta x$ , and whose base is unit area parallel to  $yz$ .

Let  $N$  be the number per unit of volume of molecules  $M$  at the left-hand face (towards  $A$ ) of that cylinder. Then the number at its right-hand face is

$$N + \delta x \frac{dN}{dx}, \quad \text{that is } N - \delta x \frac{dn}{dx}.$$

The number of  $M$  molecules of the class  $\lambda \mu \nu \omega^2 d\omega dS$  which enter the cylinder through its left-hand face in unit of time is

$$\lambda N \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \epsilon^{-hM\omega^2} \omega^3 d\omega dS.$$

The number of the same class which pass out of the cylinder through its right-hand-face in unit of time is

$$\lambda \left( N - \delta x \frac{dn}{dx} \right) \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \epsilon^{-hM\omega^2} \omega^3 d\omega dS;$$

and therefore, but for encounters, the number of molecules  $M$  of the class  $\lambda \mu \nu \omega^2 d\omega dS$  within our cylinder would be increased in unit of time by the quantity

$$\lambda \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \frac{dn}{dx} \delta x \epsilon^{-hM\omega^2} \omega^3 d\omega dS,$$

or the number per unit of volume would be increased by

$$\lambda \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \frac{dn}{dx} \epsilon^{-hM\omega^2} \omega^3 d\omega dS.$$

Therefore

$$\frac{\partial F}{\partial t} = \lambda \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \frac{dn}{dx} \epsilon^{-hM\omega^2} \omega.$$

This is a zonal harmonic function of the first order about the axis of  $x$ . In this case we shall assume

$$F = N \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \epsilon^{-hM\omega^2} \{ 1 + \lambda \phi(\omega^2) \},$$



where  $\phi(\omega^2)$  is an undetermined function of  $\omega$ . The disturbance is of the first order.

15. *Conduction of heat in a single gas.*—Let there be a horizontal tube, AB, filled with a single gas. Let the temperature be higher at A than at B, and be maintained constant at each of those points, and let the pressure be uniform throughout the tube, so that  $\frac{N}{h} = P$ , a constant, proportional to the pressure. With the same notation as in the last example, let us consider the molecules of the class  $\lambda \mu \nu \omega^2 d\omega dS$  which enter the elementary cylinder from the left in unit of time. Their number is, putting  $k$  for  $hm$ ,

$$\lambda N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega^3 d\omega dS.$$

The number of the same class which pass out of the elementary cylinder by its right-hand face per unit of time is

$$\begin{aligned} & \lambda N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega^3 d\omega dS. \\ & + \lambda \delta x \frac{d}{dx} \left\{ N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \right\} \omega^3 d\omega dS, \end{aligned}$$

$N$  and  $k$  being variable.

Therefore, but for encounters, the number of the class within our elementary cylinder would be increased in unit of time by

$$-\lambda \delta x \frac{d}{dx} \left( N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \right) \omega^3 d\omega dS,$$

or the number of the class per unit of volume would be increased in unit of time by

$$-\lambda \frac{d}{dx} \left( N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \right) \omega^3 d\omega dS;$$

that is by

$$\lambda P \epsilon^{-k\omega^2} \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \omega^3 d\omega dS \left( k\omega^2 - \frac{5}{2} \right) \frac{dk}{dx}.$$

This is positive or negative according as  $k\omega^2 >$  or  $< \frac{5}{2}$ .

For high values of  $\omega$  there is an increase, for low values a diminution. This increase or diminution is in steady motion compensated by encounters, because molecules with high velocities are on average moving more to the right than to the

left, and lose velocity in direction  $x$  by encounters. Here

$$\frac{\partial F}{\partial t} = \lambda P \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega \left( k\omega^2 - \frac{5}{2} \right) \frac{d\omega}{dx}.$$

And we assume

$$F = N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} (1 + \lambda \phi(\omega^2)),$$

where  $\phi(\omega^2)$  is an undetermined function. The disturbance is of the first order.

16. *Viscosity of a single gas.*—A gas on either side of the plane of  $xz$  is uniform throughout as regards temperature and density. On the negative side of the plane  $y = -a$  the gas has, and is constrained to maintain, a constant velocity,  $v$ , of simple translation in direction  $x$ . And on the positive side of the plane  $y = +a$ , a constant velocity  $-v$  of simple translation in that direction. The problem is to find the quantity of  $x$  momentum which under those circumstances is carried across unit area of the plane of  $xz$  per unit of time in the positive direction by molecules crossing that plane. Take any two planes parallel to  $xz$  and distant  $\delta y$  from each other. Suppose for a moment that on the negative side of the negative plane the gas has a velocity,  $v$ , of simple translation in direction  $x$ . Then the number of the class

$$\lambda \mu v \omega^2 d\omega dS$$

per unit of volume is

$$N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega^2 d\omega dS \{1 + 2\lambda k\omega v\}.$$

The number of this class which cross the negative plane in the positive direction per unit of area and time is

$$N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega^3 d\omega dS \{ \mu + 2\lambda \mu k\omega v \}.$$

The number of the same class that cross the positive plane in the positive direction per unit of area and of time is

$$N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega^3 d\omega dS \left\{ \mu + 2\lambda \mu k\omega \left( v + \delta y \frac{dv}{dy} \right) \right\}.$$

And, but for encounters, the class within the layer between the planes would gain in number per unit of volume and time by the quantity

$$- N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega^3 d\omega dS \cdot \lambda \mu \cdot 2k\omega \frac{dv}{dy}.$$

In steady motion the number of the class in question is diminished by encounters by the same quantity.

The motion of the gas is a motion of simple translation with velocity  $v = -gy$  in direction  $x$ , where  $g$  is constant, combined with a disturbance of the second order symmetrical about the plane  $x=y$ . In this case we should assume

$$F = N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} e^{-k\omega^2} (1 + \lambda\mu\phi(\omega^2)),$$

where  $\phi(\omega^2)$  is an undetermined function, and

$$\frac{\partial F}{\partial t} = -N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} e^{-2k\omega^2} \lambda\mu \cdot 2k\omega^2 \frac{dv}{dy}.$$

17. The complete solution of any problem of the kind would have to be found from the equation

$$\frac{dF}{dt} + \frac{\partial F}{\partial t} = 0,$$

expressing the steadiness of the motion for each class of molecules. It does not appear that in case of diffusion we can obtain a solution by assuming the two gases to have a motion of simple translation, one in one direction and the other in the opposite.

#### *Relation of Diffusion &c. to Temperature.*

Without obtaining a complete solution of any of these problems, we can by means of the equation

$$\frac{dH}{dt} + \frac{\partial H}{\partial t} = 0$$

determine the relation in which the solution, whatever it may be, stands to the absolute temperature of the system.

18. When the disturbance is of the first order the solution proposed is, using  $X$  to denote the disturbance as in (13),

$$X = \lambda\chi(h)\phi(hM\omega^2),$$

in which  $\chi(h)$  is a function of  $h$  to be determined, and  $\phi(hM\omega^2)$  is a function of  $hM\omega^2$ , containing only odd positive powers of  $\omega \sqrt{hM}$ , as for instance

$$\phi(hM\omega^2) = C_0\omega \sqrt{hM} + C_1(hM)^{\frac{3}{2}}\omega^3 + \&c.,$$

where the  $C$ 's are numerical.

Similarly in dealing with two gases, we shall assume

$$x = \lambda'\chi(h)\phi'(hm\psi^2),$$

and  $\phi'$  has similar form. With these values of  $X$  and  $x$ ,

$$\iint X dS = \chi(h) \iint \lambda\phi(hM\omega^2) dS,$$

the integration being over the spherical surface, described about C, as in (6).

Now, if  $\lambda_c \mu_c \nu_c$  be direction-cosines of OC, and  $OP = \omega$ ,

$$\lambda\omega = \lambda_c(V - R \cos E) + \sqrt{1 - \lambda_c^2} R \sin E \cos \gamma,$$

where E is the angle OCP, and  $\gamma$  is the angle between the plane OCP and a fixed plane, and therefore the second term disappears when we form the integral

$$\iint dS \lambda \omega \frac{\phi(hM\omega^2)}{\omega}.$$

Also, since  $\omega^2 = V^2 + R^2 - 2VR \cos E$ , we may write, expressing Taylor's theorem,

$$\frac{\phi(hM\omega^2)}{\omega} = \epsilon^{-2VR \cos E} \frac{\phi(hM\overline{V^2 + R^2})}{\sqrt{V^2 + R^2}},$$

where

$$p = \frac{d}{dV^2}.$$

Thus we obtain

$$\iint X dS = \lambda_c \chi(h) \int_0^\pi dE 2\pi \sin E (V - R \cos E) \epsilon^{-2VR \cos E} \frac{\phi(hM\overline{V^2 + R^2})}{\sqrt{V^2 + R^2}}.$$

The integration according to E can now be effected in a series, and with the assumed form of  $\phi(hM\omega^2)$  no negative powers of V or R will appear.  $\iint x dS$  can be treated in the same way.

By an extension of this method we might form  $\frac{dF_P}{dt}$  in a series of positive powers of  $\omega$ , and we should then have theoretically sufficient data for determining the coefficients  $C_0, C_1$ , &c. in the expression for  $\phi(hM\omega^2)$  by equating to zero the coefficients of powers of  $\omega$  in the expression

$$\frac{dF_P}{dt} + \frac{\partial F_P}{\partial t} = 0.$$

In order to find  $\chi(h)$  we resume the discussion of the equation

$$\frac{dH}{dt} + \frac{\partial H}{\partial t} = 0.$$

19. If in the expression

$$\left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \int_0^\infty dV \epsilon^{-h\overline{M+m}V^2} V^2 \int_0^\infty dR \epsilon^{-\frac{hM}{m}\overline{M+m}R^2} R^2 \phi(hM\overline{V^2 + R^2})$$

all the integrations were effected, the result would be independent of  $h$ , whatever the form of  $\phi$  might be. As we



may express it, the above function is, as a function of  $h$ , of zero dimensions. Therefore, since  $X = \lambda \chi(h) \phi(hM\omega^2)$  &c., the expression

$$\left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \int_0^\infty dV \epsilon^{-h\overline{M+m}V^2} V^2 \int_0^\infty dR \epsilon^{-h\frac{M}{m}\overline{M+m}R^2} \pi s^2 \rho \\ \times \int_0^\pi d\alpha 2\pi \sin \alpha \overline{X+x}^2$$

must have, as a function of  $h$ , dimensions  $\frac{(\chi(h))^2}{\sqrt{h}}$ , the factor  $\sqrt{h}$  appearing in the denominator on account of the introduction of  $\pi s^2 \rho$ , or  $\pi s^2 \frac{M+m}{m} R$ ,  $\pi s^2$  being in the cases now considered independent of  $\rho$ .

In like manner the expression

$$\left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \int_0^\infty dV \epsilon^{-h\overline{M+m}V^2} V^2 \int_0^\infty dR \epsilon^{-h\frac{M}{m}\overline{M+m}R^2} R^2 \pi s^2 \frac{M+m}{m} R \\ \times \int_0^\pi d\alpha 2\pi \sin \alpha \iint (\overline{X+x})^2 dS$$

will, as a function of  $h$ , have dimensions  $\frac{(\chi(h))^2}{\sqrt{h}}$ .

And therefore  $\frac{dH}{dt}$  (see (13)) will, as a function of  $h$ , have dimensions  $\frac{(\chi(h))^2}{\sqrt{h}}$ .

20. We have next to treat  $\frac{\partial H}{\partial t}$  in the same way. The result will be different for diffusion and for conduction of heat. In diffusion

$$\frac{\partial F}{\partial t} = \lambda \left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \epsilon^{-hM\omega^2} \omega \frac{dn}{dx},$$

$$\frac{\partial f}{\partial t} = \lambda' \left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \epsilon^{-hm\psi^2} \psi \frac{dn}{dx}.$$

Also

$$\log F = \log \left\{ N \left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \right\} - hM\omega^2 + \lambda \chi(h) \phi(hM\omega^2),$$

$$\log f = \log \left\{ n \left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \right\} - hm\psi^2 + \lambda' \chi(h) \phi'(hm\psi^2).$$

Now if we form

$$\frac{\partial H}{\partial t} = \iiint dx dy dz \left\{ \frac{\partial F}{\partial t} \log F + \frac{\partial f}{\partial t} \log f \right\},$$

the terms containing  $\lambda$  or  $\lambda'$  in the first degree disappear, and so

$$\begin{aligned} \frac{\partial H}{\partial t} = & \chi(h) \frac{dn}{dx} \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \iiint dx dy dz \lambda^2 \epsilon^{-hM\omega^2} \omega \phi(hM\omega^2) \\ & + \chi(h) \frac{dn}{dx} \left( \frac{hm}{\pi} \right)^{\frac{3}{2}} \iiint dx' dy' dz' \lambda'^2 \epsilon^{-hm\psi^2} \psi \phi'(hm\psi^2), \end{aligned}$$

where

$$\omega^2 = x^2 + y^2 + z^2,$$

$$\psi^2 = x'^2 + y'^2 + z'^2.$$

As a function of  $h$ , this expression has dimensions  $\frac{\chi(h)}{\sqrt{h}}$ ,  $\sqrt{h}$  appearing in the denominator in consequence of the factors  $\omega$  and  $\psi$ .

21. Now by virtue of the equation

$$\frac{\partial H}{\partial t} + \frac{\partial H}{\partial t} = 0,$$

$\frac{dH}{dt}$  and  $\frac{\partial H}{\partial t}$  will, as functions of  $h$ , have the same dimensions. And therefore in diffusion  $\frac{(\chi(h))^2}{\sqrt{h}}$  has the same dimensions as  $\frac{\chi(h)}{\sqrt{h}}$ , or  $\chi(h)$  is a constant, independent of  $h$ .

But the stream of gas M through the tube, that is the *rate of diffusion* for given space variation of density, is

$$N \left( \frac{hM}{\pi} \right)^{\frac{3}{2}} \int_0^\infty d\omega \epsilon^{-hM\omega^2} \omega^2 \omega \chi(h) \phi(hM\omega^2),$$

and therefore varies as  $\frac{1}{\sqrt{h}}$ , or as the square root of the absolute temperature. This is a consequence of the assumption that  $\pi s^2$  is independent of  $R$ , and therefore holds only for elastic spheres.

22. We will now treat conduction of heat in the same way. Since the disturbance is of the first order, we shall as before assume for the solution  $\lambda \chi(k) \phi(k\omega^2)$ ,  $k$  being written for  $hm$ .

Then  $\frac{dH}{dt}$  will, as a function of  $k$ , have the same dimensions as before, viz.

$$\frac{(\chi(k))^2}{\sqrt{k}}.$$

In forming  $\frac{\partial H}{\partial t}$  we have now the factor  $P\omega \frac{dk}{dx}$ , instead of  $\omega \frac{du}{dx}$  as in diffusion. Also  $k = \frac{3}{2\tau}$ , if  $\tau$  be the absolute temperature and

$$\frac{dk}{dx} = -\frac{3}{2\tau^2} \frac{d\tau}{dx} = -\frac{2}{3} k^2 \frac{d\tau}{dx}.$$

We have now to compare two systems in each of which  $P$  is constant throughout the tube, but has not necessarily the same constant value in both systems, and  $k$  has different values in the two systems.

We may make

(1)  $P$  the same, that is  $\frac{N}{k}$  the same, in both systems.

(2)  $N$  the same in both systems.

In case (1)  $\frac{\partial H}{\partial t}$ , as a function of  $k$ , has dimensions  $k^2 \frac{\chi(k)}{\sqrt{k}}$ .

In case (2) it has dimensions  $k \frac{\chi(k)}{\sqrt{k}}$ .

Now the flow of heat per unit of time through a section of the tube, that is the *rate of conduction*, is

$$N \left( \frac{k}{\pi} \right)^{\frac{3}{2}} \int_0^\infty d\omega e^{-k\omega^2} \omega^4 \chi(k) \omega \phi(k\omega^2),$$

and therefore varies

in case (1) as  $\sqrt{k}$ , or as  $\frac{1}{\sqrt{\tau}}$ ,

in case (2) as  $\frac{1}{\sqrt{k}}$ , or as  $\sqrt{\tau}$ .

We have then the following result. Assuming that the molecules may be treated, as regards their mutual encounters, as elastic spheres, the *rate of conduction of heat* between points of equal pressure but unequal temperature varies, as between two systems with the same pressure, inversely, and as between two systems with the same density directly, as the square root of the absolute temperature.

23. When the disturbance is of the second order, as in the problem of viscosity, the mean value of  $\lambda\mu$ , given  $E$ , is (see figure, § 6)

$$\frac{3}{2} \cos^2 \text{COP} - \frac{1}{2}, \text{ or } \frac{3}{2} \left( \frac{V - R \cos E}{\omega} \right)^2 - \frac{1}{2}.$$

In order in this case to prevent the appearance of negative

powers of  $V$  and  $R$  in the differentiation, we should assume  $\phi(k\omega^2)$  to consist of even powers of  $\omega\sqrt{k}$ .

As the result when all the integrations are effected,  $\frac{dH}{dt}$  will be a function of  $k$  of dimension  $\frac{(\chi(k))^2}{\sqrt{k}}$ . And  $\frac{\partial H}{\partial t}$  of dimensions  $\chi(k)$ .

So we should obtain

$$\frac{(\chi(k))^2}{\sqrt{k}} = \chi(k) \text{ or } \chi(k) = \sqrt{k}.$$

But the excess of momentum carried in the positive direction through unit area of the plane of  $xz$ , on which the viscosity depends, varies as

$$\left(\frac{k}{\pi}\right)^{\frac{3}{2}} \int_0^\infty d\omega e^{-k\omega^2} \omega^4 \chi(k) \phi(k\omega^2);$$

that is varies as  $\frac{1}{\sqrt{k}}$ , or as the square root of the absolute temperature.

24. The above results are obtained on the hypothesis that  $\pi s^2$  is independent of  $\rho$  or  $R$ , and therefore only on the hypothesis that the molecules may be treated as elastic spheres. On any other hypothesis  $\pi s^2$  is a function of  $R$ , and as such will affect the integration according to  $R$ , and the degree in  $h$  or  $k$  which  $\frac{dH}{dt}$  assumes as the result of that integration. For instance, if the molecules be centres of force repelling one another with a force varying as  $\frac{1}{\rho^5}$ ,  $\pi s^2 \propto \frac{1}{\rho}$ . In this case, in dealing with diffusion  $\frac{dH}{dt}$  will be proportional to  $(\chi(h))^2$ , instead of  $\frac{(\chi(h))^2}{\sqrt{h}}$  as in the case of elastic spheres, and the rate of diffusion would vary as  $\frac{1}{h}$ , that is as the absolute temperature, instead of as the square root of the absolute temperature.

If the experiments from which it appeared that the rate of diffusion varies as the square root of the temperature can be relied on as giving exact, and not merely approximate, results, they afford ground for the inference that molecules of gases may, as regards their mutual encounters, be treated as elastic spheres.



XXXVI. *A New Periodic Property of the Elements.*

By WILLIAM SUTHERLAND, M.A., B.Sc.\*

TO help towards getting some insight into the physical basis of the periodicity in the properties of the elements unfolded by Newlands, Mendelejeff, Meyer, Carnelley, and others, it occurred to me to investigate some property in which the period would be a real time-period. With the same object in view many workers have attacked the spectra of the elements; but though interesting results have been obtained, the complications of the subject have proved too entangled to unravel to a simple issue as yet. But if we start from the usual idea that in solids the molecules vibrate about a mean position, then at some characteristic temperature each solid ought to have a period of vibration characteristic of its molecule. The question is, At what temperature? At the melting-point in each case the vibratory motion just breaks down, so that we ought to expect some simple relation amongst the periods of vibration of the elements at their melting-points. To find relative values of these periods we may proceed thus:—Suppose a molecule of mass,  $M$ , and specific heat (mean),  $C$ , heated up from rest at absolute zero to its melting-point,  $T$ . It receives heat,  $MCT$ , which we will take to be proportional to its kinetic energy  $\frac{1}{2}Mv^2$ , where  $v$  is the velocity of the molecule at the melting-point: this would be strictly true only if we kept the body from expanding while being heated. Now, by Dulong and Petit's law,  $MC$  is approximately constant for the elements, so that  $v$ , the mean velocity of the molecule in its vibrations at the melting-point, is proportional to  $\sqrt{T/M}$ . Knowing thus the mean velocity of the vibration, if we can find its length  $L$  then its time or period  $L/v$  is obtainable. Let  $d$  be the density of the substance, then  $M/d$  represents the volume occupied by the molecule; and if  $a$  is the mean coefficient of linear expansion of the substance between absolute zero and  $T$ , then  $aT(M/d)^{\frac{1}{3}}$  represents the increase in the linear dimensions of the space occupied by a molecule when heated from zero to  $T$ , and therefore represents the length or amplitude of the vibration just as the molecule is going to leave the vibratory state characteristic of the solid. Hence the periodic time  $p$  of the molecule at the melting-point is proportional to

$$aT(M/d)^{\frac{1}{3}}\sqrt{MCT/M}.$$

\* Communicated by the Author.

All the quantities in this expression are known for a large number of substances ; but it so happens that  $a$  has not been determined for several of the bodies in Mendelejeff's most interesting families—those of Li and Be. To get over the want of these data it might seem advisable to use R. Pictet's empirical formula  $aT(M/d)^{\frac{1}{3}} = \text{constant}$  (*Comptes Rendus*, lxxxviii., and Meyer's 'Modern Theories of Chemistry,' translated by Bedson and Williams, p. 135). But this formula applies with accuracy only to the harder and heavier metals, for which the mean value of the constant is  $\cdot 045$  ; instead of which for Mg we get  $\cdot 066$ , and for Al  $\cdot 057$ , while for Na the discrepancy is greater : this formula fails, then, just where we need it at present. But I have found an empirical equation which will suit our purpose, namely  $aTM^{\frac{1}{3}} = \text{constant}$ , the constant lying between  $\cdot 04$  and  $\cdot 05$  for all the metals for which data are available except Sb, Bi, and Sn (Ir also falls to  $\cdot 037$ ). This formula includes Mg, Al, and Na, and may therefore be hopefully applied to the other metals of the same families, as will appear in the result. Taking  $\cdot 045$  as the mean value of the constant and substituting for  $aT$ , we get  $p$  proportional to  $(M/d)^{\frac{1}{3}}M^{\frac{1}{3}}/\sqrt{T}$ , dropping the constants  $\cdot 045$  and  $MC$ . Using the values for  $d$  and  $T$  obtainable from Meyer's 'Modern Theories of Chemistry,' and in our uncertainty as to the true molecular weight of the solid elements, taking  $M$  as atomic weight, we get the following relative values of the periods of vibration of the members of the lithium family at the melting-point:—

Li.	Na.	K.	Rb.	Cs.
$\cdot 21$	$\cdot 43$	$\cdot 66$	$\cdot 96$	$1\cdot 23$

At a glance these numbers are seen to run as 1, 2, 3, 4·5, 6.

For the next family we get

Be.	Mg	Ca.	Sr.	Ba.
$\cdot 35$	$\cdot 70$	$1\cdot 04$	$1\cdot 62$	$1\cdot 88$

These numbers run as 1, 2, 3, 4·5, and 5·3, not 6 exactly.

Considering the nature of the assumptions we have been forced to make, we must allow that these numbers show beautifully simple harmonic relations to exist between the periodic times of the molecules of solid metals at their melting-points. Taking now Cu and Ag, which are subsidiary relatives of the Li family, we get periods  $\cdot 21$  and  $\cdot 30$ , which are nearly as 2 to 3, and involve the same fundamental constant as the main family. Again, Zn and Cd, which stand in the same relation to the second main family

as Cu and Ag to the first, have periods  $\cdot 32$  and  $\cdot 47$ , again as 2 to 3, and involving a fundamental constant very close to that of the main family. In the next main family the only members for which data are available are Al and La, for which we get  $\cdot 20$  and  $\cdot 56$ , which are nearly as 2 to 6, that is, nearly as Na to Cs or Mg to Ba, as they ought to be. But the subsidiary members Ga and In give  $\cdot 54$  and  $\cdot 57$ , which are not related in the same way as Cu and Ag or Zn and Cd; so that here complete analogy between the families breaks down when we reach the family that marks the transition to the non-metallic families. The following three groups of values are worth notice :—

Mn.	Fe.	Co.	Ni.	Ru.	Rh.	Pd.	Os.	Ir.	Pt.
$\cdot 16$	$\cdot 16$	$\cdot 16$	$\cdot 17$	$\cdot 21$	$\cdot 20$	$\cdot 23$	$\cdot 23$	$\cdot 25$	$\cdot 27$

The following values of  $(M/d)^{\frac{1}{3}} M^{\frac{1}{3}} / \sqrt{T}$  are added ; though not of much use, because in many cases we know  $\alpha TM^{\frac{1}{3}}$  not to be near enough to  $\cdot 045$ .

Au.	Hg.	Tl.	Sn.	Pb.	P.	As.	Sb.	Bi.
$\cdot 35$	$\cdot 94$	$\cdot 65$	$\cdot 55$	$\cdot 63$	$\cdot 33$	$\cdot 36$	$\cdot 49$	$\cdot 71$
S.	Se.	Te.	Cl.	Br.	I.			
$\cdot 41$	$\cdot 50$	$\cdot 50$	$\cdot 68$	$\cdot 80$	$\cdot 75$			

It is interesting now to pass on to the case of compounds, extending to them the formula  $p = (M/d)^{\frac{1}{3}} M^{\frac{1}{3}} / \sqrt{T}$ , taking  $M$  as the ordinary molecular weight, and remembering now that  $MC$  is constant only for similarly constituted molecules, being proportional to the number of atoms in the molecule. Carnelley has given the melting-points of many compounds (Phil. Mag. [5] xviii.). Let us consider first the compounds of the Li family with the halogens ; the study of the numbers tabulated below shows that the period  $p$  of any such compound is the sum of two periods characteristic of each of its atoms. These characteristic periods are as follows :—

Li.	Na.	K.	Rb.
$\cdot 075$	$\cdot 150$	$\cdot 225$	$\cdot 375$
F.	Cl.	Br.	I.
$\cdot 116$	$\cdot 232$	$\cdot 348$	$\cdot 464$

For the lithium family these numbers run as 1, 2, 3, 5, almost the same as the series for them in the free state. For the halogens the numbers run as 1, 2, 3, 4. The soundness of these conclusions is shown in the following Table, where the values of  $p$  or  $(M/d)^{\frac{1}{3}} M^{\frac{1}{3}} / \sqrt{T}$ , obtained from experiment

and from the above values for the metals and halogens, are compared.

		Li.	Na.	K.	Rb.
F	{ exp.	·19	·25	·34	
	{ cal.	·19	·27	·34	
Cl	{ exp.	·32	·36	·44	·60
	{ cal.	·31	·38	·46	·61
Br	{ exp.	...	·49	·56	·69
	{ cal.	...	·50	·57	·72
I	{ exp.	...	·62	·69	·81
	{ cal.	...	·61	·69	·84

It is worthy of notice that the relation holds from the light molecule LiF to the heavy one RbI. To the same type of compound belong the haloid compounds of Ag and the thallic compounds as well as the mercurous and cuprous, if we treat the latter sets as on the type CuCl, HgCl, and so on. Thus we get for the periodic time of Cu in the cuprous state ·24, and of Ag ·32, numbers which are nearly in the same ratio to one another as the ·21 and ·30 before, but standing now no longer in the same relation to those of the main family. For Hg in the mercurous state we get a value ·55, and for Tl ·52. Subjoined is a comparison as before:—

		Cu.	Ag.	Hg.	Tl.
Cl	{ exp.	·53	·57	...	·77
	{ cal.	·47	·54	·78	·75
Br	{ exp.	·58	·67	·85	
	{ cal.	·59	·67	·90	
I	{ exp.	·68	·76	1·04	·94
	{ cal.	·70	·78	1·01	·98

The agreement here is not so good; in fact these numbers by themselves would prove nothing, but in conjunction with what has gone before they show that we have got approximately the periods which these four metals carry into their compounds.

Coming to compounds of the type  $\text{CaCl}_2$ , we must remember that MC is 1·5 times its value in the previous class of compounds, so that to get comparable values of  $p$  we must take  $p = (M/d)^{\frac{1}{2}} M^{\frac{1}{2}} / \sqrt{1·5 T}$ .

Again  $p$  is found to be for each molecule the sum of parts due to each atom, and we find the following values for these:

Mg.	Ca.	Sr.	Ba.
·10	·15	·20	·25

numbers which run as 2, 3, 4, 5. Be, the first member of



the family, is absent through want of experimental data. For the halogen atoms as  $F_2$ ,  $Cl_2$ ,  $Br_2$ , and  $I_2$ , the following are the values :—·156, ·312, ·468, and ·624 ; again, the series 1, 2, 3, 4, although the value ·156 of the constant of the family is not double the previous value ·116 for the single atoms. But it must be remembered that we are using the empirical relation  $aTM^{\frac{1}{2}} = \text{constant}$  without knowing whether the value of the constant may not change with change of type of compound. This does not affect the present purpose, which is to show the existence of harmonic relations.

To prove the substantial correctness for the values given for the Be family, and the double halogen atoms, the following comparison is furnished :—

	Mg.	Ca.	Sr.	Ba.
$F_2$ { exp.	·28	·30	...	·44
cal.	·26	·31	...	·41
$Cl_2$ { exp.	·42	·46	·50	·53
cal.	·41	·46	·51	·56
$Br_2$ { exp.	...	·61	·68	·68
cal.	...	·62	·67	·72
$I_2$ { exp.	...	...	·87	·84
cal.	...	...	·82	·87

As the comparison ranges from the light molecule  $MgF_2$  to the heavy one  $BaI_2$ , it proves the main principle under discussion, in spite of some noticeable disagreements in the two series of values. The following are some values for other dyad elements :—

Cd.	Hg.	Cu.	Pb.
·27	·53	·22	·39

giving the following comparison :—

	Cd.	Hg.	Cu.	Pb.
$Cl_2$ { exp.	·59	·82	·53	·71
cal.	·58	·84	·53	·70
$Br_2$ { exp.	...	1·01	...	·82
cal.	...	1·00	...	·86
$I_2$ { exp.	·88	1·15	...	1·04
cal.	·89	1·15	...	1·01

The only compounds of this type which are thoroughly irregular are those of zinc ; ·66 for  $ZnCl_2$ , ·76 for  $ZnBr_2$ , and ·85 for  $ZnI_2$ , which give a smaller value for  $Br_2-Cl_2$ , and for  $I_2-Br_2$  than holds in the other dyad compounds. For compounds of metals of higher atomicity than the dyads there are not enough data to give useful conclusions ; the haloid compounds of As and Sb give irregular results.

It is established then that *the periods of vibration of the molecules of solids at their melting-points show very simple harmonic relations.*

It is an interesting speculation in molecular physics as to whether by the analysis of the whole radiation from melting solids with bolometer and spectroscope similar harmonic relations could be found and so demonstrate the communication of impressed vibrations to the æther from the oscillating molecules. A similar study to the above made on organic compounds might yield useful information about the harmonic connexions of the organic radicals.

Melbourne, July 1890.

### XXXVII. *Electrical Oscillations in Air.*

By JOHN TROWBRIDGE and W. C. SABINE\*.

THE experiments of Hertz on electrical waves have opened a wide field for investigations in electromagnetism. The qualitative results of Henry and of Feddersen have been expressed in a quantitative manner by Sir William Thomson. Hertz, collecting together the results of previous observers, and reasoning upon the factors in the formula of Sir W. Thomson,—which expresses a relation between the capacity of a Leyden jar and the self-induction of the circuit through which this jar is discharged,—has detected wave-motion with its nodal points and ventral segments, on a wire over which electrical oscillations take place.

Hertz has also pointed out that the experimental results confirm Maxwell's theory, that light and heat are electromagnetic phenomena, and that all energy comes to us from the sun in electrical pulsations.

There can be no question of the phenomena of so-called resonance discovered by Hertz. Roughly speaking, the results obtained by Hertz's resonators satisfy the formula

$t = \frac{2\pi}{v} \sqrt{LC}$  ; in which  $t$  is the period of the electrical oscillations,

$L$  is the inductance of the circuit, and  $C$  is the capacity of the jar, or that of the terminals between which the electrical discharge takes place.

Professor J. J. Thomson has based a method of measuring the capacities of dielectrics upon this formula and upon Hertz's work †.

\* From the Proceedings of the American Academy of Arts and Sciences. Advance proof communicated by the Authors.

† Proceedings of the Royal Society, June 20, 1889.

The researches of Feddersen upon electrical oscillations\* were more quantitative than those of Joseph Henry: and Lorenz†, by his repetition of Feddersen's results, and by his mathematical analysis of them, apparently gave subsequent observers a solid basis for calculation.

The results of Feddersen and of Lorenz were obtained by photography. An image of the electric spark drawn out by means of a revolving mirror was photographed, and the distances between the successive oscillations, shown by dark bands on the photograph, were measured. Lorenz assumed the ratio between the electrostatic units and the electromagnetic units,  $v=300 \times 10^6$  metre, as that of the velocity of

light; and by means of the formula  $t = \frac{2\pi}{v} \sqrt{LC}$  obtained a

satisfactory agreement between the result of experiment and the theory. He showed, apparently, that a certain lack of agreement between theory and experiment, which Feddersen had noticed, was due to taking the dielectric constant of glass too small.

It will be noticed that the method of Feddersen, by means of which the electrical oscillations are photographed, apparently affords an accurate method of determining  $v$ . For the factors  $L$  and  $C$  occur under the square root, and the percentage errors of determination of  $L$  and  $C$ , being under the square, are halved. Lorenz did not repeat the entire work of Feddersen, but only obtained a sufficient number of photographs—taken under definite conditions in regard to capacity and inductance of the circuit—in order to measure  $t$ , the time of oscillation. The accuracy of the results which can be obtained for  $v$  depends upon the limits of accuracy of the measurements of the photographs, and of the determinations of the dielectric capacity for oscillatory charges.

In reasoning upon the mode of electrical oscillations in dielectrics, it occurred to us that the medium of the dielectric must greatly influence the result. At the instant the electrical oscillations occur, the glass of the Leyden jar is subjected to a strain which is more or less periodic. It is not probable that the capacity of a condenser is the same for rapid charges and discharges as for slow ones, and the measurements of capacity by the ordinary slow methods form no criterion of the capacity of glass under electrical influences which last but three millionths of a second. We therefore concluded to

\* Poggendorff's *Annalen*, vol. ciii. p. 69 (1858); vol. cviii. p. 497 (1859); vol. cxii. p. 452 (1861); vol. cxiii. p. 437 (1861); vol. cxv. p. 336 (1862); vol. cxvi. p. 132 (1862).

† Wiedemann's *Annalen*, vol. vii. p. 161 (1879).

employ an air condenser instead of one of glass, in order to detect, if possible, the effect of the medium of the dielectric upon electrical oscillations. In order to obtain sufficient capacity for a suitable spark, we were obliged to use the cylindrical form of condenser. The first condenser we employed was made of sheet zinc and consisted of nineteen coaxial cylinders. The inner cylinder had a diameter of 15.1 centim., and the outer one of 60.4; the height of the cylinders was 92 centim. The capacity was computed from the formula

$$C = \frac{1}{2} \frac{l}{b \log \frac{a}{b}};$$

in which  $l$  is the height, and  $b$  and  $a$  are radii.

A correction for the ends was made as follows. The radius of curvature of the boundary of the cylindrical plates was considered so large in comparison with the distance between them that the boundary was treated approximately as a straight line. We may consider that each zinc cylinder constituted a plate between infinite imaginary planes which were at zero potential, these planes being equipotential surfaces. The zinc cylinder was supposed to have its area extended by a strip of uniform breadth around its boundary, and the surface-density was assumed to be the same on the extended plate as on the parts not near the boundary. Following Maxwell (vol. i. § 196), we have

$$\frac{B}{\pi} \log_e 2 \cos \frac{\pi \beta}{B} \text{ for the correction for length.}$$

$B = a - b =$  distance between cylinders.

$\beta =$  thickness of cylinder.

$l =$  height of cylinder.

This air condenser was connected with a circuit of parallel wires, which was carefully strung by means of silk thread through the centre of a large unoccupied room. The length of this circuit was about fifty feet. It returned upon itself to the sparking terminal of the air condenser. The jar was charged by a Holtz machine, which worked fairly well under all conditions of the atmosphere. The revolving mirror was a plane one, 4 × 5 inches, silvered upon the front face. It revolved upon a horizontal axis with an average speed of three thousand revolutions per minute. The frame which carried the mirror bore also a brass arm provided with a minute brush, which rubbed upon a brass sector let into a large disk of ebonite. When the brush rested upon this brass disk the electrical charge could pass to two terminals of tin,



between which the discharge took place. A concave silvered glass mirror, of 313 centim. radius and 16·5 centim. aperture, placed at a distance of 230 centim. from the spark, received the image of the spark and reflected it back to the revolving mirror. From the revolving mirror the image was reflected to a photographic plate, which was at a distance of 259·7 centim. from the rotating mirror.

The adoption of a plane revolving mirror, and a stationary concave mirror of long focus, enabled us to place the photographic plate at a distance from the revolving apparatus, and therefore to employ less speed for the revolving mirror. There was no sensible aberration of the image. Great care was taken to balance the mirror. Its large size and weight made it very important, on account of the danger of the apparatus flying apart, that it should revolve with uniformity. The axis of the mirror was placed horizontally. This precaution proved to be a wise one, for twice during the course of the many runs which were made the mirror flew into pieces; the excursions of the fragments, however, were confined to a vertical plane. This liability to accident is perhaps inherent in a method which employs a large plane mirror. The increased amount of light which results from the use of a large mirror, however, forms a valuable compensation. The revolving mirror was driven by a gas-engine.

In order to determine the speed of the mirror at the instant the spark passed, the following apparatus was devised. The same shaft which carried the revolving mirror also carried a brass cylinder 5 centim. in diameter and 21 centim. long. This cylinder was covered at each trial with paper which was coated with lampblack. A stylus moving along a stationary rod beside the shaft could be made to draw a spiral upon the revolving cylinder. One terminal of a Ruhmkorff-coil was connected with the brass cylinder, and the other with the stylus. A second pendulum was made to break the circuit of the primary of the Ruhmkorff-coil at intervals of one second, and at the middle point of its swing. When the stylus was drawn along the stationary rod which served to guide it, it was made to release automatically at the beginning of the second another pendulum held up by an electromagnet. This latter pendulum, at the middle of its swing, discharged the air condenser through the inductance-circuit at the instant that the mirror was in a suitable position to reflect the image of the electric spark into the photographic camera. While the stylus was being drawn upon the revolving cylinder, the spark from the Ruhmkorff-coil left its trace upon the blackened paper. The record on the chronograph consisted of a strongly

marked spiral line of over fifty turns. The two sparks from the Ruhmkorff-coil left their trace upon the blackened paper as spires, which therefore measured the number of revolutions of the cylinder between the swings of the pendulum, and thus gave the rate at which the mirror was revolving. The chronograph record enabled us to measure the time to  $\frac{1}{500}$  of a second.

In any operation which requires that an electrical spark should make a record upon a disk or cylinder revolving at great speed a large Ruhmkorff-coil and a strong battery are necessary, especially if the primary circuit of the Ruhmkorff-coil is broken by a pendulum. With the ordinary automatic break, such as is commonly employed upon induction-coils, the failure of a single break is unimportant. If, however, a single break fails when a pendulum-break is employed, the record of the experiment is an imperfect one. An excess of battery-power and a large battery are therefore necessary. A metallic breakpiece also was found to be more inconstant for our purposes than a mercury-break.

It was found that a certain simplicity of contrivance was necessary in the method of discharging the air condenser through the inductance-circuit. No arm connected with the revolving mirror could be trusted to break or make an electrical circuit by throwing in or out any form of switch. The great speed at which it revolved broke all arrangements which were tried. By placing a short stiff brush of minute size upon the end of the flying terminal connected with the revolving mirror, and allowing this brush to rub against a brass plate set in an ebonite circle of 41 centim. in diameter, constancy of action was secured.

In order to obtain the same difference of potential at each run, experiments were first made with various forms of unit-jars and pith-ball electrometers. These devices were speedily given up in favour of a simple balance-electrometer. One of the pans of a delicate balance was replaced by a metallic disk. A similar disk, which was stationary, was placed immediately below the movable one. By properly weighting the remaining balance-pan great delicacy and range of indication were obtained. This apparatus constitutes, in fact, an absolute electrometer. A suitable guard-ring can be placed around the movable disk.

When the air condenser had been charged to a definite potential, the movable disk of the electrometer closed an electrical circuit in which was included an electrical bell. The observer stationed at the chronograph, at the instant he heard the bell, drew the carriage connected with the stylus

along the guides which kept the stylus on the blackened cylinder.

Calling  $L$  the coefficient of self-induction, we have

$$\frac{L}{l} = 2 \log \frac{b^2}{a^2} + 1^*$$

in which  $l$  is the length of conductors contained between two parallel planes;  $b$  the distance apart of the conductors;  $a$  the radius of wires.

In our case the effect of the ends was found to be inappreciable. The induction due to the ends can be calculated by the repeated employment of the formulæ for geometric mean distance† for two lines whose directions intersect at right angles.

Lord Rayleigh has given the following formula for inductance under rapid oscillations:—

$$L' = l \left( A + \sqrt{\frac{\mu R}{2\rho l}} \right);$$

in which  $A$  is a constant, depending on form of circuit;  $\mu$  is permeability;  $R$  is resistance;  $\rho = \frac{2\pi}{t}$ , where  $t$  is time of oscillation;  $l$  is length to and fro of inductance-circuit.

The final value of  $L'$  for our case is  $L' = 39697$ .

The radius of the wire employed was  $a = .0501$  centim.

The length was measured in three sections:—

No. 1, length 1197.0 cm., distance between wires  $b_1 = 31.55$  cm.

No. 2, " 281.0 " " "  $b_2 = 16.1$  cm.

No. 3, " 103.0 " " "  $b_3 = 11.3$  cm.

The ohmic resistance of the wires was  $.742 \times 10^9$  for direct current, and  $1.54 \times 10^9$  for alternating currents of period  $t = .0000031$ .

The difficulty in the process of photographing the spark consisted in discharging the air condenser through the induction-circuit at the instant the revolving mirror was in a position to reflect the image of the spark to the photographic plate. The terminal connected with the revolving mirror, which allowed the electrical discharge to pass when the mirror was in the desired position, had to be adjusted with extreme care. The speed of the image at the photographic plate was about 1 mile per second.

The photographs were measured by means of a dividing-engine. At first an objective of low power was used on the microscope of the dividing-engine. It was found, however,

\* Maxwell, § 685, vol. ii.

† Ibid. § 692, vol. ii.

that a simple cross-hair, unaided by a lens, moving directly against the negative, was better than any eyepiece. Measurements were made of the intervals between the electrical oscillations at both terminals.

In later experiments a smaller air condenser was employed, for reasons which will appear in the conclusions of our paper.

A summary of the details and dimensions employed is given herewith.

Small air-condenser (No. 2), cylindrical.

19 zinc cylinders.

Height 30.47 centim.

Diameter of inner cylinder 7.60 centim.

Diameter of outer cylinder 25.95 centim.

Average distance apart .5 centim.

Capacity (geometric) 5317.9 absolute units—corrected for the capacity of ends.

Capacity of wire, 200.

Self-induction in three sections, radius .0501.

1. Length, 1197.

Distance apart of parallel wires, 31.55.

2. Length, 281.

Distance apart, 16.10.

3. Length, 103.

Distance apart, 11.3.

For alternations of slow period.

Ohmic resistance, .742.

Self-induction, 41090.

Theoretical time with these values, .00000310 sec.

For alterations of period, .00000310 sec.

Ohmic resistance, 1.54.

Self-induction, 39700.

Theoretical time, .00000304.

Distance from spark to concave mirror, 230 centim.

Distance from rotating mirror to negative, 259.7 centim.

Sparking distance, .23 centim.

The following is a sample record (see figs. 5 and 6, p. 332). Each negative was measured three or more times, and the mean taken. The lengths are given in centimetres. The last line is the time in millionths of a second.

Right Terminal.

.289	.541	.561	.598	.552	.511	.544	.560	
.295	.528	.560	.595	.542	.542	.550	.585	.492
.290	.528	.582	.602	.518	.538	.550	.570	.532
.292	.518	.585	.592	.540				
.291	.529	.572	.597	.540	.528	.549	.572	.512
1.65	3.00	3.24	3.38	3.06	3.00	3.11	3.24	2.90



## Left Terminal.

·461	·611	·582	·522	·508	·551	·554
·464	·609	·567	·543	·500	·585	·556
·462	·607	·574	·532	·502	·570	·542
·462	·609	·574	·532	·503	·569	·551
2·62	3·45	3·25	3·01	2·85	3·22	3·12

Number of revolutions per second, 54·06.

Length of spark, ·23 centim.

The discharge of a glass Leyden-jar gave the following values, when reduced to seconds, different lengths of spark being used.

Length of Spark.	Terminal.	Time of Successive Oscillations.						
·4 centim.	{ Right	1·66	3·22	3·30	3·44			
	{ Left	3·33	3·37	3·30	3·36			
1·3     "	{ Right	1·71	3·32	3·45	3·37	3·42		
	{ Left	3·30	3·43	3·42	3·43	3·42	3·50	

Fig. 7 shows that the length of the spark exerts an inappreciable effect.

The following table gives the values in millionths of a second of the successive oscillations on six negatives taken with small air condenser under the conditions given on the preceding page. The first on the right terminal is a half-oscillation. The rest are double oscillations.

## Right Terminal.

1·65	3·00	3·24	3·38	3·06	2·91	3·11	3·24	2·90
1·68	3·22	2·99	3·35	3·03	2·97			
1·90	3·11	3·01	3·31	3·00	3·29			
1·95	2·95	3·00	3·08	3·06	3·20	3·03	3·03	3·16
1·62	3·01	3·34	3·04					
1·64	3·18	3·14	3·18	3·03				
1·74	3·08	3·12	3·22	3·04	3·09	3·07	3·13	3·03

## Left Terminal.

2·62	3·45	3·25	3·01	2·85	3·22	3·12		
2·89	3·50	3·08	3·21					
3·11	3·12	3·30	2·96	3·35	3·39	3·16	3·06	
2·75	3·63	3·02	2·97	3·48	3·22	3·00	3·18	3·19
2·84	3·19	3·36	2·89	3·41	3·00			
2·88	3·19	3·13	2·90	2·96				
2·85	3·39	3·19	2·99	3·21	3·21	3·09	3·12	3·19

The values for the different negatives are plotted in figs. 1, 2; the mean values, in figs. 3, 4. The time of the first half-oscillation was doubled in plotting. On each ordinate is

plotted the time of one oscillation—on the first ordinate the time of the first oscillation, on the second the time of the second. It should be noted that the curved lines are mean-

Fig. 1.

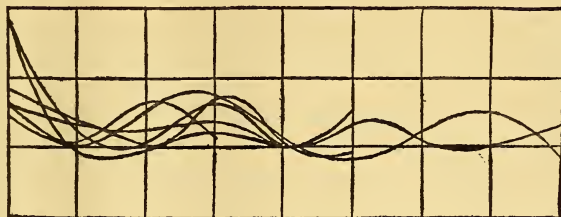


Fig. 2.

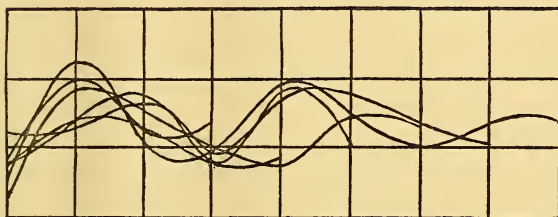


Fig. 3.

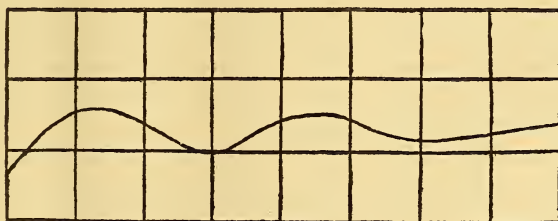
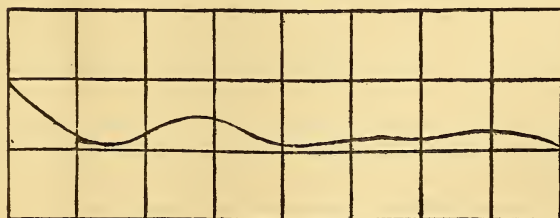


Fig. 4.



ingless, except where they cross the vertical ordinates, serving merely to connect the points belonging to one negative.

The difference in the time of oscillations cannot be explained by the vibration of the discharging arm lengthening and shortening the sparking distance, since this would necessitate a vibration frequency of 100,000 per second, and an

Fig. 5.

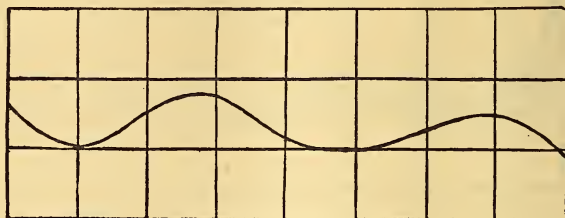
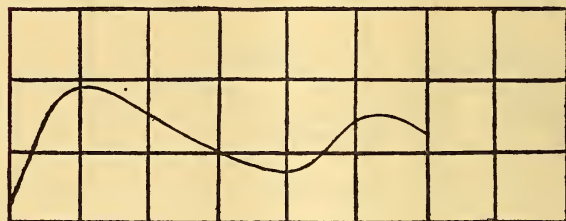


Fig. 6.



amplitude of at least one millimetre ; a velocity and momentum impossible for the apparatus either to acquire or endure. This cause also would tend to make the variation range equally above and below the calculated value as the sparking distance increased or diminished.

Another explanation may be sought in the varying ohmic resistance of the path of the spark, although this explanation is inadequate to explain the whole effect. In order to test it, a long (1·3 centim.) and short (·4 centim.) spark were taken from a glass Leyden-jar (see fig. 7). Not only could no appreciable difference between the two plates be detected, but there was no variation in the time of successive oscillations.

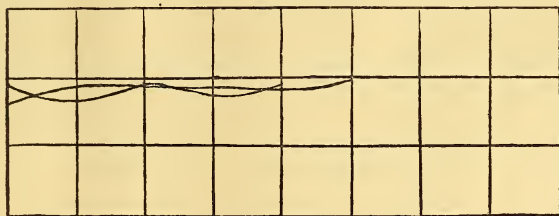
In regard to the measurement of the negatives on the dividing-engine, the following points may be worthy of mention. At the time the measurements were made, it was expected that the sparks from the glass condenser would show the variations, and that the air condenser would give the constant and theoretical period of oscillation. The reverse of this appeared when the results of the measurements were reduced. Moreover, the measurements were made by a run of the dividing-engine from one end of the negative to the

other ; so that if an error was made in the setting of the cross-hair on the image of one discharge—for example, making the measurement of that oscillation large—a corresponding amount would be deducted from the measurement of the next oscillation. The result of this would be that if the apparent variations were due to errors in measurement, the periods of discharge would be alternately large and small, or at least as often and as far below the theoretical value as above it. But this is conspicuously not the case.

A consideration of the curves which represent our results shows that with quick oscillations which result from the employment of a small air condenser, the air dielectric did not have time to recover completely, in the time of one oscillation, from the strain to which it was subjected. With the larger air condenser, the oscillations being slower, more time was given for this recovery, and hence the periodicity which we have discovered was not so marked. It seems, therefore, that not only should an electrical resonator be turned for capacity and self-induction, but also for a certain periodicity of strain in the dielectric.

In the case of glass, we should not expect to obtain evidence of this periodical recovery from a quick strain, since it is well known that the recovery from strain is so slow that the discharge from a Leyden-jar is incomplete after a discharge lasting a second. The curve we give for glass (fig. 7) shows

Fig. 7.



that this periodical recovery is too slow to manifest itself during the time of quick oscillation.

It is perhaps unnecessary to call attention to the fact that the capacity of a dielectric for rapid discharges is very different from its capacity for slow discharges. In the paper of Lorenz, already cited, the value of the dielectric capacity of glass was determined by slow methods, and used to test an equation in which the capacity of glass appears under very rapid charging and discharging.

*Phil. Mag. S. 5. Vol. 30. No. 85. Oct. 1890. 2 A*



Boltzman\* and Klemencin† have experimented on the specific inductive capacity of gases and vapours, and it is seen from their results that the agreement between the square root of the capacities of the simple gases and  $\mu$ , the index of refraction for light of these gases, is quite close, as is demanded by Maxwell's electromagnetic theory of light. A marked difference, however, was found to exist in the case of more complicated molecules—sulphurous acid, or ethyl bromide, for instance. It is probable that the changes of specific capacity of heterogeneous media under rapidly alternating forces constitute an important factor in considering the possible agreement between Maxwell's theory of light and the results of experiment.

In order to see if an intense magnetic field could modify the transmission of electrical waves through a dielectric, the following experiment was tried. A glass Leyden-jar, 2·5 centim. in diameter and 28 centim. in height, connected with our inductance-circuit, was placed inside a coil consisting of 728 windings of large wire. The outer and inner radii of this coil were 27·7 centim. and 34 centim. Its height was 40·5 centim. The magnetic field in this coil was supplied by a Gramme machine, which gave a current through the coil of approximately 30 amperes. It was expected that a certain amount of the energy spent in producing the electrical waves would be consumed in a reaction on the magnetic field. The total duration of the electrical discharge did not appear to be notably affected by the magnetic field. Certain experiments seemed to show a decrease in the total number of electrical oscillations. A large number of experiments will be necessary to decide upon the effect of a magnetic field upon the passage of electrical waves through a dielectric. The difficulty of obtaining an electrical discharge under the same difference of potential made the experiment an extremely difficult one. The method seems to us to promise a discovery of Maxwell's displacement currents in dielectrics; and we are therefore continuing our researches in this direction with a modified form of apparatus.

### *Conclusion.*

1. The electrical oscillations in the air between the plates of an air condenser show a periodicity extending through the entire range of oscillations. We believe that this periodicity

\* Pogg. *Ann.* cli. p. 403 (1875).

† Abstract of Journal of the Society of Telegraph Engineers (1886), p. 108.

is the analogue of the phenomenon of hysteresis in magnetism. A certain amount of the energy of the electrical discharge is spent in overcoming the dielectric viscosity of the air, and in straining the air dielectric. This strain is not immediately released in unison with the electrical surgings.

2. The discussion of our entire results shows unmistakably that electrical oscillations in air are not represented fully by the theoretical equations employed by Hertz. Since the latter writer has taken the term *resonance* from the subject of acoustics, and has given it a new significance in relation to electrical waves, we are tempted to draw also an analogy from the subject of sound. Laplace showed that the discrepancy between the value for the velocity of sound in air calculated from the theoretical equation, and that obtained by experiment, was due to a transformation of energy in heating and cooling the air during the passage of the sound wave. Our experiments on the transmission of electrical waves through the air show also that the values calculated from the theoretical equation do not agree with the experimental values. The discrepancy, we believe, can be explained also by a consideration of the transformation of energy in the dielectric.

3. The periodicity which we have studied is most manifest when the variable capacity of the air condenser bears a suitable relation to the time of the electrical surgings.

4. The electrical waves are apparently unaffected by passing through glass which is placed in an intense magnetic field, the direction of the electrical strain being perpendicular to that of the magnetic strain. The displacement currents of Maxwell in this case do not appear to affect the time of electrical surgings. This conclusion, however, may be modified by experiments which we shall try on a more extended scale.

### XXXVIII. On Magnetic Circuits.

By H. E. J. G. DU BOIS\*.

A CONSIDERABLE extension of our knowledge of magnetic induction has lately taken place. This, like many other additions to the realm of science, was chiefly called for in order to meet the wants of designers of electric machinery; and it has accordingly been arrived at in an essentially practical way. The aim of this preliminary communication is to show how physical science may draw advantage from some of these results, and may obtain them by unobjectionable purely

\* Translation communicated by the Author, being the abstract of a paper read before the Physik. Gesellschaft, Berlin, June 27, 1890.

physical methods. In doing so I shall not so much use the conception of lines of force, but shall rather start from the consideration of magnetization. For it is the latter quantity, which for experimental reasons (Phil. Mag. [5] xxix. p. 303, 1890) I believe must be taken as the fundamental one from the physical standpoint, much more so than induction, to which such importance has lately been attached.

The idea of an analogy (even when only in mathematical treatment) of magnetic systems with other systems of fluxes (hydrokinetic, thermal, electric) dates back as far as Euler. Faraday (and following him Maxwell) and Sir W. Thomson then each developed it in his own way. It has been worked out and practically applied, however, during the last century.

Bosanquet (1883), Rowland (1884), W. v. Siemens (1884), Gisbert Kapp (1885), especially consider the analogy with the flow of electricity, and accordingly apply Ohm's law to magnetic circuits. As, however, this law essentially implies the resistance being constant, independent of the current flowing, the above extension of its most characteristic meaning can hardly be conceded from the physical point of view; nothing is thereby meant to be said against certain practical advantages gained by introducing an (essentially variable) magnetic resistance. Quite lately, again, Pisati (1890) has laid much stress upon the analogy with thermal circuits, and accordingly has applied Fourier's law to certain magnetic systems. This appears perhaps less objectionable in so far as thermal conductivity is not necessarily a constant as its electric analogue is, though Fourier originally introduced the former as such. But even then it depends upon temperature, not upon its space-variation or upon the flow of heat: the analogy is therefore in no case a complete one, magnetic conductivity being of course independent of magnetic potential.

No physical objection, however, appears to exist to the totally different treatment the question received at the hands of J. and E. Hopkinson (1886): they started from two safely established mathematical propositions, and only made some auxiliary assumptions in order to simplify the (approximate) calculations. They so arrived at their graphic construction, now used to a certain extent in machine design, and which will be reverted to below.

Poisson's old theory of magnetic induction, extended by Neumann and Sir W. Thomson, as laid down *e. g.* in Maxwell's treatise, is known to rest on the fundamental assumption of constant susceptibility; it therefore applies to all substances except "ferromagnetics" (iron, cobalt, nickel, magnetite, and any substance which may yet be found to behave similarly).

Kirchhoff then introduced a new theory (in 1853) by making the more general assumption that magnetization is a function (capable of experimental determination) of the total magnetic intensity. Besides the important solutions of certain particular cases (ellipsoid, closed ring), he restricted himself to giving a few integral equations in the place of Poisson's. However, these were of but little practical use, and are hardly more so now that Duhem has lately taken up the analytical problem anew.

A more geometrical treatment of the new theory showed the distributions of the vectors concerned to be as follows:—*(a)* magnetic intensity : lamellar ; *(b)* magnetization : complex-lamellar ; *(c)* induction : solenoidal ; *(d)* also the three vectors are easily seen to have the same direction at every point. The proof and further discussion of these propositions cannot be given here. It may be remarked that homogeneous, isotropic ferromagnetic substance is assumed, through which no electric currents are supposed to flow ; neither is hysteresis taken into account.

The simple type of a circuit not completely closed is a thin ring containing a radial air-gap and subjected to a uniform tangential magnetizing force. This particular case, a solution of which has to my knowledge never been attempted, is reducible to the known case of an ellipsoid of revolution. In fact it is only necessary that the “self-demagnetizing factor” be capable of calculation ; *i. e.* the number into which the magnetization has to be multiplied in order to obtain the intensity of the self-demagnetizing effect. Let this numerical factor be, as usual, denoted by  $N$  ; for sufficiently long ovoids (prolate ellipsoids of revolution) of axial ratio  $m$  it is found by the well-known equation

$$N = \frac{4\pi}{m^2} (\log_e 2m - 1).$$

Now let the gap of our ring have the angular value  $\alpha$  ; *i. e.* an arbitrary concentric circle in it being considered, the  $\alpha/360$  part of this will lie in air, the  $(360 - \alpha)/360$  part in the ferromagnetic substance. A consideration of the line-integral of the self-demagnetizing intensity, which must vanish along any such closed circular line of integration, leads as a first approximation to the result that

$$N = \frac{4\pi\alpha}{360 - \alpha} [\text{approx. } \div 0.35\alpha].$$

The proof cannot well be given without a diagram. Both particular cases are now comparable in every respect, as the following short table shows :—



Ovoid. <i>m.</i>	Factor. N.	Ring. <i>a.</i>
20	·0848	2·41
30	·0432	1·22
40	·0266	·76
50	·0181	·52
100	·0054	·15
$\infty$	0	0

Now Lord Rayleigh has given a graphic construction for ovoids, which Ewing expresses in the following words:— From the ordinary curve of magnetization for infinitely long ovoids, that corresponding to a given finite one may be obtained by shearing the diagram parallel to the axis of abscissæ through an angle, which is simply determined by N, therefore also by the given ratio of axes. By the above the curve for closed rings may now, in the same way, be sheared into a diagram for a ring with a given angular gap.

The analogy of this process with the Hopkinsons's well-known graphic method is obvious, though at first essential differences appear to exist; *e.g.* the quantities used for co-ordinates are not the same in both cases. However, a comparison in detail finally leads to the identification of both constructions, so that in any given particular case the curves would exactly overlap, supposing the coordinates to be measured to proper scales. Our problem, a solution of which was first necessitated and afterwards approximately given by machine practice, has therefore now been solved to the same order of approximation by physical methods.

The degree of this approximation, the allowable limits for thickness of ring and width of air-gap, the amount of "leaking" of lines of force, &c., can only be determined by experiment on as large a scale as possible.

### XXXIX. *The Isometrics of Liquid Matter.*

By CARL BARUS\*.

[Plates IX., X., XI.]

IT was my original intention to communicate the second part of this paper only; but I found that the data there given would not be intelligible without a clear account of the method of the work. Accordingly I supplied the first part from the 'Proceedings' of the American Academy (June 1890), where a fuller account of my compressor may be found.

\* Communicated, with the permission of the Director of the U.S. Geological Survey, by the Author.

The literature of the subject, which I submitted at some length elsewhere\*, need not be repeated here.

The work was suggested by Mr. Clarence King, and it represents a stage of physical progress of an inquiry in which we are conjointly interested.

# *I. The Method of obtaining and of measuring High Pressures.*

1. Andrews's screw-compressor has an advantage, inasmuch as the acting stress is brought to bear within the compass of the barrel. In other arrangements, such, for instance, in which a cylindrical plunger is forced home, stress must be exerted on the bed-plate, or applied in a way tending to flexure the plunger. The screw-compressor may therefore be taken as the model of an apparatus of greater strength and efficiency than was necessary in Andrews's† work. Hannay and Hogarth‡ were the first to carry an improvement of the screw into execution. They obtained pressures but little short of 900 atmospheres, stating that their reasons for stopping work at this datum were quite apart from the efficiency of their apparatus. With the screw-compressor described below, I reach and hold 2000 atmospheres with facility (§§ 17, 23). It is so constructed that a large volume of liquid may be operated on, admitting of a compression of five cubic inches. Special provision has been made for the insulation of parts, thus enabling the observer to apply the essential electric methods § in studying his test samples.

Particular notice should here be given of the remarkable modification of Desgoffes's differential manometer, by which Amagat || has measured over 3000 atmospheres; but Prof. Tait ¶ recently described the "manomètre à pistons libres" in connexion with his own researches. The Bourdon gauge has just been discussed by Prof. Greenhill\*\* and Mr. Worthington††. The Bourdon gauge used below is of the kind described by the former.

\* American Journal, [3] xxxix. pp. 478 to 481 (1890); cf. *ibid.* [3] xxxviii. p. 407 (1889). In these papers I endeavour to reach the isometrics through the isothermals.

† Andrews himself seems to have entertained this opinion. See Prof. J. D. Everett's account in 'Nature,' xxxix. p. 556 (1889).

‡ Hannay and Hogarth, *Chem. News*, xli. p. 103 (1880).

§ I have special reference to Prof. Tait's device. See *Proc. Roy. Soc. Edinb.* xiii. p. 2 (1884-1885); *Beiblätter*, x. p. 149 (1886).

|| Amagat, *C. R.* ciii. p. 429 (1886).

¶ Tait, 'Challenger Reports' (1873-1876), *Physics and Chemistry*, II.; see 'Nature,' xli. p. 361 (1890).

\*\* Greenhill, 'Nature,' xli. p. 517 (1890).

†† Worthington, 'Nature,' xli. p. 296 (1890).

*Screw-Compressor.*

2. The apparatus (Plate IX. fig. 1) consists essentially of a strong wrought-iron barrel, A B C, the head of which, A A, is suitably threaded, so that a steel screw, S S T, can be forced into it. The piezometer tube is attached at the end, C C, of the barrel. Barrel and tubes are quite filled with oil.

3. To obviate leakage I make use of two special devices, the first of which is the tinned screw. This is an ordinary well-cut machine screw of iron or steel, covered with a uniform thin adhesive layer of ordinary solder, by dipping it (after cleansing with soldering-salts) in a vessel of the fused metal. When forced into their sockets, these screws secure complete freedom from leakage, even at 2000 atmospheres and more. Gauges and other appurtenances may thus be attached to the barrel, and removed from it, with facility.

The other device is the gasket of marine glue\*, or other highly viscous liquid. A stuffing-box is easily made, by which this substance is kept pressed against the threads of the screw, or against the smooth surface of a cylindrical plunger. The cement admits of being shaped by pressure to fill up any cavity, but it is far too viscous to flow through capillary interstices. In a preceding paper† I found its viscosity to be 20 billion times the viscosity of water. Pressure, moreover, tends to close up all fissures between nut and screw, thus making the apparatus more efficient at high pressures than at low pressures, even if the cement should not itself increase in viscosity.

4. To rotate the screw S S T (figs. 1 and 3) it is provided with a lever (three feet long) and ratchet, L D R. The steel ratchet-wheel, R R, forged to the shaft T of the screw, is square-cut to correspond with the right-and-left click D. A pin, E, sliding in a socket of the lever, L, and actuated by a spring (fig. 1), enables the operator to adjust the ratchet either for forward or retrograde motion of the screw S T.

The screw S S is one inch in diameter with twelve threads to the inch.

5. The barrel, B B, is secured between guides, on the planed front of the bed-plates, F F, by two bolts (figs. 1 and 4). The rear of the bed-plate is hollowed to catch drippings.

The gland, K K, of the stuffing-box is of steel, and is provided with a large flange for screwing it forcibly in place.

\* Supplied, among others, by Ducretet of Paris, and by the Société Gènevoise. Perhaps pitch, or even molasses candy, would be similarly serviceable.

† Barus, Phil. Mag. xxix. p. 337 (1890).

If a thread be cut both in the end of the barrel and in K K, these parts tend to act as lock nuts on each other at high pressures. To obviate this annoyance, I devised the method shown in fig. 2. Here the thread *aa* is movable, being on the inside of a ring, *rr*, of steel, which fits snugly in a socket of the barrel. Rotation of *rr* is prevented by the projection *s*, corresponding to a slot in the barrel. In this way a tight stuffing-box is obtained. The same number of threads are cut both on the outside (*cc*) and the inside (*bb*) cylindrical surface of K K. Thus it can be rotated without moving the screw, S S T. The gasket of marine glue is shown at *mm*.

7. The barrel is perforated by four or more holes, suitably threaded to admit the tinned machine-screws (diameter  $\frac{3}{8}$  inch with 16 threads to the inch), at the end of the gauges or other appurtenances.

8. The piezometer tubes, U U U, of cold-drawn, weldless steel tubing\* are inserted in such a way as to insulate them electrically from the barrel-end C C. A screw is cut on the end of U U U, fitting into an iron flange, W W, between two cylindrical jackets, X X and Y Y, of hard rubber or ivory. X and Y fit the hole in the barrel and the aperture of the gland Z Z very snugly. All other space within C C is filled with marine glue, by compressing the thick gasket *dd*. To obviate electric contact X X is flanged and W is of smaller diameter than the hole in the end C C of the barrel.

9. The outer end of U U U is closed by a tinned screw V (fig. 5). The substance to be examined is here introduced, usually in glass tubes (see next section, § 24). As a rule these tubes are adjusted within the compass of the copper vapour-bath *ff* (fig. 5), which surrounds U U excentrically. This bath is a long cylinder of brazed sheet copper, containing the liquid *yy* to be boiled. Vapours escaping are condensed in a lateral tube (not shown) and run back, thus making the ebullition continuous. A number of these baths are at hand. In order to pass from one temperature to another, it is merely necessary to slip off one vapour-bath and slide on another. The copper vessels are thickly jacketed with asbestos, and the tubulures *hh* are either closed by perforated corks, or at high temperatures (200°–300°) by stuffing-boxes (not shown) appressing the corks. The tubulure *g* receives the insulated platinum/platinum-iridium thermocouple for measuring the temperature of the bath. Tubes or jackets through which cold water

\* Obtained from John S. Leng, New York, or Philip S. Justice, Philadelphia, U.S.A. Both these gentlemen are Agents of an English house whose address is not known to me.



flows must surround U U, between the barrel and the vapour-bath, and between this and the end-screw V. It is essential that vapour be directly in contact with the piezometer. For fine temperature-work (§ 30, next section) and below 200°, I use the drum *ff* merely for the reception of vapour, leading it in at one end of the bottom, and suitably withdrawing it at the other. Low temperatures are obtained by a jacket of circulating water.

10. In figure 4, O P Q indicates the method of filling the barrel with oil. It is quite as convenient, however, to simply pour it in, after removing one of the screws M, fig. 1.

11. A case of two-inch plank closely surrounding the machine is easily devised. A barricade should be placed beyond the end V of the piezometer tube.

12. A vertical piezometer similar to C C U U, but smaller in dimensions, and ending below in a finely perforated steel screw, may be attached at M (§ 23).

### *Pressure Measurement.*

13. Pressures are measured in terms of the volume increase of a long, cold-drawn steel tube, closed at one end, while the other end communicates with the interior of the barrel B B, fig. 4. It may be called a Tait gauge, since the elastics of this case were specifically investigated by Prof. Tait\*. This gauge is inserted at N, and is shown at *qq*, *tt*, *ss*. To measure the expansion of the steel tube *qq*, it is surrounded by a close-fitting glass tube *ttt*, one end of which is joined to *qq* by an internal layer of marine glue, *vv*, surmounted by a tight cap of fusible metal. This joint is rigid as well as reliably hermetic. The other end, of *tt*, communicates with the capillary tube *ss*, by which the volume increase is measured. In fig. 4 *ss* is shown vertically; but it is expedient to bend it horizontally, parallel and close to the water-jacket *uu*, to which *ss* is rigidly fastened directly over a glass millimetre-scale. Pressure on the outside of *tt* appreciably displaces the meniscus in *ss*, an error to be guarded against.

The shell-like space between steel tube *qq* and glass tube *tt* is quite filled with a liquid of small coefficient of expansion. Neither mercury nor alcohol were found satisfactory. I therefore used pure water, coloured with a little fuchsine. This is introduced through *ss*, by repeatedly evacuating *tt* and boiling out all traces of air.

I obtained the requisite constancy of temperature by sur-

\* Tait, 'Challenger Reports,' II. 1885, App. A, p. 26.

rounding *tt* with a jacket *uu* of circulating cold water, coming directly from the hydrant. The meniscus in *ss* may be raised or lowered, and coloured when faded, by inserting filamentary glass suction-tubes into the capillary (§ 14). Water free from air scarcely attacks steel.

14. To graduate this gauge, I compared it with a large Bourdon gauge\* reading from 0 to 1000 atmospheres (§ 1). This comparison is a check on both instruments, though it affords no means of testing the standard atmosphere employed. Since both gauges are based on Hooke's law and provided with suitable scales of equal parts, relations are well indicated. In Table I.,  $2a_0$ ,  $2a_1$ , and  $L$  denote the internal and the external diameters, and the length, respectively, of the steel tube  $qq$ , fig. 4;  $2\rho$  is the bore of the capillary *ss*.

TABLE I.—Comparison of Tait Gauge and Bourdon Gauge.

$2a_0 = \cdot 54$  centim.;  $2a_1 = 1\cdot 00$  centim.;  $L = 100$  centim.;  
 $\rho = \cdot 034$  centim.

Time .....	—	15 m.	30 m.	45 m.	75 m.	90 m.
Gauge ...	Bourdon.	Tait.	Tait.	Tait.	Tait.	Tait.
	atm.	centim.	centim.	centim.	centim.	centim.
	0	1·90	2·10	2·00	2·18	2·16
	100	3·58	3·70	3·60	3·85	
	200	5·20	5·50	5·35	5·55	
	300	7·05	7·25	7·20	7·45	7·30
	400	8·70	9·00	8·90	9·10	
	500	10·50	10·72	10·70	10·85	
	600	†12·50	12·50	12·45	12·55	12·70
	700	14·10	14·10	14·10	14·20	
	800	15·65	15·70	15·70	15·85	
	900	17·22	17·20	17·30	17·45	
	1000	18·80	19·00	19·00	19·10	19·20
	900	16·62	16·70	16·80	16·80	
	800	14·65	14·70	14·63	14·70	
	700	12·80	12·80	12·75	12·92	
	600	10·95	11·00	11·00	11·12	11·00
	500	9·30	9·28	9·23	9·35	
	400	7·55	7·55	7·50	7·60	
	300	5·95	6·00	6·10	6·15	5·85
	200	4·50	4·55	4·60	4·60	
	100	3·04	3·12	3·15	3·20	
	0	1·74	1·90	1·90	2·00	1·60
Rate in centimetres } per atmosphere... }		·0169	·0171	·0172	·0172	

† Break in the measurements.

\* Furnished by the Société Génèvoise.

15. The table contains five series of observations made at the times (minutes) stated. Not more than two or three minutes were allowed per observation. Comparing data on the same or corresponding horizontal rows, the maximum difference is .40 centim., or 24 atmospheres. Comparing the two zero readings of the last column (work intentionally hastened), the difference of reading is .56 centim., or 33 atmospheres. This is the maximum index of error in case of unreasonably hasty work (§ 18).

16. A second point of view is obtained by comparing the data of the pressure "on" and the pressure "off" phases of the above experiments. This is done in the chart, fig. 6 (Pl. X.) No. 0. The accordance in the "on" phase is satisfactory, since the errors are not above 10 atmospheres, and the loci very nearly straight. The "off" data do not return in the lines of the "on" data. Indeed the two curves, "on" and "off," enclose a band the maximum width of which is 1.5 centim. or 90 atmospheres.

17. To interpret this curious phenomenon I compared the gauges after several months' use. At least five minutes were allowed per observation. Two complete series are given in Table II. This table also gives some data on the constancy of the zero after very high pressure. Slight shifting equivalent to 5 or 10 atmospheres is observable after 2000 atmospheres.

TABLE II.—Comparison of the Bourdon Gauge and the Tait Gauge, No. 0, four months later.

Large Bourdon.	First Series.		Second Series.		Factor.	Mean Factor.	High Pressure Tests.	
	Pressure "on."	Pressure "off."	Pressure "on."	Pressure "off."			Pressure.	Reading.
atm.	centim.	centim.	centim.	centim.	cm./atm.	cm./atm.	atm.	centim.
100	6.40	6.30	6.35	6.20	.01715	.01722	0	4.90
200	8.10	7.95	8.03	7.88	.01725		2110	40.93
300	9.87	9.70	9.80	9.60	.01720		0	5.10
400	11.57	11.39	11.50	11.32	.01728		2160	41.95
500	13.29	13.23	13.20	13.12			0	5.20

The character of Tables I. and II. is identical. Hence to account for the apparent hysteresis it is necessary to construct other Tait gauges. This I did with much care.

18. The new gauges are No. 1, about of the same length as No. 0, and No. 4, which is much shorter. The glass tube (*tt*, fig. 4) is as close-fitting as practicable, and the capillary

TABLE III.—Comparison of large Bourdon Gauge with the Tait Gauge No. 1.

$\rho = .0220$  centim. ;  $L = 100$  centim. ;  $a_1 = 1$  centim. ;  
 $a_0 = 27$  centim.

Large Bourdon.	Pressure "on." No. 1.	Pressure "off." No. 1.	Large Bourdon.	Pressure "on." No. 1.	Pressure "off." No. 1.
Atm.	centim.	centim.	Atm.	centim.	centim.
0	17.81	17.96	0	5.96	6.21
100	21.30	21.00	100	9.42	9.14
200	25.03	24.31	200	13.17	12.36
300	28.85	27.75	300	17.00	15.74
400	32.63	31.32	400	20.74	19.13
500	36.50	35.12	500	24.60	22.84
600	40.35	39.11	600	28.45	26.75
700	44.05	43.10	700	32.15	30.76
800	47.55	47.12	800	35.78	34.75
900	51.25	51.27	900	39.57	39.00
			1000	43.36	43.40

TABLE IV.—Comparison of Tait Gauges Nos. 1 and 4.

No. 1.  $L = 100$  centim. ;  $a_0 = .27$  centim. ;  $a_1 = 1$  centim.

No. 4.  $L = 58$  centim. ;  $a_0 = .27$  centim. ;  $a_1 = 1$  centim.

No. 1.	No. 4.	Small Bourdon.	No. 1.	No. 4.	F <sub>1</sub> .	F <sub>4</sub> .
centim.	centim.	atm.	centim.	centim.	cm./atm.	cm./atm.
— 0.40	12.40	0	— 1.30	12.02	3.65	1.63
+ 8.38	16.45	100	+ 2.28	13.63	3.69	1.67
18.23	20.85	200	6.00	15.29	3.60	1.67
28.43	25.40	300	9.66	16.97	3.73	1.61
38.36	29.80	300	9.65	16.96	3.69	1.66
50.04	34.91	200	5.90	15.26		
59.93	39.41	100	+ 2.20	13.62		
*63.75	41.25	0	— 1.30	12.04		
55.03	37.33					
42.89	32.06					
31.90	27.19					
20.09	21.86					
+ 9.02	16.78					
— 0.55	12.30					

\* Respectively 1780 and 1790 atmospheres.

of No. 1 is of small bore, to insure special accuracy of reading. Both capillaries were calibrated. Of the many series of observations made, two for No. 1 are given in Table III., and



a long range comparison between No. 1 and No. 4 is given in Table IV. Five minutes were allowed per observation. In the second part of Table IV. both gauges are standardized by a comparison with a small, very sensitive Bourdon Gauge, found identical with the large Bourdon Gauge, used above.  $F_1$  and  $F_4$  are the factors found. In other series similar to Table III., the agreement of observations occupying like positions in like series is always very close, the mean difference being 1.2 atmospheres. Nevertheless the data of Table III. still show decided hysteresis. See fig. 6, No. 1 (Pl. X.). The maximum distance apart of the "on" and "off" series is about 40 atmospheres. Indeed I was even able to grade the cycles.

19. It is expedient to examine the chief sources of error involved. The cycles cannot be attributed to an imperfect Bourdon mechanism; for in adjusting the pressure at any given value just before observing, the actual pressures must as frequently be incremented as decremented, both in the "on" and the "off" series. Thus the aggregate error must be *nil*. Liquid adhering to the walls of the capillary tube *ss*, would show its largest discrepancy at zero atmospheres, following high pressure. Similarly, slight changes of temperature of the water in *uu* might displace the fiducial zero, but they would produce no persistent cyclic effects.

I think the clue for the interpretation of the apparent hysteresis is given by the form of the cycles, which is that of an archer's bow with the cord uppermost. Bearing in mind that the liquid in *tt* is heated by compression during the "on" series, and that even though gradually parting with its heat increment, it is, nevertheless, *continually* hotter than the surrounding medium; bearing in mind, moreover, that in the "off" series the water in *tt* is cooled by expansion, but that the water is hotter than the surrounding medium only during the high-pressure stages, and colder than this medium during the low-pressure stages (heat having been continually dissipated)—an explanation of the bow-shaped cycles is suggested. Tait gauges considered as thermometers are relatively very sensitive instruments; even my best gauges show displacements of 1 or 2 centim. per degree. Regarding the small cycle (17 atmospheres) of Table IV., it will be remembered that the error here occurs differentially.

A bow-shaped cycle may also be conceived to result as a viscous phenomenon, if strain (set) were gradually impressed on the gauges during the "on" series, which strain asserts itself during the "off" series. (*Cf.* § 34.) I must reserve my opinion until further experiments have been made, in which Amagat's "manomètre" (*l. c.*) is employed.

It follows, in general, that to obtain trustworthy data pressure observations must be recorded during the pressure-increasing phase of work only. In most cases (see next section) this condition is easily fulfilled, since the pressures sought are reached from zero.

20. From the dimensions  $a_0$ ,  $a_1$ ,  $L$ ,  $\rho$ , (Table I.), the increase of the external volume of the steel gauge-tube is  $47/10^6$  per unit of external volume, per centimetre of displacement of the thread in the capillary tube  $ss$  (fig. 4). This corresponds to a volume increment

$$v'/V = .0000008 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

per unit of external volume, per atmosphere.

Tait's formula (*l. c.*) modified to suit the present case is  $v'/V = \Pi a_0^2 (1/k + 1/n) / (a_1^2 - a_0^2)$ , where  $\Pi$  is the internal pressure, and  $1/k$  and  $n$  the compressibility and rigidity, respectively, of the steel employed. Taking  $k$  and  $n$  from Everett's\* tables, viz.,  $k = 1.84 \times 10^{12}$  and  $n = 8.2 \times 10^{11}$ , and putting  $\Pi = 10^6$  dynes,

$$v'/V = .0000007. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This result is of the same order as (1), § 19.

Similar results could be obtained for Tables II. and III. I think this method can be made sharp enough for the experimental measurement of  $1/k + 1/n$ .

21. In addition to the work done with Tait gauges, I spent some time in constructing a direct-reading, helical Bourdon. The results are not of interest here.

22. Instead of having a screw enter the barrel, similar results must be obtainable by forcing a cylindrical shaft into the barrel. The device shown within C C, fig. 1, proves that the gasket of marine glue is quite as serviceable for smooth cylinders as for screws.

The labour necessary in producing the above pressures decreases nearly as the fourth power of the diameter of the screw, *cet. par.* Similar advantages are gained by increasing the number of threads to the inch. Hence, supposing the initial pressures produced by a thick screw (diameter 1 inch say) at one end of the barrel, and the final pressures (above 2000 atmospheres, when the enclosed liquids have become much *less* compressible) produced by a thinner screw (diameter  $\frac{1}{2}$  inch say) at the other end of the barrel, the efficiency of the screw-compressor would be increased. In such a case the piezometer tube must be vertical, § 12. My purpose,

\* J. D. Everett, 'Units and Phys. Constants' (Macmillan, 1873), p. 53.

however, in limiting these experiments to 2000 atmospheres was to avoid straining the gauges, § 17. I add in concluding, that among the special facilities of the above screw-compressor is the micrometric accuracy with which pressure can be raised to and maintained at a given value, for any reasonable length of time.

II.—*The Isometrics\* of Ether, Alcohol, Thymol, Diphenylamine, and Para-toluidine.*

23. By aid of the machine, described in the foregoing section, I made the following investigation of the isometrics of liquids. The nature of the problem is clearly defined by the results of an earlier paper†, where it appears conformably with the inferences of Dupré, Levy, Ramsay and Young, and Fitzgerald, that liquid isometrics are lines of small curvature.

*Apparatus.*

24. The apparatus to be constructed is such that the criterion for constant volume is given by a reliable electric contact. Figs. 7 and 8 show the tube of constant volume. It consists of three parts:—the reservoir *ef* (diameter .3 centim. to .4 centim.), and the two capillary stems *ed* and *da* (diameter about .08 centim.), separated by the enlarged portion *d*, into which a platinum terminal *c* penetrates. Other dimensions are given in fig. 7. Fig. 8 (diagram) shows the tube ready for use. The end *g* has been sealed, holding the platinum wire (the other terminal) *mhn*, which passes through *fe* into the capillary. The substance to be tested quite fills *ef* and about one half the adjoining stem. The remainder of the tube is filled with mercury *lk*.

The tube thus adjusted is inserted into the piezometer U U, fig. 5, and the terminal *c* put in metallic connexion with the walls of the steel tube near V. The terminal *mo* is suitably insulated by surrounding it with a glass tube, and after passing quite *through* the piezometer into the barrel, fig. 1, is there put in metallic connexion with one of the screws M. The constant-volume tube *ag*, fig. 8, is thus held in horizontal position within the steel piezometer, by aid of its two tense terminals.

\* The word "isometric" is used by J. Willard Gibbs in his beautiful researches on graphic methods in the thermodynamics of fluids (Trans. Connecticut Acad. II. [2] p. 311, 1873; *cf. ibid.* p. 382). It has the advantage of priority if not of expressiveness, and I do not feel the need of withdrawing "isometric" in favour of "isochore," as is done by Ramsay and Young (Phil. Mag. [5] xxiii. p. 435, 1887).

† Barus, American Journal [3] xxxix. pp. 497 *et seq.* (1890).

25. The method of experiment is easily inferred. The glass tube being in place and quite surrounded with oil, piezometer and barrel are put in a simple circuit containing a battery and a galvanoscope. The electric contact, made or broken by forcing the screw SST in or out, is sharp and thoroughly reliable, even at 2000 atmospheres and 200°.

26. In passing from one constant temperature to another, there is danger either of forcing the mercury thread, *lk*, out of the tube *ag*, or into the reservoir *ef*. Hence when the temperature of *uu* is increasing, the pressure is to be increased in such a way as to keep the electric contact just made; and when temperature decreases the pressure is to be relieved in such a way as to keep the electric contact just broken. In these adjustments the screw and ratchet is very serviceable.

27. When a series of isometrics is to be mapped out, the volume of liquid between meniscus *k* and the free end *n* is suitably changed. This volume may be conceived to be either positive or negative.

28. The operation of filling the glass tube *ag* calls for some skill; but a description is beyond the scope of the present paper. I make extensive use of filamentary glass funnel-tubes, and of filamentary glass connexion-tubes communicating with the mercury air-pump.

Solid substances, like diphenylamine, must be kept fused after filling in a hot-water-bath, and the tubes *ag* are to be introduced into a hot piezometer.

29. The greatest care must be taken to have all parts of the tube clean, and to avoid rubber connexions or other material impregnated with sulphur. When the mercury appears dead, the tube is worthless.

30. Seeing that the piezometer tube is a good conductor, constancy of temperature cannot be guaranteed nor its value measured, unless the vapours of the bath be directly in contact with the tube, § 7. Methyl alcohol, 66°, water, 100°, amyl alcohol, 130°, turpentine, 160°, naphthaline, 215°, benzoic acid, 250°, diphenylamine, 310°, phenanthren, 340°, are available for boiling. They form a convenient series. A low (fiducial) temperature is given by ice, or by circulating water. It is essential that the vapour-baths slide on and off the piezometer easily. Jarring may break the thread of the constant-volume tube within.

31. To measure the temperatures I used a platinum/platinum-iridium thermocouple, with its junction in contact with the piezometer tube, near the centre of the vapour-bath. Thermoelectric force was expressed in terms of the *twist* of the platinum fibre which suspended the given astatic system of



the torsion-galvanometer\*. To calibrate this instrument the boiling-points of water and of mercury were first used. Finally, I made extensive comparisons with the glass re-entrant air-thermometer (§§ 35, 36).

32. Pressure was measured as shown in Section I., and the factor of the Tait Gauge frequently checked by aid of a small sensitive 300-atmosphere Bourdon Gauge. About 20 or 30 minutes were allowed to secure isothermal conditions, both for the gauge and the piezometer tube. Leaks must be avoided; otherwise the operator is apt to pump heat into the liquids. Particular care was taken to redetermine the initial pressure and temperature ( $17^\circ$  and  $68^\circ$ , respectively) *before* and *after* each high-temperature observation. This is a certain and an essential check on the validity of the results. At any high temperature at least four readings were made, about five minutes apart. The last two of these, if coincident, were taken.

#### OBSERVATIONS.

33. In the Tables below the notation used is as follows:—

$N'_\theta$ , deflexion in degrees of arc observed at the torsion-galvanometer.

$t$ , temperature of cold junction of thermocouple.

$n_\theta$ , correction by which  $N'_\theta$  is reduced to

$N_\theta$ , the deflexion which would be observed at the torsion-galvanometer, if  $t = 20^\circ$ .

$\theta$ , temperature of the substance in the constant-volume tube;  $\theta$  is computed from  $N_\theta$  and is identical with the temperature of the vapour-bath surrounding the piezometer.

$N_p$ , reading in centimetres at the capillary tube of the pressure-gauge.

$p$ , pressure corresponding to  $N_p$ , in atmospheres. Hence  $p$  is the pressure bearing on the substance in the constant-volume tube.

$\Delta\theta$  } temperature and pressure obtained by shifting the  
 $\Delta p$  } coordinates, so that the initial temperature and pressure may be zero.

34. For illustration I will give a full example of two of the many series of results obtained for ether and the other substances. Each series contains at least one observation at the boiling-point of water, the importance of which will presently be seen, § 35. Since the relation between  $p$  and

\* Cf. Barus, Phil. Mag. [5] xxix. p. 146 (1890).

$v$  is nearly linear, the gauge-reading for  $p=0$  is of secondary importance within the limits of the present paper. It was not noted carefully.

TABLE V.—Isometrics of Ether Observations.

$N_{\theta}'$	$t$	$n_{\theta}$	$N_{\theta}$	$\theta$	$N_p$	$p$	Series No.	Time.
°	°C.	°	°	°C.	centim.	atm.	XIV.	h m
7.147	21.2	.104	7.251	98.2	29.79	816		0 50
7.132	21.3	.112	7.241	98.0	29.86	819		1 25
.....	.....	.....	.....	18.0	4.29	118		1 30
20.080	21.7	.146	20.266	218.8	64.30	1761		1 55
20.071	21.8	.155	20.226	218.8	64.30	1761		2 45
.....	.....	.....	.....	18.1	5.19	142		2 50
4.144	22.2	.192	4.336	67.8	21.14	579		3 20
4.147	22.3	.200	4.347	68.0	21.14	579		4 0
.....	.....	.....	.....	(18.1)	(5.20)	(142)		4 5
13.177	22.3	.200	13.377	157.8	49.04	1344		5 0
13.194	22.3	.200	13.394	157.9	49.06	1344		5 5
.....	.....	.....	.....	17.9	5.39	148		5 30
.....	.....	.....	.....	17.4	4.18	114	XV.	0 52
20.371	20.0	.000	20.371	220.2	64.17	1758		1 43
20.353	20.0	.000	20.353	220.0	64.16	1758		1 50
.....	.....	.....	.....	17.4	4.23	116		2 20
7.212	20.8	.068	7.380	99.1	30.83	845		3 0
7.265	20.8	.068	7.333	98.8	30.84	845		3 5
.....	.....	.....	.....	17.4	4.45	122		3 20
4.397	21.0	.087	4.484	69.1	21.37	586		3 50
4.415	21.0	.087	4.502	69.4	21.35	585		3 56
.....	.....	.....	.....	17.4	4.43	121		4 30
13.306	21.2	.104	13.410	158.0	48.93	1341		5 45
13.330	21.3	.112	13.442	158.3	48.98	1342		5 50
.....	.....	.....	.....	17.4	4.86	133		6 10

The change of  $p$  during the course of a series is noticeable, and it is due to the fact that the gauge, which had on a former occasion been compelled to do violent work, has not yet quite viscously recovered from the strain. The series XV. is better than series XIV. in this respect, and the improvement continues in all the other data, § 37. Of the two values of fiducial  $p$  which comprehend any high pressure  $p$ , the second is very probably correct and will be used below.

35. An inspection of all my data shows that the temperature datum needs correction. The cause of discrepancy is the temperature-coefficient and perhaps also the time-coefficient of the magnetic system of the torsion-galvanometer. This correction is easily applied, since whatever magnetic state obtains affects the twists corresponding to all temperatures of a given series, uniformly. If  $N'$  be the twist for  $100^{\circ}$  on any

day of observation, and if  $N_\theta$  be the corresponding twist on the day of final calibration, both observed at the same torsion-galvanometer, then  $N_\theta/N_\theta'$  is the reduction factor.

To test this inference I adduce two independent calibrations, over a month apart. If  $N_\theta = a(T-t) + b(T^2-t^2)$ , and  $t = 20^\circ$ , the data are expressed in Table VI.

TABLE VI.—Behaviour of the Torsion-Galvanometer\*.

April 20th  $\begin{cases} a' = .0844 \\ b' = .0000717 \end{cases}$  May 27th  $\begin{cases} a = .0829 \\ b = .0000694 \end{cases}$

T.	$N_\theta'$	$N_\theta$	$N_\theta/N_\theta'$	T.	$N_\theta'$	$N_\theta$	$N_\theta/N_\theta'$
$^\circ\text{C.}$				$^\circ\text{C.}$			
50	2.683	2.632	.9810	250	23.865	23.377	.9796
100	7.440	7.298	.9809	300	30.057	29.430	.9792
150	12.557	12.311	.9804	350	36.611	35.831	.9787
200	18.031	17.670	.9800	400	43.520	42.578	.9784

The change of  $N_\theta/N_\theta'$  is less than .3 per cent. for the whole interval  $50^\circ$  to  $400^\circ$ , a satisfactory result. Small reciprocal changes of  $a$  and  $b$  would wipe out this discrepancy without appreciably slighting the observations.

36. A more serious question, relative to the degree of truth of the interpolation equation  $N_\theta = a(T-t) + b(T^2-t^2)$  remains for solution. This can only be decided by direct air-thermometer comparisons. I used a re-entrant air-thermometer bulb †, and determined constancy of volume by aid of an electric contact. The bulb was heated in a closed cylindrical paraffin bath, 7 inches in diameter and about 7 inches long, heavily jacketed (1 inch thick) with asbestos. The disposition met was such as placed the thermoelectric junction at the centre of the bulb, which in its turn was at the centre of the bath. Observations were made in time series during the period of cooling down from  $300^\circ$ . I give an example of one of the three series of comparisons made in Table VII., where  $T_{a,t}$  is the temperature measured by the air-thermometer,  $N_\theta$  the corresponding twist at the torsion-galvanometer.  $T_{t,c}$  is the temperature computed from  $N_\theta$ , by aid of Table VI. Again,  $V$  is the zero volume of the air-thermometer bulb,  $v'$  and  $v''$  the volumes of the hot and cold parts of the stem and capillaries, and  $h_0$  is the tension of the gas at zero Centigrade.

\* Computed from observations at  $100^\circ$  and  $327^\circ$ .

† Bull. U.S. Geol. Survey, No. 54, pp. 168 *et seq.*, 188 *et seq.*, 1889.

TABLE VII.—Comparisons of Thermocouple and Air-thermometer.

$V = 239.93$  cub. centim.;  $v' = .030$  cub. centim.;  $v'' = .694$  cub. centim.;  $h_0 = 48.28$  centim.

Time.	$T_{a,t}$	$N_{\theta}$	$F_{t,c}$	Diff.	Time.	$T_{a,t}$	$N_{\theta}$	$F_{t,c}$	Diff.	
h m	° C.		° C.	° C.	h m	° C.		° C.	° C.	
0 53	299.6	30.147	305.0	-5.4	4 18	122.5	9.629	123.4	-0.9	
1 05	295.3	29.261	301.2	-5.9	4 29	117.2	9.077	118.0	-0.8	
1 16	292.0	29.175	297.3	-5.3	4 38	113.1	8.696	114.3	-1.2	
1 25	289.1	28.836	294.8	-5.7	4 52	107.1	8.086	108.0	-0.9	
1 33	236.3	22.355	241.2	-4.9	5 29	94.0	6.717	94.0	$\pm 0.0$	
1 42	232.2	21.814	236.5	-4.3	5 39	90.9	6.430	91.0	$\pm 0.1$	
1 55	226.9	21.179	231.0	-4.1						
2 09	222.0	20.597	225.8	-3.8						
3 03	167.7	14.549	171.2	-3.5	* {	16	100.0	7.313	100.1	-0.1
3 13	160.9	13.794	164.1	-3.2		28	100.1	7.329	100.3	-0.2
3 24	153.4	12.911	155.6	-2.2		37	100.1	7.207	100.1	$\pm 0.0$
3 36	145.4	12.076	147.7	-2.3						

\* Comparisons in steam.

Series of this kind show at once that throughout every stage of cooling the temperature registered by the thermocouple is persistently higher than the corresponding temperature of the air-thermometer. Inasmuch as the system cools from the outside of the thermometer-bulb, this may be regarded as a mere indication of too rapid cooling. I must note, however, that by retarding or accelerating cooling, I did not materially change this discrepancy. Hence, without passing further judgment, I deduced both  $T_{a,t}$  and  $T_{t,c}$ , for all the observations below.

37. After correcting the temperature in the manner stated, I obtained the data for the five isometrics given in Table VIII. Temperatures  $\theta_{a,t}$  and  $\theta_{t,c}$  are measured by the air-thermometer and the thermocouple respectively. Two data under  $\Delta\theta$  are to be similarly interpreted.  $\Delta p$  is defined above, § 33. Slight irregularities of  $\theta$  still appear, showing that if temperature is to be measured by the torsion-galvanometer, check readings of the boiling-point of water must be made before and after each series of temperature observations. Two independent series are usually given for each substance.



TABLE VIII.—Isometrics of certain Liquids.

Substance.	$\theta_{t,c.}$ $\theta_{a,t.}$	$\Delta\theta.$	$\Delta p.$	Substance.	$\theta_{t,c.}$ $\theta_{a,t.}$	$\Delta\theta.$	$\Delta p.$
Ether (14).	17.8	0	0	Alcohol (2).	17.0	0	0
	99.7	81.9	712		100.4	83.4	899
	99.7	81.7	701		100.2	83.4	893
	18.0	0	0		16.8	0	0
	{ 223.1	{ 205.1	1643		{ 161.4	{ 144.6	1592
	{ 219.9	{ 201.9			{ 160.0	{ 143.2	
	{ 223.1	{ 205.0	1619		{ 161.4	{ 144.5	1582
	{ 219.9	{ 201.8			{ 160.0	{ 143.1	
	18.1	0	0		16.9	0	0
	{ 68.6	{ 50.5	437		{ 68.2	{ 51.3	541
	{ 69.2	{ 51.1			{ 68.9	{ 52.0	
	{ 68.6	{ 50.5	437		{ 68.1	{ 51.1	533
	{ 69.5	{ 51.4			{ 68.8	{ 51.8	
	(18.1)	(0)	(0)		17.0	0	0
	{ 160.4	{ 142.3	1202		100.4	83.4	895
	{ 159.2	{ 141.1			100.2	83.2	884
	{ 160.6	{ 142.7	1196				
{ 159.4	{ 141.5						
17.9	0	0					
Ether (15).	17.4	0	0	Thymol (1).	{ 67.7	{ 50.5	704
	{ 222.4	{ 205.0	{ 68.5		{ 51.3		
	{ 219.2	{ 201.8	1644		{ 68.2	{ 51.0	705
	{ 222.3	{ 204.9	1642		{ 68.9	{ 51.7	
	{ 219.0	{ 201.6	100.0		82.9	1555	
	17.4	0	0		99.9	82.7	1556
	100.2	82.8	729		{ 68.8	{ 51.6	714
	99.8	82.4	723		{ 69.2	{ 52.0	
	17.4	0	0		{ 69.8	{ 52.6	715
	{ 69.8	{ 52.4	464		17.2	0	
	{ 70.2	{ 52.8			100.0	82.8	1169
	{ 69.9	{ 52.5	464		100.0	82.8	1160
	{ 70.4	{ 53.0			17.2	0	0
	17.4	0	0		{ 124.9	{ 107.7	1508
	{ 159.5	{ 142.1	1220		{ 124.6	{ 107.4	
	{ 158.1	{ 140.7			1209	{ 124.8	{ 107.6
	{ 159.7	{ 142.1	{ 124.5			{ 107.3	
{ 158.4	{ 141.0	17.2	0	0			
17.4	0	0					
Alcohol (1).	17.2	0	0	Thymol (2).	17.0	0	0
	{ 70.1	{ 52.9	562		{ 68.5	{ 51.5	721
	{ 70.6	{ 53.4			{ 69.1	{ 52.1	
	{ 70.2	{ 53.0	556		{ 68.4	{ 51.5	729
	{ 70.9	{ 53.7			{ 69.0	{ 52.1	
	17.2	0	0		16.9	0	0
	100.2	83.0	891		100.1	83.2	1166
	100.2	83.0	888		100.3	83.5	1171
	17.2	0	0		16.8	0	0
	{ 160.8	{ 143.6	1583		{ 126.1	{ 109.3	1512
	{ 159.6	{ 142.4			{ 125.8	{ 109.0	
	{ 160.8	{ 143.6	1575		{ 126.9	110.1	1506
	{ 159.6	{ 142.4			{ 126.5	109.7	
	17.2	0	0		16.8	0	0

Table VIII. (continued).

Substance.	$\theta_{t, c.}$ $\theta_{a, t.}$	$\Delta\theta.$	$\Delta p.$	Substance.	$\theta_{t, c.}$ $\theta_{a, t.}$	$\Delta\theta.$	$\Delta p.$
Paratoluidine.	$\left\{ \begin{array}{l} 68.4 \\ 69.1 \\ 68.2 \\ 68.9 \end{array} \right.$ $\left\{ \begin{array}{l} 99.9 \\ 31.1 \\ 30.4 \end{array} \right.$ $\left\{ \begin{array}{l} 68.6 \\ 69.3 \\ 68.5 \\ 69.2 \end{array} \right.$ $\left\{ \begin{array}{l} 124.8 \\ 124.6 \\ 125.0 \\ 124.8 \end{array} \right.$ $\left\{ \begin{array}{l} 68.3 \\ 68.9 \\ 68.5 \\ 69.2 \end{array} \right.$ $\left\{ \begin{array}{l} 158.8 \\ 157.4 \\ 159.0 \\ 157.8 \end{array} \right.$ $\left\{ \begin{array}{l} 68.5 \\ 69.0 \\ 68.5 \\ 69.0 \end{array} \right.$	0  0  56.3 55.4 56.7 55.9 0 0 90.3 88.2 90.5 88.8 0 0 0 0	0 452 441  809 799  0 0 1137 1124  0 0	Diphenyl-amine (2).	$\left\{ \begin{array}{l} 163.7 \\ 162.4 \\ 163.4 \\ 162.2 \end{array} \right.$ $\left\{ \begin{array}{l} 69.0 \\ 69.6 \\ 69.2 \\ 69.8 \end{array} \right.$ 99.9 100.2 $\left\{ \begin{array}{l} 69.5 \\ 70.1 \\ 69.7 \\ 70.5 \end{array} \right.$ $\left\{ \begin{array}{l} 127.1 \\ 126.8 \\ 127.6 \\ 127.3 \end{array} \right.$ $\left\{ \begin{array}{l} 70.0 \\ 70.8 \\ 69.8 \\ 70.6 \end{array} \right.$	$\left\{ \begin{array}{l} 94.7 \\ 92.8 \\ 94.4 \\ 92.6 \end{array} \right.$ 0 0 $\left\{ \begin{array}{l} 30.7 \\ 30.0 \\ 30.7 \\ 30.1 \end{array} \right.$ 0 0 0 $\left\{ \begin{array}{l} 57.4 \\ 56.3 \\ 57.6 \\ 56.5 \end{array} \right.$ 0 0 0 0	1346 1345   481 479  0 0 914 904  0 0
				* Thymol (3).	25.9 100.0 100.0 26.0 125.1 125.5 26.0	0 74.1 74.0 0 99.1 99.5 0	0 1048 1038 0 1388 1390 0
Diphenyl-amine (1).	$\left\{ \begin{array}{l} 68.3 \\ 69.0 \\ 68.2 \\ 69.0 \end{array} \right.$ 100.0 100.0 $\left\{ \begin{array}{l} 69.2 \\ 69.8 \\ 69.4 \\ 69.9 \end{array} \right.$ $\left\{ \begin{array}{l} 126.5 \\ 126.0 \\ 127.0 \\ 126.6 \end{array} \right.$ $\left\{ \begin{array}{l} 68.7 \\ 69.4 \\ 68.8 \\ 69.6 \end{array} \right.$	0  31.8 31.0 30.8 30.2 0 0 57.1 56.1 58.3 57.2 0 0 0 0	0 499 487  0 0 915 900  0 0	* Corroborative measurements made nearly two months <i>after</i> the preceding measurements. See § 42, end.			

38. Corrections are now to be applied for the thermal and elastic volume-changes of glass. Direct measurements of the elastic constants of my glass tubes, throughout an interval of  $300^{\circ}$  and 2000 atmospheres, are at present out of the question. Hence I selected liquids of large compressibility. Fortunately the correction is differential, and it will vanish in proportion as the isometrics of glass approach those of the above liquids (§ 43).

For the expansion of glass throughout long intervals ( $0^{\circ}$  to  $300^{\circ}$ ), results of Dulong and Petit\* and of Recknagel† are available. The coefficients of the former are the smaller. I will therefore accept them, seeing that inasmuch as the thermal variations of the compressibility of glass are not known, the smaller coefficients of expansion ( $\beta$ ) are preferable. Dulong and Petit found:—

$$0^{\circ} \text{ to } 100^{\circ}, \quad \beta = 26/10^6,$$

$$0^{\circ} \text{ to } 200^{\circ}, \quad \beta = 28/10^6,$$

$$0^{\circ} \text{ to } 300^{\circ}, \quad \beta = 30/10^6.$$

From these the volume of the constant-volume tube in terms of its capacity at  $20^{\circ}$  and  $70^{\circ}$ , respectively, are to be computed.

39. The compressibility of glass taken from Everett's tables (*l. c.*) agrees fairly well with the values due to Regnault, and more recently to Amagat‡; but apart from the fact that compressibility increases in marked degree with temperature, little further can be conjectured. Hence, for want of data, the volume of the glass tube under any hydrostatic pressure  $p$  (atm.) must be taken as  $1 - p \times 10^6/k$ , where  $k = 4 \times 10^{11}$ , irrespective of temperature.

The present and preceding paragraphs suffice for the computation of a table of double entry (the arguments being  $p$  and  $\theta$ ), from which the volume-changes  $\delta v$  of the glass constant-volume tubes, corresponding to any of the pairs of values of  $\Delta p$  and  $\Delta \theta$  in Table VIII., may be at once designated. A list of the values  $\delta v$  is given in Table IX., corresponding in arrangement with Table VIII. The curious feature of these data is that  $\delta v$ , as here computed, is sometimes positive and sometimes negative.

40. Having given these data, it is finally necessary to find what correction  $\delta p$  is to be added to  $\Delta p$  in order to com-

\* Dulong and Petit, *Ann. de Ch. et Phys.* [2] vii. p. 113 (1817).

† Recknagel, *Ber. k. Bayrischen Acad.* [2] p. 327 (1866).

‡ Amagat, *Comptes Rendus*, cvii. p. 618 (1888); cviii. p. 1199 (1889); he finds  $1/k = 2405/10^9$ .

pensate for  $\delta v$ , or, as it were, to annul it. The compressibilities of the liquids must therefore be known under the given conditions of *actual* pressure  $p$  and temperature. The results of my earlier paper\* are available for this purpose, except in the case of ether at high temperature, where the compressibility is estimated. Table IX. enumerates the divers compressibilities ( $d\frac{v}{V}/dp$ ) as well as the values of  $\delta p$  corresponding to each  $\delta v$ .

41. Utilizing these values I constructed the final Table X., in which the values of  $\Delta p$  and  $\Delta \theta$  are such as would be observed if the constant-volume tube were quite rigid. For  $\Delta \theta$  I give the thermoelectric values only (§ 36), believing these to be more nearly correct. The Table also contains  $p_0$  and  $\theta_0$ , which are the initial or fiducial pressures used in constructing  $\Delta p$  and  $\Delta \theta$ . For diphenylamine and toluidine  $p_0$  and  $\theta_0$  are estimated.

TABLE IX.—Corrections ( $\delta p$ ) for Thermal and Elastic-volume changes of Glass. (Cf. Table VIII.)

Substance.	$\Delta p$ .	$\delta v \times 10^6$ .	$10^6 \times d\frac{v}{V}/dp$ .	$\delta p$ .	Substance.	$\Delta p$ .	$\delta v \times 10^6$ .	$10^6 \times d\frac{v}{V}/dp$ .	$\delta p$ .
Ether (14).	705	+ 400	95	+ 4	Thymol (1).	705	—500	46	—11
	1630	1750	60	30		1155	—750	44	—17
	440	200	100	2		715	—500	46	—11
	1200	800	80	10		1165	—750	44	—17
						1500	—950	42	—23
Ether (15).	1640	+1700	60	+28	Thymol (2).	725	—500	46	—11
	730	350	95	4		1170	—750	44	—17
	465	200	100	2		1510	—850	42	—20
	1210	800	80	10					
Alcohol (1).	560	— 100	66	— 2	Para- toluidine.	450	—300	52	— 6
	890	— 50	63	— 1		810	—410	50	— 8
	1580	— 100	51	— 2		1130	—300	45	— 7
Alcohol (2).	900	— 100	63	— 2	Diphenyl- amine (1).	490	—450	43	—10
	1590	— 100	51	— 2		910	—650	40	—16
	540	$\pm$ 0	66	$\pm$ 0	Diphenyl- amine (2).	1345	—800	38	—21
	890	— 50	63	— 1		480	—400	43	— 9
						910	—700	40	—18

\* Am. Journ. [3] xxxix. p. 501 (1890).



TABLE X.—Isometrics. Digest of probable Results.

Substance.	$\Delta\theta$ .	$\Delta p$ .	Substance.	$\Delta\theta$ .	$\Delta p$ .
	° C.	atm.		° C.	atm.
Ether.	50.5	439	Thymol.	51.5	718
$\theta_0=18^\circ$ .	81.8	705	$\theta_0=17^\circ$ .	83.3	1154
$p_0=30$ atm.	142.5	1206	$p_0=80$ atm.	109.7	1486
	205.0	1649			
Ether.	52.5	466	*Para-	31.4	435
$\theta_0=17^\circ$ .	82.6	727	toluidine.	56.5	792
$p_0=30$ atm.	142.1	1219	$\theta_0=80$ atm.	90.4	1117
	205.0	1670			
Alcohol.	53.0	554	*Diphenyl-	31.3	477
$\theta_0=70^\circ$ .	83.0	887	amine.	57.7	884
$p_0=50$ atm.	143.6	1573	$\theta_0=68^\circ$ .		
Alcohol.	51.2	551	*Diphenyl-	30.7	469
$\theta_0=17^\circ$ .	83.4	888	amine.	57.5	886
$p_0=50$ atm.	144.5	1580	$\theta_0=68^\circ$ .	94.5	1324
Thymol.	51.3	700			
$\theta_0=17^\circ$ .	82.7	1141			
$p_0=80$ atm.	107.7	1472			

\*  $p=400$  atm., approximately. The Table assumes that for  $\Delta\theta=0$ ,  $\Delta p=0$ .

## DEDUCTIONS.

42. It conduces to clearness to express graphically both the data of Table VIII. and of Table X., as has been done in Pl. XI. figs. 9 and 10 respectively. In the latter the points are connected by straight lines, to emphasize the changes of curvature. Turning first to fig. 9, it is seen that below 1000 atmospheres the curves are so nearly linear that they may be accepted as such with an error no larger than  $2^\circ$  or  $3^\circ$  at 1000 atmospheres. An inspection of the individual points shows this to be within the limits of error. Regarding diphenylamine and toluidine, it is well to remember that the initial temperature is nearly  $70^\circ$ .

Above  $1000^\circ$  all the isometrics show definite curvature, in a way which often appears somewhat abrupt. This is particularly the case with diphenylamine and with toluidine, and to a smaller degree with ether. As a rule the curves are concave downwards, showing that the pressure-increments do not keep pace with the temperature-increments. The reverse, however, is to some extent true for alcohol, while the isometrics of thymol are practically straight within 1500 atmospheres. It is well to note that thymol has been undercooled

from 53° to 17°, without solidifying under the initial pressure.

Comparing figs. 9 and 10, the following slopes are found for the respective isometrics :—

TABLE XI.—Observed Initial Slopes of the Isometrics.

	Ether.	Alcohol.	Thymol.	Diphenyl-amine.	Paratoluidine.
	° C./atm.	° C./atm.	° C./atm.	° C./atm.	° C./atm.
Not corrected for volume- changes of glass tube (fig. 9) }	{ .114 .115 }	} .095	.071	.063	.070
Corrected for volume-changes of glass tube (fig. 10)..... }	{ .116 .114 }		.073 .072	.065 .065	} .072
Initial temperature, $\theta_0 =$ .....	17°	17°	17°	68°	68°
Initial pressure, $p_0 =$ .....	30 atm.	50 atm.	80 atm.	(400) atm.	(400) atm.
Boiling-point = .....	34°	78°	233°	310°	198°
Melting-point = .....	...	...	53°	54°	43°

It is seen from this Table as well as Table IX., that the correction for non-rigidity of the constant-volume tube does not exceed 2 per cent. In most cases, and for pressures not too high, it may be disregarded.

The slopes thus obtained (Table XI.) have no absolute value, since the data must vary with the initial volume under consideration. Volume-measurements are beyond the scope of the present paper. I may state, however, that a study of the thermodynamic surfaces of liquids, by the aid of consecutive isometrics, promises to be experimentally the most precise (§ 27).

If the change of curvature (figs. 9 and 10) above 1000 atmospheres were due to an unwarranted application of Hooke's law in case of the gauge, the curvatures of all the isometrics would change in somewhat similar ways at the same pressure. This is not observed in the figures, where each isometric is found to have an individual character. Tests made with thymol at the close of the above work reproduced the straight isometric very beautifully, showing that the curves for diphenylamine and toluidine are not influenced by marked gauge-errors (see Table VIII., end).

43. A singularly curious inference is suggested on comparing the approximate isometrics of solid glass computed in §§ 38, 39, with the liquid isometrics of Tables X. and XI. For glass the initial slope of the isometric is about .1° per atmosphere, a datum which comes very near (in order) to the slopes of the liquid isometrics, varying as they do between .07° per atm. and .12° per atm. This proximity of the solid

and the liquid isometric of compound matter is exceedingly striking. Solid metallic isometrics are quite different from the above (Table XI.). If  $1/k$  be the compressibility and  $\beta$  the coefficient of thermal expansion, the quantity  $10^6/k\beta$  is an estimate of the initial slope of the isometric, in degrees per atmosphere. Taking  $k$  and  $\beta$  from Everett's tables (*l. c.*), the slopes for steel, iron, and copper respectively are only  $\cdot 014^\circ$ ,  $\cdot 016^\circ$ , and  $\cdot 011^\circ$  per atmosphere. They thus preserve an order of magnitude smaller than that of glass, or the above organic liquids.

44. For the time being the above results admit of the following interpretation:—Whenever a substance passes from the liquid to the gaseous state, no matter whether this takes place continuously above the critical temperature, or discontinuously below it, the underlying cause is a change of molecule from a more complex to a less complex type. As long as the molecule remains unchanged the isometrics are straight. When the change of molecule takes place so as to begin with the liquid molecule and pass continuously into the gaseous molecule, the isometrics curve continuously for the linear isometric of the true liquid to that of the true gas. Such an explanation is of course tentative. It rests on evidence purely experimental and therefore of uncertain interpretation; and it is suggested by a controversy which I have summed up elsewhere\* as follows:—"The linear relation was predicted from theoretical considerations by Dupré (1869) and by Lévy (1884)—considerations soon proved to be inadequate by Massieu, H. F. Weber, Boltzmann, and Clausius. Ramsay and Young (1887) established† the relation in question experimentally for vapours, but not, I think, very fully for liquids decidedly below their critical points. Reasoning from these data, Fitzgerald (1887) investigated the consequences of the law; viz.:—(1) specific heat under constant volume is a temperature-function only; (2) internal energy and entropy can be expressed as a sum of two terms, one of which is a volume-function only and the other a temperature-function only. Thus Ramsay, Young, and Fitzgerald arrive substantially at the same position from which Dupré and Lévy originally started."

However, too much care cannot be taken in keeping clearly in mind that pressures which, in relation to the usual laboratory facilities, are exceptionally large, may yet be mere

\* *Am. Journal* [3] xxxviii. p. 407 (1889).

† For a pressure-interval not exceeding about 80 atmospheres for a group of isometrics, nor about 30 atmospheres for a single isometric. See Ramsay and Young, *Phil. Mag.* [5] xxiii. p. 435 (1887).

vanishing increments when mapped out on the scale of the molecular pressures of liquids and solids. It is from this point of view that I am about to make further experiments on the thermodynamics of fluid matter.

Physical Laboratory, U.S. Geological Survey,  
Washington, D.C., U.S.A.

## XL. *Intelligence and Miscellaneous Articles.*

### THE MAGNETO-OPTICAL GENERATION OF ELECTRICITY.

BY SAMUEL SHELDON, PH.D.

WHILE experimenting upon the effects of alternating currents of electricity upon the plane of polarized light, results were obtained which made it feasible to try a series of experiments, in which the Faraday arrangements were reversed. Although the series is incomplete, yet the little that has been accomplished seems worthy of publication.

It is well known\* that if a beam of plane-polarized light be passed through a tube containing bisulphide of carbon, and if the tube and beam lie in the direction of the lines of force of an electromagnet about to be excited, the plane of the emergent beam will be rotated upon exciting the magnet. The direction of rotation will be the same as that of the exciting current, and the amount of rotation will depend upon the strength of the current. If the current be reversed, the plane will be rotated in an opposite direction and by exactly the same amount. Thus the rapidly alternating current would produce a rapid swinging to and fro of the plane of light.

Now if a difference of potential, under these conditions, produces such a rotation of the plane, why should not a rapid rotation of the plane under exactly the same conditions produce an inverse difference of potential between the terminals of the coil? A continuous rotation should produce a continuous current of electricity, and an oscillating of the plane an alternating current. The experiments which have been performed verify the latter supposition.

The coil employed was wound upon a thin brass tube as a core. This was closed at each end by plates of glass, and was provided with holes for filling with carbon bisulphide. Its length was 175 millim. and its diameter 23 millim. Upon this was wound the coil from double silk-covered copper wire of 0.85 millim. diameter. When wound, the length of the coil was 150 millim. and its diameter 45 millim. The resistance was 7.21 ohms.

A quantitative measurement of the Faraday effect was first made and in the following manner:—A beam of light from an incandescent lamp, after passing through a large nicol, was made to traverse the bisulphide of carbon in the coil. Upon emerging,

\* Faraday, Exp. Res. 2146, vol. iii. p. 1.



the beam was brought to extinction by the proper adjustment of an analysing nicol. A measured current of electricity was now passed around the coil. This necessitated a readjustment and rotation of the analysing nicol to reproduce extinction of the beam. Within the limits tried, this rotation was proportional to the current strength. As a mean of many measurements, it was found that a current of 1 ampere required a rotation of 78 minutes of the analyser. Accordingly 278 amperes would be required to rotate the plane through  $360^\circ$ , providing the proportionality between current strength and rotation remained unaltered.

Now, if we consider a plane-polarized ray of light to be made up of two opposite circularly-polarized rays, then a particle of æther in the bisulphide of carbon describes a simple harmonic oscillation in a plane. This motion in a straight line is the resultant of the two oppositely directed, equiperiodic, circular rotations of equal amplitude. If now a magnetic field be created, the particle undergoes an instantaneous circular electric displacement which results in the retardation of one and the acceleration of the other component rotation. The line of oscillation suffers rotation as a result, and assumes a new position. The displacement must be instantaneous, for, were it continuous, the line of oscillation would continue to rotate and the analyser could not be made to produce extinction. If, now, instead of allowing the magnetic field to produce this circular displacement, we superimpose, by mechanical means, a third rotation upon the two existing components, then a magnetic field should result and an electromotive force be induced in a coil surrounding that field. Such a result would be obtained by rotating the polarizing nicol. The rapidity of rotation must be very great, and, if it requires 278 amperes (an impressed electromotive force of 2000 volts) to rotate the plane through  $360^\circ$ , then to produce this electromotive force the polarizer must be revolved with a frequency of the same order as of the oscillations of light. But a nicol cannot be revolved much above 200 times per second. The centrifugal force resulting from a higher rate will, owing to the strain produced, interfere with the performance of its functions as a polarizer. This rate of 200 revolutions per second would produce, in the apparatus employed, an electromotive force of perhaps 0.000000001 volt, giving a current too small to be detected by any galvanometer in my laboratory. Hence use was made of the extreme delicacy of the telephone as a substitute, and a swinging of the plane instead of a revolution.

The arrangement of apparatus was as follows:—Light from an arc lamp, after passing through a large nicol, was reflected, at a very obtuse angle, from a small movable mirror and then passed through the bisulphide of carbon in the coil before-mentioned. The two terminals of the coil were carried to a room three stories below and in another part of the building. Here they were con-

nected through a telephone and a switch. The mirror ( $10 \times 30$  millim.) was fixed in a brass frame free to rotate about an axis nearly parallel with the ray of light. This frame was connected by an eccentric and gears to the main shaft in the workshop. By this arrangement the mirror was made to oscillate through  $45^\circ$  about 300 times each second. The plane of polarization was thus twisted through twice that amount, or  $90^\circ$ , in the same time. While this oscillation was going on in the workshop, an ear placed at the telephone at the other end of the circuit could easily distinguish a tone, which, however, was the octave above that made by the moving mirror. When the circuit was broken the sound ceased to be heard, but upon again closing the tone became audible. With a rate of 200 oscillations per second the note was not so easily distinguished. But upon closing the circuit that peculiar sizzling noise so common in telephone-circuits was heard.

During the experiments the mirror was frequently broken by the high rate of vibration. But another was quickly substituted by my assistant, Mr. Baker, whom I have to thank for this and the construction and management of the rotating apparatus.—*American Journal of Science*, September 1890.

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#### ON THE OBSERVATION OF ELECTRODYNAMIC WAVES.

BY EMIL WIECHERT.

If the occurrence of electrodynamic waves of short period is observed in the manner originally indicated by Hertz, considerable difficulties arise from the very feeble light of the scintillæ. This difficulty is greatly diminished if the scintillæ are observed through a microscope, which sends to the eye a very large cone of light proceeding from the scintilla.

I made up such a microscope from a system of lenses which belongs to a polarizing microscope, and is used in this for observation with strongly convergent light, and the object-glass of a telescope. The linear magnification is about fiftyfold. The microscope gives diffused indistinct pictures, but fulfils its purpose so well that, in observing with it, the place of observation need not be darkened; in bright daylight scintillæ stand out clearly which the naked eye can only see with difficulty in darkness.

Another method is not only more sensitive, but enables a large number of persons simultaneously to observe the scintillæ; and can also be used with ordinary light.

Imagine a secondary conductor formed just as if the object were to observe the occurrence of scintillæ. Suppose that at first the secondary waves do not act. Let both halves of the secondary conductor be insulated from each other, and one put to earth while

the other is connected with a source of electricity which supplies electricity *slowly*. When the potential has reached a certain limit a scintilla passes between the two halves of the conductor; the potential then falls rapidly, then increases again until a fresh scintilla again diminishes it, and so on. If electrodynamic waves produce electrical vibrations in the secondary conductor, the sparks will obviously occur with a smaller accumulation of electricity than otherwise; this is the fundamental idea of the new method of observation.

In practically carrying out the observation I connect the half of the secondary conductor which is to be electrified with an ordinary electroscope, which contains two aluminium leaves which hang near each other. Each spark is then manifested by a sudden collapse of the aluminium leaves: attention is to be directed to this phenomenon. If electrodynamic waves act, the greatest angular deflexion of the aluminium leaves diminishes.

If the action of the electrodynamic waves is so violent that, even without artificial electrification of the secondary conductor, scintillæ occur in its spark-gap, the aluminium leaves remain almost without change.

I used at first a water-electrification machine as source of electricity; I now use a Wimshurst machine. A thread of proper length connects one electrode with the half of the secondary conductor which is to be electrified; in order to avoid too high tensions both electrodes are provided with points. If the machine is kept at work for a few seconds and is then left to itself, the store of electricity remaining in the Leyden jars is sufficient to keep up the play of the phenomenon.

The author points out the similarity of his method of observation to that of Boltzmann (Phil. Mag. [5] xxx. p. 126), which he had only seen after his paper was sent off. Hedwells on the very distinct way in which his method illustrates the phenomena.—Wiedemann's *Annalen*, vol. xl. p. 640 (1890).

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#### CONTRIBUTIONS TO THE DEMONSTRATION OF HERTZ'S EXPERIMENTS. BY G. BARTANIEK.

The author uses small incandescent lamps which have become useless owing to a break in the carbon filament, and which he inserts in the interval of Hertz's resonator. It is only necessary to connect one wire with one sphere of the resonator. At the break small green scintillæ appear with an aureole. On touching the glass side the light streams to the part touched, which acquires a green phosphorescence.—*Beiblätter der Physik*, vol. xiv. p. 654.

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XII. *On Refraction and Dispersion in certain Metals.*  
By H. E. J. G. DU BOIS and H. RUBENS\*.

[Plate XII.]

§ 1. **INTRODUCTORY.**—A method has been worked out by Prof. Kundt, by means of which the laws of propagation of light may be studied in exceedingly thin metallic prisms. By this method he has succeeded in obtaining, for a number of metals, the refractive index for light normally transmitted, the approximate value of the dispersion, and the effect of temperature on the former. As his papers† are everywhere easy of access, we shall often refer to them below in order to avoid needless repetition.

§ 2. Working on the same lines we have now made observations with light obliquely transmitted, in order in the first place to obtain an empirical rule of refraction. We then attempted to determine the dispersion as accurately as possible by using four colours defined by spectral lines. The three metals experimentally examined were iron; cobalt, and nickel; these were chosen for the following reasons:—

\* Translated by one of the Authors from the Berlin Acad. *Sitzungsberichte*, July 24, 1890, p. 955. The principal results were also communicated to Sect. A of the Brit. Assoc. at Leeds, Sept. 4, 1890.

† Kundt, Berlin *Sitzungsberichte*, Feb. 1888, p. 255, and Dec. 1888, p. 1387; referred to below as (A) and (B) respectively. Reprinted in Wied. *Ann.* xxxiv. p. 469 (1888), and xxxvi. p. 824 (1889). Transl., *Phil. Mag.* [5] xxvi. p. 1 (1888).



In the first place Dr. Lobach\* and one of us† published data for the dispersion of Kundt's and Kerr's magneto-optic phenomenon respectively in these three substances; those numbers refer to the same colours we have now used again. We so hope to contribute towards the experimental determination of strictly comparable optical constants.

Secondly, it is comparatively easy to obtain these metals electrolytically in wedge-shaped films. We may therefore safely assume that our metal prisms left little to be desired.

Lastly, the considerable amount of their refraction contributes towards the accuracy of measurement. In addition we shall occasionally have to discuss the behaviour of certain metals with much smaller refractive indices; however, we have not made any experiments on these (see § 16).

§ 3. *The experiments* were carried out almost in the same manner and with the same spectrometer as those made by Prof. Kundt in Berlin (B. pp. 1389-91). We did not use the heating arrangement there described; certain other special appliances were, however, devised, to be described in due time. Readings had previously either been taken off the spectrometer's divided circle or with a micrometer-eyepiece. Neither of these plans was adhered to in the present case; the adjustments being made instead by turning the micrometer-screw of the spectrometer's telescope (magnifying 10-fold). This having been done by one of the observers, the reading on the divided head of the micrometer-screw was taken by the other, observing through an auxiliary telescope placed at a distance. One division on the divided head corresponded to a rotation of  $4''\cdot20$  of the telescope round the spectrometer's vertical axis.

Refracting angles and deviations are always given in seconds, each being obtained from 20 readings. Generally the collimation was checked before each such set by observations through the lateral windows, according to the rules laid down by Prof. Kundt (B. p. 1390).

§ 4. *Checks* have been applied to the method in considerable number by Prof. Kundt (A. pp. 263-265). We have therefore only had to add a few measurements in order to test the method of collimation. A perfectly plane and parallel glass proof-plate of Steinheil's was blackened in such manner as to leave open four windows, of breadth  $\cdot2$  centim. and height  $1\cdot0$

\* Lobach, *Inaugural dissert.* Berlin 1890; reprinted Wied. *Ann.* xxxix. p. 358 (1890).

† du Bois, Wied. *Ann.* xxxix. p. 38 (1890); Phil. Mag. [5] xxix. p. 264 (1890).

centim., occupying the same relative positions as the prisms and windows of our metallic biprisms (see Plate XII. fig. 1). The collimation of the two outer windows was adjusted as usual, with the result that the inner pair of windows now gave an apparent angle of  $\cdot 2''$ , and an apparent deviation of  $\cdot 4''$ . A platinized glass plate treated in the same manner gave values  $1''\cdot 3$  and  $1''\cdot 8$  respectively; this had been previously labelled "middling," and was less perfectly plane than any of those carrying the biprisms finally experimented upon. The latter plates were of course carefully selected and tested by means of a Gauss's eyepiece.

These observations prove the method of collimation to have been sufficiently accurate for the object in view, as the refracting angles of the prisms\* lay between  $15''$  and  $25''$ , the deviation generally exceeding  $20''$  (up to  $200''$ , compare § 11). As regards the measurement of the angles and deviations, it may be remarked that these cannot appreciably have been interfered with through multiple inner reflexions. In fact the prisms were in every case so thick that films of double the thickness would have proved almost quite opaque†.

§ 5. It is impossible to give a general estimate of the accuracy reached; each prism exhibiting its particular individuality in this respect. In order therefore to enable the reader to form a judgment on our measurements, we have given a few detailed sets of observations (Tables I. and III.) besides the final values (Tables II. and IV.).

Our prisms were always kept in exsiccators, and proved to remain quite unaltered when thus treated. Thus we found the refracting angle as well as the deviation of a cobalt prism (Co III.), which had been left to itself for six months, not to have changed appreciably during this interval. The same was the case with an iron prism (Fe III.), the black coating of which had moreover been removed and replaced by a new one: this also proves the surfaces of the metal to have been sufficiently plane, as the reflecting patches left open on blackening certainly had not exactly the same boundaries in both cases.

We may remark that certain other experiments were occasionally made in this laboratory by Mr. Shea, using our prisms with a spectrometer by Schmidt and Haensch; these always quite confirmed our results.

\* As it is necessary to keep the thinner part of the prisms  $> 3 \times 10^{-6}$  centim. and the thicker part  $< 13 \times 10^{-6}$  centim., it follows that prisms with an angle much exceeding the highest value given in the text cannot be used. The mean breadth of the prisms may be estimated at  $\cdot 15$  centim.

† Compare Wernicke, *Pogg. Ann.* clv. p. 88 (1875); also Rathenau, *Inaugural dissert.* Berlin, 1889.

## I. REFRACTION.

§ 6. Measurements of the deviation on oblique transmission of light through the prisms would have possessed but little intrinsic interest. We had therefore first to find a legitimate way of developing, from our measurements, the relation which must needs exist between the inclinations of the wave-fronts in metal and air respectively to the surface separating both media. In doing so we wished to avoid all auxiliary hypotheses, and to base our inferences on none of the optical theories at present in vogue. The following treatment of the problem before us will show how far we have reached the end in view on the lines thus prescribed.

§ 7. *Notation.*—Accurately “parallel” light having been always used, we have to consider plane wave-fronts, and in particular the direction of their normals. Let the angles of these directions with the normals to the prisms’ surfaces be denoted by  $i_m$  in the metal,  $i$  in the air. These are evidently also the inclinations of the wave-fronts on either side of the bounding surface metal | air. For the refractive index we write the usual symbol  $n$ ; it has to be borne in mind that the index has a strictly physical meaning only when Snellius’s sine law\* holds absolutely or infinitely nearly (see § 12).

The angle between the normals  $N_1$  and  $N_2$  to the two surfaces of the biprism, as directly measured by Gauss’s eyepiece, will be called the “refracting angle”  $\beta$ ; it is the sum of the angles of the two prisms. The angle between two pencils of light, originally parallel, then each transmitted through a different prism, is the deviation  $\alpha$ .  $\beta$  as well as  $\alpha$  may be considered infinitely small for our present purpose; the mathematical treatment of the subject is thereby reduced to great simplicity.

§ 8. *Mode of Calculation.*—Fig. 1 represents a horizontal cross-section of our biprisms, of course not drawn to scale. The two surfaces are numbered 1 and 2, these numbers being also used as suffixes to distinguish quantities related to one or the other surface. Now consider two infinitely thin pencils of light, 1 and 2, parallel to one another; evidently these will continue parallel in the metal  $M$  up to points  $A_1$  and  $A_2$  infinitely near the surfaces 1 and 2. This is still the case if the glass plate or the film of platinum or both be wedge-shaped (as indeed they always are more or less). The paral-

\* The ordinary law of refraction still often goes by the name of Descartes; however, there can be no doubt but that the Dutch mathematician Willebrord Snell was the first to enunciate it.

lelism of both pencils cannot in any way be interfered with by anything happening at the bounding surfaces  $a, b, c$ . In fact this parallelism is only destroyed by refraction at the fourth boundary metal | air; therefore our experiments can only teach us something about what happens at this boundary, in particular about how  $i$  depends upon  $i_m$ . For our purpose it is, however, better to consider  $i$  the independent variable, as this angle is the one directly measured.

We therefore put  $i_m = f(i)$ , evidently a single-valued odd function, unknown as yet. From the diagram in fig. 1 it follows at once that

$$\nless N'_1 A_2 N_2 = i_{m2} - i_{m1} = di_m = \beta$$

and

$$i_2 - i_1 = di = \alpha + \beta$$

$$\therefore \frac{di_m}{di} = f'(i) = \frac{\beta}{\alpha + \beta}$$

and

$$f(i) = \int_0^i \frac{\beta di}{\alpha + \beta} \dots \dots (1)$$

§ 9. Now from our measurements we know the values of  $\alpha$ , and therefore also of  $\beta/(\alpha + \beta)$ , for a set of values of  $i$ . We therefore in a certain sense obtain an experimental differential equation of the simplest kind, which we have only to integrate in order to obtain the relation sought for between  $i_m$  and  $i$ . This we have actually carried out; with abscissæ  $i$  values of  $\beta/(\alpha + \beta)$  were plotted as ordinates, the points thus obtained joined by a smooth curve, and the values of the integral  $f(i)$  arrived at by graphical integration, starting from the initial value  $f(0) = 0$ , evident for reasons of symmetry.

§ 10. If the prisms be for a moment supposed to consist of ordinary transparent matter of index  $n$ , Snellius's law would hold, *i. e.*

$$i_m = f(i) = \sin^{-1} \left( \frac{\sin i}{n} \right), \dots \dots (2)$$

and this would give by differentiation the explicit equations

$$n = \sqrt{\left\{ \left( \frac{\alpha}{\beta} + 1 \right) \cos i \right\}^2 + \sin^2 i}, \dots \dots (3)$$

and

$$\alpha = \beta \left\{ \frac{\sqrt{n^2 - \sin^2 i}}{\cos i} - 1 \right\}, \dots \dots (4)$$

which will be repeatedly used below for purposes of calcula-



tion according as  $\alpha$  or  $n$  be considered given in addition to  $i$  and  $\beta$ . A discussion of equation (4) shows that at the minimum of deviation (for  $i=0$ )

$$\alpha = \beta(n-1) \quad [\text{or } n = \frac{\alpha}{\beta} + 1]. \quad . \quad . \quad . \quad (5)$$

Of course  $\alpha$  changes but slightly near its minimum (compare A. p. 259). When  $i$  approaches  $90^\circ$ ,  $\alpha$  tends towards infinite values; at least so long as  $n > 1$ , and accordingly no total reflexion ensues (see § 15).

§ 11. *The experiments* were begun by adjusting the biprism vertically on the spectrometer platform. By means of the latter's divided circle, the normal to the prism could be set

TABLE I. (Prism Fe III.).

$\beta$ .	Deviation $\alpha$ at Inclination $i$ :						
	$0^\circ$ .	$\pm 30^\circ$ .	$\pm 40^\circ$ .	$\pm 50^\circ$ .	$\pm 55^\circ$ .	$\pm 60^\circ$ .	$\pm 65^\circ$ .
du Bois.							
26.1 25.0 25.5	51.4 50.7 50.4 52.0	63.7 67.5	74.7 72.2	91.6 107.2	105.3 105.7	122.5 122.8	147.0 159.5
25.7	51.1	65.6	73.5	99.4	105.5	122.7	153.3
Rubens.							
27.8 23.4 26.4	51.5 51.2 53.1 53.8	65.5 70.2	74.9 71.4	88.5 106.8	114.4 103.7	119.5 137.9	155.5 153.5
25.9	52.4	67.9	73.2	97.7	109.1	128.7	154.5
Mean Values.							
25.8	51.7	66.7	73.3	98.5	107.3	125.7	153.9

at any angle to the left (+) or right (−) of the telescope's axis. After a few preliminary trials we made regular measurements for values of  $i=0^\circ, 30^\circ, 40^\circ, 50^\circ, 55^\circ, 60^\circ, 65^\circ$ , because with these intervals the increments of the deviation were most uniform. In certain cases we could still observe at  $70^\circ$  inclination; the deviations obtained in this case were considerable, *e.g.* with a cobalt prism we found  $\alpha=200''$ , *i. e.* over three minutes. However, the projection of the prism on the objective lens now becomes too narrow; consequently the image of the slit is so considerably drawn out by diffraction that measurement becomes uncertain and inaccurate notwithstanding the strong deviation.

For these observations the source of light was a Linnemann's zirconia burner seen through red glass. For the reasons stated above (§ 5) a complete set of observations is given in Table I. It will be seen that each observer determined one deviation for + and one for − inclination (each by 20 readings); these are seen to agree on the whole. The angle  $\beta$  was measured three times by each of us, the deviation with normal transmission four times; this was done on account of the preponderating influence of these values on the final results. The mean values for the two observers were used in the subsequent calculation.

We have carried out this part of our work with but one prism of each metal, while using three for the measurements of dispersion. In the latter the results prove quite independent of the refracting angle (§ 18), and it may therefore be inferred that such is also the case with oblique transmission. It was not so much our object here to find numerical constants as it was in the second part of our work, where a great number of observations had to be collected in order to obtain sufficient accuracy\*.

§ 12. *The results* for the three metals are given in Table II. From the observed values of  $\alpha$  (first horizontal line in each section of the table) values of  $n$  were first calculated by equation (3) (third line); this was done only in order to see whether Snellius's law might apply. Now it is evident that for nickel the values of  $n$  at last begin to increase with  $i$ ; such is also the case for cobalt, though to a less degree. For iron the deviations from Snellius's law appear to lie within the errors of observation. However, we feel bound to assume that the latter metal differs from the two others only quantitatively, not qualitatively.

\* Compare the check by an independent observer mentioned in the last paragraph of § 5, which was applied here.

Now  $n$  loses its physical meaning as soon as it ceases to be constant; and we have given the variable values only to show that they can be of no further use. A deviation of the metals

TABLE II. ("Red" Light).

$i$ .	0°.	30°.	40°.	50°.	55°.	60°.	65°.
Prism Fe III. ; $\beta = 25''.7$ ; $n = 3.06$ .							
$\alpha$ , obs. ....	51.7	66.7	73.3	98.5	107.3	125.7	153.9
$\alpha$ (SNELL.) ...	53.0	64.0	74.7	92.8	106.4	125.3	152.0
$n$ , calc. ....	{ 3.01	3.15	3.02 }	3.20	3.03	3.07	3.09
$i_m$ , integr. ...	0	9.3	12.0	14.4	15.4	16.3	17.1
$i_m$ (SNELL.) ..	0	9.4	12.1	14.5	15.5	16.4	17.2
Diff. ....	—	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1
Prism Co III. ; $\beta = 23''.6$ ; $n = 3.10$ .							
$\alpha$ , obs. ....	47.0	61.2	72.2	95.1	113.0	124.0	152.4
$\alpha$ (SNELL.) ...	49.7	59.9	70.0	86.9	99.6	117.2	142.6
$n$ , calc. ....	{ 3.00	3.15	3.17 }	3.32	3.42	3.24	3.28
$i_m$ , integr. ...	0	9.2	11.8	14.0	14.9	15.7	16.4
$i_m$ (SNELL.) ..	0	9.3	11.9	14.3	15.3	16.2	17.0
Diff. ....	—	-0.1	-0.1	-0.3	-0.4	-0.5	-0.6
Prism Ni III. ; $\beta = 27''.7$ ; $n = 1.93$ .							
$\alpha$ , obs. ....	27.3	31.3	36.8	51.0	61.2	84.4	114.4
$\alpha$ (SNELL.) ...	25.8	31.9	38.2	48.6	56.7	67.9	83.9
$n$ , calc. ....	{ 1.98	1.91	1.90 }	1.98	2.02	2.20	2.35
$i_m$ , integr. ...	0	14.7	19.2	23.1	24.8	26.2	27.3
$i_m$ (SNELL.) ..	0	15.0	19.5	23.4	25.1	26.6	28.0
Diff. ....	—	-0.3	-0.3	-0.3	-0.3	-0.4	-0.7

from the sine law is thus shown to exist, but to become sensible only for inclinations above say 40°. We believe that the nature of this deviation will be better understood if the behaviour of each metal be compared with that of an ideal transparent substance, which we assume to exist for this purpose, and to possess a refractive index equal to the mean of those found for the metal at inclinations of 0°, 30°, and 40°, which are equal within the limit of experimental errors.

We have now calculated  $\alpha$  and  $i_m$  for these imaginary substances by equations (4) and (2), *i. e.* according to Snellius's law (second and fifth lines). Lastly, the values of  $i_m$ , found for the metal by graphic integration, are given in the fourth line of each of the three sections of Table II.

For the sake of clearness we have also graphically illustrated the contents of Table II. In fig. 2,  $\alpha$  is plotted as a function of  $i$ ; the dotted curves refer to the ideal substances, the broken straight lines to the metals\*. For iron both lines almost coincide; for cobalt, and especially for nickel, it is easy to see the difference.

In the same way fig. 3 gives the relation between  $i_m$  (ordinate) and  $i$  (abscissa); the dotted curves again refer to the ideal substance. The points  $\odot$ , corresponding to the metals, all lie somewhat towards the axis of abscissæ.

§ 13. *Synopsis.*—The results may be condensed into three statements:—

I. Light, on passing from Fe, Co, and Ni (and probably also from a number of other metals) into air, begins by following Snellius's sine law for small angles of emission†.

A refractive index may therefore be inferred from observations with approximately normal transmission, but from such only; in fact this is what was done by Prof. Kundt, and what may be mathematically expressed as follows:—

II. The refractive index of metals is defined as  $\lim_{i=0} (\sin i / \sin i_m)$ .

The expression in parentheses differs but little from its limit even for considerable values of  $i$ ; at least for the three metals we have examined.

III. The actual metals deviate from ideal substances, supposed to possess the index thus defined, in the following sense: to a given  $i_m$  corresponds a *greater* value of  $i$ , or to a given  $i$  a *lesser* value of  $i_m$ .

The differences become more marked the greater the inclination, and are given empirically by our Table II. (sixth line); for the three metals they decrease in the order Ni, Co, Fe.

§ 14. *The method of observation* we used has the advantage that considerable differences in the deviation observed finally lead to comparatively slight differences in the relation obtained by integration.

\* On account of the almost identical behaviour of Co and Fe, the ordinates of all the iron curves (in figs. 2–4) had to be plotted from the auxiliary axis of abscissæ, in order to prevent the curves from overlapping.

† This law is then easily seen to hold as well for emission into any other transparent medium within the same range.



In many cases, where the object is rather qualitative, it further appears advisable to work at considerable inclination; the fittest angle is  $60^\circ$ ; the deviation is then increased about three-fold. The apparent breadth of the prism, however, is only halved ( $\cos 60^\circ = 0.500$ ), so that the diffraction effect does not yet present too great an obstacle. As remarked above, however, refractive indices can only be calculated from measurements with normal transmission; we have therefore adhered to the latter method for our measurements of dispersion.

§ 15. *Other Metals.*—These remarks can only apply to metals having a high index, such as those now examined. For these metals one condition is always fulfilled, which appears important to us, viz. that the values of  $i_m$  hardly exceed  $30^\circ$ , an angle the cosine of which is still near unity\*. For Fe and Co  $i_m$  even remains below  $20^\circ$ ; accordingly the deviations from Snellius's law are most considerable for Ni, which has the smallest index.

We have also given theoretical curves for silver and gold in fig. 3; we began by assuming the sine law to hold and took the indices given by Kundt (A, p. 266): Ag (white) 0.27; Au (white) 0.58; Au (blue) 1.00. Of course in the latter case a deviation should never occur, and  $i_m = i$  always.

These theoretical curves show that for  $i > 15^\circ.66$  (Ag) and  $i > 35^\circ.45$  (Au), total reflexion ought to commence; greater angles of emission into air would then be impossible. The deviation curves in fig. 2 have been calculated for prisms with a refracting angle  $\beta = 25''$ ; they should more properly lie under the axis of abscissæ, as the deviations all become *negative*. The curves show that for these metals also the numerical values of  $\alpha$  ought to increase with  $i$ , finally to reach the value  $\beta$  for the critical values of the abscissa given above (see equation (4) § 10); at this point the curves must come to a dead stop.

§ 16. It is evident, however, from the most casual observation that silver or gold films may be looked through at any angle. This shows that the assumption of Snellius's law, made above for the sake of further discussion, must be quite beside the truth in this case, even as a rough approximation.

For different reasons it appeared to us unadvisable at present to attempt to pursue this question experimentally. It may be indeed foreseen that the advantages offered by

\* As is seen from fig. 3,  $i_m$  hardly increases any more when  $i$  increases from  $65^\circ$  to  $90^\circ$ ; we should therefore probably have learned nothing more even if we had been able to push the inclination beyond  $65^\circ$ .

our method in the case of Fe, Co, and Ni would not subsist when applying it to Au or Ag. In fact we should have had to determine the large deviation from Snellius's law, which doubtless exists, by small differences in the quantities observed. We could hardly have successfully attempted this without refining the observations.

However, it is possible to foretell the actual shape of the silver and gold curves (fig. 3). They must start from the origin along the same tangent as the dotted curves drawn; then bend more and more concavely towards the axis of abscissæ; they cannot intersect  $\overline{PQ}$ , as this would mean total reflexion, and must abut normally on  $\overline{QR}$ . Their character therefore is essentially the same as that of our curves obtained for Ni &c.

## II. DISPERSION.

§ 17. *The experiments* had to be made at the minimum of

TABLE III.

du Bois.					RUBENS.				
$\beta$ .	Deviation $\alpha$ .				$\beta$ .	Deviation $\alpha$ .			
	Li $\alpha$ .	D.	F.	G.		Li $\alpha$ .	D.	F.	G.
Prism Co. III.									
$\overset{''}{22\cdot4}$ 21·8 19·5	$\overset{''}{48\cdot2}$ 46·2	$\overset{''}{40\cdot0}$ 41·7	$\overset{''}{29\cdot8}$ 36·4	$\overset{''}{25\cdot1}$ 29·0	$\overset{''}{23\cdot8}$ 24·7 21·6	$\overset{''}{51\cdot4}$ 52·0	$\overset{''}{48\cdot8}$ 45·5	$\overset{''}{33\cdot4}$ 37·7	$\overset{''}{20\cdot0}$ 28·4
21·2 $n=$	47·2 3·23	40·8 2·92	33·1 2·56	27·1 2·27 Mean	23·4 $n=$ $n=$	51·7 3·21 3·22	47·1 3·02 2·97	35·6 2·52 2·54	24·2 2·04 2·16
Prism Ni II.									
$\overset{''}{22\cdot2}$ 22·7 22·3	$\overset{''}{17\cdot6}$ 22·0	$\overset{''}{15\cdot7}$ 18·9	$\overset{''}{16\cdot8}$ 15·7	$\overset{''}{10\cdot1}$ 11·4	$\overset{''}{22\cdot3}$ 21·8 23·4	$\overset{''}{19\cdot7}$ 23·3	$\overset{''}{21\cdot3}$ 14·2	$\overset{''}{17\cdot6}$ 16·0	$\overset{''}{16\cdot4}$ 9·1
22·4 $n=$	19·8 1·89	17·3 1·77	16·2 1·72	10·7 1·48 Mean	22·5 $n=$ $n=$	21·5 1·96 1·93	17·8 1·79 1·78	16·8 1·75 1·74	12·8 1·57 1·52

deviation, as remarked above. In the plane of the spectrometer's slit a small spectrum from an arc lamp was projected. By slightly turning the collimator the slit could be adjusted to given positions in the spectrum. For this purpose the divided circle had been calibrated by observations with the spectral lines of Li, Na, and H, and the readings corresponding to the wave-lengths of Li  $\alpha$ , D, F, and G noted once for all. The refractive index was calculated by equation (5) (§10).

We begin by giving two full sets of observations in Table III., which explains itself. We worked with three prisms of each metal, in order to get our results freed as much as possible from the individuality of the prisms and from other sources of error.

§ 18. *The results* are given in Table IV.; the numbers in prominent type are the arithmetic means of the indices obtained for the three prisms. Beneath these we moreover give figures headed "means B;" these were calculated by giving different weight to the indices derived from different prisms proportional to the refracting angle of the latter. As the numbers B show no systematic differences against A, the results are really independent of the refracting angle (compare A, p. 264). The means B are of no further use, as the observations with the steeper prisms are for various reasons not more trustworthy than those with the flatter ones. The indices for "red" light are those obtained above (Table II.); they correspond to a wave-length of about  $64.4 \times 10^{-6}$  centim.\*

§ 19. *Discussion.*—A comparison of some of our numbers with those found by Prof. Kundt for Ni and Fe with light only approximately homogeneous (A, p. 266) leads to the following remarks:—

1. For Ni the coincidence is sufficiently near, considering the preliminary character of Prof. Kundt's measurements and the uncertainty about the wave-length which has to be attributed to his "blue" light;

2. For Fe deviations appear, rather insignificant at the blue end but increasing towards the red.

It is of course at present impossible to decide whether these deviations may be explained by Kundt's prisms not having been free from oxide (lesser index, normal dispersion A, p. 267) or by his electrolytic iron baths not having been chemically pure. Considering the improvements since introduced into the method, mainly by Prof. Kundt himself, we believe our

\* du Bois, Wied. Ann. xxxi. p. 956 (1887).

numbers to be approximately correct; however, rather a large range of error must be allowed in consequence of the difficulties of observation.

Our refractive indices are plotted as a function of the wave-

TABLE IV.

No.		Refractive Index $n$ .				
Colour .....		Red.	"Red."	Yellow.	Blue.	Violet.
Line .....		Li $\alpha$ .	—	D.	F.	G.
$\lambda \times 10^6$ centim.		67.1	64.4	58.9	48.6	43.1
Iron.						
Fe.	$\beta$ .					
I.	17.0	3.34	—	3.03	2.61	2.23
II.	20.9	3.01	—	2.84	2.63	2.15
III.	26.0	3.00	—	2.59	2.08	1.78
Means A.....		3.12	3.06	2.72	2.43	2.05
Means B.....		3.02	—	2.71	2.40	2.01
Cobalt.						
Co.	$\beta$ .					
I.	13.5	3.02	—	2.42	2.23	2.01
II.	14.5	3.42	—	2.88	2.41	2.14
III.	22.3	3.22	—	2.97	2.54	2.16
Means A.....		3.22	3.10	2.76	2.39	2.10
Means B.....		3.22	—	2.86	2.41	2.11
Nickel.						
Ni.	$\beta$ .					
I.	16.5	2.12	—	1.89	1.71	1.46
II.	22.4	1.93	—	1.78	1.74	1.52
III.	27.7	2.08	—	1.85	1.68	1.63
Means A.....		2.04	1.93	1.84	1.71	1.54
Means B.....		2.02	—	1.83	1.72	1.56



length in air (fig. 4). These curves of anomalous dispersion are seen to have an analogous shape for the three metals. The values for "red" light lie well between those for D and  $\text{Li}\alpha$ , considering its imperfect homogeneity.

There appears to be no simple relation between this dispersion of refraction and that of either Kundt's or Kerr's phenomenon (compare § 2).

### III. CONCLUSION.

§ 20. We have from the beginning guarded ourselves against basing in any way upon any of the various elastic or electric optical theories proposed (§ 6). In the present paper we have attempted to restrict ourselves to the communication of facts which may be simply inferred from our experiments. We believe that the realm of fact in the optics of metals is as yet too little extended to serve as a successful criterion for the theories; any slight extension of it, to which we may have contributed, hardly changes this state of affairs.

A valuable contribution towards the experimental investigation of this part of Optics has been lately published by Dr. Drude; he determined the two ordinary constants of reflexion for a number of metals with the utmost care. By means of the particular elastic theory advocated by him, he then calculated indices of refraction and of extinction and reflecting powers which he compared with experimental data by Kundt (A, p. 266), Wernicke\*, and one of us†. Of the refractive indices obtained in this way four‡ are directly comparable with ours, and even show a certain amount of coincidence.

In answer to our inquiry Dr. Drude was good enough to promise measurements on cobalt also, eventually with regard to dispersion. We therefore think it advisable to wait for those further determinations, as these are sure to afford Dr. Drude a safer base for judging any coincidence or discrepancy than the data at present to hand can possibly do.

Physic. Inst. Univ. Berlin, July 20, 1890.

\* Wernicke, *Pogg. Ann. Erg.* viii. p. 75 (1878).

† Rubens, *Wied. Ann.* xxxvii. p. 267 (1889).

‡ Drude, *Wied. Ann.* xxxix. p. 481 (1890). The values meant are  $n'$  (red) and  $n$  (sodium light) for nickel and steel in his table on p. 537.

XLII. *On a Method of Determining the Absolute Density of a Gas.* By J. JOLY, B.E., M.A.\*

THE method still in general use for the accurate determination of the density of a gas is that of Regnault, improved from the conception of Biot and Arago, by the addition principally of the counterpoising vessel. This method is not free from objections.

The gas is weighed in the vessel in which its volume is measured, and as this is necessarily a large vessel, of considerable weight, the weight of the gas bears but a very small proportion to the total weight observed. Again, from the great bulk and surface of the containing vessel, it is in itself a difficult object to weigh with a high degree of accuracy, more especially when exposed, as it is, between the first and second weighings, to the manipulation incident in filling it at a known temperature.

Further, in the determination of the volume of this vessel there arises, as Lord Rayleigh has lately shown†, an error due to the variation of pressure within the vessel when it is weighed, vacuous in the first instance, full in the second. This error, which escaped Regnault, is very considerable in this method.

If, again, there is an object in economizing the gas, Regnault's method is wasteful, as the "washing out" of so large a vessel with the gas necessitates a far greater expenditure of gas than is subsequently required for the actual determination. Without referring again to these objections to the method of Regnault, it will be seen that they are either much reduced in importance or eliminated in the method to be described.

In this new method the measurements of the volume and of the weight of the gas are effected in separate vessels. That in which the gas is weighed is small, the gas being under high pressure within it. That in which the volume is subsequently measured may, on the other hand, be as large as may be desired. We are not concerned with its weight.

The vessel which I have in use for holding the gas, when being weighed, is of copper, spherical in form, about 6·7 centim. in diameter, made up of two hemispheres, the walls being about 1 millim. in thickness. The hemispheres are brazed (not soft-soldered) together within a belt of copper about

\* Reprinted from the Scientific Proceedings of the Royal Dublin Society, June 18, 1890.

† Proc. Roy. Soc. xliii. p. 356.

$4\frac{1}{2}$  millim. wide, and 1 millim. in thickness. The vessel must be quite staunch. Its internal volume is just 160 cub. centim. It is closed by a small screw-valve, having a side tubulure for attachment to the various apparatus. The valve-spindle of steel works through a small stuffing-box to prevent the escape of gas along the shaft of the spindle when the vessel is being filled or emptied.

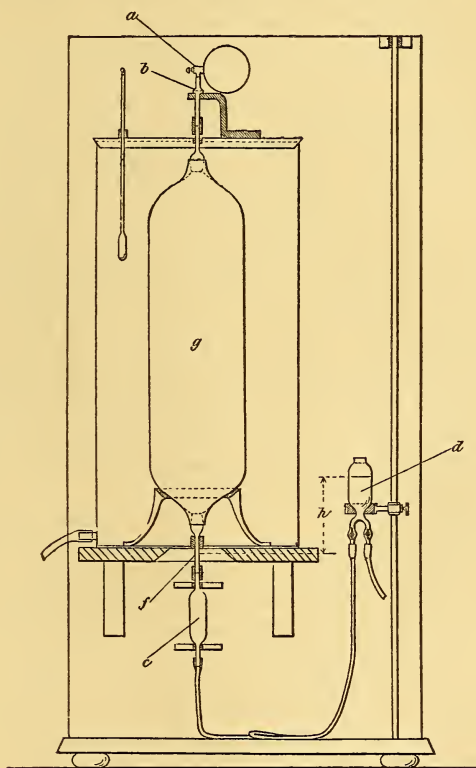
This vessel is tested hydraulically to 1000 lb. in the square inch. It may be safely filled to pressures of 20 or 25 atmospheres. I am daily using such vessels in the steam calorimeter in determining the specific heats of gases; here they are raised to the temperature of  $100^{\circ}$  C., bringing the pressure to near 30 atmospheres in many cases. For the purpose of compressing the gas into this vessel I use a pump of special construction, a description of which I hope shortly to publish. But, obviously, any compression-pump which will deliver the gas without contamination of oil or moisture will answer.

A counterpoising sphere of the same bulk and weight approximately is required. Against this, after the required quantity of gas has been inserted in the weighing-sphere, the latter is equilibrated. This operation is readily performed in an ordinary chemical balance to an accuracy of one tenth or one twentieth of a milligram. The weight of a copper vessel of the strength described will be from 80 to 90 grammes. It will be seen later that one sufficiently strong to hold 2 litres safely need not exceed some 40 grammes in weight.

The vessel in which the volume is determined is next to be considered. It is lettered *g* in the diagram, where it is shown connected with the weighing-sphere, the latter screwed to the steel connexion *b* provided for it, and through the fine bore (1 millim.) of which it delivers its contents into *g*. The volumenometer is of glass, cylindrical, closed at each end by ground stoppers with tubulures attached. The upper tubulure is of fine bore, hardly 1 millim., the lower tubulure of some 3 or 4 millim. bore. The volumenometer is surrounded by a copper jacket, having two large openings cut in its cover for the admission of broken ice or water, and also a tubulure for admitting a thermometer. A fine mark is etched on the lower tubulure at *f*, and this tubulure is continued by attachment to a smaller vessel *c*, as shown. This again is connected by a rubber-tube connexion with the vessel *d*, which can be raised or lowered, as will be understood from the diagram. The volume of the volumenometer is best determined with water. If water is subsequently to be used in it the procedure is as follows:—

The coupling *b* is removed and the vessel *g* inverted in the copper jacket. The wide tubulure is now uppermost, the narrow one below. This is attached to *d*, and the upper one to an air-pump, and distilled air-free water drawn into *g* through the lower tubulure till it is quite full. The vessel *d* is now raised, the connexion with the air-pump removed, and when *d* is so high that water is just welling out of the tubulure this is closed with a short pinched rubber tube.

Broken ice is now filled in round the volumenometer, and after the lapse of some hours the connexion below with *d* is



broken and the fine tubulure closed with a little piece of wax. The upper tubulure is now opened, and the level in the tubulure lowered by applying bibulous paper till it sinks to the mark etched upon the glass. It is then closed with rubber tubing as before. The ice being next removed, *g* is lifted out, dried carefully, and weighed. This done it is replaced



in the copper cylinder, this time in its normal position, and the water allowed to run out. The ice is now returned to the jacket, and after the lapse of some time the volumenometer is closed as before, when the height  $H$  of the barometer is read. Another weighing is now made, and by difference the weight of water at  $0^{\circ}\text{C.}$  which has quitted the vessel is calculated, allowing for the weight of saturated air at  $0^{\circ}\text{C.}$  and  $H$  contained in the vessel at the second weighing. One or more such operations may be performed, and from the known density of water at  $0^{\circ}\text{C.}$  the volume at the temperature  $0^{\circ}\text{C.}$  calculated. To this must be added, for the complete volume, the volume at ordinary temperatures of the small steel connexion with the sphere. It is obvious that the error arising from the inconstant temperature of this fine tube or of the short tubulure exposed at  $f$  need not be attended to.

If mercury is subsequently to be employed in the volumenometer the volume should be determined on a slightly different procedure. Water should still be used, however—not mercury, or a distending effect, due to the great weight of the latter, might give rise to error—but the weight of the vessel, when containing air, should be *first* ascertained when the walls within are dry. In this way the capacity of the *dry* volumenometer is obtained, which is that required with the use of mercury. It is evident that the use of mercury is on this account much preferable to water in subsequent work, as the volume of residual water in the vessel from one experiment to another will not be accurately constant. Again, no hygrometric correction on the pressure of the gas contained in the volumenometer will be requisite.

The volume of this vessel (which is but an enlarged Sprengel tube) being ascertained once for all at the temperature  $0^{\circ}\text{C.}$ , it follows that it will afford a ready means of dealing with a gas contained in the weighing-sphere. It is filled with mercury or water, and surrounded by ice. The vessel  $d$  is then raised till the liquid in the volumenometer has risen to the top of the fine steel tubulure  $b$ , the weighing-sphere removed from the balance, screwed on to  $b$ , and the vessel  $d$  lowered. The valve at  $a$  is next screwed back a little till the mercury is seen to rise in  $d$ . The right-hand stop-cock on  $d$  is now opened, and the mercury let flow into a tall graduated or marked vessel, so that it may be known about when the operation of filling  $g$  is approaching completion. Presently, the surface level of the mercury sinks into the vessel  $c$ . This possesses such capacity as to give time to close the valve of the sphere before any gas is lost;  $d$  is now raised slowly, till the overflow gas in  $c$  is compressed back into

the volumenometer. All must now be let to stand till  $t_0^\circ$  is attained (half-an-hour will suffice), and the final adjustment of the mercury level to the mark  $f$  then effected. By means of a cathetometer the height  $h$ , the difference of level between the surfaces at  $d$  and  $f$ , is read. This will only be some 5 or 6 millim. in general. For this a temperature correction is hardly required; but a capillary correction, ascertained experimentally once for all, must be applied owing to the different areas of the surfaces in the two tubes. This might be eliminated in the construction by conferring an equally small area on  $d$ , but it is probably more convenient to make the simple correction required. The barometer is now read, and the pressure of the gas in  $g$  computed. Its temperature is  $0^\circ \text{C.}$ , and its volume that of the vessel,  $= V$ . The sphere is now returned to the balance, re-weighed, and the weight of gas, subject to a small correction, found by difference.

The correction mentioned is due to the shrinkage of the copper sphere on the relief of pressure, and corresponds to that occurring in the case of Regnault's glass vessel. Experiments (two, closely agreeing, have been made on this sphere) reveal a shrinkage which may be taken as  $0.1732$  cub. centim. on the removal of  $4.3525$  grammes of air at the temperature  $12^\circ \text{C.}$ , a fall of pressure of  $22.01$  atmospheres, closely. At  $760$  millim. this weight of air occupies about  $3.367$  litres. This would be a needlessly large volume to confer on the volumenometer, except for very special work. Even in the case of hydrogen (1 litre at  $760$  and  $0^\circ \text{C.}$ , weighing  $0.0895$  gram.) two litres will suffice for a very accurate estimation of the weight of gas dealt with. At the pressure corresponding to the compression of two litres into the sphere of  $160$  cub. centim. capacity, a much lighter weighing-sphere than that previously described will suffice. Thus I use one weighing but  $41$  grammes, which has been tested up to  $500$  lb. in the square inch. The thickness of its walls is somewhat less than half a millimetre, its volume a little greater than  $160$  cub. centim. There is no difficulty in weighing such a vessel to the one-twentieth of a milligram., or closer. Using the heavier vessel the correction for shrinkage will be the shrinkage due to two litres, *i.e.*  $0.1029$  cub. centim. multiplied into the normal density of air. This gives a displacement effect of  $0.000127$ . This correction is on a weight of  $2.5878$  gram. of air or the correction on  $w$ , which is subtractive, is for air one part in  $25,000$  q.p. In the case of hydrogen one part in  $1790$ . Assuming the use of the lighter sphere the experimentally determined shrinkage is  $0.26359$  cub. centim. for a lowering of pressure of  $12.82$  atmospheres,

a little more than the pressure due to two litres. The shrinkage is, in fact, closely 0.257 cub. centim., and the correction on the weight of gas released is 0.000318. This is higher than with the heavier sphere, but the correction is perfectly definite [and easily ascertained once for all by successive weighings, before and after emptying, in distilled water]\*; and on the other hand the use of the lighter vessel will probably confer still greater accuracy on the weighings.

Turning our attention to the volumenometer it appears possible that a similar correction may arise in the assumption made as to its capacity. For, in the experiments in which its volume is determined, its walls are exposed to the pressure due to the weight of the water contained in it; subsequently, when it is occupied by a gas, this pressure does not obtain. Hence there might be reason to fear some small excess in the value ascribed to its capacity. To make this a matter of experiment, I filled the jacket with water, and provided a wide tube dipping into it, syphon-wise, enabling the water to be all run off within a short space of time. The volumenometer within was filled with air, the upper tubulure was closed, the lower one being arranged to dip into a vessel of water, the water standing some little height in the tube, nearly to the etched mark. Thick baize was now folded round and over the jacket, and after the lapse of some time the cross wire of a cathetometer was brought to read the level of the water in the lower tubulure. A few minutes' observation sufficed to show when this level was stationary. The syphon was now put into operation; and while the water was running out of the jacket the level of the liquid on the tubulure was observed. No movement was perceivable. It is thus, I think, legitimate to conclude that no appreciable error arises from this source, the experiment being a delicate one.

Comparing the previous figures with those obtained in the exact experiments of Lord Rayleigh, using Regnault's method, which experiments may be fairly taken as representative of modern refinement on the method, the following numbers are obtained, assuming the same weight of hydrogen to be dealt with in the present method as was used by Lord Rayleigh, and the lighter sphere to be used.

\* Two experiments on the heavier sphere afforded: (1) a shrinkage of 0.1013 cub. centim. for the release of 2.5728 grammes of air at 15°; (2) a shrinkage of 0.1732 cub. centim. for 4.3525 grammes of air at 12° C.

Two experiments on the lighter sphere gave: (1) 0.1720 cub. centim. shrinkage for the release of 1.6046 grammes of air at 16°; and (2) a shrinkage of 0.2636 cub. centim. for 2.5284 grammes of air at 14° 3.



Volume of vessel in which the gas is weighed :—

For Regnault's method 1800 cub. centim.

„ new „ 160 „

Weight of vessel in which the gas is weighed :—

For Regnault's method 200 grams.

„ new „ 41 „

Error of buoyancy on the weight of gas :—

For Regnault's method 1 in 280.

„ new „ 1 in 560.

Ratio of weight of gas to weight of vessel in which it is weighed :—

For Regnault's method 1 to 1261.

„ new „ 1 to 258.

Regarding the last numbers I may observe that the case assumed is unfavourable to the new method. The compression of 1800 cub. centim. (at 760 millim.) in the sphere raises the pressure to 12·5 atmospheres, but it may safely be filled to 17, or, it will carry some 36 per cent. more gas than is assumed above.

The volumenometer which I am about to take into use in estimating the density of the samples of gas used in my experiments on the specific heats of gases has only lately been constructed. A first and hasty experiment on the density of dry air may, however, indicate the magnitudes dealt with, and the accuracy obtainable when restricted to the use of water in the volumenometer. The interior volume of the volumenometer determined by weighing it filled with water at 15°·67, and again filled with air, but wet on the walls, was found to be 1751·0 cub. centim. This is with great probability correct to unity, the first place of decimals being perhaps open to small error.

The data in the experiment on air density are as follows :—  
 Weight of air inserted = 2·1092 less 0·0001 for error of buoyancy = 2·1091. Temp. of water jacket = 15°·70. Bar. 760·32 reduced to 0° C. Head of water 0·388 inches (= *h*) + 0·120 inches correction for capillarity (by subsequent experiment). Total press. 760·32 + 0·95 millim. = 761·27. Max. vapour tension of water at 15·7 = 13·3 millim.; hence the pressure, finally, is 747·97 millim. The volume for the experiment may be taken as 1751 cub. centim., neglecting the temperature effect of 0°·03.



From these data the density of dry air at 747·97 millim., and at the temperature 15·70, is found to be 0·0012046. The last figure is doubtful, as being beyond the limit of accuracy with which the volume is known.

If, for confirmation of this result, reference is made to accepted results from the *Tabellen* of Landholt and Börnstein, the density of dry air under the same conditions of pressure and temperature is deduced as 0·0012033. From Biedermann's *Chemiker-Kalender* (1888) is deduced the number 0·0012052. The mean of these two closely agrees with the experimental result, absolutely indeed to the fourth significant figure, the last reliable one in the determination.

In conclusion, I may point out that this method leaves the gas finally in a vessel, which, by the addition of a small side way to the connexion *b*, may be made a most convenient one for the subsequent transference of the gas into any apparatus for its analysis.

The present method may, as in the case of Regnault's, be by obvious procedures applied to the determination of the variation of the density with change of temperature, or change of pressure. And its application to the determination of vapour densities suggests itself. In this case the temperature of the volumometer would, perhaps, best be adjusted by the use of a vapour in the jacket, and an arrangement for controlling its pressure.

XLIII. *On the Tension of Water Surfaces, Clean and Contaminated, investigated by the Method of Ripples.* By Lord RAYLEIGH, Sec. R.S.\*

NUMEROUS and varied phenomena prove that the tension of a water surface is lowered by the presence of even a trace of grease. In the case of olive-oil, a film whose calculated thickness is as low as 2 micro-millimetres is sufficient to entirely alter the properties of the surface in relation to fragments of camphor floating thereupon. It seemed to me of importance for the theory of capillarity to ascertain with some approach to precision the tensions of greasy surfaces; and in a recent paper † I gave some results applicable to the comparison of a clean surface with one just greasy enough to stop the camphor movements and also with one saturated with olive-oil. The method employed was that depending upon the

\* Read September 6 before Section A of the British Association at Leeds. Communicated by the Author.

† Proc. Roy. Soc. March 1890, vol. xlvii. p. 367.

rise of liquid between parallel plates of glass ; and I was not satisfied with it, not merely on account of the roughness of the measurement, but also because the interpretation of the result depends upon the assumption that the angle of contact with the glass is zero. In the opinion of Prof. Quincke, whose widely extended researches in this field give great weight to his authority, this assumption is incorrect even in the case of pure liquids, and, as it seemed to me, is still less to be trusted in its application to contaminated surfaces, the behaviour of which is still in many respects obscure. I was thus desirous of checking my results by a method independent of the presence of a solid body.

The solution of the problem was evidently to be found in the observation of ripples, as proposed by Prof. Tait, upon the basis of Sir W. Thomson's theory. Thomson has shown that when the wave-length is small, the vibration depends principally upon capillary tension ; so that a knowledge of corresponding wave-lengths and periods will lead to a tolerably accurate estimate of tension.

Besides some early observations of my own\*, made for the most part for another purpose, I had before me the work of Matthiessen†, who has compared Thomson's formulæ with observation over a wide range of wave-length. The results are calculated on the basis of an assumed surface-tension, and are exhibited as a comparison of calculated and observed wave-lengths. On the whole the agreement is fair ; but the accuracy attained seemed to be insufficient for the purpose which I had in view. As will presently appear, an error in the wave-length is multiplied about three times in the tension deduced from it, so that, in a reversal of Matthiessen's calculations, the errors would appear much magnified.

Quite recently Mr. Michie Smith has published an account of experiments made by Thomson's method for the determination of the tension of mercury. Some anomalies were met with ; and it seems not improbable that the vibrations observed were in some cases an octave below those of the vibrating source‡.

When it is remembered that Thomson's theory is one of infinitely small vibrations, it will be seen that for my purpose it was necessary above all things that the amplitude of vibration should be very moderate. The sub-octave vibrations of

\* "On the Crispations of Fluid resting upon a Vibrating Support," *Phil. Mag.* July 1883.

† *Wied. Ann.* xxxviii. p. 118 (1889).

‡ Faraday, *Phil. Trans.* 1831. See also Rayleigh, *Phil. Mag.* April and July 1883.

Faraday are especially to be avoided as almost necessarily of large amplitude. At the same time the limitation is not without its inconvenience. One of the great difficulties of the experiment is to see the waves properly, and this is much increased when the vibrations are extremely small.

In considering the problem thus presented, it occurred to me that it was essentially the same as that so successfully solved by Foucault in relation to the figuring of optical surfaces. The undisturbed surface of liquid is an accurate plane; the waves upon it may be regarded as deviations from optical truth, and may be made evident in the same way as any other deviations from truth in a reflecting surface. Guided by this idea, I was able to work with waves of which nothing whatever was to be seen by ordinary observation of the surface over which they were travelling.

In the application of Foucault's method it is necessary that light from a radiant point, after reflexion from the surface under test, should be brought to a focus, in the immediate neighbourhood of which is placed the eye of the observer. Any small irregularities in the surface then render themselves conspicuous to the eye focused upon it. In the present case the reflector is plane, and the formation of a real image of the radiant requires the aid of a lens. In my experiments this was usually a large single lens of 6 inches diameter and 34 inches focus. On one occasion an achromatic telescope-lens was substituted, but the aperture was too small to include the number of waves necessary for accuracy. Although the want of achromatism was prejudicial to the appearance of the image, it is not certain that the accuracy of the determinations was impaired, at least after experience in observation had been acquired. The lens was fixed horizontally near the floor, a few inches above the surface of the water under examination. The radiant point, a very small gas-flame, was situated in the principal focal plane, but a little on one side of the axis of symmetry, so that the image formed after reflexion from the water and a double passage through the lens might be a little separated from the source. For greater convenience reflecting strips of looking-glass were introduced at angles of  $45^\circ$ , or thereabouts, so that the initial and final directions of the rays were horizontal.

The smallness of the disturbance is not the only obstacle to its visibility. Even with Foucault's arrangement for viewing minute departures from planeness, nothing could usually be seen of the waves here employed without a further device necessary on account of the rapidity with which all phases are presented in succession. A clear view of the waves must be



an intermittent one, isoperiodic with the vibrations themselves, and may be obtained in the manner first described by Plateau. In the present case it was found simplest to render the light itself intermittent. Close in front of the small gas-flame was placed a vibrating blade of tin-plate rigidly attached to the extremity of the prong of a large tuning-fork, and so situated that once during each vibration the light was intercepted by the interposition of the blade. The vibrations of the fork were maintained electromagnetically in the usual manner, and the intermittent current furnished by the interrupter fork was utilized, as in Helmholtz's vowel-sound experiments, to excite a second, in unison with itself. The second fork generated waves in the dish of water by means of a dipper attached to its lower prong.

When the action is regular, the vibrations of the two forks are strictly isochronous, even though the natural periods may differ somewhat\*. The view presented to the observer is then perfectly steady, and corresponds to one particular phase of the vibration, or rather, since the illumination is not instantaneous, to an average of phases in the neighbourhood of a particular one.

Even in the case of a perfectly regular train of waves, the appearance will depend upon the precise position occupied by the eye. It is evident that the light most diverted from its course is that reflected from the shoulders of the waves—the points midway between the troughs and crests, for it is here that the slope of the surface is greatest. Thus if the eye be moved laterally outwards from the focal point, until all light has nearly disappeared, the residual illumination will mark out the instantaneous positions of one set of shoulders, all other parts of the complete wave remaining dark. This is one of the most favourable positions for observation. If the deviation from the focal point be in the opposite direction, the other set of shoulders will be seen bright.

The aspect of the waves was not always equally pleasing. Sometimes the formation of stationary waves, due to reflexions, interfered with regularity. A readjustment of the walls of the vessel relatively to the dipper would then often effect an improvement. The essential thing is that there should be no

\* A dirty condition of the mercury sometimes leads to the failure of several successive contacts. During the interval the vibrations of the second fork, being unconstrained, take place in their natural period. In this way a phase-discrepancy may set in, to be subsequently corrected when the regular contacts are reestablished. Such a state of things is to be avoided as distracting to the eye, and unfavourable to accurate observation.



ambiguity in the wave pattern over the measured part of the field. It would occasionally happen that in certain positions of the eye a change of phase would occur in the middle of the field, so that the bright bands in one part were the continuation of the dark bands of another part. Near the transition the bands would appear confused, a sufficient indication that no measurement must be attempted. On the other hand, it is not necessary that the contrast between the dark and bright parts should be very great. Indeed the measuring marks were better seen when no part of the field was very dark.

Fig. 1 gives a general idea of the appearance of the field. On the right is seen a general paper with a notched edge, the use of

Fig. 1.



which was to facilitate the counting. The measuring arrangement was something like a beam compass. Stout brass wires, attached to a bar of iron, were shaped at their ends like brad-awls, and the edges were placed parallel to the crests of the waves. In order to avoid residual parallax, the rod was so supported that the edges were in close proximity to the water surface.

In many of the experiments the distance between the edges was set beforehand, *e.g.* to 10 centim., and was not altered when the wave-lengths varied with the deposition of grease. The number of wave-lengths included was determined by

counting, and estimation of tenths. Usually the discrepancy between Mr. Gordon's estimation and my own did not exceed a single tenth, and in a large proportion of cases there was no difference. Probably the mean of our readings would rarely be wrong by more than  $\frac{1}{20}$  of a wave-length, when the pattern was well seen. In the experiments specially directed to the determination of the tension of a clean surface, it was found advisable to work with an unknown distance; otherwise the recollection of previous results interfered with the independence of the estimates.

It is probable that somewhat greater accuracy in single measurements might have been attained had the distance been adjustable by a smooth motion within reach of the observer. Each measuring edge might then have been set to the most favourable position, that is, to the centre of a bright band. The frequent removal of the apparatus for comparison with a scale would, however, be rather objectionable; and it was thought doubtful whether any final gain would accrue in the mean of several observations.

Some trouble was experienced from the communication of vibrations through unintended channels. In order to prevent the direct influence of the interrupter fork upon the liquid surface, it was found advantageous to isolate it from the floor by supporting it upon a shelf carried upon the walls across a corner of the laboratory. On one occasion it was noticed that the waves were visible without the aid of the arrangement for making the light intermittent. This was traced to a tremor of one of the mirrors, supported upon the same shelf as the interrupter fork. Such a method of rendering the waves visible is objectionable, since it destroys the definition of the measuring points. The tremor was eliminated by the introduction of rubber tubing under the stand of the interrupter.

During the experiments on greasy surfaces one pair of forks only was employed. The frequency of the interrupter was about 42 per second, so that the intermittent current could be used to excite a fork of about 126. The beats between this and a standard Koenig fork of 128 were counted at intervals, and found to be sufficiently constant. The pitch of the standard has been verified by myself\*, and at the temperature of the laboratory may be taken with sufficient accuracy to be 128. If we take the number of beats per minute at 98, we have for the frequency of the interrupter

$$f = \frac{1}{3} \left( 128 - \frac{98}{60} \right) = 42.12.$$

\* Phil. Trans. 1883, p. 316.

In the case of clean water another pair of forks of about 128 was employed as a check. The number of beats was 184 per minute, and

$$f = 128 - \frac{184}{60} = 124.9.$$

The water was contained in a shallow  $12'' \times 10''$  porcelain dish; and before commencing observations its surface was purified with the aid of an expansible hoop of thin sheet brass. The width of the hoop is greater than the depth of water, and it is deposited in the dish so as to include the dipper, but otherwise in as contracted a condition as possible. It is then opened out to its maximum area with the effect of attenuating many times the thickness of the greasy film, which no amount of preliminary cleaning seems able to obviate. It not unfrequently happened that the first attempt to get a clean surface was a partial failure, but a repetition of the operation was usually successful. It seems as if impurity attaches itself to the brass so obstinately that only contact with a clean water surface will remove it.

In the earlier experiments the waves were generated by a dipper of circular section, a closed tube of glass, somewhat like a test-tube. The measurements were quite satisfactory, but I felt doubts as to a possible influence of curvature upon wave-length. In order to avoid any risk of this kind, and to render the waves straight from the commencement, a straight horizontal edge of glass plate, about  $2\frac{1}{2}$  inches long, was afterwards substituted, and worked very satisfactorily. It is not necessary or desirable that the dipper should pass in and out of the water. In most cases the vibrations employed were very small, and the edge of the dipper was immersed throughout.

The purity of the water surface could be judged by the result of the observation of the number of wave-lengths; the smallest number corresponding to the purest surface. But it soon became apparent that a more delicate test was to be found in the general appearance of the wave pattern. Upon a clean surface there is a strong tendency to irregularity, dependent no doubt upon reflexions, which become more important when the propagation is very free. In order to meet this, it was often found necessary to weaken the vibrations of the secondary fork, either by putting it more out of tune with the primary, or by shifting its magnet to a less favourable position, or, finally, by shunting the current across. A slight trace of grease would then render itself evident by a damping down of the waves before any change

could be observed in the wave-length. After a little experience with the forks in a given state of adjustment, a momentary glance at the pattern was sufficient to enable one to recognize the condition of the surface.

The interpretation of the observations depends upon the following formula, due to Thomson :—

Let  $U$  = velocity of propagation,  
 $\lambda$  = wave-length,  
 $\tau$  = periodic time,  
 $\rho$  = density,  
 $T$  = superficial tension,  
 $h$  = depth of water,

then (Basset's 'Hydrodynamics,' vol. ii. p. 177)

$$U^2 = \frac{\lambda^2}{\tau^2} = \left( \frac{g\lambda}{2\pi} + \frac{2\pi T}{\rho\lambda} \right) \tanh \frac{2\pi h}{\lambda};$$

so that to find  $T$  we have

$$T = \frac{\rho\lambda^3}{2\pi\tau^2} \coth \frac{2\pi h}{\lambda} - \frac{g\lambda^2\rho}{4\pi^2}.$$

In the present experiments the effect of the limitation of depth is negligible. We have  $h = 1.8$  centim., and for the greatest value of  $\lambda$  about .7 centim. Now

$$\coth \frac{2\pi h}{\lambda} = \frac{1 + e^{-4\pi h/\lambda}}{1 - e^{-4\pi h/\lambda}} = 1 + 2e^{-4\pi h/\lambda},$$

approximately, when  $h$  is relatively large; so that

$$\coth (2\pi h/\lambda) = 1 + 2e^{-30} = 1,$$

with abundant accuracy. Again, in the case of water we have  $\rho = 1$ ; and thus

$$T = \frac{\lambda^3}{2\pi\tau^2} - \frac{g\lambda^2}{4\pi^2},$$

which is the formula by which the calculation of  $T$  is to be made. The second term will be found to be small in comparison with the first, so that approximately  $T$  varies as  $\lambda^3$ . A one per cent. error in the estimation of  $\lambda$  will therefore involve one of three per cent. in the deduced value of  $T$ . In many of the experiments about 15 waves were included between the marks. An error of  $\frac{1}{10}$  of a wave is thus 1 in 150, leading to a two per cent. error in  $T$ . We may expect the final mean value to be correct to less than one per cent., but we must not be surprised if individual results show discrepancies of two per cent.

An example (August 2) will now be given in which the surface of clean water was greased with oleic acid. The dish



after rinsing was filled with water drawn from a tap in connexion with a cistern supplied mainly by rain water, and placed in position. On expansion of the brass hoop the number of waves included between the measuring points was estimated to be 13·7, 13·8 by the two observers. A piece of paper was then greased with oleic acid, and with this a platinum wire, previously cleaned by ignition, was wiped. On introduction of part of the wire into the water contained within the hoop, the number of waves rose to 15·4, 15·3. Upon this surface camphor scrapings were found to be quite dead, so that the mark had been overshot.

The dish was then refilled. Upon expansion the number of waves upon the clean surface was 13·7, 13·7. On contamination with a little oleic acid, 14·8, 14·8. Camphor was now moderately active. More oleic was added. Readings were now 15·4, 15·4, and camphor was quite dead.

The point to be fixed evidently lay between 14·8 and 15·4. A fresh surface was taken, and on addition of a little oleic the readings were 14·8, 14·8. Camphor was then tried and found moderately active. Reading still 14·8. A little more oleic added; readings 15·1, 15·1; camphor scrapings were now "nearly dead." More oleic; 15·2, 15·2; camphor "very nearly dead." More oleic; 15·4, 15·4; "not absolutely dead." More oleic; 15·5, 15·5; camphor "absolutely dead." The temperature of the water was 63° F.

On a previous occasion (July 29) accordant results had been obtained. Clean water 13·7, 13·7. Oleic added; 15·0, 15·0; camphor nearly dead. More oleic; 15·2, 15·25: camphor very nearly dead. Oleic; 15·55, 15·6; camphor dead. On both days the distance over which the waves were measured was 9·20 centim.

It may be well to exhibit in full the calculation for the clean water:—

$\log 9\cdot2 = \cdot9638$	$\log g = 2\cdot9917$
$\log 13\cdot7 = 1\cdot1367$	$\log \lambda = 1\cdot8271$
$\log \lambda = 1\cdot8271$	$1\cdot8271$
	$\hline 2\cdot6459$
	$\log 4\pi^2 = 1\cdot5962$
$\log \lambda^3 = 1\cdot4813$	$\log 11\cdot2 = 1\cdot0497$
$\log 42\cdot12 = 1\cdot6245$	
$1\cdot6245$	
$\hline 2\cdot7303$	
$\log 2\pi = \cdot7981$	
$\log 85\cdot5 = 1\cdot9322$	

$$\text{Finally, } T = 85\cdot5 - 11\cdot2 = 74\cdot3.$$

If we take as the reading when the camphor is nearly dead 15·2, we find in like manner

$$T = 62\cdot7 - 9\cdot1 = 53\cdot6.$$

After this example a summary of results may suffice. The interest attaching to the determination of the tension of a clean surface led me to strive after a higher degree of accuracy than perhaps would otherwise have been necessary. The following table contains the results obtained with both forks:—

Date.	Distance.	Frequency.	Tension.	Water.	Temp. F.	Remarks.
1890.						
June 23...	9·05	40·9	72·3	Tap	..... 73	Telescope lens.
25...	4·12	40·9	74·5	"	66	
26...	11·70	40·9	73·7	"	61	
30...	11·27	40·12	74·0	"	61	
July 1...	9·96	42·12	73·2	"	62	Strip dipper introduced.
2..	9·96	42·12	74·7	"	64	
4...	9·96	42·12	74·7	Distilled	60	
8...	9·96	42·12	74·7	"	65	
25...	10·00	42·12	74·2	Tap	65	
25...	9·20	42·12	75·2	"	68	
28...	9·20	42·12	74·3	"	68	
28...	9·20	42·12	74·3	Distilled	68	
29...	9·20	42·12	74·3	"	.....	
Aug. 2...	9·20	42·12	74·3	Tap	63	
July 23...	10·00	124·9	74·1	Tap	65	
23...	9·49	124·9	73·2	"	66	
23...	8·13	124·9	73·5	Distilled	66	

The mean result with the graver fork is  $T=74\cdot2$ ; and with the quicker one  $T=73\cdot6$ . The discrepancy of nearly one per cent. marks the limit of accuracy. It should be remarked that some of the consecutive results where no variation occurred in the distance between the points cannot be regarded as quite independent.

On several occasions distilled water proved a less satisfactory subject than tap water. The surface seemed more unwilling to become and remain clean. Sometimes after expansion a notable increase of readings would occur in the course of a few minutes without assignable cause.

I was very anxious to satisfy myself that in the surfaces experimented upon by the wave method a high degree of purity was really attained. In the experiments of July 28 a Plateau needle vibrating upon a portable stand was introduced. After the examination by the method of waves the dish was brought out into a good light, and the quality of the surface tested by observation of the motion of motes when the needle

lying upon it was caused to vibrate by an external magnet\*. In making the necessary arrangements there was some risk of introducing contamination, so that the discovery of an unclean surface would prove nothing definite. If, however, the behaviour of the surface under the needle test was good, it could be inferred with confidence that the measured waves were not affected by impurity. On two occasions the test succeeded fairly well.

The observations with the 128 fork were rather difficult, the waves being about twice as close as in the other case. In the calculation of results it appears, as was to be expected, that the importance of the second term, due to gravity, is diminished. Thus for July 22,

$$T = 76.5 - 2.4 = 74.1.$$

The general result that at temperatures such as  $65^{\circ}$  ( $18^{\circ}$  C.) the tension of clean water surfaces is about 74.0 C.G.S. absolute units of force per centimetre seems entitled to considerable confidence. It agrees with some former observations † of my own upon the transverse vibrations of jets, as has been remarked by Mr. Worthington ‡. Some interesting experiments upon the vibrations of falling drops by Lenard § point also in the same direction. On the other hand it deviates largely from the higher value, about 81, which Prof. Quincke thinks the most probable. The deviation from 81 is certainly not due to contamination. It has been explained that great care was taken in this respect during the present experiments; and in the jet method the surfaces are probably the purest attainable. The method favoured by Quincke depends upon the measurement of large flat bubbles confined under the horizontal surface of a solid body. In default of experience I must leave it to others to judge whether a systematic error due to optical or other causes could enter here. Mr. Worthington contends that some of Quincke's deductions from his measurements require correction for curvature perpendicular to the meridional plane. To this and other criticisms Prof. Quincke has replied ||.

Experimenters upon capillary tubes have generally been led to adopt the lower value, but here the interpretation involves an assumption that the angle of contact  $\theta$  is zero. What these measurements give in the first instance is  $T \cos \theta$ ; so that if  $\theta = 30^{\circ}$ , or thereabouts, the higher value of  $T$  is the one really

\* "On the Superficial Viscosity of Water," Proc. Roy. Soc. June 1890, vol. xlviii. p. 139.

† Proc. Roy. Soc. 1879, vol. xxix. p. 71.

‡ Phil. Mag. 1885, vol. xx. p. 51.

§ Wied. Ann. Bd. xxx. (1887).

|| *Ibid.* xxvii. p. 219 (1886).

indicated. This is the view adopted by Quincke, who in an important series of observations\* has shown that the edge angle between water and glass has frequently a considerable value dependent upon the impurity of glass surfaces, even when carefully cleaned by ordinary methods. But I confess that the argument does not appear to me conclusive. The angles recorded are maximum angles. If after a drop has been deposited some of the liquid is drawn off, the angle may be diminished almost to zero. Observations upon capillary heights correspond surely to the latter condition of things, for no experimenter measures the gradual rise of liquid in a dry tube. I am disposed to think that the assumption  $\theta=0$  is legitimate, and thus that the lower value of  $T$  is really supported by experiments of this class.

Leaving now the results for pure surfaces, let us pass on to those found for water contaminated with grease up to the point where the camphor scrapings were judged to be "very nearly dead." It must be remembered that the additions of oil were discontinuous, and that the point could not always be hit with precision. On any one day it is possible to set up a fairly precise standard of what one means by "very nearly dead;" but the standard is liable to vary in one's own mind, and is of course impossible to communicate to another. Too much importance therefore must not be ascribed to exact agreement or the failure of it. On one day experiments were made by varying the areas enclosed within the hoop. Thus, if the motions were a little too lively, they could be deadened to the required point by contraction of the area and consequent concentration of grease. This procedure was not so convenient as had been hoped, in consequence of the mechanical disturbance attending a motion of the hoop. In all cases an observation, for the most part recorded in the previous table, was made first upon a clean surface, so as to ensure that the contamination was all of the kind intended. The results are collected in the annexed table:—

Date.	Water.	Oil.	Tension.	Remarks.
June 30.....	Tap	Olive-oil	53·7	Not quite independent.
July 1.....	"	"	51·1	
2.....	"	"	52·1	
4.....	Distilled	"	53·0	
7.....	"	"	53·0	
11.....	"	"	53·0	
29.....	Tap	Oleic Acid	53·6	
Aug. 2.....	"	"	53·6	Another sample.
2.....	"	Olive-oil	52·4	
2.....	"	"	52·4	

\* Wied. Ann. 1877, vol. ii. p. 145.



The tension of the surface when the camphor movements are just stopping may thus be reckoned at 53·0 C.G.S., or about 72 per cent. of that of a clean surface. There is some reason to infer that the tension is the same whatever kind of grease be used. In the last experiment the sample of oil was one of which it was necessary to take decidedly more than usual (in the ratio of about 3 : 2) in order to stop the motions. This was proved by the balance in the manner described in a former paper. I have other grounds for thinking it probable that the tension does not depend upon the kind of oil, and hope to investigate the matter further by a more appropriate method.

On several occasions the effect of large additions of oil was tried. The limit did not appear to be very definite; for a second and even a third drop gave a sensible indication. The results were June 30, 38·8; July 1, 40·3; July 7, 41·0; July 8, 41·7; July 26, 38·9; mean 40·1. They relate to olive-oil; and it is possible that the largeness of the quantity required to approach the limit depends upon the heterogeneous character of the substance.

Two observations were made of the effect of additions of oleate of soda to distilled water. When the limit seemed nearly attained final readings were taken with the results: July 8, 25·3; July 11, 24·6; mean 25·0. It will be seen that the tension is lowered very much further by soap than by oil.

The principal results of the present experiments may be thus summarized. The tension of a water surface, reckoned in C.G.S. measure, is in the various cases :—

Clean .....	74·0	100
Greasy to the point where the camphor motions } nearly cease .....	53·0	72
Saturated with olive-oil .....	41·0	54
Saturated with oleate of soda .....	25·0	34

In the last column the tensions are exhibited as fractions of that of a clean surface.

#### POSTSCRIPT, *Sept.* 19.

It appeared probable that the tension of otherwise pure water saturated with camphor would be the same as that of greasy water upon which camphor fragments were just dead ;

and before the above paper was written I had already attempted to examine this point. The experiment, however, did not succeed. The camphorated water had decidedly too much tension (wave-number 14·7 instead of 15·5), but on the other hand the liquid was clearly not saturated, inasmuch as fresh camphor scrapings were lively upon an expanded surface. I have recently returned to the subject with water which has stood in contact with excess of camphor for more than a month.

Sept. 15. Fresh clean water. Expanded 13·7, 13·7. Motes still. Olive-oil added, 15·2, 15·2; camphor fragments moderately active. More oil, 15·3, 15·3; camphor nearly dead. More oil, 15·5, 15·5; camphor dead. Fragments of camphor and motes quite still.

The saturated solution of camphor was now substituted. Surface expanded; 15·5, 15·5. Expanded, 15·5. This number could not be reduced by any number of expansions of the surface.

It was observed that the surface was usually in motion, as evidenced by an irregular drift of motes and camphor fragments. The latter had no individual motion, all neighbouring particles moving together. The effect is probably due to local evaporation of camphor and accompanying increase of tension. Associated with this was a fluctuation backwards and forwards of the number of waves, such as was never observed with pure or simply greasy water.

We are thus justified in the conclusion that saturated solution of camphor has the same tension as is found for greasy water when camphor fragments are just dead. When the saturated solution was diluted with about an equal volume of water, the wave-number was reduced to 14·7. In these experiments the distance between the points was 9·20 centim., and the frequency was 42·12, so that the observations are directly comparable with those in the example calculated at length.

The comparison of tensions for clean and camphorated water may also be effected by the method of capillary heights. Some observations by Mr. Gordon gave the following:—

Clean water .....	7·94,	7·91,	7·92
Water changed .....	7·92,	7·90,	7·90
Saturated camphor .....	5·63,	5·68,	5·65
Clean water .....	7·97,	7·90,	7·92
Water changed .....	7·94,	7·96,	7·93
Saturated camphor .....	5·62,	5·63,	5·66

Thus, as a mean, capillary height for clean water is 7.93 centim., and for water saturated with camphor 5.64. The ratio of these is .71.

Observations by myself upon the same tube, but read in a somewhat different manner, gave

Clean water..... 8.04, 8.03, 8.04, 8.05.

Water changed ... 8.02, 8.02.

Camphorated water 5.77, 5.80, 5.79, 5.80, 5.80, 5.83.

As means we may take 8.03 centim. and 5.80 centim., giving for the ratio .71, as before.

The ratio of tensions thus found agrees remarkably well with that deduced from the observations upon ripples, viz. .72. It will be remembered that the latter might be expected to be somewhat higher, as corresponding with a condition of things where camphor fragments were *nearly*, but not quite dead.

October 8.—I take this opportunity of recording that a film of grease, insufficient to check the motion of camphor fragments, exercises a marked influence upon the reflexion of light from the surface of water in the neighbourhood of the polarizing angle. In the case of a clean surface and at the Brewsterian angle the reflexion of light polarized perpendicularly to the plane of incidence appears to vanish in accordance with the formula of Fresnel.

XLIV. *The Expansion of Water and other Liquids.*  
By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.\*

[Plates VII. & VIII.]

MY investigation of various properties of sulphuric acid (Journ. Chem. Soc. 1890, pp. 65, 331, and Phil. Mag. 1890, xxix. p. 427) showed that the curved figures representing these properties, or the figures representing the rate of change of these properties with change in percentage composition—the first differential coefficient, obtained by dividing the difference between the values obtained for two different solutions by the difference in their percentage strength—indicated the existence of more or less sudden changes of curvature at certain points corresponding to the composition of definite hydrates. The method adopted in examining any curved figure, to ascertain whether it was a single continuous curve

\* Communicated by the Author.

or not, consisted in applying to the experimental points of which it was composed a ruler bent by the hands, and ascertaining whether the whole figure could be drawn in one section, or whether it could only be drawn in several independent sections. The mere fact of the latter being the case did not prove that there was any real change of curvature at the point where two sections met, it simply suggested the possibility of this being the case: this possibility was, however, converted, in my opinion, into certainty, by finding that each of these sections was a simple parabola (although a ruler may be bent to form curves of a non-parabolic nature); by finding that some seven or eight different curved figures of totally different characters, and representing, either different properties, or the same property under different conditions, all gave indications of changes of curvature at the *same* points; and by finding that these points certainly corresponded to definite hydrates, wherever the solutions were strong enough to permit of such evidence being obtainable.

The culminating proof, however, of these changes of curvature, and of the hydrates which they represent, has been obtained from the law of the freezing-points which I have formulated, and which has reduced the proof of their existence to a mere question of mathematics (Chem. Soc. Proc. 1889, p. 149). So far as I have gone at present, every one of the hydrates which the changes of curvature indicated has been established beyond all reasonable doubt.

Such results afford conclusive proof of the validity of the method which I used to recognize these changes of curvature, and justify me in publishing the results of a similar treatment of the curves representing the density of water at different temperatures, although the changes shown by them are much more doubtful than in the majority of the cases previously examined, and although there is little or no evidence from any other source available for confirming their existence.

In an examination of the effect of temperature on the densities of sulphuric-acid solutions (Journ. Chem. Soc. 1890, p. 120), I determined the value of the water-contents of a 25 cubic centim. bottle at every 2° between 6° and 38° (for the method see *ibid.* p. 69). The results, which are given in Table I., when plotted out (fig. 11, Plate VII., which, however, does not show the whole of them), suggested the existence of some change of curvature at about 18°: on differentiating the experimental values, a differential ( $dw/dt$  in Table I.) was obtained which also suggested a change at this temperature, though a change of a very doubtful nature: this differential is shown in fig. 1, Plate VII., and appears to consist of two nearly straight



TABLE I.—Weights of Water contained in a 25-cubic-centim. Density-bottle at  $t^{\circ}$ .

$t^{\circ}$ .	$dt$ .	$w$ .	$dw$ .	$\frac{dw}{dt}$ .	$t^{\circ}$ .	Alternate determinations.	
						$\frac{dw}{dt}$ .	$t^{\circ}$ .
38.203	.....	$\left\{ \begin{array}{l} 24.87660 \\ 24.87670 \\ 24.87660 \\ 24.87665 \\ 24.87670 \end{array} \right\} 24.87667$					
	2.100	.....	—0.1733	—0.0083	37.15		
36.103	.....	24.89400					
	2.013	.....	—0.1585	—0.0079	35.10		
34.090	.....	24.90985					
	2.025	.....	—0.1560	—0.0077	33.08		
32.075	.....	24.92545					
	2.015	.....	—0.1385	—0.0069	31.07		
30.060	.....	24.93930					
	1.996	.....	—0.1351	—0.0068	29.06		
28.064	.....	$\left\{ \begin{array}{l} 24.95329 \\ 24.95232 \end{array} \right\} 24.95281$					
	2.028	.....	—0.1274	—0.0063	27.05		
26.036	.....	24.96555					
	2.201	.....	—0.1225	—0.0056	24.94		
23.835	.....	24.97780					
	1.930	.....	—0.1010	—0.0052	22.87		
21.905	.....	24.98790					
	2.024	.....	—0.0940	—0.0046	20.89		
19.881	.....	24.99730					
	1.956	.....	—0.0954	—0.0049	18.90		
17.925	.....	$\left\{ \begin{array}{l} 25.00757 \\ 25.00666 \\ 25.00602 \end{array} \right\} 25.00684$				—0.0040	17.91
	1.979	.....	—0.0636	—0.0032	16.94		
15.946	.....	25.01320					
	2.007	.....	—0.0665	—0.0033	14.94		
13.939	.....	$\left\{ \begin{array}{l} 25.02010 \\ 25.01960 \end{array} \right\} 25.01985$					
	1.973	.....	—0.0468	—0.0024	12.95		
11.956	.....	$\left\{ \begin{array}{l} 25.02450 \\ 25.02456 \end{array} \right\} 25.02453$					
	1.961	.....	—0.0412	—0.0021	10.98		
9.995	.....	$\left\{ \begin{array}{l} 25.02880 \\ 25.02865 \\ 25.02899 \\ 25.02816 \end{array} \right\} 25.02865$				—0.0015	9.96
	2.017	.....	—0.0174	—0.0009	8.99		
7.978	.....	$\left\{ \begin{array}{l} 25.03050 \\ 25.03050 \\ 25.03050 \\ 25.03006 \end{array} \right\} 25.03039$					
	1.963	.....	—0.0143	—0.0007	7.00		
6.015	.....	$\left\{ \begin{array}{l} 25.03165 \\ 25.03191 \end{array} \right\} 26.03182$					

lines meeting at about 18°. The determinations at 10° and 18° appeared to be anomalous, although they were repeated several times, and it is therefore better to omit them entirely; an omission which gives us the differential points given in Table I. under the heading of "alternate determinations," and marked in the plate by crosses.

A differentiation of the smoothed curve representing the experiments gave the values quoted in Table II., and the figure reproduced in fig. 2, Plate VII. This figure, like the other, suggests a change of curvature at 18°, as well as another change at about 10°.

TABLE II.—Weight of Water contained in a 25-cubic-centim. Density-bottle at  $t^{\circ}$ .

Differentiation of the Smoothed Curve representing the Weights.

$t^{\circ}$ .	$w$ .	$\frac{dw}{dt}$ .	$t^{\circ}$ .	$t^{\circ}$ .	$w$ .	$\frac{dw}{dt}$ .	$t^{\circ}$ .
38	24.87835	—00825	37.5	23	24.98215	—00500	22.5
37	24.88660	—00805	36.5	22	24.98715	—00480	21.5
36	24.89465	—00795	35.5	21	24.99195	—00465	20.5
35	24.90260	—00785	34.5	20	24.99660	—00470	19.5
34	24.91045	—00770	33.5	19	25.00130		
33	24.91815	—00745	32.5	17	25.00900	—00395	16.5
32	24.92560	—00710	31.5	16	25.01295	—00350	15.5
31	24.93270	—00690	30.5	15	25.01645	—00305	14.5
30	24.93960	—00710	29.5	14	25.01950	—00285	13.5
29	24.94670	—00645	28.5	13	25.02235	—00225	12.5
28	24.95315	—00630	27.5	12	25.02460	—00200	11.5
27	24.95945	—00615	26.5	11	25.02660	—00150	10.5
26	24.96560	—00580	25.5	10	25.02810	—00120	9.5
25	24.97140	—00535	24.5	9	25.02930	—00100	8.5
24	24.97675	—00540	23.5	8	25.03030	—00075	7.5
23	24.98215			7	25.03105	—00060	6.5
				6	25.03165		

My determinations were not nearly numerous enough to establish either of the changes here suggested, and were taken only as hinting the possibility of the existence of such ; but they showed the advisability of examining the more numerous results of other physicists in the same manner.

In all cases except one the differentiation of these was performed on the experimental values themselves. The exception was that of Kopp's determinations, which, though they may approximate to the truth more nearly than in several other cases, show such experimental errors in consecutive determinations as to be useless for purposes of direct differentiation. The smoothed curve representing the experiments was therefore differentiated in this case. In other cases also the smoothed experimental curves were differentiated, but only with the view of supplementing the evidence derived from a direct differentiation.

The differentiation of the several results requires some manipulation in order to combine the various series which several of the experimenters have made, and in order to get fairly equal differences between the consecutive determinations. One or two determinations which were evidently erroneous have been omitted. I have not considered it necessary to reproduce here the voluminous tables containing these results.

It is scarcely necessary to point out that only the experimental values themselves were taken, and that values calculated from equations purporting to represent them would be of no use for such purposes as the present.

Some of the results refer to volumes, others to weights : in some water at  $0^{\circ}$  is taken as unity, in others water at  $4^{\circ}$  : in some, again, the weights or volumes are uncorrected for the expansion of the glass. None of these differences will affect the question at issue—the existence or position of sudden changes of curvature—they will only affect (and that to a very small extent) the inclination, and, possibly, the curvature (if the coefficient of expansion of glass is represented by a curve instead of a straight line as is generally assumed) of the differential. Where densities are taken, the sign of the differential will be the opposite of what it is where volumes are taken : in the Plates I have represented them so that this difference shall not interfere with a comparison of the various figures.

It must be remembered that the figures here given illustrate

the results only imperfectly. In examining determinations in the manner here described many different scales must be employed; and the scales must be altered to suit the accuracy of the determinations of different experimenters, and of the same experimenter when working at different temperatures.

The illustrations which I give of the results are confined almost exclusively to the differentials.

The following details may be noted as to the various results obtained.

Pierre's values (*Ann. Chim. Phys.* xv. p. 325) exhibit great regularity up to  $20^{\circ}$ ; they are very numerous, and extend down to  $-13^{\circ}$ . The direct differential up to  $20^{\circ}$ , and that from the smoothed experimental curve from  $20^{\circ}$  to  $95^{\circ}$  (Table III.), is shown in fig. 3, Plate VII. The direct differential for these higher temperatures is given on a less open scale in fig. 12, Plate VIII. The irregularity which suggests two changes at  $0^{\circ}$  and  $-2^{\circ}5$  respectively is so peculiar that it must be regarded with considerable distrust: but some one change, however, somewhere about this temperature seems certain, since the results from  $-13^{\circ}$  to  $10^{\circ}$  cannot be represented by any one line or curve. The change at about  $18^{\circ}$  is also doubtful, since the curve from  $50^{\circ}$  to  $18^{\circ}$  could be extended down to  $10^{\circ}$  (but not lower) with but little increase in the apparent experimental error.

Despretz (*Ann. Chim. Phys.* lxx. p. 1) made four series of determinations between  $-10^{\circ}$  and  $17^{\circ}$ . That one which gives the most regular results indicates a possible change at about  $10^{\circ}$  (see fig. 4); and the mean values which he deduced from the four series gives a similar indication, though at a somewhat higher temperature (fig. 5). There appears to be some irregularity below  $0^{\circ}$ , but the nature of the figure here is uncertain. One series of determinations extending to  $100^{\circ}$  which he made by another method gave no certain indications of any change at higher temperatures, and are not sufficiently numerous to show any changes which might exist at lower temperatures. They have not been reproduced here.

The differential obtained from the smoothed curve representing Kopp's results (*Pogg. Ann.* lxxii. p. 45) is shown in fig. 6. Tables III. and IV. contain the numerical values. They suggest a change at about  $60^{\circ}$  and  $10^{\circ}$ .



TABLE III.—Vol. of Water at Temperatures from 33° to 101°. Differentiation of the Smoothed Curves representing Pierre's and Kopp's results. Volume at 0°=1.

$t^{\circ}$ .	Pierre.		Kopp.		$t^{\circ}$ .
	$v$ .	$\frac{dv}{dt}$ .	$v$ .	$\frac{dv}{dt}$ .	
101	.....	.....	1.04357	.00075	100
99	1.04312	.00096	1.04207	.00074	98
97	1.04160	.00087	1.04060	.00077	96
95	1.04007	.00086	1.03907	.00073	94
93	1.03855	.00074	1.03762	.00071	92
91	1.03707	.00072	1.03620	.00070	90
89	1.03563	.00073	1.03480	.00069	88
87	1.03418	.00072	1.03342	.00070	86
85	1.03225	.00070	1.03203	.00069	84
83	1.03135	.00070	1.03065	.00068	82
81	1.02995	.00065	1.02930	.00065	80
79	1.02865	.00068	1.02800	.00064	78
77	1.02730	.00064	1.02672	.00066	76
75	1.02603	.00064	1.02540	.00066	74
73	1.02476	.00064	1.02412	.00061	72
71	1.02349	.00062	1.02290	.00059	70
69	1.02226	.00061	1.02172	.00059	68
67	1.02105	.00059	1.02055	.00059	66
65	1.01988	.00057	1.01938	.00057	64
63	1.01875	.00058	1.01825	.00055	62
61	1.01760	.00056	1.01715	.00054	60
59	1.01648	.00056	1.01607	.00051	58
57	1.01536	.00052	1.01505	.00049	56
55	1.01433	.00052	1.01408	.00048	54
53	1.01330	.00049	1.01313	.00047	52
51	1.01232	.00046	1.01220	.00045	50
49	1.01140	.00045	1.01130	.00045	48
47	1.01050	.00044	1.01040	.00040	46
45	1.00962	.00043	1.00960	.00042	44
43	1.00876	.00042	1.00877	.00040	42
41	1.00793	.00037	1.00797	.00039	40
39	1.00720	.00038	1.00720	.00037	38
37	1.00645	.00037	1.00647	.00037	36
35	1.00572	.....	1.00573	.00035	34
33	.....		1.00503		

TABLE IV.—Volume of Water at Temperatures from 0° to 39°.

Differentiation of the Smoothed Curve representing Kopp's results. Volume at 0° = 1.

$t^{\circ}$ .	$v$ .	$\frac{dv}{dt}$ .	$t^{\circ}$ .	$t^{\circ}$ .	$v$ .	$\frac{dv}{dt}$ .	$t^{\circ}$ .
39	1·007147	·000382	38·5	19	1·001367	·000187	18·5
38	1·006765	·000365	37·5	18	1·001180	·000168	17·5
37	1·006400	·000355	36·5	17	1·001012	·000159	16·5
36	1·006045	·000350	35·5	16	1·000853	·000150	15·5
35	1·005695	·000340	34·5	15	1·000703	·000141	14·5
34	1·005355	·000332	33·5	14	1·000562	·000122	13·5
33	1·005023	·000323	32·5	13	1·000440	·000113	12·5
32	1·004700	·000320	31·5	12	1·000327	·000102	11·5
31	1·004380	·000300	30·5	11	1·000225	·000095	10·5
30	1·004080	·000297	29·5	10	1·000130	·000080	9·5
29	1·003783	·000282	28·5	9	1·000050	·000067	8·5
28	1·003501	·000276	27·5	8	0·999983	·000055	7·5
27	1·003225	·000262	26·5	7	0·999928	·000033	6·5
26	1·002963	·000253	25·5	6	0·999895	·000022	5·5
25	1·002710	·000248	24·5	5	0·999873	+·000001	4·5
24	1·002462	·000235	23·5	4	0·999872	—·000010	3·5
23	1·002227	·000227	22·5	3	0·999882	—·000025	2·5
22	1·002000	·000225	21·5	2	0·999907	—·000038	1·5
21	1·001775	·000210	20·5	1	0·999945	—·000055	0·5
20	1·001565	·000198	19·5	0	1·000000		
19	1·001367						

Rosetti's results (Pogg. Ann. Erg.-Bd. v. p. 268) give a differential which suggests a change at about 60° and another at 18° (fig. 7); but the determinations at the higher temperatures are not very numerous, and those from 3° to —6°

show irregularities too great to permit of any satisfactory conclusions being drawn from them.

Matthiessen's determinations (*Pogg. Ann.* cxxviii. p. 527, and fig. 8) indicate a change at about  $20^{\circ}$ , but none at  $50^{\circ}$ – $60^{\circ}$ : they would not be sufficiently numerous to show any which existed at temperatures below  $20^{\circ}$ . I have represented a portion of the experimental curve itself in fig. 12: the close similarity with my own as regards the change near  $20^{\circ}$  will be noticed, though the curves, referring as they do to weights and volumes respectively, differ as to their position. Rosetti's experimental curve is of a precisely similar nature.

Jolly's values (*Sitzungsber. d. Akad. zu München*, 1864, (i) p. 141) give a differential represented by fig. 9. They indicate a change at about  $50^{\circ}$ , but they would not be sufficiently numerous to show any changes at lower temperatures. Jolly quotes some results obtained by Henrici, but they are not sufficiently numerous for the present purposes.

Hagen's determinations (*Abhandl. d. k. Akad. d. Wissenschaft. z. Berlin*, 1855; *Math. Abhandl.* i.) are very numerous, and for the purposes of direct differentiation must be arranged in two series. They indicate changes at  $50^{\circ}$ ,  $20^{\circ}$ , and  $10^{\circ}$ , but the exact form of the figure between  $20^{\circ}$  and  $10^{\circ}$  is doubtful: the changes at these two temperatures depend on the fact of the curves above and below them ceasing to be applicable below and above the two temperatures respectively. The points given by the second series into which his results were divided have not been inserted here owing to lack of room: they do not extend above  $34^{\circ}$ . Hagen's values refer to actual weights; they have been multiplied by  $\frac{3}{4}$  so as to reduce them to about the same relative magnitude as those results which are expressed as volumes or densities.

None of these results, if taken separately, would be sufficient to prove the changes which they indicate, but when taken together they certainly afford sufficient evidence for the assertion that these changes are highly probable. The evidence may be summarized as follows:—

Change at	Indicated by the results of
$50^{\circ}$ – $60^{\circ}$ . .	Hagen, Jolly, Kopp, Pierre, and Rosetti.
$17^{\circ}$ – $20^{\circ}$ . .	Hagen, Kopp, Matthiessen, Pickering, Pierre, and Rosetti.
$9^{\circ}$ – $11^{\circ}$ . .	Hagen, Kopp, Pickering, and Pierre.
$0^{\circ}$ . .	Despretz's results showing some irregularity at these low tem- peratures.
$-2^{\circ}$ – $5$ . .	

Such concordance in the results of different observers can

scarcely be accidental. The cases in which the individual results fail to show any one of the above changes are chiefly those where the results are deficient in number or accuracy. The most marked exceptions to this statement being the absence of indications of any change at  $50^{\circ}$ – $60^{\circ}$ , by Despretz's or Matthiessen's results, and the absence of indications of change at  $10^{\circ}$  by Rosetti's results.

It is true that there is some discrepancy as to the nature of the first differential lines in some cases according to the different observers; but a very small difference, or a constant source of error, such as might occur in taking the temperature, would account for this; the important point is the *position* of the changes.

The existence of more or less sudden alterations in the rate at which density varies with temperature must, I think, from reasons other than experimental ones be regarded as not improbable. It can scarcely be doubted that liquids are composed of various partially dissociated aggregates of their fundamental molecules, and the instability of such complicated bodies would, no doubt, be so great that a rise of a few degrees would be sufficient to exterminate some particular one of them, and such extermination would result in the alteration in the rate at which temperature would affect the density. The existence of such changes, moreover, is in harmony with that of similar changes in the curves representing the effect of temperature on the heat of dissolution of weak salt-solutions (Trans. Chem. Soc. 1887, p. 290).

Further confirmation of the change at  $50^{\circ}$ – $60^{\circ}$  has been found in some recent work of Tschernay (*J. Russ. Chem. Soc.* 1880, pp. 430 and 486). This physicist has examined the expansion of solutions of six different nitrates and nine chlorides, and finds that in all cases a change occurs at about  $50^{\circ}$ , necessitating the use of different equations to represent the determinations above and below that temperature\*. I had at first attributed this change to some peculiarity in the expansion of glass, since it is well known that at about  $50^{\circ}$  glass begins to experience some change which prevents it reverting at once to its original volume on cooling; but I now think that this explanation cannot be held, for most of the other liquids which I have examined do not exhibit any change at this temperature, and those which do so exhibit a change of a very different magnitude from that exhibited by water. It may also be pointed out that definite changes in the rate of expan-

\* I have not examined Tschernay's data to see whether they give evidence of any changes besides that at  $50^{\circ}$ .



sion of a solid must imply sudden changes in its constitution, just as they do in the case of a liquid ; and in the case of a solid, where the molecules are practically fixed, such changes present far greater difficulties than in the case of liquids, where the mobility of the particles is great, and where we have a state particularly favourable for dissociation.

An examination of the densities of some other liquids has added confirmation to my conclusions respecting water. The changes which they exhibit are placed at various temperatures, showing that they cannot be attributed to constant errors in the instruments used, and some of them are moreover of a much more pronounced character than those in the case of water.

Pierre's memoir above cited gives the results obtained with eleven other liquids ; these I have differentiated directly, and the differentials are plotted out in Plate VIII. They are arranged roughly according to the magnitude of the rate of change: the scale adopted for  $dv/dt$ , it must be specially noted, is only one-fifth of that used in Plate VII.

With ethyl chloride the results are not very regular: they appear to form a continuous straight line throughout.

With methyl bromide they form a slight curve continuous throughout, but there are not sufficient points to admit of any definite conclusions being drawn from them.

In the case of ether we get two straight lines meeting at about  $14^{\circ}$ , and showing the existence of a change at that temperature, which is further emphasized by the very non-conformable point existing there (see Trans. Chem. Soc. 1890, p. 67). There seems to be another change at  $-10^{\circ}$ , but the data are insufficient to prove it.

With ethyl formate the results are represented by a straight line from  $60^{\circ}$  to  $-21^{\circ}$ , where there seems to be a change ; but it is uncertain in its character.

Ethyl bromide gives two straight lines showing a change at about  $39^{\circ}$ .

With methyl acetate we get a continuous and very slight curve ; but it might well be a straight line from  $65^{\circ}$  to about  $-10^{\circ}$ , followed by a different line down to  $-34^{\circ}$ .

Methyl iodide gives two straight lines showing a change at  $10^{\circ}$ . The points are not in very good agreement with the upper of these two lines, but if we take the means between consecutive points the agreement is perfect.

Methyl alcohol gives three straight lines with changes at  $44^{\circ}$  and  $16^{\circ}$ .

With ethyl iodide we get a perfectly continuous straight line throughout.

Carbon disulphide gives a fairly straight line from  $-20^{\circ}$  up to  $45^{\circ}$ ; at this last point some irregularity begins to show itself, and we get two points at A and B which are nonconformable to an extraordinary extent. The difference at B would correspond to an error of some  $3^{\circ}$ , and though it is difficult to imagine how such an error could occur (as it would have to exist in all the determinations above  $51^{\circ}$ ), it is still more difficult to imagine that the results are true.

Ethyl alcohol gives three straight lines with changes at  $53^{\circ}$  and  $19^{\circ}$ , noticeable as being nearly coincident with two of those shown by water.

Fig. 12 gives Pierre's results with water, the portion below  $15^{\circ}$  being copied from fig. 3, Plate VII. The character of this curve and the lowness of its position is remarkable by the side of the other curves.

The boiling-points of the various liquids are inserted in the Plate (b.-p.), but they do not seem to correspond to any sudden changes when the substance still remains liquid.

Although we cannot attribute very much weight to the results obtained with these volatile liquids, the general character of all the curves is in favour of the view that the first differential is a series of straight or nearly straight lines, and that consequently the density, as a function of temperature, is represented by a series of parabolic curves of the second order. Methyl bromide and acetate are the only doubtful exceptions amongst the non-aqueous liquids examined; and in the diagrams for water the portion between  $18^{\circ}$  and  $55^{\circ}$  is the only one which appears to be uniformly curved.

Mendeleëff's work on the expansion of alcoholic solutions, Tschernay's on that of salt-solutions, and my own determinations with sulphuric-acid solutions given above (Trans. Chem. Soc. 1890, p. 119), may also be cited as further proof of the rectilinear character of the first differential in such cases.

That the arguments brought forward in this communication in favour of the existence of more or less sudden changes in the rate of alteration of the density with temperature can be regarded as absolute proof cannot for a moment be maintained; nor must it be supposed that the evidence here is in any respect on the same footing with that on which the conclusions in my previous communications depend. In the present case the various changes depend on differences as small as any in the most doubtful cases in former investigations, and the conclusions drawn from them must always be doubtful. The evidence derived from the data given by the different

physicists are, moreover, not in absolute agreement, though it would be unreasonable to look for greater concordance in such a difficult case. But the weakness of the evidence here in comparison with that in the previous work lies in the fact that we are here dealing with only one property, instead of with the accumulation of confirmatory evidence from wholly independent sources. For this reason only we must be satisfied with regarding the results more as important suggestions than as definite proof.

XLV. *On the Relation between the Boiling-Points, Molecular Volumes, and Chemical Characters of Liquids.* By ORME MASSON, M.A., D.Sc., Professor of Chemistry in the University of Melbourne\*.

IN one of his papers on the Periodic Law (Phil. Mag. 1885, p. 259) Professor Carnelley pointed out several relations between the alkyl compounds of the elements with regard to the variation of boiling-point and of specific gravity. If, instead of considering the specific gravities themselves, we calculate from them the molecular volumes of, say, the ethyl compounds of the various elements and plot a curve with these values as ordinates and the atomic weights of the elements in question as abscissæ, the manner in which they vary from one compound to another and from one period to another may be compared with the variation of the boiling-points, similarly plotted; and, in spite of the broken character of the curves, due to want of data and the nonformation of ethides by many of the elements, the general resemblance between the alteration of molecular volume and the alteration of boiling-point is rendered very striking. The molecular volumes are, however, not really comparable, being calculated from densities at ordinary temperatures; and they cannot therefore serve for the study of whatever exact relation may exist between boiling-points and molecular volumes. For this purpose densities at the boiling-points are required, and these are known in the case of only five of the twenty or more known ethides (Clarke's Table of Specific Gravity).

Intending ultimately to complete as far as possible the study of the molecular volumes of these substances at their boiling-points under atmospheric pressure, I commenced recently with the haloid compounds of ethyl, using Ramsay's method, slightly modified; and certain considerations have been suggested by a comparison of these first results with the work of

\* Communicated by the Author.



other observers, which I believe are of sufficient interest to warrant me in discussing them now. It is not claimed that the law which will be put forward is at all complete or final in form ; but the evidence certainly shows that it is at least a first approximation to an exact law. Before proceeding further, I should state that I find that the relation in question has already been to a certain extent noticed by J. A. Groshans, who cited one or two instances of it in a paper published four years ago and discussed these instances in the light of his " Law of Density Numbers " (*Berichte*, xix. p. 974). So far as I am aware, it has not otherwise been noticed.

To save circumlocution, I shall use the phrase *compounds of the same group* to signify compounds of the same hydrocarbon radical with elements of the same natural group. Thus ethyl fluoride, chloride, bromide, and iodide form one group ; the oxide, sulphide, selenide, and telluride form another ; ethylene halides a third ; and chloroform and bromoform belong to a fourth. The law may then be stated as follows :—The ratio of the molecular volume at the boiling-point to the temperature of ebullition reckoned from absolute zero is a constant quantity for all compounds of the same group. More fully stated it amounts to this :—

*If liquid compounds of the same group be compared at temperatures at which their vapour-pressures are equal, the volumes occupied by unit weights are inversely proportional to the molecular weights and directly proportional to the absolute temperature ; or*

$$\frac{M}{D_T \times T} = \frac{V_T}{T} = \text{a constant } (c) \quad . \quad . \quad . \quad (1)$$

for each group, vapour-pressure being equal. In this formula  $M$ =molecular weight,  $D_T$ =density of the liquid at  $T^\circ$ ,  $T$ =absolute temperature of ebullition, and  $V_T$ =molecular volume at  $T^\circ$ . It will be shown that, so far as the law can be at present tested, the deviations are small but real.

This may be compared with the following, which is but a special statement of two familiar laws of much wider application :—If vapours of the same group [or any vapours] be compared at different temperatures but equal pressure, the volumes occupied by unit weights are inversely proportional to the molecular weights and directly proportional to the absolute temperatures : or

$$\frac{M}{d_T \times T} = \frac{v_T}{T} = \text{a constant } (c'), \quad . \quad . \quad . \quad (2)$$



vapour-pressure being equal. Here also the deviations are small but real.

If these two expressions be taken together, we get the following rider to the first law :—

*Different compounds of the same group are expanded equally in changing from liquid at the boiling-point to vapour at the boiling-point ; for*

$$\frac{v_T}{T} : \frac{V_T}{T} = \frac{v_T}{V_T} = \frac{c'}{c}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we neglect deviations from normal vapour-density, and if all measurements be expressed in grammes and cubic centimetres, the actual value of  $v_T$  for any vapour at atmospheric pressure is  $\frac{22326 T}{273}$ . Hence  $c' = 81.7766$ , and

$$\frac{v_T}{V_T} = 81.7766 \frac{T}{V_T};$$

and this ratio is of constant value in each group of compounds. It may be called the coefficient of *ebullition expansion*. (Compare J. A. Groshans, Phil. Mag. 1885, xx. p. 197.)

The chief evidence in support of the law is afforded by the compounds of the hydrocarbon radicals with the halogens. The data they afford are brought together in Table I., where they are divided into eleven groups according to the constitution of the radical. It will be seen that the examples are of various kinds, monohalides of different homologous series, both saturated and unsaturated, being represented, and also dihalides and trihalides. The molecular volumes are calculated from the densities recorded by various observers, but as far as possible the same observer has been quoted for the compounds of the same group, so as to ensure comparable results within that group.

The different columns of Table I. give (1) the name of the compound, (2) its formula, (3) the molecular weight,  $M$ , (4) the liquid density,  $D_T$ , at the boiling-point under atmospheric pressure, (5) the observer's name, (6) the found molecular volume,  $V_T$ , (7) the boiling-point on the absolute scale,  $T$ , (8) the value of the ratio  $\frac{V_T}{T}$ , and (9) the number  $81.7766 \frac{T}{V_T}$ , which is, as already explained, the measure of what may be called the ebullition expansion.

TABLE I.

Liquid.	Formula.	M.	D <sub>r</sub> .	Observer.	V <sub>r</sub> .	T.	$\frac{V_r}{T}$ .	Ebullition expansion.
Methyl chloride .....	CH <sub>3</sub> Cl ...	50.34	.99145	{ Vincent and Delachanal }	50.77	249.8	.2037	401.5
Methyl iodide .....	CH <sub>3</sub> I .....	141.50	2.2146	Dobriner.	63.89	315.8	.2023	404.2
Ethyl chloride .....	C <sub>2</sub> H <sub>5</sub> Cl ...	64.31	.89769	Masson.	71.64	286.5	.2500	327.0
Ethyl bromide .....	C <sub>2</sub> H <sub>5</sub> Br ...	108.69	1.41783	"	76.65	311.4	.2462	332.2
Ethyl iodide .....	C <sub>2</sub> H <sub>5</sub> I .....	155.47	1.81425	"	85.69	344.3	.2489	328.6
Propyl chloride .....	C <sub>3</sub> H <sub>7</sub> Cl ...	78.28	.8536	Zander.	91.71	319.5	.2870	284.9
Propyl bromide .....	C <sub>3</sub> H <sub>7</sub> Br ...	122.66	1.2639	"	97.05	344	.2821	289.9
Propyl iodide .....	C <sub>3</sub> H <sub>7</sub> I .....	169.44	1.3867	"	106.79	375.5	.2844	287.5
Butyl chloride .....	C <sub>4</sub> H <sub>9</sub> Cl ...	92.25	.8094	Ramsay.	113.97	350.6	.3251	251.6
Butyl iodide .....	C <sub>4</sub> H <sub>9</sub> I .....	183.41	1.4308	Dobriner.	128.19	402.9	.3182	257.0
Isopropyl chloride .....	C <sub>3</sub> H <sub>7</sub> Cl ...	78.28	.8326	Zander.	94.02	309.5	.3038	269.2
Isopropyl bromide .....	C <sub>3</sub> H <sub>7</sub> Br ...	122.66	1.2368	"	99.18	333	.2978	274.6
Isopropyl iodide .....	C <sub>3</sub> H <sub>7</sub> I .....	169.44	1.5650	"	108.27	362	.2991	273.4
Isobutyl chloride .....	C <sub>4</sub> H <sub>9</sub> Cl ...	92.25	.8073	Schiff.	114.27	341	.3351	244.0
Isobutyl bromide .....	C <sub>4</sub> H <sub>9</sub> Br ...	136.63	1.1456	"	119.27	363.5	.3281	249.2
Isobutyl iodide .....	C <sub>4</sub> H <sub>9</sub> I .....	183.41	1.4335	"	127.95	387.5	.3302	247.7
Amyl chloride .....	C <sub>5</sub> H <sub>11</sub> Cl ...	106.22	.7903	Schiff.	134.40	372.5	.3608	226.6
Amyl bromide .....	C <sub>5</sub> H <sub>11</sub> Br ...	150.60	1.0881	"	138.42	391.5	.3536	231.3
Amyl iodide .....	C <sub>5</sub> H <sub>11</sub> I ...	197.35	1.3098	"	150.69	421	.3579	228.5
Allyl chloride .....	C <sub>3</sub> H <sub>5</sub> Cl ...	76.28	.9002	Zander.	84.74	319	.2656	307.9
Allyl bromide .....	C <sub>3</sub> H <sub>5</sub> Br ...	120.66	1.3333	"	90.50	343.5	.2635	310.4
Allyl iodide .....	C <sub>3</sub> H <sub>5</sub> I .....	167.44	1.6601	"	100.86	375.6	.2685	304.5
Phenyl fluoride .....	C <sub>6</sub> H <sub>5</sub> F .....	95.8		Young.	101.59	358.1	.2837	288.3
Phenyl chloride .....	C <sub>6</sub> H <sub>5</sub> Cl ...	112.2	Young gives volumes, not densities.	"	114.26	404.9	.2821	239.8
Phenyl bromide .....	C <sub>6</sub> H <sub>5</sub> Br ...	156.6		"	119.94	429	.2796	292.5
Phenyl iodide .....	C <sub>6</sub> H <sub>5</sub> I .....	203.4		"	129.86	461.5	.2814	290.6
Ethylene chloride .....	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> ...	98.68	1.15635	Thorpe.	85.34	356.5	.2394	341.6
Ethylene bromide .....	C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> ...	187.44	1.93124	"	97.06	404.5	.2407	340.7
Ethylene chloriodide .....	C <sub>2</sub> H <sub>4</sub> ClI ...	189.84	1.87915	"	101.03	413.1	.2446	334.4
Chloroform .....	CHCl <sub>3</sub> .....	119.08	1.40877	Thorpe.	84.53	334.2	.2529	323.3
Bromoform .....	CHBr <sub>3</sub> .....	252.22	2.43611	"	103.53	424.2	.2441	335.1

The figures in the last two columns of the foregoing Table afford, I think it may be claimed, sufficient proof of the truth of the law under discussion, so far as the elements of the seventh natural group are concerned. They show that the different halides of the same radical give an almost

constant value for  $\frac{V_T}{T}$ , the deviation from perfect constancy in only two cases amounting to 2 per cent. of the total value. But an inspection of the figures also proves, I think, that the deviations, such as they are, are real; for in every case but one the bromide has the lowest value, and in every case but two the iodide has a value intermediate between those of the chloride and the bromide. If we assume, as seems fair, that the fluoride possesses the highest value in each group, as it does among the phenyl compounds, then the magnitude of  $\frac{V_T}{T}$  appears to undergo a small periodic variation within the group, falling from RF to RBr and rising again at RI to almost the value of RCl.

Other points are suggested; but before entering into a discussion of these, it will be best to bring forward the evidence which, as it appears to me, justifies the extension of the law beyond the elements of the seventh group. Unfortunately direct experimental evidence is not as yet available; for though the densities of some of the alkyl oxides and nitrides at their boiling-points have been recorded, there is a total absence of data with regard to the sulphides, phosphides, &c. The boiling-points of many of these compounds are known, however; and a fair approximation to their molecular volumes at the boiling-point can be almost certainly arrived at by making use of the average atomic-volume values of Kopp or Thorpe. Those here employed are C=11, H=5.5, S=22.6, P=25.3, As=26.3, Sb=28.6, Si=30.3, Sn=40.8 (Thorpe, *Trans. Chem. Soc.* xxxvii. p. 393).

Table II. gives the results of such calculation. It will be seen that, if the method may be trusted at all, proof is afforded of the close approximation to a constant value for  $\frac{V_T}{T}$  in the compounds of the sixth, fifth, and fourth groups of elements. It does not, of course, enable us to compare the extent of the deviations from absolute constancy with that exhibited by the compounds of the seventh group. The successive columns of Table II. give (1) the formula of the compound, (2) the mole-

cular weight,  $M$ , (3) the liquid density at boiling-point,  $D_T$  (if observed), with the observer's name, (4) the value of  $V_T$  found ( $= \frac{M}{D_T}$ ), or (5) this value calculated from atomic-volume numbers, (6) the absolute boiling temperature,  $T$ , and (7) the value of the ratio  $\frac{V_T}{T}$ .

TABLE II.

Formula.	M.	$D_T$ .	$V_T$ .		T.	$\frac{V_T}{T}$ .
			Found.	Calculated.		
$(C_2H_5)_2O$ ...	73·84	·69566 (Masson)	106·14	.....	307·9	·3447
$(C_2H_5)_2S$ ...	89·86	.....	.....	121·6	365	·3332
$(C_3H_7)_2O$ ...	101·78	·6743 (Zander)	150·94	.....	363·7	·4150
$(C_3H_7)_2S$ ...	117·80	.....	.....	165·6	405·5	·4084
$(C_4H_9)_2O$ ...	129·72	·6575 (Dobrinier)	197·29	.....	413·9	·4767
$(C_4H_9)_2S$ ...	145·74	.....	.....	209·6	455	·4607
$(C_2H_5)_3N$ ...	100·83	·6621 (Schiff)	152·29	.....	362	·4207
$(C_2H_5)_3P$ ...	117·78	.....	.....	173·8	400	·4345
$(C_2H_5)_3As$ ...	161·72	.....	.....	174·8	413	·4233
$(C_2H_5)_3Sb$ ...	206·82	.....	.....	177·1	431	·4109
$(C_2H_5)_4Si$ ...	144·06	.....	.....	228·3	426	·5359
$(C_2H_5)_4Sn$ ...	233·56	.....	.....	238·8	454	·5260
$(C_3H_7)_4Si$ ...	199·94	.....	.....	316·3	486	·6508
$(C_3H_7)_4Sn$ ...	289·44	.....	.....	326·8	498	·6562

The atomic volumes of selenium and tellurium are not even approximately known. Ethyl selenide boils at  $108^\circ C$ ., and the telluride at  $98^\circ C$ . If these compounds follow the rule, therefore, tellurium must have a smaller atomic volume than selenium. If a value for  $\frac{V_T}{T}$  be assumed slightly smaller than

that obtained by direct experiment with the oxide, viz. ·34 instead of ·3447, we get  $V_T = 129·5$  for  $(C_2H_5)_2Se$  and  $V_T = 126·1$  for  $(C_2H_5)_2Te$ ; whence, if  $C_2H_5 = 49·5$ ,  $Se = 30·5$ , and  $Te = 27·1$ , as approximate values.



To revert to Table I., it may be pointed out that the variation in value of  $\frac{V_T}{T}$  is fairly constant as we pass from the halide of one alkyl radical to that of its next homologue. This is exemplified in Table III., where the experimental figures for the chlorides and iodides of the first four normal fatty radicals are compared with consecutive multiples of the figure .041.

TABLE III.

Radical.	$\frac{V_T}{T}$ found.		<i>n</i> .	<i>n</i> × .041.
	Iodide.	Chloride.		
CH <sub>3</sub> .....	.2023	.2037	5	.205
C <sub>2</sub> H <sub>5</sub> .....	.2489	.2500	6	.246
C <sub>3</sub> H <sub>7</sub> .....	.2844	.2870	7	.287
C <sub>4</sub> H <sub>9</sub> .....	.3182	.3251	8	.328

In this table it is intended merely to call attention to the comparative regularity of the increase with each successive addition of CH<sub>2</sub> to the radical, so far as can be judged from the examples quoted. The evidence is at present insufficient to warrant speculation on this point.

There is no doubt whatever that the law, at all events in its most obvious form, cannot be extended beyond the range of carbon compounds. To test the question, the values of  $\frac{V_T}{T}$  have been calculated for all the inorganic substances included in Thorpe's research which fall into natural groups. The results are given in Table IV. The first column contains the formula of the substance, the second gives Thorpe's experimental value for  $V_T$ , the third gives his value for  $T$ , and the ratio  $\frac{V_T}{T}$  is given in the last column.

TABLE IV.

Formula.	$V_T$ .	T.	$\frac{V_T}{T}$ .
Br <sub>2</sub> .....	53.48	332.27	.1609
ICl .....	56.18	374.3	.1501
SOCl <sub>2</sub> .....	78.01	351.8	.2217
S <sub>2</sub> Cl <sub>2</sub> .....	90.28	411.12	.2196
SO <sub>2</sub> Cl <sub>2</sub> .....	86.29	342.95	.2516
CrO <sub>2</sub> Cl <sub>2</sub> .....	88.21	388.9	.2268
PCl <sub>3</sub> .....	93.34	348.95	.2675
PBr <sub>3</sub> .....	108.28	445.9	.2428
AsF <sub>3</sub> .....	53.84	333.4	.1615
AsCl <sub>3</sub> .....	94.37	403.21	.2340
SbCl <sub>3</sub> .....	96.72	496.5	.1948
POCl <sub>3</sub> .....	101.37	380.23	.2666
POBrCl <sub>2</sub> .....	107.38	410.6	.2615
PSCl <sub>3</sub> .....	116.11	398.12	.2916
VOCl <sub>3</sub> .....	106.25	400.19	.2655
CCl <sub>4</sub> .....	103.68	349.74	.2964
CBrCl <sub>3</sub> .....	108.43	377.07	.2876
SiCl <sub>4</sub> .....	120.8	330.57	.3654
TiCl <sub>4</sub> .....	124.47	409.4	.3040
SnCl <sub>4</sub> .....	131.07	386.9	.3388

It is evident from these figures that the apparently simple relation which obtains among the compounds of hydrocarbon radicals with elements of the same group does not extend to compounds of elements of one group with elements of another group. In some cases the ratio has nearly the same value in similar compounds, *e. g.* SOCl<sub>2</sub> and S<sub>2</sub>Cl<sub>2</sub>, or POCl<sub>3</sub>, POBrCl<sub>2</sub>, and VOCl<sub>3</sub>; but in others there is a large variation, as in the simple halogen compounds of the phosphorus group. But the law, if fully understood, might be found to explain and embrace these cases.

It appears, then, from a comparison of Table IV. with Tables I. and II., that similarity of chemical constitution is not the only condition required for equality of the ratio  $\frac{V_T}{T}$ .

Some clue may be obtained to the more precise nature of the relation by an examination of the very interesting work on benzene and its monohalogen derivatives published last year by Professor Sydney Young (Trans. Chem. Soc. lv. p. 486).

I may perhaps be allowed to briefly recapitulate his chief results, in so far as they affect this question.

(1) The critical pressures of  $C_6H_5F$ ,  $C_6H_5Cl$ ,  $C_6H_5Br$ , and  $C_6H_5I$  are equal, or very nearly so. Equal pressures are therefore corresponding pressures. But  $C_6H_6$  has a different critical pressure.

(2) Compared at equal pressures, from 5 millim. up to the critical point, the absolute boiling-temperatures of the four halogen derivatives (but not of benzene) bear constant ratios to one another.

(3) At all equal pressures the molecular volumes at boiling-points of the four halogen derivatives also bear constant ratios to one another.

Young gives the values of  $V_T$  and  $T$  for each compound at various pressures, and also the constant ratio numbers applicable to any pressure for comparison of the fluoride with the chloride &c. in respect to each of these variables.

In Table V. the second column gives Young's boiling-temperature ratios, the third gives his molecular volume-ratios, and in the last are the values of the ratios  $\frac{V_T}{T}$  which I have calculated from them. They are good for any equal pressure.

TABLE V.

Compound.	Comparative Values of		
	T.	$V_T$ .	$\frac{V_T}{T}$ .
$C_6H_5F$ .....	1.0000	1.0000	1.0000
$C_6H_5Cl$ .....	1.1308	1.1244	0.9943
$C_6H_5Br$ .....	1.1974	1.1800	0.9854
$C_6H_5I$ .....	1.2884	1.2772	0.9913

The figures in the last column prove (1) that the approximate equality of the ratio  $\frac{V_T}{T}$  exhibited by these four compounds at a pressure of 760 millim. holds good at other pressures ; (2) that the deviations from perfect equality, such as they are, characterize all pressures alike, at all events up to the limits actually reached in Young's experiments.

This being the case with one of the groups of compounds quoted in Table I., it seems only fair to conclude from the perfect analogy of the others at atmospheric pressure, that the same conclusions might be drawn in their cases also, were experimental data available. Hence, in all probability, equality of the ratio  $\frac{V_T}{T}$  in different compounds at equal pressure depends on a combination of the following :—

(1) Similarity of chemical constitution, of a kind akin to that concerned in isomorphism; (2) equality of critical pressure; and implies also (3) constancy of the ratios  $V : V'$  and  $T : T'$  at all equal pressures. It is possible that the slight deviations from perfect equality of  $\frac{V_T}{T}$ , to which attention has been directed, are connected with slight differences of critical pressure.

Young's work further enables us to study the manner in which  $\frac{V_T}{T}$  for one and the same liquid varies with variation of pressure. Very interesting curves are obtained by plotting the ratios  $\frac{V_T}{T}$  as ordinates and  $P$ ,  $P_T$ , or  $T$  as abscissæ. In the case of fluorbenzene the first curve shows a descent which is very rapid at first, then gradually slows off till a minimum is reached at about 7000 millim., then a slow but steadily increasing rise, which becomes rapid as the critical point is approached. The actual extreme values are ·3559 at 5 millim., ·2631 at 7000 millim. (minimum), and ·4164 at 33912 millim. (critical). The value at 760 millim., already given, is ·2837. The curves for the chloride, bromide, and iodide are perfectly similar as far as they go. Those plotted with  $V_T$  measured as abscissæ are nearly parabolic in form.

Obviously it would be of considerable interest if we were enabled to compare the curves of the halogen compounds of different radicals with one another and these with the curves for their compounds with oxygen, nitrogen, and elements of other natural groups. We should, then, in all probability attain to a fuller understanding of the relations between boiling-point, molecular volume, and chemical character.

Melbourne, 12th August, 1890.

*Postscript.*—It has been suggested to me by Mr. E. F. J. Love, Lecturer in Natural Philosophy in this University, that the relation discussed in the foregoing Paper, when taken



together with certain of Ramsay and Young's results (Phil. Mag. 1885 and 1886), leads to the following conclusion:—

*If different compounds of the same group be compared when boiling at equal pressure, the latent heats of vaporization are inversely proportional to the molecular weights and directly proportional to the absolute temperatures of ebullition: or*

$\frac{M \cdot L}{T} = \text{a constant for each group, pressure being equal.}$

This may be demonstrated in the following manner, starting with the thermodynamic formula

$$\frac{L}{S_1 - S_2} = \frac{T}{J} \cdot \frac{dp}{dt},$$

where  $S_1$  and  $S_2$  represent the specific volumes of the same substance at the boiling-point in the gaseous and liquid conditions respectively.

Ramsay and Young have shown that the value of  $T \cdot \frac{dp}{dt}$  is a constant for closely allied substances such as the halides of ethyl and phenyl, *i. e.* for different members of the same group; whence also (if we distinguish quantities belonging to two such compounds by dashes)

$$\frac{L}{S_1 - S_2} = \frac{L'}{S'_1 - S'_2}.$$

Substituting molecular weights for unit weights, we get

$$\frac{M \cdot L}{v_T - V_T} = \frac{M' \cdot L'}{v'_{T'} - V'_{T'}}, \quad \dots \dots \dots (1)$$

where  $v_T$  and  $V_T$  are used as in the foregoing paper. But it has there been shown that

$$\frac{v_T}{T} = \frac{v'_{T'}}{T'} \text{ and } \frac{V_T}{T} = \frac{V'_{T'}}{T'}.$$

Hence

$$\frac{v_T - V_T}{T} = \frac{v'_{T'} - V'_{T'}}{T'}. \quad \dots \dots \dots (2)$$

Combining (1) and (2), we get

$$\frac{M \cdot L}{T} = \frac{M' \cdot L'}{T'}. \quad \dots \dots \dots (3)$$

The molecular latent heats and the molecular volumes, both liquid and gaseous, therefore follow the same law as regards their relation to temperature.

There are very few actual determinations of latent heat by which this conclusion can be tested. In the cases, however, of methyl chloride and iodide and ethyl chloride and iodide, the values found at atmospheric boiling-points agree fairly well with the theory. But it should be remembered that such determinations are not to be relied on as more than near approximations to the truth (compare Ramsay and Young, *Phil Mag.* Dec. 1885).

Formula.	L.*	M.	T.	$\frac{M \cdot L}{T}$
CH <sub>3</sub> Cl .....	96·9	50·34	249·3	19·57
CH <sub>3</sub> I.....	46·1	141·50	315·8	20·66
C <sub>2</sub> H <sub>5</sub> Cl .....	100·1	64·31	285·5	22·55
C <sub>2</sub> H <sub>5</sub> I .....	46·9	155·47	344·3	21·18

Melbourne, 18th August, 1890.

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XLVI. *On the Relation between the Boiling-points, Molecular Volumes, and Chemical Characters of Liquids.* By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol †.

THE appearance of the preceding very interesting paper under the above title by Professor Masson has induced me to bring forward the following considerations at a somewhat earlier period and in a probably less complete state than I had originally intended.

In his dissertation 'On the Continuity of the Gaseous and Liquid States' Van der Waals has proposed the following generalizations as applicable to all substances:—"If two substances be compared at absolute temperatures which are proportional to their absolute critical temperatures, their vapour-pressures will be proportional to the critical pressures, and their specific volumes (both of liquid and saturated vapour) will be proportional to their critical volumes."

Assuming the truth of these relations, we may calculate the

\* The figures in this column are taken from Ramsay and Young's paper (*loc. cit.*), where the authorities are not given; except that for methyl chloride, which is quoted from J. Chappuis (*Chem. Soc. Abstr.*, 1887, p. 627).

† Communicated by the Author.

ratio of the specific or molecular volumes of two substances at "corresponding" pressures if we know their critical temperatures and pressures and their boiling-points under low pressures, provided, as is usually the case, the saturated vapours at these low pressures behave as normal gases.

For the molecular volume of the saturated vapour of any substance under such conditions will be given by the equation

$$v = 22.32 \times \frac{T}{273} \times \frac{760}{p},$$

where  $T$  is the boiling-point on the absolute scale of temperature, and  $p$  is the pressure. So also the molecular volume of the saturated vapour of any other substance at the "corresponding" pressure  $p' =$

$$v' = 22.32 \times \frac{T'}{273} \times \frac{760}{p'}.$$

The ratio of the molecular volumes of the saturated vapours will therefore be

$$\frac{v}{v'} = \frac{T}{T'} \times \frac{p'}{p}.$$

The ratio of the molecular critical volumes will be the same; and as the critical volumes apply equally to the gaseous and liquid states, the ratio of the molecular volumes of the liquids at corresponding pressures will also be given by the equation

$$\frac{V}{V'} = \frac{T}{T'} \times \frac{p'}{p}.$$

In the special case of the haloid derivatives of benzene, the critical pressures of which are equal, the equation becomes

$$\frac{V}{V'} = \frac{T}{T'};$$

and this relation Prof. Masson has shown to apply not only to this group of compounds, but also to other groups of haloid compounds of hydrocarbon radicals.

So far the experimental results extend only to the liquid state, but I hope to be able to determine the densities of the saturated vapours of the benzene derivatives within sufficiently wide limits to test the accuracy of the relation for the gaseous state also.

When the critical pressures of two substances are not the same it would seem improbable that the relation  $\frac{v}{v'} = \frac{V}{V'} = \frac{T}{T'} \times \frac{p'}{p}$  would really hold good; for it is quite certain that for such

bodies, when the absolute temperatures are proportional to the absolute critical temperatures, the vapour-pressures are (at any rate in the cases examined) *not* proportional to the critical pressures. In the case of benzene and fluorbenzene, for instance, between about 0° C. and the critical points the ratios of the vapour-pressures at “corresponding” temperatures, instead of being constant, vary from 1·340 to 1·073.

I have, however, shown (Trans. Chem. Soc. 1889, lv. p. 514) that at “corresponding” pressures the ratio of the molecular volumes of benzene and fluorbenzene remain approximately constant within wide limits; and this is also the case, though the deviations are greater, with the liquids (methyl, ethyl, and propyl alcohol and ethyl ether) examined by Professor Ramsay and myself, when compared either with fluorbenzene or among themselves. It is therefore possible to obtain an approximate value for the ratio of the molecular volumes of such substances at “corresponding” pressures and to compare these values with those given by the equation

$$\frac{V}{V'} = \frac{T}{T'} \times \frac{p'}{p}.$$

The experimental data from which the ratios have been calculated are given below:—

Substance.	Formula.	Absolute Critical Temperature.	Critical Pressure, in millim.
Fluorbenzene .....	C <sub>6</sub> H <sub>5</sub> F	559·55	33190
Benzene.....	C <sub>6</sub> H <sub>6</sub>	561·5	36390
Methyl alcohol.....	CH <sub>3</sub> OH	513·0	59760
Ethyl alcohol .....	C <sub>2</sub> H <sub>5</sub> OH	516·1	47850
Propyl alcohol .....	C <sub>3</sub> H <sub>7</sub> OH	536·7	38120
Ethyl ether .....	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	466·8	27060
Carbon tetrachloride ...	CCl <sub>4</sub>	556·15	34180
Tin tetrachloride .....	SnCl <sub>4</sub>	593·0	28230

In the following Table the values of  $\frac{V}{V'}$ , calculated from the above data, are compared with those obtained from the experimental results at corresponding pressures. The percentage-differences between the values obtained by the two methods are also given, and the Table is arranged in the order of these differences.



Substances compared.	$\frac{T}{T'} \times \frac{p'}{p}$ .	Approximate ratio of molecular volumes at "corresponding" pressures.	Percentage-difference.
$C_3H_7OH/C_2H_5OH$ ...	1·305	1·30	0·4
$(C_2H_5)_2O/C_6H_5F$ .....	1·045	1·04	0·5
$C_6H_6/C_6H_5F$ .....	·935	·945	1·1
$CCl_4/SnCl_4$ .....	·775	·795*	2·8
$C_2H_5OH/C_6H_5F$ .....	·640	·61	4·7
$C_3H_7OH/C_6H_5F$ .....	·853	·80	6·2
$SnCl_4/C_6H_5F$ .....	1·246	1·34*	7·5
$CCl_4/C_6H_5F$ .....	·965	1·07*	10·9
$C_2H_5OH/CH_3OH$ ...	1·256	1·44	14·7
$C_3H_7OH/CH_3OH$ ...	1·640	1·89	15·2
$CH_3OH/C_6H_5F$ .....	·509	·42	17·5

The number of comparisons is hardly great enough to allow of very certain generalizations; but it may be pointed out that in three out of the four cases where there is the closest concordance between the values calculated by the two methods, we have to do with bodies which, as far as constitution is concerned, are closely related. Of the seven remaining comparisons only two are between compounds which are so related, and in both cases methyl alcohol is one of the compounds. The want of concordance exhibited by methyl alcohol when compared with the other alcohols of the same series, both in this case and in many of its properties, may perhaps be due to the preponderating influence of the hydroxyl as against the alkyl group.

The following conclusions may perhaps be tentatively drawn from the foregoing data:—

1. When the critical pressures of two closely related substances are equal, the ratio of their molecular volumes in the liquid state (and probably also in that of saturated vapour) at their boiling-points under any equal pressures is equal to the ratio of their boiling-points measured on the absolute scale of temperature, and therefore also to the ratio of their absolute critical temperatures.

2. When the critical pressures of two nearly related substances are unequal, their molecular volumes at their boiling-points under "corresponding" pressures are (approximately)

\* Calculated from single readings of volume, taking that of  $SnCl_4$  at the boiling-point under 760 millim. pressure and the others at "corresponding" pressures.



Make O the zero point. The lengths of the divisions are to be such that C'O shall contain  $1000 \div f$  of them.

[In the actual apparatus  $f$  was  $5\frac{1}{2}$  in. and C'O contained 190 divisions, shown in the figure as 19.]

L is a concave lens of focal length  $f'$  which may be inserted at F. This has the effect of increasing the length of the scale by moving its zero to a greater distance.

G is an inclined plane on which is placed the object to be viewed. The object which I usually prefer is a series of equal black circular spots with narrow white intervals. The middle interval has a mark by which it may be recognized, and it is helpful that every 10 divisions of the scale should correspond to exactly one spot or exactly two. Being looked at very obliquely, the spots appear as very flat ellipses with minor axes about a fifth of their major axes, separated at the extremities of their minor axes by very narrow white spaces.

3. Let P be a point in the object at distance  $u$  from the lens, Q the image of P, and let  $FQ = v$ . Then

$$\frac{1}{v-f} = \frac{1}{u} - \frac{1}{f}; \text{ whence } \frac{1}{v} = \frac{f-u}{f^2}.$$

Consequently the divergence of the refracted pencil as it passes F and enters the eye is indicated by the number on the scale under the luminous point. For, an inch being  $\frac{1000}{f^2}$  divisions,  $(f-u)$  inches is  $\frac{1000}{f^2} (f-u)$  or  $\frac{1000}{v}$  divisions.

Each division represents an amount of divergence equal to that of a pencil whose vertex is 1000 inches distant.

Applying this to the object on the inclined plane G when its position is that shown in the figure, we see that its points are viewed by means of *converging* pencils varying in convergence from 0 to 180 units of the scale.

4. The apparent magnitude of the object is unaltered by the motion of the table, the eye being supposed at F. For the rays which go through that point from two given points of the object are before incidence parallel to the axis, and strike the lens at points which are not changed by the motion of the table. Hence we see that the arrangement enables us to offer to the eye an object which gives on the retina an image of constant size and shape, but which makes, in its different parts and in its movement, a continuously changing demand on the power of accommodation.

5. The range of convergence which can be offered to the eye is from O to B, and that of divergence from O to C'. It

is often necessary to increase the latter. This is done by inserting at F the lens L. If  $f'$  be the focal length of this lens,

$$\frac{1}{v} = \frac{f-u}{f^2} + \frac{1}{f'} = \frac{f-u + \frac{f^2}{f'}}{f^2}.$$

Thus we see that the insertion of the lens has no other effect than to remove the zero of divergence outwards by a distance  $\frac{f^2}{f'}$ , which in units of the scale is  $\frac{1000}{f'}^*$ .

[In the actual case this was 240 degrees of the scale, so that when using the lens we must increase by 240 every number read from the scale, but, in doing so, we must recollect that the numbers from O to B are negative.]

It may be noted here that the power of any lens is the displacement which its introduction at F causes on the scale.

6. Suppose that we wish to ascertain the *punctum remotum*, that is the least divergence suitable for the eye (in hypermetropia, the greatest convergence). Begin with the table at its farthest, and move it up slowly. Clearness at last appears at the lower part of the object, that is, the narrow white interval between two consecutive ellipses ceases to encroach on them. This clearness gradually includes more and more of the object, and the observer meanwhile has his attention occupied in noticing the progress of its upper limit. Let him arrest the motion when the upper limit of clearness arrives at the middle. The scale now shows the divergence corresponding to the *punctum remotum*.

If the nearest point, or greatest useful divergence, has to be observed, we may proceed in the same way but beginning at the nearer end. For most eyes it will be necessary to insert the lens L, and for some even a lens of shorter focal length.

The difference between the two numbers read from the scale gives the *accommodating power*.

7. The object observed so far has been virtually a series of horizontal lines, so that what has been determined as the least divergence is the least divergence suitable for a vertical section of the eye. Now let the inclined plane be laid on its side, the major axes of the ellipses will become vertical, and the white intervals may be called vertical lines.

On determining afresh the least divergence it will often be

\* Each reading  $h$  of the scale should receive the small correction  $-\partial h^2 \div 1000$ ,  $\partial$  being distance of eye from F, in inches.



found to differ from that previously obtained, being usually less. The difference between the two is the amount of *astigmatism* of the eye.

In what precedes I have supposed the principal meridians of the eye to be horizontal and vertical. The modifications required by their deviation from these directions are sufficiently obvious. The amount of the deviation may be found by means of a series of concentric circles with intervals of about the same breadth, say  $\cdot 025$  inch, viewed directly. When this object is placed on the table and moved up slowly, a band of clearness at last appears along a nearly horizontal diameter. This diameter shows one meridian, the other is shown by the tangent at the middle of any of the clear segments, and these are the directions in which the lines above called horizontal and vertical are supposed to lie.

8. As an example illustrating the use of the apparatus, I will take an actual case, remarking that each result given is the mean of several observations.

L, R,  $v$ ,  $h$ , stand for left eye, right eye, vertical lines, horizontal lines.

Referring to the position, in the scale, of the *punctum remotum*, I found  $Lv = -200$ ,  $Lh = -115$ ,  $Rv = -216$ ,  $Rh = -144$ . These observations show that the eyes are both greatly affected by hypermetropia and astigmatism, for in a perfect eye all these numbers are equal and do not differ much from  $0^*$ .

$Lh - Lv = 85$  is the astigmatism of the left eye; and  $Rh - Rv = 72$ , that of the right.

9. To remedy these defects I had glasses ground, of the same form for both eyes. They were intended to have a spherical convex front surface, of power  $\dagger 212$ , and a concave cylindrical back surface with axis horizontal, of power 62.

The eyes while using these glasses were tested, and gave the following results:—

$$Lv = 14, Lh = 37, Rv = 15, Rh = 14.$$

These show that the glasses very nearly destroy the astigmatism of the right eye and leave 23 of astigmatism in the left, which was in several respects an inferior instrument. Also by comparing these numbers with those given above we may deduce the forms of the lenses. Thus:— $Lv$  is increased

\* The meridians of greatest and least curvature were not exactly horizontal and vertical, but the difference was small enough to be neglected.

† By this I mean the power of a lens having the surface named on one side and a plane surface on the other.

from  $-200$  to  $+14$ , that is by  $214$ ; this then is the power of the left lens for viewing vertical lines, and is consequently the power of the spherical surface.

$Lh$  is increased by  $152$ ; this is the difference between the powers of the two surfaces, indicating for the cylindrical surface a power of  $62$ . Similarly it will be found that the power of the spherical surface of the right lens indicated is  $231$ , and that of the cylindrical surface  $73$ .

10. If to the numbers  $Lv=14$ ,  $Lh=37$ ,  $Rv=15$ ,  $Rh=14$ , the accommodating power, which time has reduced to about  $40$ , be added, and account is also taken of the influence of convergence of the optic axes\*, we see that the patient has acquired by means of the spectacles a very satisfactory power of vision within the range most useful for work. For out-of-door use another pair was provided, having  $25$  less power on the spherical side, so that distant objects might be clearly seen.

Hampstead, August 26th, 1890.

#### XLVIII. Notes on Hydrogen Gas.

By J. ALFRED WANKLYN and W. J. COOPER†.

THE record of some experiments in the laboratory will not be quite without interest to chemists. The wonderful passivity of hydrogen gas is illustrated by the following experiments:—

I. A strong solution of perchloride of iron, made by dissolving the solid chloride in water, was placed in a graduated tube which was inverted in the usual manner so as to form a receptacle for gas.  $26$  cubic centim. of hydrogen gas was then introduced into the tube and allowed to remain in contact with the iron-solution for forty hours. At the expiration of that time the volume of the gas was found to be unaltered. The gas was then burnt.

II. A solution of platinic chloride containing  $5$  per cent. of platinic chloride was allowed to act upon hydrogen gas in a Hempel absorption-pipette.  $95$  cubic centim. of hydrogen was taken for experiment. After twenty-eight hours' exposure the volume of the gas was found unchanged.

III. Ferricyanide of potassium, the solution containing  $25$  per cent. of the dry salt, was employed in the Hempel absorption-pipette. No absorption of hydrogen took place.

\* Donders, on Accommodation and Refraction, p. 111.

† Communicated by the Authors.

A repetition of the experiment in which potash was added to the solution of the ferricyanide, and with exposure to bright sunlight, showed no absorption of hydrogen during a period of eight days.

IV. Nitric acid (spec. grav. 1.42) was tried. An exposure of hydrogen for sixteen hours to the action of the acid produced no change in the volume of the gas, and on examining the gas it was found to be devoid of nitric oxide.

V. A mixture of oil of vitriol and strong nitric acid was altogether without action on the gas.

VI. Aqua regia was also tried and found to be without action on hydrogen. In this case the volume of gas was gradually increased, viz. from 67.5 up to 110 cubic centim. The increase was due to evolution of chlorine. On washing with water the chlorine was dissolved, and there remained 66.5 cubic centim. of hydrogen which burnt in a satisfactory manner. This experiment was made in diffused daylight; in bright sunlight reaction between the chlorine and the hydrogen must take place.

VII. Even solution of chromic acid was found to be without action on hydrogen at ordinary temperatures. The duration of the exposure was twenty-four hours, and the readings were:—

Volume of hydrogen before	. .	64.8 cubic centim.		
"                  "	after	. .	65.0	" "

The activity of hydrogen is illustrated as follows:—

When solution of permanganate of potash—whether it be strongly alkaline, or neutral, or strongly acid—is brought into an atmosphere of hydrogen, it is attacked by the hydrogen even at ordinary temperatures. The rate of the action depends upon a variety of circumstances which we are carefully studying.

In one experiment the Hempel gas-pipette was charged with a solution containing about 30 per cent. of caustic potash and about 2 per cent. of permanganate of potash. The readings were:—

Vol. of gas taken	. . .	65 cub. cent. on June 24, 1890.		
"          after absorption	46	" "	28,	"
"          "	35.8	" "	July 2,	"
"          "	33.2	" "	3,	"
"          "	26.8	" "	6,	"
"          "	21.4	" "	10,	"
"          "	19.5	" "	12,	"

The gas employed in this experiment was a mixture of hydrogen and air, consisting of about 3 volumes of hydrogen and 1 volume of air.

It will be noted that at the beginning of the absorption the rate is about 5 cubic centim. in twenty-four hours; then 2·5 cubic centim., and lastly 1 cubic centim. The retardation evidently depends upon the diminishing proportion of hydrogen in the gaseous mixture.

The next experiment was made with a saturated solution of neutral permanganate (containing 6·5 grams permanganate of potash in 100 cubic centim. of solution):—

Volume of gas taken . . . .	79·4 cubic centim.
After absorption for 26 hours .	39·0   "   "
"   "   further 14   "   .	27·4   "   "
"   "   "   12   "   .	22·8   "   "
"   "   "   13   "   .	20·8   "   "
"   "   "   24   "   .	19·8   "   "

The gas consisted of:—

	Vols.
Hydrogen . . . .	75
Air . . . . .	25
	<hr/>
	100

In this instance the surface of the permanganate solution was enlarged by the employment of glass beads about 4 millimetres in diameter.

In another experiment the details were:—

Volume of gas taken . . . .	29·0 cubic centim.
After absorption for 1 hour .	25·8   "   "
"   further 16 hours .	10·4   "   "
"   "   9   "   .	6·2   "   "
"   "   15   "   .	5·2   "   "
"   "   21   "   .	5·0   "   "

The solution of permanganate was the same as before, and the glass beads were used.



XLIX. *Notices respecting New Books.*

*Elliptic Functions, an Elementary Text-book for Students of Mathematics.* By A. L. BAKER, C.E., Ph.D. (New York: Wiley & Sons, 1890. Pp. iv+118.)

THE Editor's object is to put within reach of the English (? English-speaking) student "a tolerably complete outline of the subject [of Elliptic Functions], clothed in simple mathematical language and methods," and so to "smooth the road" to this important branch of Mathematics. Abundant material is to be found in the works of Abel, Euler, Jacobi, and Legendre, not to mention the writings of mathematicians of more recent date. The earlier matter is not easily accessible to the ordinary student, and Mr. Baker deserves our thanks for his labour in the volume before us. He has not aimed at originality, which is not to be looked for in the description of work he has undertaken, but he has tried to simplify the methods in use, so as to make them intelligible to the average student. He adopts the Gudermannian notation as being simpler than the Jacobian, and employs zero subscripts "to indicate decreasing series in the Landen transformation, and of numerical subscripts to indicate increasing series." He gives a list of works consulted, and states that he has refrained from any reference to the Gudermann or Weierstrass functions "as not within the scope of this work." There are seventeen chapters in all, with an introductory chapter which is a condensation of an article on the subject by the late Prof. Moseley. There are several typographical errors, of an elementary character, and now and again the compiler uses terms which are explained subsequently. The last chapter contains applications to the Lemniscate, the ellipse, and hyperbola, and besides there are exercises scattered throughout the rest of the book.

*An Introduction to the Logic of Algebra, with Illustrative Exercises.* By E. W. DAVIS, Ph.D. (New York: Wiley & Sons, 1890. Pp. xv+119.)

WE have read this *Introduction*, which is a good piece of solid work, with much interest. The author states that "the book is precisely described by the title, and is mainly the outgrowth of a conviction that the *logic* of Algebra is a very much neglected study." Some idea of the writer's mode of treatment will be got from the following statement of the various sources drawn upon in its compilation. The more important works consulted are:—*Argand*, Sur le manière de représenter quantités imaginaires; *Clifford*, Common Sense of the Exact Sciences; *De Morgan*, Trigonometry and Double Algebra, and Introduction to his Calculus; *Dirichlet*, Zahlen-theorie; and *Tannery*, Théorie des fonctions

d'une Variable seule. There is a good analysis of the contents, in which the subject-matter of each article is carefully stated.

An extract from the last article, in which Mr. Davis rapidly glances over the route pursued, will most concisely represent what he has attempted.

"The commutative, associative, distributive, and index laws that held with the first simplest numbers have been made to hold throughout. Finally, by our extensions, we have made the three primary operations and their four inverses always possible, *i. e.* always resulting in a number belonging to our scheme. In the reasoning first employed for the handling of incommensurables, and further developed in the treating of growths and rates, we have the germ of . . . the Infinitesimal Calculus. The Graphic representation leads to the Analytical Geometry of Des Cartes. The theory of sines and cosines with its geometric applications is Trigonometry, and leads, by the introduction of new numbers and conceptions, to the Function Theory. The theory of double numbers is simple and restricted, and but a faint suggestion of what is to be found in the beautiful developments proposed by Hamilton and Grassmann, the Peirces, and Sylvester. These are a few only of the lines of thought open to the student. Yet, in whatsoever direction investigation may carry him, he will find his work essentially the same in character. Definitions and conventions and their logical consequences and relations make up the whole of it. These relations form the universe wherein the Mathematician lives; a universe, to be sure, of his own construction, a product of his brain, but none the less real and substantial to him. Here he observes and compares, and experiments; here he reasons out connections, discovers causes, and foretells results."

It is only in these closing words that Mr. Davis leaves the beaten track, his feelings at having finished his task, we suppose, getting the upper hand of his usual sobriety. The rest of his work is characterized by great clearness in exposition and by fertility of illustration. His Argand diagrams make many points clear. The printing of such a work as this makes great demands upon the author and the printers, yet we have detected but few errors. On p. 7, line 8 up, *b* has been omitted: p. 10, line 7 up, for *first a* read *b*: p. 12, line 13 up, for *d* read *b*: p. 32, line 2 up, last statement appears to be wrong: p. 42, line 6, ? last statement: p. 45, line 6 up, " $+10$ ," should be " $-10$ ": p. 67, line 14 up, same error: p. 73, line 6, for " $-2$ " read " $=2$ ": p. 74, line 5, dele last 2. We have noticed some other trivial errors which are easily corrected.

The student may consult, when using this book, Prof. Chrystal's 'Text-book of Algebra' for further illustrations on the subject of Graphs.

*Theory of Differential Equations.*—Part I. *Exact Equations and Pfaff's Problem.* By A. R. FORSTH, *Sc.D., F.R.S.* (Cambridge: University Press, 1890. Pp. xiv + 340.)

THE work before us is the first instalment in fulfilment of a promise made by the author in his 'Treatise on Differential Equations' (1885), and is written after the same thorough fashion as the earlier volume. The author's aim is "to include every substantial contribution to the development of the particular subject herein dealt with; and the historical form, into which the treatment has been cast, has facilitated the indication of the continuous course of the development." He has drawn upon all available sources, duly acknowledging his indebtedness to the several previous explorers in this field, and has further contributed investigations of his own. A few illustrative examples have been made up or culled from the memoirs above referred to.

The first part consists of 13 chapters. The first two chapters discuss the single exact equation and a system of exact equations. Under the former head we have a full account of the methods of solution given by Euler, Bertrand, Collet, Natani, and Du Bois-Reymond; and under the latter head we have a generalization of the above method given by Euler, with an examination of Natani's method and of a theorem by Mayer in development of this method. Frobenius's conditions for uncanonical form are also discussed. The next 4 chapters are devoted to a historical summary of methods of treating Pfaff's problem, Pfaff's reduction as completed by Gauss and Jacobi, Grassmann's method, and Natani's method. Chapter vii. contains the application of previous results to partial differential equations of the first order. The next four chapters are occupied, in order, with Clebsch's method, tangential transformations, Lie's method, and Frobenius's method. Chapter xii. gives an abstract of Darboux's method. The closing chapter discusses Systems of Pfaffians, and is prefaced with a list of the memoirs which form the principal sources of our information on this subject. The whole treatise is a splendid piece of work, but, from the nature of the subject, is "caviare to the general." A full index makes consultation easy. We have detected only two trivial typographical errors (on pp. 92 and 99).

### *L. Intelligence and Miscellaneous Articles.*

ACTINOELECTRICAL INVESTIGATIONS. BY A. STOLTETOW.

THE author sums up as follows the results of his researches, which have extended over almost two years, and some of which have already appeared.

1. When the rays of the voltaic arc fall on a plate charged with negative electricity it is discharged; this discharge is accompanied by a marked fall of potential or not according as the discharge occurs more or less rapidly.



2. The action of the rays is strictly unipolar ; positive electricity is not carried away.

3. The apparent charge of neutral bodies by the rays may probably be ascribed to the same cause.

4. By far the strongest action is possessed by rays of the highest refrangibility ( $\lambda < 295 \times 10^{-6}$  millim.), which are wanting in the sun's spectrum.

5. It is necessary that the rays be absorbed by the surface of the body ; the discharge is accordingly greater, the greater the absorption.

6. All metals are sensitive to this action ; some colouring-matters (aniline colours) are the most sensitive. Water, which is transparent for the active rays, was found to be insensitive.

7. There is no appreciable interval of time between the moment of illumination and the corresponding discharge.

8. Other things being equal, the discharge is proportional to the energy of the active rays, and of the illuminated surface.

9. The action is perceptible even with very small densities ; its magnitude depends on the density, and at first increases more rapidly than the latter and afterwards more slowly.

10. Two plates between which a difference of potential due to voltaic contact exists, represent a kind of voltaic element as long as the electrically negative plate is illuminated by active rays.

11. We are entitled to consider this actinoelectrical discharge as an electrical current ; the air (either by itself or by the action of the particles mixed with it) plays the part of a bad conductor ; the apparent resistance does not follow Ohm's law.

12. The actinoelectric action is increased by the temperature.

The author states in conclusion that the phenomena described are only to be observed in gases. Experiments with solid and with liquid insulators always gave a negative result. It follows from this that actinoelectrical currents represent a kind of convection current. (Compare the results of Bichat, Righi, Blondlot, Lenard, and Wolff.) If it be assumed that at the boundary of metal and air there is a difference of potential due to contact, then from the discharge of the negatively electrical body, we may in some way explain the charge of the feebly positively charged or neutral body. Whether in this there is an electrolysis of gas (Arrhenius) or not must be left an open question.

Convection explains only the further progress of the phenomenon ; the first step of the electromotive excitation remains an enigma.

The hypothesis of E. Wiedemann appears to the author very rich in consequences ; but the inactivity of ordinary luminous rays (that is, visible), as well as the decidedly unipolar character of the action, is unintelligible. The analogy between the phenomena described and the well-known discharges in Geissler's and Crookes's tubes is striking.

As regards the observations of Borgmann (see below), the author  
*Phil. Mag.* S. 5. Vol. 30. No. 186. Nov. 1890. 2 H



observes that he has repeated the experiments with success; they may be explained by assuming that the telephone which is sensitive for a circuit is not so when the same quantity of electricity acts as a feebly intermittent current. By experiments with intermittent illumination and a rotating commutator it is proved that any possible retardation of the action could not amount to  $\frac{1}{1000}$  of a second.—*Journal of the Russian Physicochemical Society*, vol. xxi. p. 159, 1889; *Beiblätter der Physik*, vol. xiv. p. 322.

ON ACTINOELECTRIC PHENOMENA. BY J. BORGMANN.

The net condenser of Stoltetow is illuminated by a rotating disk with sectors cut out; the galvanometer is replaced by the telephone. On closing the circuit a distinct shock is heard in the telephone, but this is not the case with intermittent illumination. The author concludes from this that the actinoelectrical discharge is not instantaneous.—*Ibid.*

STATIONARY LUMINOUS VIBRATIONS. BY O. WIENER.

The author has published in Wiedemann's *Annalen*, vol. xl. p. 203, an important Memoir, in which by photographic methods he has demonstrated the existence of stationary luminous vibrations. The memoir is accompanied by phototypic illustrations of the results of his experiments. His conclusions are given by himself as follows:—

By the foregoing research the experimental proof has been furnished for the existence of stationary waves of light. A sensitive, perfectly transparent collodion lamina, the thickness of which was small in comparison with the wave-length of light ( $\frac{1}{30}$  about) was placed between two glass plates at a small distance from a metal mirror and making a small angle with this. After protracted exposure to the spectral rays the lamina was developed, and bands were formed which it was proved could only be due to the action of stationary waves.

A more accurate investigation of stationary waves showed that with perpendicular reflexion at the optically denser medium, the nodal points of the chemical luminous action are at distances equal to the multiple of half a wave-length from the reflecting surface; the ventral segments are between these, that is at distances equal to the odd multiples of a quarter wave-length.

Experiments in which two rectilinearly polarized waves of light were used, which crossed each other at right angles, showed that a chemical action on the sensitive plate due to an inference of the two rays occurred when their planes of polarization coincided, but failed when they were at right angles to each other. It was to be concluded from this, that the chemically active vibrations of a rectilinearly polarized wave of light are at right angles to their plane of polarization.

The results of the experiments in their bearing on the theory of light were discussed. It may merely be mentioned that the most obvious conception of the processes brought to light by the experiments is obtained by assuming that vibrations of the luminiferous medium produce vibrations of the solid particles in the same direction, which effect a photochemical change of the sensitive lamina. On the basis of this assumption the experiments lead to a decision between the mechanical theories of light, and that in favour of Fresnel's.

Expressed in the language of the electromagnetic theory of light the experiments teach that the chemical action of a rectilinearly polarized wave of light is connected with the presence of electrical and not of magnetic vibrations.

As regards the method of investigation here employed, the thin sensitive lamina represents in a certain sense a transparent eye which can simultaneously take up luminous impressions from opposite directions. While in investigating the motion of light we have hitherto been restricted to one locality in drawing a conclusion as to the motion transmitted to the eye; the possibility is now open of investigating the luminous motion in the place itself as regards its amplitude, phase, and the direction of its vibrations.—Wiedemann's *Annalen*, vol. xl. p. 203, 1890.

OBSERVATIONS ON A PAPER BY MR. FLUX "ON THE SHAPE OF  
NEWTON'S RINGS." BY A. WANGERIN.

In the March number of the Philosophical Magazine a paper is published by Mr. Flux which discusses the theory of Newton's rings, and leads to the same results as those which I developed in 1880 in connexion with the observations of Prof. Sohncke\*, and which I had published in abstract in the *Monatsberichte* of the Berlin Academy, November 4, 1880, and more fully in the *Annalen*, vol. xii. p. 201 (1881). Mr. Flux, it is true, mentions my priority in two places; yet from the words at the conclusion he seems to raise the claim of being by his theory the first to arrive at a satisfactory conclusion. In opposition to this view I find myself compelled to prove that everything which Mr. Flux adduces in reference to Newton's rings in reflected light, is completely covered by the contents of my research, with the exception of one unimportant result. In the first place, Mr. Flux has not added a single new result to those which I have already found. But the agreement between our papers is not restricted to the results, but extends, not only to the details of the calculation, but also to the greater part of the nomenclature, and even to the figures. The proof of

\* Before I began my theoretical investigations Prof. Sohncke had already established experimentally several of the results given in our joint paper, and he has subsequently tested other deductions from the theory.

Mr. Flux, apart from a different arrangement of the matter, contains nothing which was not taken literally, or in the ordinary sense, from the paper already cited or from another on the same subject\*. In one point only does the statement of Mr. Flux differ from mine, without, however, leading to any new results.

In order to establish the statement I have just made I may be allowed to sketch the separate sections of Mr. Flux's paper, and at the same time refer to the corresponding ones of my own. [For these the reader is referred to the original paper in Wiedemann's *Annalen*, No. 8, 1890, p. 738.]

The author gives the detailed comparison and thus concludes:—In what I have said, where I have gone into all the apparent or actual deviations between Mr. Flux's research and my own, the contention made at the beginning of this article will appear abundantly justified. Apart from the alteration of a proof, the research of Mr. Flux, both as regards results and their establishment, is nothing further than a repetition of what I had already carried out in my two researches or what Herr Gumlich had done in his paper which is connected therewith.

In conclusion, it may be mentioned that the confirmation which my theoretical investigations had met with in the careful observations of Prof. Sohncke is mentioned by Mr. Flux, but dismissed in less than two lines.—*Abstract of communication from the Author.*

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FLUORESCENT VAPOURS. BY F. WIEDEMANN.

Professors Ramsay and Young† had described an experiment according to which solutions of eosine fluoresce above the critical temperature, without, however, as they themselves state, considering it to be strictly proved. Independently of them I made at the same time an analogous experiment which, however, gives perfectly certain results, and which I here communicate from the Proceedings of the Societas Physico-medica at Erlangen for the year 1888.

Experiments with liquids which were sealed in capillary tubes gave a very distinct fluorescence above the critical temperature for solutions of eosine and Magdala red in alcohol. That it is not diffused light with which we have to deal is shown if we use as source of light that which has passed through ammoniacal copper sulphate, which contains no yellow or red rays. The fluorescent light contains these rays; this is distinctly seen when a lens is used, the cone of light is distinctly seen continued in the vapour, and is especially beautiful with Magdala red. Experiments with saffranine gave no results, as it is decomposed. With Magdala red there is also a feeble decrease in coloration after heating.—Wiedemann's *Annalen*, No. 10, 1890.

\* A. Wangerin, Wied. *Ann.* xx. pp. 177 *et seqq.* (1883).

† Chemical News, vol. liii. p. 205 (1886).

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LI. *On the Dynamical Theory of Electromagnetic Action.*

By Professor ANDREW GRAY, M.A.\*

THE use of the term potential energy in electromagnetic theory is somewhat vague. For example, an expression for the potential energy of a circuit and a magnetic shell is obtained by replacing the former by its equivalent shell and proceeding as in the magnetic theory of two shells. This expression gives the potential energy of the system in terms of the configuration of the two shells, and so enables the mutual forces between the shell and the circuit, and therefore also the work done in any relative displacement, to be calculated. But, in the presentation of the theory, the assumption is then made that this work is wholly due to the expenditure of the potential energy of the substances in the battery, and nothing is credited to a change in the intrinsic or potential energy which the system possesses irrespective of the store of energy contained in the battery.

But when we consider the case of two circuits, we have always to take into account the change in intrinsic energy. For example, when two rigid circuits are allowed to approach one another infinitely slowly, the battery, as is well known, is drawn upon for twice as much energy as is required for the work done by electromagnetic forces between the two circuits, the balance going to increase the intrinsic energy of the system.

\* Communicated by the Author.



When the circuits are separated again by external forces applied to overcome the electromagnetic forces, the intrinsic energy is diminished by the same amount, and the battery is saved just as much energy in the reverse displacement as it supplied in the direct.

If the displacement do not take place infinitely slowly, we have to take into account the change in the intrinsic energy due to the change of the current in each circuit.

Thus the change in the intrinsic energy is here very important.

Again, when we consider two magnets which are displaced by their mutual forces, we find the change in the intrinsic energy, expressed in terms of the configuration of the system, the only thing to be taken into account. The mutual forces set the magnets into motion, or displace them against external resistance, and thus do work. This work can be obtained from no other source than the intrinsic or configuration energy of the system.

Thus in the case of two circuits and in that of two magnets, change of intrinsic energy plays a part; in the case of a magnet and a circuit it apparently does not; and I have never seen the reason of the apparent exception anywhere clearly stated. I think that the treatment of the intrinsic energy in the presentation of this part of the theory of electromagnetic action is a source of difficulty to many, and prevents clearness of ideas regarding what is certainly not found an easy subject when an attempt is made to master it in all its bearings.

This difficulty is met with in the perusal of the writings of even the greatest masters of the science of Electricity. Thus Clerk-Maxwell, in his 'Electricity and Magnetism' (vol. ii. p. 179), has given a treatment of the problem of two circuits, in which the change of intrinsic energy is left out of account, and a correct result is obtained only by what seems an inadmissible process\*. This passage is a pretty close rendering of one in Helmholtz's famous essay, *Die Erhaltung der Kraft*, in which the same treatment occurs. It is evident that here the change of intrinsic energy has not been present to the minds of the writers, and the result is a statement of theory which may have caused thoughtful students considerable embarrassment.

Again, I have observed what seem to me traces of this want of clearness in attempts to deduce directly from the expressions for the intrinsic energy of a magnetic field due to any distribution of currents, the energy dissipated per unit of volume of the medium, in carrying the substance round a closed cycle of magnetization. The correct way of

\* See McConnel, 'Nature,' vol. xxxv. p. 172.

regarding the intrinsic energy gives, as shown below, exactly the amount of energy, per unit of volume of the medium, spent in any change of magnetization, whether a complete cycle or not, *otherwise* than in increasing the intrinsic energy, and therefore gives at once the energy dissipated in carrying the medium through a complete cycle from one given state as to intrinsic energy back to the same state again.

Everything seems to point to the conclusion that what we are in the habit of regarding as potential energy is really kinetic energy. Every increase of scientific knowledge of matter furnishes additional proof that all its properties have their explanation in motion, and the conviction is more and more forced upon every physical student that the ordinary division of energy into potential and kinetic results from our incomplete knowledge of the material system considered. If we had perfect knowledge of the coordinates of all the parts of the system and their velocities at a given instant, and, further, knew fully the conditions to which these coordinates are subject, we should *ipso facto* be able to define the configuration at any time of any portion of the system, and to state how at that time the whole kinetic energy is divided between that portion and the rest of the system. Thus the ordinary transformation of potential into kinetic energy, and *vice versa*, is only a process of redistribution of kinetic energy between the different parts of the system.

It can in fact be proved that if a dynamical system be specified partly by a certain group of position coordinates ( $\phi$ ) and partly by velocities of other coordinates ( $\psi$ ), so that the kinetic energy is the sum of two corresponding parts  $T_\phi$ ,  $T_\psi$ , of which the first is expressed as a quadratic function of the velocities of the type  $\dot{\phi}$ , and the other as a quadratic function of the momenta corresponding to the velocities  $\dot{\psi}$ , the alterations of the position coordinates will take place precisely as if the system had a quantity of kinetic energy  $T_\phi$ , and a quantity of potential energy  $T_\psi^*$ . For there being no potential energy we can in this case write the Lagrangian equation for a  $\phi$ -coordinate as follows† :—

$$\frac{d}{dt} \frac{d(T_\phi - T_\psi)}{d\dot{\phi}} - \frac{d(T_\phi - T_\psi)}{d\phi} = 0;$$

or, since  $dT_\psi/d\dot{\phi} = 0$ ,

$$\frac{d}{dt} \frac{dT_\phi}{d\dot{\phi}} - \frac{dT_\phi}{d\phi} = - \frac{dT_\psi}{d\phi};$$

\* See J. J. Thomson's 'Applications of Dynamics to Physics and Chemistry,' p. 13.

† Routh, 'Stability of Motion,' p. 61; Thomson and Tait's 'Natural Philosophy,' vol. i. part 1, p. 323.



The quantities  $N_1, N_2$ , &c. are generalized components of electrokinetic momentum.

Using Lagrange's equations of motion and introducing Lord Rayleigh's Dissipation Function  $F$ , we have, since the coefficients in  $T$  do not contain the coordinates  $y$ , for the impressed electromotive forces in the different circuits the typical equation

$$\frac{dN_k}{dt} + \frac{dF}{dy_k} = E_k. \quad (4)$$

But

$$F = \frac{1}{2} \sum R_k \dot{y}_k^2,$$

where  $R_k$  is the resistance in the circuit indicated by the suffix  $k$ . Hence

$$\frac{dN_k}{dt} = E_k - R_k \dot{y}_k. \quad (5)$$

The electromotive forces of the type  $dN_k/dt$  are the parts of the impressed electromotive forces which are employed in working against the electromotive forces due to induction. Thus  $-dN_k/dt$  is the type of the actual electromotive force due to induction. Since this may be written in the form

$$-\frac{d}{dt} \frac{dT}{dy_k},$$

we see that the inductive electromotive force tends to diminish the electrokinetic energy.

Again, the forces which must be applied to work against the reacting internal electromagnetic forces are

$$-\frac{dT}{dx_1}, \quad -\frac{dT}{dx_2}, \quad \&c.,$$

where  $x_1, x_2$ , &c. are coordinates determining the geometrical positions of the circuits. Thus, the mutual electromagnetic forces having equal and opposite values to these, tend to *increase* the electrokinetic energy. These two results must be kept clearly in mind in what follows.

This dynamical theory, if applicable to a system of ordinary circuits, must, if Ampère's theory of magnetism be true, be also applicable to a system of magnets, or a system composed partly of ordinary circuits and partly of magnets; otherwise Ampère's theory cannot be a complete expression of the facts of the case. Maxwell has applied it only to the case of two circuits, and its applicability to the case of a circuit and a



magnetic shell has been questioned by Mr. S. H. Burbury (Proc. Camb. Phil. Soc. 1888). I shall endeavour to test its applicability by a comparison of its consequences in the three simple typical cases :—(1) two ordinary circuits, (2) an ordinary circuit and a magnetic shell, (3) two magnetic shells.

(1) In this case let  $L_1, L_2, M$  be the coefficients of self-induction, and the coefficient of mutual induction for the two circuits. Then we have

$$T = \frac{1}{2} (L_1 \dot{y}_1^2 + 2M \dot{y}_1 \dot{y}_2 + L_2 \dot{y}_2^2). \quad \dots \quad (6)$$

If  $E_1, E_2$  be the electromagnetic forces,  $R_1, R_2$  the resistances, equation (5) gives

$$\left. \begin{aligned} E_1 - \frac{d}{dt} (L_1 \dot{y}_1 + M \dot{y}_2) &= R_1 \dot{y}_1, \\ E_2 - \frac{d}{dt} (L_2 \dot{y}_2 + M \dot{y}_1) &= R_2 \dot{y}_2. \end{aligned} \right\} \quad \dots \quad (7)$$

We shall suppose that the circuits are rigid, so that  $L_1, L_2$  are invariable. Then if the circuits be subjected only to those changes which take place from their mutual action, and  $dT$  be the change in  $T$  which takes place in a small interval of time  $dt$ ,

$$dT = L_1 \dot{y}_1 d\dot{y}_1 + M(\dot{y}_2 d\dot{y}_1 + \dot{y}_1 d\dot{y}_2) + L_2 \dot{y}_2 d\dot{y}_2 + \dot{y}_1 \dot{y}_2 dM. \quad (8)$$

The work  $dW$  done by electromagnetic forces has the value  $dT/dx \cdot dx$ . Hence

$$dW = \dot{y}_1 \dot{y}_2 dM. \quad \dots \quad (9)$$

This work is spent in producing kinetic energy in the displaced conductors (or if these are not free, in moving them against external resistance, or in both ways).

The work done by the impressed electromotive forces over and above that dissipated is

$$\left( E_1 - \frac{dF}{d\dot{y}_1} \right) \dot{y}_1 dt + \left( E_2 - \frac{dF}{d\dot{y}_2} \right) \dot{y}_2 dt,$$

which, by (7), has the value

$$L_1 \dot{y}_1 d\dot{y}_1 + M(\dot{y}_1 d\dot{y}_2 + \dot{y}_2 d\dot{y}_1) + L_2 \dot{y}_2 d\dot{y}_2 + 2\dot{y}_1 \dot{y}_2 dM,$$

or, by (8) and (9), the value  $dT + dW$ , so that the energy is all accounted for.

This agreement (as also that in each of the cases which follow) is of course only a consequence of the equations given above ; but its exhibition tends to give a clearer notion of the dynamical meaning of these equations.

Here part of the impressed electromotive forces  $E_1, E_2$  in each case is employed in working against the inductive electromotive force, and thus in increasing the electrokinetic energy. By the electromagnetic forces the electrokinetic energy is increased by the amount  $\dot{y}_1\dot{y}_2 dM$ , which also is the amount of work spent in moving the circuits.

If the conductors are displaced from rest to rest again, so that  $\dot{y}_1, \dot{y}_2$ , have resumed their steady values  $d\dot{y}_1=0, d\dot{y}_2=0$ , the energy furnished by the batteries is  $2\dot{y}_1\dot{y}_2 dM$ , of which one half is accounted for in  $dT$ , the other by the work done in moving the circuits, which has its equivalent in work done against the external resistance by which the conductors were brought to rest. This result was obtained by Sir William Thomson so long ago as 1851.

(2) Assuming, according to Ampère, that a magnetic shell is equivalent to a current round its edge, and putting  $\dot{y}_2$  for this current, we have, since  $E_2=0, R_2=0$ , instead of (7),

$$\left. \begin{aligned} E_1 - \frac{d}{dt}(L_1\dot{y}_1 + M\dot{y}_2) &= R_1\dot{y}_1 \\ \frac{d}{dt}(L_2\dot{y}_2 + M\dot{y}_1) &= 0. \end{aligned} \right\} \cdot \cdot \cdot (10)$$

As before we get

$$\left. \begin{aligned} dT &= L_1\dot{y}_1 d\dot{y}_1 + M(\dot{y}_2 d\dot{y}_1 + \dot{y}_1 d\dot{y}_2) + L_2\dot{y}_2 d\dot{y}_2 + \dot{y}_1\dot{y}_2 dM, \\ dW &= \dot{y}_1\dot{y}_2 dM. \end{aligned} \right\} \cdot (11)$$

The energy furnished by the battery is, as before,

$$L_1\dot{y}_1 d\dot{y}_1 + M\dot{y}_1 d\dot{y}_2 + \dot{y}_1\dot{y}_2 dM.$$

By the other circuit no energy is given. But multiplied by  $\dot{y}_2$ , the second of (10) gives

$$L_2\dot{y}_2 d\dot{y}_2 + M\dot{y}_2 d\dot{y}_1 + \dot{y}_1\dot{y}_2 dM = 0.$$

Thus

$$\left. \begin{aligned} dT &= L_1\dot{y}_1 d\dot{y}_1 + M\dot{y}_1 d\dot{y}_2, \\ dT + dW &= L_1\dot{y}_1 d\dot{y}_1 + M\dot{y}_1 d\dot{y}_2 + \dot{y}_1\dot{y}_2 dM, \end{aligned} \right\} \cdot \cdot (12)$$

which again, of course, is the energy furnished by the battery.

Here, if the changes are estimated for the system when brought to rest,  $d\dot{y}_1=0$ . The other current  $\dot{y}_2$  does not, however, remain constant, and we have to inquire what is its effect upon the magnet. We know that the moment of a hard magnet is not seriously altered by a displacement produced by the mutual forces if  $\dot{y}_1$  is moderate; and the small alteration

generally observed is opposite to that which would be produced by the inductive change in  $\dot{y}_2$ . We are led to conclude that  $\dot{y}_2$ , on which, according to Ampère's theory, the intensity of magnetization depends, must remain practically constant. Writing, then, the second of (10) in the form

$$L_2\dot{y}_2 + M\dot{y}_1 = L_2\gamma,$$

where  $\gamma$  is the initial current before the magnet was brought into the field of the circuit, we see that if the dynamical theory is applicable,  $M\dot{y}_1/L_2$  must be a quantity small in comparison with  $\gamma$ . This gives  $d\dot{y}_2$  a small quantity of the second order, and makes the value of  $dT$ , the change in the electrokinetic energy, depend only on the term  $L_1\dot{y}_1d\dot{y}_1$ , which is zero if the system is not in relative motion. Thus the fact that the mechanical value of a current in a conductor is not affected by bringing permanent magnets into its neighbourhood is not contradicted by the dynamical theory, if the supposition here made as to the value of  $M\dot{y}_1/L_2$  be actually true. We have to inquire what physical reasons can be adduced in support of it.

Suppose that, instead of a simple magnetic shell, we have a solenoid made up of equal distinct circuits, in each of which a current  $\gamma$  flows. If the number of circuits per unit of length be  $n$ , the coefficient of self-induction per unit of length is  $4\pi n^2 A$ , where  $A$  is the area of the circuit, and the total induction through the solenoid (neglecting the effect of its ends) is  $4\pi n^2 l \gamma A$ , if  $l$  be its length. If the circuit carrying the current  $\dot{y}_1$  consist of  $n'$  turns of wire closely surrounding the solenoid, the induction through it and the solenoid is  $4\pi n n' \gamma A$ . Thus the maximum value of  $M$  is  $4\pi n n' A$ . Thus we get

$$\frac{M}{L_2} = \frac{n'}{nl};$$

that is, the ratio, which the theory indicates must be vanishingly small, is equal to the ratio of the number of turns in the circuit to the number of circuits in the solenoid. Thus we are led to the supposition, probable on other grounds, that the number of molecular circuits in the solenoid is exceedingly great.

It is also necessary, in order that the Amperian molecules may give an inductive magnetization in iron agreeing with experiment, that the self-induction of each molecular circuit must be great, that is  $A/L_2$  must be small. If the current flow in a ring channel this condition, as Maxwell has pointed out\*, may be fulfilled by supposing the radius  $R$  of the mean

\* Maxwell, 'Electricity and Magnetism,' vol. ii. § 844.

line of the channel great in comparison with  $r$  the radius of the channel, since  $L_2$  depends on  $\log R/r$ .

(3) Considering now the case of two shells, we have the same expressions for  $dT$  and  $dW$  as in (11); but the equations (10) become, since now  $R_1=0$ ,  $E_1=0$ ,

$$\left. \begin{aligned} L_1 \dot{y}_1 d\dot{y}_1 + M \dot{y}_1 d\dot{y}_2 + \dot{y}_1 \dot{y}_2 dM &= 0, \\ L_2 \dot{y}_2 d\dot{y}_2 + M \dot{y}_2 d\dot{y}_1 + \dot{y}_1 \dot{y}_2 dM &= 0. \end{aligned} \right\} \dots \dots (13)$$

Thus substituting in (11) we find

$$dT = -\dot{y}_1 \dot{y}_2 dM, \dots \dots \dots (14)$$

which is equal and opposite to the work done by the electromagnetic forces in moving the system. Here, it is to be observed, the electrokinetic energy is diminished through the action of the electromotive forces by just double the amount by which the electromagnetic forces increase it.

The performance of a finite amount of work by electromagnetic forces in overcoming external forces, or in giving the magnets kinetic energy, and the diminution of the electrokinetic energy by an equal amount, are quite consistent with only a slight alteration of  $\dot{y}_1$ ,  $\dot{y}_2$ , and therefore of the magnetic moments of the magnets. Indeed, the alteration in the magnetic moments of the magnets actually produced is opposite in sign to that which would be caused by  $d\dot{y}_1$ ,  $d\dot{y}_2$ , and is due no doubt to magnetization produced by a turning round of magnetic molecules in the body. But in an ideal case, in which the molecules could undergo no such alteration of position, it is only necessary to suppose that  $L_1$ ,  $L_2$  are each great in comparison with  $M$  to enable the effect of  $d\dot{y}_1$ ,  $d\dot{y}_2$  on the magnetic moments to be small, a supposition which is very possibly in accordance with fact.

There does not seem to me, therefore, to be any insuperable physical difficulty in the way of the application of the general dynamical equations to magnets as well as to circuits carrying currents. Of course our ignorance of the current strength, &c., in the former case prevents us from making practical use of these equations; but their theoretical application gives I think a clearer view of the energetics of electromagnetic (and magnetic) action than can be obtained without them.

I shall now consider from this dynamical point of view the inductive magnetization produced in iron and other substances when placed in a magnetic field. As is well known, the expression in (1) or (3) for the electrokinetic energy can be reduced to a definite integral. The following method of performing this reduction seems more direct and simple than



that used by Maxwell, which is the method I think generally pursued. Starting from equation (3), viz.,

$$T = \frac{1}{2}(N_1\dot{y}_1 + N_2\dot{y}_2 + \dots + N_k\dot{y}_k + \dots),$$

take any circuit, say that through which the induction is  $N_k$ , and draw any surface in the field so as to form a cap with that circuit as bounding edge. Then, by the well-known theorem as to the work done in carrying a unit pole in a closed path round a circuit, we have

$$4\pi\dot{y}_k = \oint H_k \cos \theta_k ds,$$

where the integration is taken round any closed path embracing the circuit,  $H_k$  is the magnetic force *due to the current in that circuit*, and  $\theta_k$  the angle which  $H_k$  makes with  $ds$ , an element of the path. Hence, since the total induction through every such surface is the same, we have

$$N_k\dot{y}_k = \frac{1}{4\pi} \int N_k H_k \cos \theta_k ds. \quad . \quad . \quad (15)$$

Now let the surface be taken at right angles to the lines of induction everywhere. These lines are closed curves round the conductors, and each threads through one or more of the circuits. It is possible to divide up the whole field by successive surfaces, each having for bounding edge *any given circuit*, so that every one of those surfaces shall be everywhere at right angles to the lines of induction. Every one of these, if it cut through a system of closed lines belonging to any *one* circuit, will pass through every point of that circuit. Of course no one of the closed tubes of induction which the surface thus cuts through contributes anything to the total induction through the surface.

Now let the direction of the closed curve, round which the integral of  $H \cos \theta ds$  is taken, be everywhere at right angles to these surfaces, and let  $B$  be the value of the induction at any point where this curve cuts one of these surfaces. Then, if  $dS$  be the area of an element of the surface at that point, the induction through it is  $BdS$ . Thus we get

$$N_k\dot{y}_k = \frac{1}{4\pi} \iint B H_k \cos \theta_k ds dS,$$

where one integral is taken over the surface and the other round the closed curve. But this is evidently the same thing as

$$N_k \dot{y}_k = \frac{1}{4\pi} \iiint_{-\infty}^{+\infty} B H_k \cos \theta_k \, dx \, dy \, dz, \quad . \quad . \quad (16)$$

where  $x, y, z$  are the coordinates of the point at which the induction is  $B$ , and  $dx \, dy \, dz$  is an element of volume.

Finally, take any point on one of these surfaces, and let  $B$  be the induction there. For *every* such point a surface can be drawn having any one of the circuits as its boundary, and hence by (16) and (3) we have finally for  $T$  the equation :

$$T = \frac{1}{8\pi} \iiint_{-\infty}^{+\infty} B (H_1 \cos \theta_1 + H_2 \cos \theta_2 + \&c.) \, dx \, dy \, dz. \quad . \quad (17)$$

But if  $H$  be the total magnetic force at the point and  $\theta$  the angle which it makes with the normal to the surface, we have

$$H \cos \theta = H_1 \cos \theta_1 + H_2 \cos \theta_2 + \&c.$$

Hence (17) becomes

$$T = \frac{1}{8\pi} \iiint B H \cos \theta \, dx \, dy \, dz. \quad . \quad . \quad (18)$$

If we suppose, what is always the case in an isotropic medium, that  $B$  and  $H$  have the same direction, we have

$$T = \frac{1}{8\pi} \iiint_{-\infty}^{+\infty} B H \, dx \, dy \, dz = \frac{1}{8\pi\mu} \iiint_{-\infty}^{+\infty} B^2 \, dx \, dy \, dz, \quad . \quad (19)$$

since  $B = \mu H$ , if  $\mu$  be the magnetic inductive capacity or permeability of the medium.

Now let the total induction through the circuit in which the magnetizing current is flowing be increased by an amount  $dN$  produced by increasing the current in that circuit. The energy drawn from the battery is  $\dot{y} dN$ ; and clearly by the investigation given above, we have, if  $dB$  be the increase of induction at  $(x, y, z)$ ,

$$\dot{y} dN = \frac{1}{4\pi} \iiint_{-\infty}^{+\infty} H dB \, dx \, dy \, dz. \quad . \quad . \quad (20)$$

The change of electrokinetic energy  $dT$  is given by

$$dT = \frac{1}{8\pi} \iiint_{-\infty}^{+\infty} (H dB + B dH) \, dx \, dy \, dz. \quad . \quad . \quad (21)$$

Hence for the energy spent *otherwise* than in increasing the electrokinetic energy in the medium, we have

$$y dN - dT = \frac{1}{4\pi} \iiint_{-\infty}^{+\infty} \left\{ H dB - \frac{1}{2} (H dB + B dH) \right\} dx dy dz. \quad (22)$$

If the magnetization be carried through a closed cycle, so that the medium is brought back to the same state as at first, the electrokinetic energy returns to the same value, and the integral of the quantity within the inner brackets, which is  $d(BH)$ , is zero. Thus the energy furnished to the medium in the closed cycle is

$$\frac{1}{4\pi} \iiint_{-\infty}^{+\infty} \left\{ \int H dB \right\} dx dy dz,$$

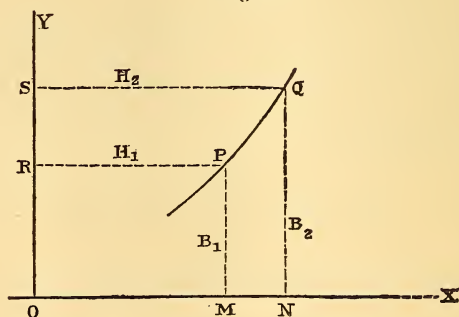
the inner integral being taken with respect to  $B$  round the cycle.

If we take the changes per unit of volume at a place where the induction is  $B$  and the magnetic force  $H$ , we have for the energy given to the medium the value  $H dB/4\pi$ , and for the increase of electrokinetic energy  $d(BH)/8\pi$ . Therefore, for the energy spent otherwise than in increasing the electrokinetic energy, we get the expression

$$\frac{1}{4\pi} H dB - \frac{1}{8\pi} (H dB + B dH).$$

Hence if  $P, Q$  (fig. 1) be two points on a curve of magnetization of which the ordinates are values of  $B$ , and the

Fig. 1.



abscissæ values of  $H$ , we have for the whole energy spent otherwise than in increasing  $T$ , in this part of the curve, the value

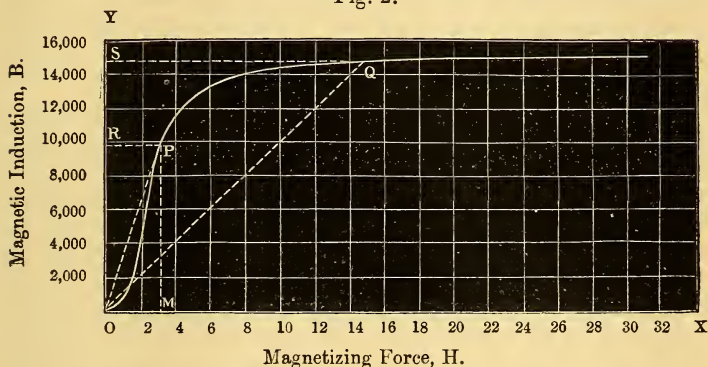
$$\frac{1}{4\pi} \left\{ \int_{B_1}^{B_2} H dB - \frac{1}{2} \int_{B_1}^{B_2} (H dB + B dH) \right\};$$

that is,

$$\frac{1}{4\pi} (\text{area } P Q S R - \frac{1}{2} \text{area } N Q S R P M).$$

The second area of course vanishes when Q coincides with P, as it does when the curve forms a closed cycle.

Fig. 2.



It is interesting to apply this result to an actual curve of magnetization in iron (fig. 2). For all points on the curve up to a little distance beyond P, the total energy given to the medium in producing the corresponding magnetization exceeds the electrokinetic energy, but for all points further from the origin the electrokinetic energy exceeds, and for points on the upper flat part of the curve very greatly exceeds, the energy given out to the medium by the battery. [The point P at which OP is a tangent to the curve marks the point at which the energy given out to the medium and the electrokinetic energy are increasing at the same rate, the former below that point is increasing faster, above that point slower than the latter.]

We are forced to conclude that for every series of magnetization steps from zero up to a certain point energy is given to the medium, and for every series from zero up to any further point the medium furnishes the balance of energy required for the electrokinetic energy. In every small step below P a balance of energy, over and above the electrokinetic energy, is given to the medium; for every small step



above P a balance is taken from the medium to make up the electrokinetic energy.

It seems to me that these results are very intimately connected with and confirm Prof. Ewing's theory of Magnetization, published in the *Philosophical Magazine* for September. In the steep part of the curve beyond the first bend we have work done by the electromagnetic forces (and probably converted into heat) at a much greater rate than elsewhere in the curve. Here, according to this theory, magnets undergo almost all the turning of their axes they receive. Hence the coefficients of mutual induction must increase here most quickly, and consequently also the work done by electromagnetic forces which depend, as shown above, on the changes in these coefficients.

Prof. Ewing supposes that the molecular magnets having been swung round into new positions of stable equilibrium vibrate about that position, generating Foucault currents in the surrounding medium, thus heating it. Now Baur, Rowland, Hopkinson, and others have shown that iron has its magnetic susceptibility increased by rise of temperature so long as a certain high magnetizing force and a certain high temperature are not exceeded. The conclusion which follows from this by thermodynamic theory is that increase of magnetization should *cool* the iron. Although of course we cannot reason rigidly for an unclosed series of changes, owing to our want of knowledge of the molecular changes, it does seem probable that the iron is really heated in the part of the curve for which the curvilinear area O Q S is greater than the triangle O Q S. The hypothesis would, however, explain this seeming contradiction; for, as I understand it, the thermodynamic theory does not take into account any expenditure in producing heat of the electromagnetic work done in altering the magnetic state. If the molecules could be laid hold of by external forces, against which they might do work in going round to their new positions, so as to be guided to rest in these positions, there would be no vibration, and the iron would show a cooling, according to thermodynamic theory. In fact the heating due to the Foucault currents, supposed to be thus generated, must be less than it otherwise would be by the thermodynamic cooling.

In the upper part of the curve it seems probable that there is a marked cooling. At present I am engaged in a careful experimental investigation of heating-effects for the whole curve.

Another point which may be here remarked is that (as

shown in equations (13) for a particular case) the inductions through the molecular circuits remain constant. Hence in a magnetizable body these inductions must be the same in the unmagnetized state of the body as in its magnetized state ; and this seems to show that the magnetization consists in the turning round, into facing on the whole in the same direction, different lines or chains of regularly arranged molecular magnets, or molecular circuits, as opposed to an alignment of a number of circuits previously perfectly mixed up in their arrangement. For if each of these chains have its component molecules all facing the same way, and the different chains be so arranged that the body has no magnetic moment in mass, the constant induction of large amount through each circuit can be accounted for ; and this appears to me to be the more natural explanation. A body which had its molecular circuits perfectly mixed up as to direction could not, it seems to me, be magnetized at all, except in so far as to produce an induction through each of the circuits equal and opposite to the integral of the magnetizing force over that circuit, unless indeed the coefficients of self-induction are in all cases so large as to give a considerable induction through each circuit due to its own current alone. If the latter were the case, the result of causing all the molecular circuits to face one way would be to produce an induction, in the same direction, over every part of a section of the body across the direction of the magnetizing force ; if it were not the case, the induction across such a section would be everywhere small, in consequence of the fact that the surrounding circuits before the alignment contribute on the whole nothing to the induction through a particular circuit, which induction must afterwards still have the same small value.

Thus, if the current in each circuit does not by itself produce an induction in itself considerable, a moderate magnetizing force, applied to a body composed of molecules perfectly mixed as to the directions of their axes, ought to produce diamagnetic quality, in consequence of the creation of the magnetic induction required to keep the total induction through each circuit at its former value.

Of course diamagnetic quality is most simply accounted for by supposing the molecules immovable. The only effect of placing the body in a magnetic field would then be to produce induced currents corresponding to diamagnetization.

LII. *On the Theory of Surface Forces.*

By Lord RAYLEIGH, *Sec. R.S.*

[Continued from p. 298.]

WE may apply the same formulæ to compare the pressures at the centre and upon the surface of a spherical mass of fluid, surrounded by vacuum. If the radius be  $r$ , we have at the centre

$$V = 4\pi \int_0^r f^2 \Pi(f) df,$$

and at the surface

$$V = 2\pi \int_0^{2r} \left(1 - \frac{f}{2r}\right) f^2 \Pi(f) df;$$

so that the excess of pressure at the centre is

$$4\pi \int_0^r f^2 \Pi(f) df - 2\pi \int_0^{2r} f^2 \Pi(f) df + \frac{\pi}{r} \int_0^{2r} f^3 \Pi(f) df. \quad (34)$$

If  $r$  exceed the range of the forces, (34) becomes

$$2\pi \int_0^\infty f^2 \Pi(f) df + \frac{\pi}{r} \int_0^\infty f^3 \Pi(f) df = K + \frac{2T}{r}, \quad (35)$$

as was to be expected. As the curvature increases from zero, there is at first a rise of pressure. A maximum occurs when  $r$  has a particular value, of the order of the range. Afterwards a diminution sets in, and the pressure approaches zero, as  $r$  decreases without limit.

If the surface of fluid, not acted on by external force, be of variable curvature, it cannot remain in equilibrium. For example, at the pole of an oblate ellipsoid of revolution the potential will be greater than at the equator, so that in order to maintain equilibrium an external polar pressure would be needed. An extreme case is presented by a rectangular mass, in which the potential at an edge is only one half, and at a corner only one eighth, of that general over a face.

When the surface is other than spherical, we cannot obtain so simple a general expression as (34) to represent the excess of internal over superficial pressure; but an approximate expression analogous to (35) is readily found.

The potential at a point upon the surface of a convex mass differs from that proper to a plane surface by the potential of the meniscus included between the surface and its tangent

plane. The equation of the surface referred to the normal and principal tangents is approximately

$$2z = x^2/R_1 + y^2/R_2,$$

$R_1, R_2$  being the radii of curvature. The potential, at the origin, of the meniscus is thus

$$V = \iint \Pi(f) z f df d\theta,$$

where  $f^2 = x^2 + y^2$ ; and

$$\int_0^{2\pi} z d\theta = \int \left( \frac{f^2 \cos^2 \theta}{2R_1} + \frac{f^2 \sin^2 \theta}{2R_2} \right) d\theta = \frac{\pi f^2}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right).$$

Accordingly

$$V = \frac{\pi}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \int_0^\infty f^3 \Pi(f) df = \frac{T}{R_1} + \frac{T}{R_2}.$$

The excess of internal pressure above that at the superficial point in question is thus

$$K + \frac{T}{R_1} + \frac{T}{R_2}, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

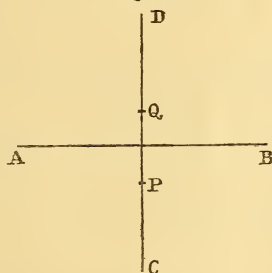
in agreement with (35).

For a cylindrical surface of radius  $r$ , we have simply

$$K + \frac{T}{r}. \quad . \quad . \quad . \quad . \quad . \quad (37)$$

Returning to the case of a plane surface, we know that upon it  $V = K$ , and that in the interior  $V = 2K$ . At a point P (fig. 2) just within the surface, the value of  $V$  cannot be

Fig. 2.



expressed in terms of the principal quantities  $K$  and  $T$ , but will depend further upon the precise form of the function  $\Pi$ . We can, however, express the value of  $\int V dz$ , where  $z$  is measured inwards along the normal, and the integration extends over the whole of the superficial layer where  $V$  differs from  $2K$ .



It is not difficult to recognize that this integral must be related to  $T$ . For if  $Q$  be a point upon the normal equidistant with  $P$  from the surface  $AB$ , the potential at  $Q$  due to fluid below  $AB$  is the same as the potential at  $P$  due to imaginary fluid above  $AB$ . To each of these add the potential of the lower fluid at  $P$ . Then the sum of the potentials at  $P$  and  $Q$  due to the lower fluid is equal to the potential at  $P$  due to both fluids, that is to the constant  $2K$ . The deficiency of potential at a point  $P$  near the plane surface of a fluid, as compared with the potential in the interior, is thus the same as the potential at an external point  $Q$ , equidistant from the surface. Now it is evident that  $\int V_Q dz$  integrated upwards along the normal represents the work per unit of area that would be required to separate a continuous fluid of unit density along the plane  $AB$  and to remove the parts beyond the sphere of influence, that is, according to the principle of Dupré,  $2T$ . We conclude that the deficiency in  $\int V_P dz$ , integrated along the normal inwards, is also  $2T$ ; or that

$$\int_0^z V_P dz = 2K \cdot z - 2T, \quad . . . . . (38)$$

$z$  being large enough to include the whole of the superficial stratum. The pressure  $p$  at any point  $P$  is given by

$$p = V_P - K,$$

so that

$$\int_0^z p dz = K \cdot z - 2T. \quad . . . . . (39)$$

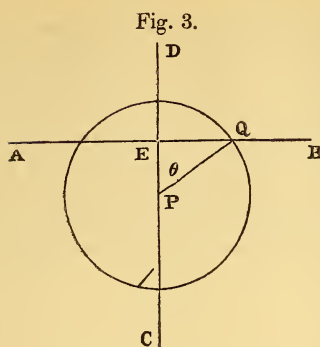
We may thus regard  $2T$  as measuring the total deficiency of pressure in the superficial stratum.

The argument here employed is of course perfectly satisfactory; but it is also instructive to investigate the question directly, without the aid of the idea of superficial tension, or energy, and this is easily done.

In polar coordinates the potential at any point  $P$  is expressed by

$$V_P = 2\pi \iint \Pi(f) f^2 \sin \theta d\theta df,$$

the integrations extending over the whole space  $ACB$  (fig. 3). If the distance  $EP$ , that is  $z$ , exceed the range of the forces, every sphere of radius  $f$ , under consideration, is complete, and  $V_P = 2K$ . But in the integration with respect to  $z$  incomplete spheres have to be considered, such as that shown



in the figure. The value of the potential, corresponding to a given infinitely small range of  $f$ , is then proportional to

$$\int_{\theta}^{\pi} \sin \theta d\theta = 1 + \cos \theta = 1 + z/f.$$

If now we effect first the integration with respect to  $z$ , we have as the element of the final integral,

$$2\pi \Pi(f) f^2 df \left\{ \int_0^f (1 + z/f) dz + \int_f^z 2 dz \right\},$$

or

$$2\pi \Pi(f) f^2 df (2z - \frac{1}{2}f);$$

and thus, on the whole,

$$\begin{aligned} \int_0^z V_P dz &= z \cdot 4\pi \int_0^{\infty} \Pi(f) f^2 df - \pi \int_0^{\infty} \Pi(f) f^3 df \\ &= z \cdot 2K - 2T, \text{ as before.} \end{aligned}$$

An application of this result to a calculation of the pressure operative between the two halves of an isolated sphere will lead us to another interpretation of  $T$ . The pressure in the interior is  $K + 2T/r$ ,  $r$  being the radius; and this may be regarded as prevailing over the whole of the diametral dividing plane, subject to a correction for the circumferential parts which are near the surface of the fluid. If the radius  $r$  increase without limit, the correction will be the same per unit of length as that investigated for a plane surface. The whole pressure between the two infinite hemispheres is thus

$$\pi r^2 (K + 2T/r) - 2T \cdot 2\pi r,$$

or

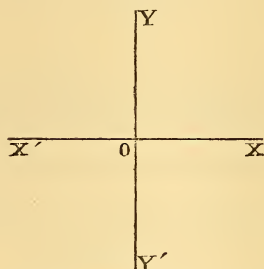
$$\pi r^2 K - T \cdot 2\pi r. \quad . \quad . \quad . \quad . \quad . \quad (40)$$

This expression measures equally the attraction between the

2 K 2

two hemispheres, which the pressure is evoked to balance. If the fluid on one side of the diametral plane extended to infinity, the attraction upon the other hemisphere, supposed to retain its radius  $r$ , would be  $\pi r^2 K$  simply; so that the second term  $T \cdot 2\pi r$  may be considered to represent the deficiency of attraction due to the absence of the fluid external to one hemisphere. Regarding the matter in two dimensions, we recognize  $T$  as the attraction per unit of length perpendicular to the plane of the paper of the fluid occupying (say)

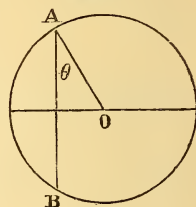
Fig. 4.



the first quadrant  $X O Y$  (fig. 4) upon the fluid in the third quadrant  $X' O Y'$ , the attraction being resolved in one or other of the directions  $O X$ ,  $O Y$ . In its actual direction, bisecting the angle  $X O Y$ , the attraction will be of course  $\sqrt{2} \cdot T$ .

We will now suppose that the sphere is divided by a plane  $A B$  (fig. 5), which is not diametral, but such that the angle  $B A O = \theta$ ;  $A O = r$ ,  $A B = 2\rho$ . In the interior of the mass, and generally along the section  $A B$ ,  $V = 2K$ . On the surface of the sphere, and therefore along the circumference of  $A B$ ,  $V = K - 2T/r$ . When  $V$  was integrated along the normal, from a plane surface inwards, the deficiency was found to be  $2T$ . In the present application the integration is along the oblique line  $A B$ , and the deficiency will be  $2T \sec \theta$ . Hence when  $r$  and  $\rho$  increase without limit, we may take as the whole pressure over the area  $A B$

Fig. 5.



$$\begin{aligned} & \pi \rho^2 (K + 2T/r) - 2\pi \rho \cdot 2T \sec \theta \\ & = \pi \rho^2 K - 2\pi \rho (2T \sec \theta - T \cos \theta). \end{aligned}$$

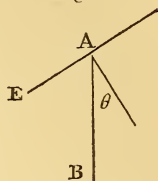
The deficiency of attraction perpendicular to  $A B$  is thus for each unit of perimeter

$$2T \sec \theta - T \cos \theta, \dots \dots \dots (41)$$

and this we may think of as applicable in two dimensions (fig. 6) to each unit of length. When  $\theta=0$ , (41) reduces to  $T$ .

The term  $T \cos \theta$  in the expression for the total pressure appears to have its origin in the curvature of the surface, only not disappearing when the curvature vanishes, in consequence of the simultaneous increase without limit of the area over which the pressure is reckoned. If we consider only a distance  $AB$ , which, though infinite in comparison with the range of the attraction, is infinitely small in comparison with the radius of curvature,  $T \cos \theta$  will disappear from the expression for the pressure, though it must necessarily remain in the expression for the attraction. The pressure acting across a section  $AB$  proceeding inwards from a plane surface  $AE$  of a fluid is thus inadequate to balance the attraction of the two parts. It must be aided by an external force perpendicular to  $AB$  of magnitude  $T \cos \theta$ ; and since the imaginary section  $AB$  may be made at any angle, we see that the force must be  $T$  and must act along  $AE$ .

Fig. 6.



An important class of capillary phenomena are concerned with the spreading of one liquid upon the surface of another, a subject investigated experimentally by Marangoni, Van der Mensbrugghe, Quincke, and others. The explanation is readily given in terms of surface-tension; and it is sometimes supposed that these phenomena demonstrate in a special manner the reality of surface-tension, and even that they are incapable of explanation upon Laplace's theory, which dealt in the first instance with the capillary pressures due to curvature of surfaces\*.

In considering this subject, we have first to express the dependence of the tension at the interface of two bodies in terms of the forces exercised by the bodies upon themselves and upon one another, and to effect this we cannot do better than follow the method of Dupré. If  $T_{12}$  denote the interfacial tension, the energy corresponding to unit of area of the interface is also  $T_{12}$ , as we see by considering the introduction (through a fine tube) of one body into the interior of the other. A comparison with another method of generating the interface, similar to that previously employed when but one body was in question, will now allow us to evaluate  $T_{12}$ .

The work required to cleave asunder the parts of the first

\* Van der Mensbrugghe, "Essai sur la Théorie Mécanique de la Tension Superficielle, &c." *Bulletins de l'Acad. roy. de Belgique*, 3<sup>me</sup> série, t. ix. no. 5, 1885, p. 12. Worthington, *Phil. Mag.* Oct. 1884, p. 364.



fluid which lie on the two sides of an ideal plane passing through the interior, is per unit of area  $2T_1$ , and the free surface produced is two units in area. So for the second fluid the corresponding work is  $2T_2$ . This having been effected, let us now suppose that each of the units of area of free surface of fluid (1) is allowed to approach normally a unit area of (2) until contact is established. In this process work is gained which we may denote by  $4T'_{12}$ ,  $2T'_{12}$  for each pair. On the whole, then, the work expended in producing two units of interface is  $2T_1 + 2T_2 - 4T'_{12}$ , and this, as we have seen, may be equated to  $2T_{12}$ . Hence

$$T_{12} = T_1 + T_2 - 2T'_{12}. \quad (42)$$

If the two bodies are similar,

$$T_1 = T_2 = T'_{12};$$

and  $T_{12} = 0$ , as it should do.

Laplace does not treat systematically the question of interfacial tension, but he gives incidentally in terms of his quantity  $H$  a relation analogous to (42).

If  $2T'_{12} > T_1 + T_2$ ,  $T_{12}$  would be negative, so that the interface would of itself tend to increase. In this case the fluids must mix. Conversely, if two fluids mix, it would seem that  $T'_{12}$  must exceed the mean of  $T_1$  and  $T_2$ ; otherwise work would have to be *expended* to effect a close alternate stratification of the two bodies, such as we may suppose to constitute a first step in the process of mixture\*.

The value of  $T'_{12}$  has already been calculated (7). We may write

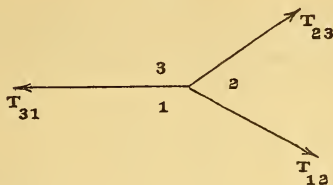
$$T'_{12} = \pi \sigma_1 \sigma_2 \int_0^\infty \theta(z) dz = \frac{1}{8} \pi \sigma_1 \sigma_2 \int_0^\infty z^4 \phi(z) dz; \quad (43)$$

and in general the functions  $\theta$ , or  $\phi$ , must be regarded as capable of assuming different forms. Under these circumstances there is no limitation upon the values of the interfacial tensions for three fluids, which we may denote by  $T_{12}$ ,  $T_{23}$ ,  $T_{31}$ . If the three fluids can remain in contact with one another, the sum of any two of the quantities must exceed the third, and by Neumann's rule the directions of the interfaces at the common edge must be parallel to the sides of a triangle, taken proportional to  $T_{12}$ ,  $T_{23}$ ,  $T_{31}$ . If the above-mentioned condition be not satisfied, the triangle is imaginary, and the three fluids cannot rest in contact, the two weaker tensions, even if acting in full concert, being incapable of balancing the strongest. For instance, if  $T_{31} > T_{12} + T_{23}$ , the second

\* Dupré, *loc cit.* p. 372. Thomson, Popular Lectures, p. 53.

fluid spreads itself indefinitely upon the interface of the first and third fluids.

Fig. 7.



The experimenters who have dealt with this question, Marangoni, Van der Mensbrugghe, Quincke, have all arrived at results inconsistent with the reality of Neumann's triangle. Thus Marangoni says\* :—"Die gemeinschaftliche Oberfläche zweier Flüssigkeiten hat eine geringere Oberflächenspannung als die Differenz der Oberflächenspannung der Flüssigkeiten selbst (mit Ausnahme des Quecksilbers)." Three pure bodies (of which one may be air) cannot accordingly remain in contact. If a drop of oil stands in lenticular form upon a surface of water, it is because the water-surface is already contaminated with a greasy film.

On the theoretical side the question is open until we introduce some limitation upon the generality of the functions. By far the simplest supposition open to us is that the functions are the same in all cases, the attractions differing merely by coefficients analogous to densities in the theory of gravitation. This hypothesis was suggested by Laplace, and may conveniently be named after him. It was also tacitly adopted by Young, in connexion with the still more special hypothesis which Young probably had in view, namely that the force in each case was constant within a limited range, the same in all cases, and vanished outside that range.

As an immediate consequence of this hypothesis we have from (3)

$$K = K_0 \sigma^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

$$T = T_0 \sigma^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

where  $K_0$ ,  $T_0$  are the same for all bodies.

But the most interesting results are those which Young† deduced relative to the interfacial tensions of three bodies. By (12), (43),

$$T'_{12} = \sigma_1 \sigma_2 T_0; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

\* Pogg. *Ann.* cxliii. p. 348, 1871 (1865). It was subsequently shown by Quincke that mercury is not really an exception.

† Works, vol. i. p. 463.

so that by (42), (45),

$$T_{12} = (\sigma_1 - \sigma_2)^2 T_0 \dots \dots \dots (47)$$

According to (47), the interfacial tension between any two bodies is proportional to the square of the difference of their densities. The densities  $\sigma_1, \sigma_2, \sigma_3$  being in descending order of magnitude, we may write

$$\begin{aligned} T_{31} &= (\sigma_1 - \sigma_2 + \sigma_2 - \sigma_3)^2 T_0 \\ &= T_{12} + T_{23} + 2(\sigma_1 - \sigma_2)(\sigma_2 - \sigma_3)T_0; \end{aligned}$$

so that  $T_{31}$  necessarily exceeds the sum of the other two interfacial tensions. We are thus led to the important conclusion, so far as I am aware hitherto unnoticed, that according to this hypothesis Neumann's triangle is necessarily imaginary, that one of three fluids will always spread upon the interface of the other two.

Another point of importance may be easily illustrated by this theory, viz. the dependency of capillarity upon abruptness of transition. "The reason why the capillary force should disappear when the transition between two liquids is sufficiently gradual will now be evident. Suppose that the transition from 0 to  $\sigma$  is made in two equal steps, the thickness of the intermediate layer of density  $\frac{1}{2}\sigma$  being large compared to the range of the molecular forces, but small in comparison with the radius of curvature. At each step the difference of capillary pressure is only one quarter of that due to the sudden transition from 0 to  $\sigma$ , and thus altogether half the effect is lost by the interposition of the layer. If there were three equal steps, the effect would be reduced to one third, and so on. When the number of steps is infinite, the capillary pressure disappears altogether."\*

According to Laplace's hypothesis the whole energy of any number of contiguous strata of liquids is least when they are arranged in order of density, so that this is the disposition favoured by the attractive forces. The problem is to make the sum of the interfacial tensions a minimum, each tension being proportional to the square of the difference of densities of the two contiguous liquids in question. If the order of stratification differ from that of densities, we can show that each step of approximation to this order lowers the sum of tensions. To this end consider the effect of the abolition of a stratum  $\sigma_{n+1}$ , contiguous to  $\sigma_n$  and  $\sigma_{n+2}$ . Before the change we have  $(\sigma_n - \sigma_{n+1})^2 + (\sigma_{n+1} - \sigma_{n+2})^2$ , and afterwards  $(\sigma_n - \sigma_{n+2})^2$ . The second *minus* the first, or the increase in

\* "Laplace's Theory of Capillarity," *Phil. Mag.* October 1883, p. 315.

the sum of tensions, is thus

$$2(\sigma_n - \sigma_{n+1})(\sigma_{n+1} - \sigma_{n+2}).$$

Hence, if  $\sigma_{n+1}$  be intermediate in magnitude between  $\sigma_n$  and  $\sigma_{n+2}$ , the sum of tensions is increased by the abolition of the stratum; but, if  $\sigma_{n+1}$  be not intermediate, the sum is decreased. We see, then, that the removal of a stratum from between neighbours where it is out of order and its introduction between neighbours where it will be in order is doubly favourable to the reduction of the sum of tensions; and since by a succession of such steps we may arrive at the order of magnitude throughout, we conclude that this is the disposition of minimum tensions and energy.

So far the results of Laplace's hypothesis are in marked accordance with experiment; but if we follow it out further, discordances begin to manifest themselves. According to (47)

$$\sqrt{T_{31}} = \sqrt{T_{12}} + \sqrt{T_{23}}, \dots \dots \dots (48)$$

a relation not verified by experiment. What is more, (47) shows that according to the hypothesis  $T_{12}$  is necessarily positive; so that, if the preceding argument be correct, no such thing as mixture of two liquids could ever take place.

But although this hypothesis is clearly too narrow for the facts, it may be conveniently employed in illustration of the general theory. In extension of (25) the potential at any point may be written

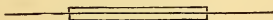
$$V = \iiint \sigma \Pi(f) dx dy dz, \dots \dots \dots (49)$$

and the hydrostatical equation of equilibrium is

$$dp = \sigma dV. \dots \dots \dots (50)$$

By means of the potential we may prove, independently of the idea of surface tension, that three fluids cannot rest in contact. Along the surface of contact of any two fluids the potential must be constant. Otherwise, there would be a tendency to circulation round a circuit of which the principal parts are close and parallel to the surface, but on opposite

Fig. 8.



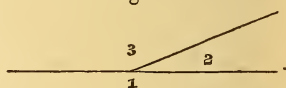
sides. For in the limit the variation of potential will be equal and opposite in the two parts of the circuit, and the resulting forces at corresponding points, being proportional also to the densities, will not balance. It is thus necessary to equilibrium that there be no force at any point; that is, that the potential be constant along the whole interface.



It follows from this that if three fluids can rest in contact, the potential must have the same constant value on all the three intersecting interfaces. But this is clearly impossible, the potential on each being proportional to the sum of the densities of the two contiguous fluids, as we see by considering places sufficiently removed from the point of intersection.

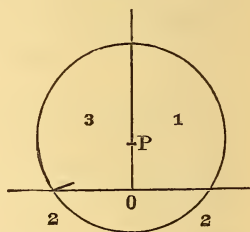
According to Laplace's hypothesis, then, three fluids cannot rest in contact; but the case is altered if one of the bodies be solid. It is necessary, however, that the quality of solidity attach to the body of intermediate density. For suppose, for example (fig. 9), that the body of greatest density,  $\sigma_1$ , is solid, and that fluids of densities  $\sigma_2, \sigma_3$  touch it and one another. It is now no longer necessary that the potential be constant along the interfaces (1, 2), (1, 3); but only along the interface (3, 2). The potential at a distant point of this interface may be represented by  $\sigma_2 + \sigma_3$ . But at the point of intersection the potential cannot be so low as this, being at least equal to  $\sigma_1 + \sigma_3$ , even if the angle formed by the two faces of (2) be evanescent. By this and similar reasoning it follows that the conditions of equilibrium cannot be satisfied, unless the solid be the body of intermediate density  $\sigma_2$ .

Fig. 9.



One case where equilibrium is possible admits of very simple treatment. It occurs when  $\sigma_2 = \frac{1}{2}(\sigma_1 + \sigma_3)$ , and the conditions are satisfied by supposing (fig. 10) that the fluid interface is plane and perpendicular to the solid wall. At a distance from O the potential is represented by  $\sigma_1 + \sigma_3$ ; and the same value obtains at a point P, near O, where the sphere of influence cuts into (2). For the areas of spherical surface lost by (1) and (3) are equal, and are replaced by equal areas of (2); so that if the above condition between the densities holds good, the potential is constant all the way up to O. The sub-case, where  $\sigma_3 = 0$ ,  $\sigma_2 = \frac{1}{2}\sigma$ , was given by Clairaut.

Fig. 10.



If the intermediate densities differ from the mean of the other two, the problem is less simple; but the general tendency is easily recognized. If, for example,  $\sigma_2 > \frac{1}{2}(\sigma_1 + \sigma_3)$ , it is evident that along a perpendicular interface the potential would increase as O is approached. To compensate this the interface must be inclined, so that, as O is approached,  $\sigma_1$  loses its importance relatively to  $\sigma_3$ . In this case therefore the angle between the two faces of (1) must be acute.

The general problem was treated by Young by means of superficial tensions, which must balance when resolved parallel to the surface of the solid, though not in the perpendicular direction. In this way Young found at once

$$T_{31} \cos \theta + T_{12} = T_{23}; \quad . \quad . \quad . \quad (51)$$

or rather, in terms of the more special hypothesis,

$$(\sigma_1 - \sigma_3)^2 \cos \theta + (\sigma_1 - \sigma_2)^2 = (\sigma_2 - \sigma_3)^2. \quad . \quad . \quad (52)$$

From this we deduce

$$\cos \theta = \frac{2\sigma_2 - \sigma_1 - \sigma_3}{\sigma_1 - \sigma_3}, \quad . \quad . \quad . \quad (53)$$

in agreement with what we found above for a special case. The equation may also be written

$$\sigma_1 \cos^2 \frac{1}{2}\theta + \sigma_3 \sin^2 \frac{1}{2}\theta = \sigma_2; \quad . \quad . \quad . \quad (54)$$

or if, as we may suppose without real loss of generality,  $\sigma_3 = 0$ ,

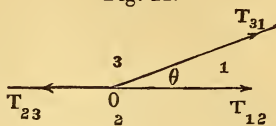
$$\sigma_1 \cos^2 \frac{1}{2}\theta = \sigma_2, \quad . \quad . \quad . \quad (55)$$

a form given by Laplace. In discussing the equation (53) with  $\sigma_3 = 0$ , Young\* remarks:—"Supposing the attractive density of the solid to be very small, the cosine will approach to  $-1$ , and the angle of the liquid to two right angles; and on the other hand, when  $\sigma_2$  becomes equal to  $\sigma_1$ , the cosine will be  $1$ , and the angle will be evanescent, the surface of the liquid coinciding in direction with that of the solid. If the density  $\sigma_2$  be still further increased, the angle cannot undergo any further alteration, and the excess of force will only tend to spread the liquid more rapidly on the solid, so that a thin film would always be found upon its surface, unless it were removed by evaporation, or unless its formation were prevented by some unknown circumstance which seems to lessen the intimate nature of the contact of liquids with dry solids."

The calculation of the angle of contact upon these lines is thus exceedingly simple, but I must admit that I find some difficulty in forming a definite conception of superficial tension as applied to the interface of a solid and a fluid. It would seem that interfacial *tension* can only be employed in such cases as the immediate representative of interfacial *energy*,

\* Works, vol. i. p. 464. I have introduced an insignificant change in the notation.

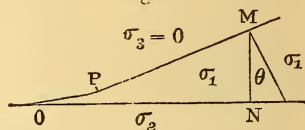
Fig. 11.



as conceived by Gauss. This principle, applied to a hypothetical displacement in which the point of meeting travels along the wall, leads with rigour to the required result.

In view of the difficulties which have been felt upon this subject, it seems desirable to show that the calculation of the angle of contact can be made without recourse to the principle of interfacial tension or energy. This indeed was effected by Laplace himself, but his process is very circuitous. Let  $O P M$  be the surface of fluid ( $\sigma_1$ ) resting against a solid wall  $O N$  of density  $\sigma_2$ . Suppose also that  $\sigma_3=0$ , and that there is no external pressure on  $O M$ . At a point  $M$  at a sufficient distance from  $O$  the curvature must be uniform (or the potential could not be constant), and we will suppose it to be zero. It would be a mistake, however, to think that the surface can be straight throughout up to  $O$ . This we may recognize by consideration of the potential at a point  $P$  just near enough to  $O$  for the sphere of influence to cut the solid. As soon as this occurs, the potential would begin to vary by substitution of  $\sigma_2$  for  $\sigma_1$ , and equilibrium would fail. The argument does not apply if  $\theta = \frac{1}{2}\pi$ .

Fig. 12.



We may attain the object in view by considering the equilibrium of the fluid  $M N O$ , or rather of the forces which tend to move it parallel to  $O N$ . Of pressures we have only to consider that which acts across  $M N$ , for on  $O M$  there is no pressure, and that on  $O N$  has no component in the direction considered. Moreover, the solid  $\sigma_2$  below  $O N$  exercises no attraction parallel to  $O N$ . Equilibrium therefore demands that the pressure operative across  $M N$  shall balance the horizontal attraction exercised upon  $O M N$  by the fluid  $\sigma_1$  which lies to the right of  $M N$ . The evaluation of the attraction in such cases has been already treated. It is represented by  $M N \cdot \sigma_1^2 K_0$ , subject to corrections for the ends at  $M$  and  $N$ . The correction for  $M$  is by (41)  $\sigma_1^2 T_0 (2 \sec \theta - \cos \theta)$ , and for  $N$  it is  $\sigma_1^2 T_0$ . On the whole the attraction in question is therefore

$$\sigma_1^2 \{ M N \cdot K_0 - 2 T_0 \sec \theta + T_0 \cos \theta - T_0 \}.$$

We have next to consider the pressure. In the interior of  $M N$ , we have  $\sigma_1^2 K_0$ ; but the whole pressure  $M N \cdot \sigma_1^2 K_0$  is subject to corrections for the ends. The correction for  $M$  we have seen to be  $2 \sigma_1^2 T_0 \sec \theta$ . In the neighbourhood of  $N$  the potential, and therefore the pressure, is influenced by the

solid. If  $\sigma_2$  were zero, the deficiency would be  $2\sigma_1^2 T_0$ . If  $\sigma_2$  were equal to  $\sigma_1$ , there would be no deficiency. Under the actual circumstances the deficiency is accordingly

$$2\sigma_1(\sigma_1 - \sigma_2)T_0;$$

so that the expression for the total pressure operative across M N is

$$\sigma_1\{M N \cdot \sigma_1 K_0 - 2\sigma_1 T_0 \sec \theta - 2(\sigma_1 - \sigma_2)T_0\}.$$

If we now equate the expressions for the pressure and the resolved attraction, we find as before

$$\sigma_1(1 - \cos \theta) = 2(\sigma_1 - \sigma_2).$$

In connexion with edge-angles it may be well here to refer to a problem, which has been the occasion of much difference of opinion—that of the superposition of several liquids in a capillary tube. Laplace's investigation led him to the conclusion that the whole weight of liquid raised depends only upon the properties of the lowest liquid. Thereupon Young\* remarks:—"This effect may be experimentally illustrated by introducing a minute quantity of oil on the surface of the water contained in a capillary tube, the joint elevation, instead of being increased as it ought to be according to Mr. Laplace, is very conspicuously diminished; and it is obvious that since the capillary powers are represented by the squares of the density of oil and of its difference from that of water, their sum must be less than the capillary power of water, which is proportional to the square of the sum of the separate quantities."

But the question is not to be dismissed so summarily. That Laplace's conclusion is sound, upon the supposition that *none of the liquids wets the walls of the tube*, may be shown without difficulty by the method of energy. In a hypothetical displacement the work done against gravity will balance the work of the capillary forces. Now it is evident that the liquids, other than the lowest, contribute nothing to the latter, since the relation of each liquid to its neighbours and to the walls of the tube is unaltered by the displacement. The only effect of the rise is that a length of the tube before in contact with air is replaced by an equal length in contact with the lowest liquid. The work of the capillary forces is the same as if the upper liquids did not exist, and therefore the total weight of the column supported is independent of these liquids.

\* Works, vol. i. p. 463.



The case of Young's experiment, in which oil stands upon water in a glass tube, is not covered by the foregoing reasoning. The oil must be supposed to wet the glass, that is to insinuate itself between the glass and air, so that the upper part of the tube is covered to a great height with a very thin layer of oil. The displacement here takes place under conditions very different from before. As the column rises, no new surface of glass is touched by oil, while below water replaces oil. The properties of the oil are thus brought into play, and Laplace's theorem does not apply.

That theory indicates the almost indefinite rise of a liquid like oil in contact with a vertical wall of glass is often overlooked, in spite of Young's explicit statement quoted above. It may be of interest to look into the question more narrowly on the basis of Laplace's hypothesis.

If we include gravity in our calculations, the hydrostatic equation of equilibrium is

$$p = \text{const.} + \sigma V - gpz, \quad . \quad . \quad . \quad . \quad (56)$$

where  $z$  is measured upwards, and  $V$  denotes as before the potential of the cohesive forces. Along the free surface of the liquid the pressure is constant, so that

$$\sigma V = \sigma^2 K_0 + gpz, \quad . \quad . \quad . \quad . \quad (57)$$

$z$  being reckoned from a place where the liquid is deep and the surface plane.

At a point upon the surface, whose distance from the wall exceeds the range of the forces,

$$\sigma V = K + T \left( \frac{1}{R_1} + \frac{1}{R_2} \right); \quad . \quad . \quad . \quad . \quad (58)$$

or, if we take the problem in two dimensions,

$$\sigma V = K + \frac{T}{R}, \quad . \quad . \quad . \quad . \quad (59)$$

where  $R$  is the radius of curvature, and  $K, T$  denote the intrinsic pressure and tension proper to the liquid and proportional to  $\sigma^2$ . Upon this equation is founded the usual calculation of the form of the surface.

When the point under consideration is nearer to the wall than the range of the forces, the above expression no longer applies. The variation of  $V$  on the surface of the thin layer which rises above the meniscus is due not to variations of curvature, for the curvature is here practically evanescent, but to the inclusion within the sphere of influence of the more dense matter constituting the wall. If the attraction

be a simple function of the distance, such as those considered above in illustrative examples, the thickness of the layer diminishes constantly with increasing height. The limit is reached when the thickness vanishes, and the potential attains the value due simply to the solid wall. This potential is  $\sigma'K_0$ , the intrinsic pressure within the wall being  $\sigma'^2K_0$ ; so that if we compare the point above where the layer of fluid disappears with a point below upon the horizontal surface, we find

$$gz = \sigma(\sigma' - \sigma)K_0. \quad . \quad . \quad . \quad . \quad . \quad (60)$$

By this equation is given the total head of liquid in contact with the wall; and, as was to be expected, it is enormous.

The height of the meniscus itself in a very narrow tube wetted by the liquid is obtained from (57), (58). If  $R$  be the radius of curvature at the centre of the meniscus,

$$gz = 2T/R; \quad . \quad . \quad . \quad . \quad . \quad (61)$$

and  $R$  may be identified with the radius of the tube, for under the circumstances supposed the meniscus is very approximately hemispherical.

The calculation of the height by the method of energy requires a little attention. The simplest displacement is an equal movement upwards of the whole body of liquid, including the layer above the meniscus. In this case the work of the cohesive forces depends upon the substitution of liquid for air in contact with the tube, and therefore not merely upon the interfacial tension between liquid and air, as (61) might lead us to suppose. The fact is that in this way of regarding the subject the work which compensates that of the cohesive forces is not simply the elevation against gravity of the column ( $z$ ), but also an equal elevation of the very high, though very thin, layer situated above it. The complication thus arising may be avoided by taking the hypothetical displacement so that the thin layer does not accompany the column ( $z$ ). In this case the work of the cohesive forces depends upon a reduction of surface between liquid and air simply, without reference to the properties of the walls, and (61) follows immediately.

Laplace's integral  $K$  was, as we have seen, introduced originally to express the intrinsic pressure, but according to the discovery of Dupré\* it is susceptible of another and very important interpretation. "Le travail de désagrégation totale d'un kilogramme d'un corps quelconque

\* *Théorie Mécanique de la Chaleur*, 1869, p. 152.

Van der Waals gives the same result in his celebrated essay of 1873.—German Translation, 1881, p. 31.

égale le produit de l'attraction au contact par le volume, ou, ce qui équivaut, le travail de désagrégation totale de l'unité de volume égale l'attraction au contact." *Attraction au contact* here means what we have called intrinsic pressure. The following reasoning is substantially that of Dupré.

We have seen (2) that  $2\pi m\sigma\psi(z)$  represents the attraction of a particle  $m$  placed at distance  $z$  from the plane surface of an infinite solid whose density is  $\sigma$ . The work required to carry  $m$  from  $z=0$  to  $z=\infty$  is therefore

$$2\pi m\sigma \int_0^{\infty} \psi(z) dz = m\sigma K_0,$$

by (4); so that the work necessary to separate a superficial layer of thickness  $dz$  from the rest of the mass and to carry it beyond the range of the attraction is  $\sigma^2 dz K_0$ . The complete disaggregation of unit of volume into infinitesimal slices demands accordingly an amount of work represented by  $\sigma^2 K_0$ , or  $K$ . The work required further to separate the infinitesimal slices into component filaments or particles and to remove them beyond the range of the mutual attraction is negligible in the limit, so that  $K$  is the total work of complete disaggregation.

A second law formulated by Dupré is more difficult to accept. "Pour un même corps prenant des volumes variés, le travail de désagrégation restant à accomplir est proportionnel à la densité ou en raison inverse du volume." The argument is that the work remaining to be done upon a given mass at any stage of the expansion is proportional first to the square of the density, and secondly to the actual volume, on the whole therefore inversely as the volume. The criticism that I am inclined to make here is that Dupré's theory attempts either too little or too much. If we keep strictly within the lines of Laplace's theory the question here discussed cannot arise, because the body is supposed to be incompressible. That bodies are in fact compressible may be so much the worse for Laplace's theory, but I apprehend that the defect cannot be remedied without a more extensive modification than Dupré attempts. In particular, it would be necessary to take into account the work of compression. We cannot leave the attractive forces unbalanced; and the work of the repulsive forces can only be neglected upon the hypothesis that the compressibility itself is negligible. Indeed it seems to me, that a large part of Dupré's work, important and suggestive as it is, is open to a fundamental objection. He makes free use of the two laws of thermodynamics, and at the same time rests upon a molecular theory which is too narrow to hold them. One is driven to ask what is the real

nature of this heat, of which we hear so much. It seems hopeless to combine thermodynamics with a merely statical view of the constitution of matter.

On these grounds I find it difficult to attach a meaning to such a theorem as that enunciated in the following terms\* :—  
 “La dérivée partielle du travail mécanique interne prise par rapport au volume égale l’attraction par mètre carré qu’exercent l’une sur l’autre les deux parties du corps situées des deux côtés d’une section plane,” viz. the intrinsic pressure. In the partial differentiation the volume is supposed to vary and the temperature is supposed to remain constant. The difficulty of the first part of the supposition has been already touched upon; and how in a fundamental theory can we suppose temperature to be constant without knowing what it is? It is possible, however, that some of these theorems may be capable of an interpretation which shall roughly fit the facts, and it is worthy of consideration how far they may be regarded as applicable to matter in a state of extreme cold.

With respect to the value of  $K$ , Young’s estimate of 23,000 atmospheres for water has already been referred to. It is not clear upon what basis he proceeded, but a chance remark suggests that it may have been upon the assumption that cohesion was of the same order of magnitude in liquids and solids. Against this, however, it may be objected that the estimate is unduly high. Even steel is scarcely capable of withstanding a tension of 23,000 atmospheres.

So far as I am aware, the next estimates of  $K$  are those of Dupré. One of them proceeds upon the assumption that for rough purposes  $K$  may be identified with the mechanical equivalent of the heat rendered latent in the evaporation of the liquid, that in fact evaporation may be regarded as a process of disaggregation in which the cohesive forces have to be overcome. This view appears to be substantially sound. If we take the latent heat of water as  $600^\circ$ , we find for the work required to disintegrate one gram of water

$$600 \times 4.2 \times 10^7 \text{ C.G.S.}$$

One atmosphere is about  $10^6$  C.G.S.; so that

$$K = 25,000 \text{ atmospheres.}$$

The estimates of his predecessors were apparently unknown to Van der Waals, who (in 1873) undertook his work mainly with the object of determining the quantity in question. He finds for water 11,000 atmospheres. The application of Clausius’s equation of virial to gases and liquids is obviously

\* *Loc. cit.* p. 47.



of great importance ; but, as it lies outside the scope of the present paper, I must content myself with referring the reader to the original memoir and to the account of it by Maxwell\*.

One of the most remarkable features of Young's treatise is his estimate of the range  $a$  of the attractive force on the basis of the relation  $T = \frac{1}{3}aK$ . Never once have I seen it alluded to ; and it is, I believe, generally supposed that the first attempt of the kind is not more than twenty years' old. Estimating  $K$  at 23,000 atmospheres, and  $T$  at 3 grains per inch, Young finds† that "the extent of the cohesive force must be limited to about the 250 millionth of an inch ;" and he continues, "nor is it very probable that any error in the suppositions adopted can possibly have so far invalidated this result as to have made it very many times greater or less than the truth." It detracts nothing from the merit of this wonderful speculation that a more precise calculation does not verify the numerical coefficient in Young's equation. The point is that the range of the cohesive force is necessarily of the order  $T/K$ .

But this is not all. Young continues :—"Within similar limits of uncertainty, we may obtain something like a conjectural estimate of the mutual distance of the particles of vapours, and even of the actual magnitude of the elementary atoms of liquids, as supposed to be nearly in contact with each other ; for if the distance at which the force of cohesion begins is constant at the same temperature, and if the particles of steam are condensed when they approach within this distance, it follows that at 60° of Fahrenheit the distance of the particles of pure aqueous vapour is about the 250 millionth of an inch ; and since the density of this vapour is about one sixty thousandth of that of water, the distance of the particles must be about forty times as great ; consequently the mutual distance of the particles of water must be about the ten thousand millionth of an inch. It is true that the result of this calculation will differ considerably according to the temperature of the substances compared.... This discordance does not, however, wholly invalidate the general tenour of the conclusion...and on the whole it appears tolerably safe to conclude that, whatever errors may have affected the determination, the diameter or distance of the particles of water is between the two thousand and the ten thousand millionth of an inch." This passage, in spite of its great interest, has been so completely overlooked that I have

\* 'Nature,' vol. x. p. 477 (1874). See also vol. xi. pp. 357, 374.

† Works, vol. i. p. 461.

ventured briefly to quote it, although the question of the size of atoms lies outside the scope of the present paper.

Another matter of great importance to capillary theory I will only venture to touch upon. When oil spreads upon water, the layer formed is excessively thin, about two millionths of a millimetre. If the layer be at first thicker, it exhibits instability, becoming perforated with holes. These gradually enlarge, until at last, after a series of curious transformations, the superfluous oil is collected in small lenses. It would seem therefore that the energy is less when the water is covered by a very thin layer of oil, than when the layer is thicker. Phenomena of this kind present many complications, for which various causes may be suggested, such as solubility, volatility, and—perhaps more important still—chemical heterogeneity. It is at present, I think, premature to draw definite physical conclusions; but we may at least consider what is implied in the preference for a thin as compared with a thicker film.

Fig. 13.

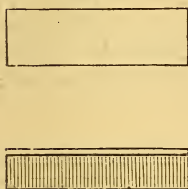


Fig. 14.

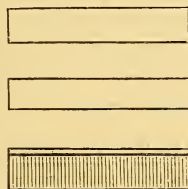
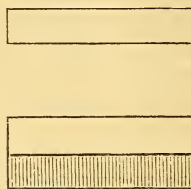


Fig. 15.



The passage from the first state to the second may be accomplished in the manner indicated in figs. 13, 14, 15. We begin (fig. 13) with a thin layer of oil on water and an independent thick layer of oil. In the second stage (fig. 14) the thick layer is split into two, also thick in comparison with the range of the cohesive forces, and the two parts are separated. In the third stage one of the component layers is brought down until it coalesces with the thin layer on water. The last state differs from the first by the substitution of a thick film of oil for a thin one in contact with the water, and we have to consider the work spent or gained in producing the change. If, as observation suggests, the last state has more energy than the first, it follows that more work is spent in splitting the thick layer of oil than is gained in the approach of a thick layer to the already oiled water. At some distances therefore, and those not the smallest, oil must be more attracted (or less repelled) by oil than by water. The reader will not fail to notice the connexion between this subject and the black of soap-films, investigated by Profs. Reinold and Rücker.

LIII. *On the Deformation of Twisted Strips.*

By G. H. BRYAN\*.

IN the March number of the Philosophical Magazine (p. 244) Professor Perry has described the behaviour of a twisted strip of metal when its ends are pulled apart, and has investigated formulæ to determine the untwisting produced. It seemed, however, that Prof. Perry's theory hardly afforded a satisfactory explanation of the phenomena, and the idea occurred to me that a better clue to the correct solution might be obtained by considering the problem as a particular case of the deformation of a thin plate. I have pursued this method in the present paper, and the results obtained will, I think, be found to agree very well with those found by experiment and described in Prof. Perry's paper.

It will be convenient to denote the breadth of the strip by  $2a$  and its thickness by  $2h$ , instead of using  $b$  and  $t$  respectively. We suppose  $h$  to be small in comparison with  $a$ , so that the strip can be treated as a thin plate. Let the strip, originally supposed plane, be twisted about its middle line into a helicoid, the twist per unit length being  $\phi$ . If we consider a fibre of the material whose distance from the axis is  $x$ , its elongation per unit length will be

$$\sqrt{(1 + x^2\phi^2)} - 1.$$

In the helicoid the lines of principal curvature will everywhere cut the generating lines at an angle of  $45^\circ$ . If  $\chi$  is the inclination to the axis of the tangent plane at the point  $x$ , we have

$$\tan \chi = x\phi,$$

$$\therefore \frac{d\chi}{dx} = \frac{\phi}{1 + x^2\phi^2};$$

whence we readily find for the principal curvatures,

$$\frac{1}{\rho_1} = -\frac{1}{\rho_2} = \frac{\phi}{1 + x^2\phi^2}.$$

We shall now make the assumption that the twist is sufficiently small to permit of our neglecting  $x^2\phi^2$ , and therefore also  $x^2\phi^2$ , *in comparison with unity*. Now  $a\phi$  is the whole angle of twist in a length of the strip equal to half its breadth, and this will certainly be small in all cases of practical interest; moreover the results which we shall obtain will fully justify our assumption. To this order of approximation the elongation

\* Communicated by the Author.

of the fibre at distance  $x$  from the axis will be

$$\frac{1}{2}x^2\phi^2,$$

and the principal curvatures will everywhere be

$$1/\rho_1 = -1/\rho_2 = \phi.$$

We now suppose that the strip is permanently twisted so that the helicoidal form may be taken as the unstrained state. We proceed to calculate the potential energy per unit length when the strip undergoes a small axial elongation  $e$  per unit length and when its twist is increased by a small amount  $\tau$ . In consequence of the lateral contraction due to longitudinal elongation, the distance of any point from the axis will be altered; let the point  $x$  thus become displaced to a distance  $x+u$  from the axis. To our order of approximation, the strains in the middle surface will be

$$\sigma_1 = \frac{du}{dx}, \quad \varpi = 0;$$

$$\sigma_2 = e + \frac{1}{2}x^2\{(\phi + \tau)^2 - \phi^2\} = e + x^2\phi\tau;$$

while, for the changes of curvature,

$$\delta\left(\frac{1}{\rho_1}\right) = -\delta\left(\frac{1}{\rho_2}\right) = \tau,$$

the directions of principal curvature being unaltered. Thus the usual expressions\* give for  $W$ , the total potential energy due to stretching and bending, per unit length of the strip,

$$W = \frac{E}{1-\mu^2}h \int_{-a}^a \left\{ \left(\frac{du}{dx}\right)^2 + 2\mu \frac{du}{dx} (e + x^2\phi\tau) + (e + x^2\phi\tau)^2 \right\} dx$$

$$+ \frac{4}{3}nh^3 \int_{-a}^a \tau^2 dx;$$

where  $E$  denotes Young's modulus,  $n$  the simple rigidity, and  $\mu$  Poisson's ratio.

Since there is no force acting perpendicular to the axis of the strip, we have by variation of  $u$ ,

$$0 = \delta W = \frac{Eh}{1-\mu^2} \int_{-a}^a 2 \left\{ \frac{du}{dx} + \mu(e + x^2\phi\tau) \right\} \frac{d\delta u}{dx} dx;$$

\* Basset finds that the potential energy also contains terms depending on the stretching of the middle surface and involving the cube of the thickness. These can, however, in the present case, be safely neglected in comparison with the corresponding terms involving the first power of the thickness. It is different with the terms depending on bending, as bending may be large in comparison with the stretching.



therefore

$$\frac{du}{dx} = -\mu(e + x^2\phi t);$$

whence

$$\begin{aligned} W &= Eh \int_{-a}^a (e + x^2\phi\tau)^2 dx + \frac{4}{3} nh^3 \int_{-a}^a \tau^2 dx^* \\ &= 2Eha \left( e^2 + \frac{2}{3} a^2\phi\tau e + \frac{1}{5} a^4\phi^2\tau^2 \right) + \frac{8}{3} nh^3 a\tau^2. \end{aligned}$$

Let  $w$  be the axial tension,  $G$  the couple about the axis required to produce the deformation. Then evidently,

$$\frac{dW}{de} = w, \quad \frac{dW}{d\tau} = G.$$

In the experiments described by Prof. Perry,  $G=0$ , and  $\tau$  is the quantity observed. We therefore have

$$0 = \frac{dW}{d\tau} = 2Eah \left( \frac{2}{3} a^2\phi e + \frac{2}{5} a^4\phi^2\tau \right) + \frac{16}{3} nh^3 a\tau,$$

$$w = \frac{dW}{de} = 2Eah \left( 2e + \frac{2}{3} a^2\phi\tau \right).$$

Eliminating  $e$ , we find

$$w = -\tau \times 16ha^2 \left( \frac{1}{15} Ea\phi + n \frac{h^2}{a^2} \cdot \frac{1}{a\phi} \right).$$

Writing  $\theta = -\tau$ , so that  $\theta$  measures the *untwisting* per unit length, this gives

$$\theta = \frac{w}{16ha^2 \left( \frac{1}{15} Ea\phi + n \frac{h^2}{a^2} \cdot \frac{1}{a\phi} \right)},$$

the required formula for  $\theta$ .

When  $a\phi$  is exceedingly small the formula gives

$$\theta = \frac{wa\phi}{16nh^3},$$

which agrees with Prof. Perry's result.

The value of  $\theta$  soon, however, attains a maximum as  $\phi$  is increased. This will be the case when

\* The first term of this expression might have been written down at once by considering the elongation of the fibres of the strip when pulled out, while the second term follows immediately by taking the same expression for the torsional rigidity as that assumed by Perry. On the whole I think the method here given is preferable, as it involves fewer assumptions, and shows more fully within what limits we may consider the results as approximately correct.

$$a^2\phi^2 = \frac{15n}{E} \frac{h^2}{a^2} = \frac{15}{2(1+\mu)} \frac{h^2}{a^2},$$

or

$$a\phi = \frac{h}{a} \sqrt{\left\{ \frac{15}{2(1+\mu)} \right\}}.$$

The square root in this expression is equal to  $2\frac{1}{4}$  if  $\sigma = \frac{13}{27}$ , and is equal to  $2\frac{1}{2}$  if  $\sigma = \frac{1}{5}$ ; hence for ordinary substances it is intermediate between  $2\frac{1}{4}$  and  $2\frac{1}{2}$ . We see that if the strip is thin, so that  $h$  is small compared with  $a$ , the above value of  $a\phi$  will be small. This shows that the maximum value of  $\theta$  will occur well within the limits in which our approximation is valid.

This maximum value is

$$\begin{aligned} \theta &= \frac{w}{32h^2a} \sqrt{\left( \frac{15}{nE} \right)} \\ &= \frac{w}{32nh^2a} \sqrt{\left\{ \frac{15}{2(1+\mu)} \right\}}. \end{aligned}$$

In order that the strip may be sensitive,  $\theta$  must be large for a given value of  $w$ . If the area  $4ah$  of the cross section be kept constant, this result may be brought about by making  $h$  as small as possible, and this fact affords a further justification of the present method of treatment.

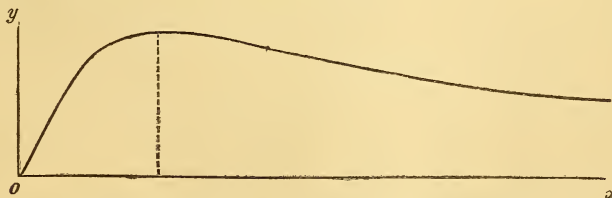
When  $\theta$  is approaching the maximum, its rate of increase will of course become less rapid, and after this maximum has been passed,  $\theta$  will diminish still more slowly than it increased. Thus if we call  $\theta'$  the maximum value of  $\theta$  and  $\phi'$  the corresponding value of  $\phi$ , the relation between  $\theta$  and  $\phi$  may be written

$$\frac{\theta}{\theta'} = \frac{2}{\phi/\phi' + \phi'/\phi}.$$

This relation may be exhibited graphically by tracing the cubic curve

$$y = \frac{2x}{x^2 + 1},$$

where  $x = \phi/\phi'$ ,  $y = \theta/\theta'$  (see figure).



The greatest negative value of  $dy/dx$  is  $-\frac{1}{4}$  and occurs when  $x = \sqrt{3}$ , while when  $x=0$  we have  $dy/dx=2$ . This

shows that the greatest rate of decrease of  $\theta$  after passing the maximum is only  $\frac{1}{5}$  of its initial rate of increase.

$$\text{When } \phi = \frac{1}{2}\phi' \text{ or } = 2\phi', \quad \theta = \frac{4}{5}\theta';$$

$$\text{when } \phi = \frac{1}{3}\phi' \text{ or } = 3\phi', \quad \theta = \frac{3}{5}\theta';$$

and if  $\phi$  be further increased beyond  $3\phi'$ , the rate of diminution of  $\theta$  will become less and less rapid.

We also notice that the maximum value of  $\theta$  is inversely proportional to  $ah^2$ , thus agreeing pretty closely with the results of Prof. Perry's first experiments.

When  $\phi$  is large compared with  $\phi'$  my formula gives approximately

$$\theta = \frac{15w}{16Eh\omega^3\phi}.$$

Owing, however, to our assumption that  $a\phi$  is small compared with unity, little value can be attached to this result. It can only hold if the strip is very thin indeed, and  $a\phi$  is a small quantity intermediate in order of magnitude between  $h/a$  and unity.

Cambridge, September 1890.

#### LIV. *Motion of Atoms in Electric Discharges.*

By JOHN TROWBRIDGE\*.

THE application of spectrum analysis to the measurement of the approach or recession of a star in a direction directly away or directly toward an observer's eye is generally regarded as one of the greatest achievements of modern science. Experiments upon the oscillating discharge of electricity led me to reflect whether the method which has been used in star-observation might not be employed to test the question whether the atoms of the metals of the terminals between which the oscillating discharge passes are conveyed to and fro by the oscillating discharge, or whether they are shaken, so to speak, by the discharge so that they emit to the æther the ripples which appeal to our senses as light and heat. No mention is made here of a convection effect, which would take place too slowly to give a spectroscopic effect.

After I had made the experiments which I will shortly describe, and while I was in doubt whether to publish my results, a paper by Professor J. J. Thomson, director of the Cavendish Laboratory, Cambridge, England, appeared in the

\* Communicated by the Author.

August number of the Philosophical Magazine (1890), "On the Velocity of the Transmission of Electric Disturbances," which contains the following passage:—

"The very rapid rate with which the electric discharge is propagated through a rare gas compels us to admit that the electricity is not carried by charged atoms moving with this velocity. For if it were, then if the discharge were to take place in air at atmospheric pressure between two parallel plates one centimetre apart, charged to a potential difference of approximately 30,000 volts, the kinetic energy which would have to be communicated to the atoms to make them move with this velocity would be greater than the original potential energy of the charged plates, assuming that the charge on each atom is that deduced from electrolytic considerations."

The unusual dispersion afforded by a Rowland concave grating led me to test this hypothesis in as far as it relates to the question, Are the molecules of metals carried with the oscillations of electricity from terminal to terminal between which the oscillations take place?

A circuit of wire giving a suitable value of self-induction was arranged in connexion with a series of Leyden jars. The time of oscillation was calculated from the well-known formula  $t = 2\pi\sqrt{LC}$ , in which  $L$  is the value of the self-induction of the circuit,  $C$  the capacity of the Leyden jars. Preliminary examination of the electric spark taken through this circuit with a revolving mirror showed that the discharge was an oscillatory one. Two different values of self-induction were employed. One gave the duration of a double oscillation  $t = \cdot 0000003$  of a second, the other gave  $t = \cdot 0000024$  of a second.

If we denote by  $V$  the velocity of light,  $-\lambda$  and  $\lambda$  wavelengths,  $S$  the speed of approach of the atom, we shall have

$\lambda = \left( \frac{V}{V+S} \right)$ . The distance across which the oscillations took

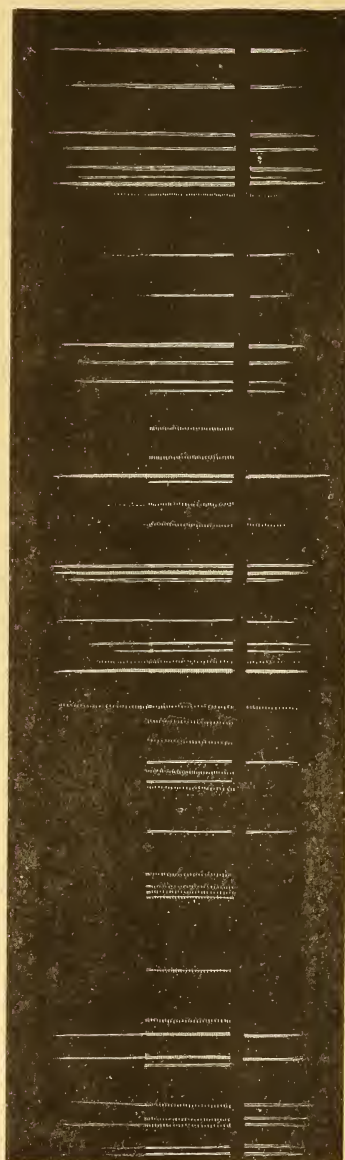
place is 6 millimetres. Calculation shows that if the iron atoms were conveyed to and fro between the terminals, a broadening of the iron lines in the spectrum would result which could be readily detected. The broadening might amount to a space equivalent to a whole tenth-metre.

The oscillating spark passed between two iron terminals. One of these terminals was hollow. The hollow terminal was placed in a line perpendicular to the slit of the spectroscope, so that the oscillation of the spark should be toward and away from the slit. If therefore the iron atoms moved to and fro with the oscillations of electricity across the air-gap, a dis-



Oscillations  
of spark  
perpendi-  
cular to slit.

Oscillations  
of spark  
parallel  
to slit.



placement of the iron lines in the spectrum of the metal would result. There would be both a displacement toward the less refrangible end caused by the recession of the atom, and one toward the more refrangible end of the spectrum caused by the approach of the atom. The great amount of dispersion afforded by a concave grating of 20,000 lines to the inch enabled me to easily detect a movement equivalent to a tenth-metre. I accordingly took a photograph of the iron lines with the terminals in the position I have described, and on the same plate immediately above this photograph a comparison photograph was taken with the terminals paral-  
lled to the slit. In this case the iron atoms did not make their supposed excursions away and toward the slit, and therefore no displacement of the spectrum-lines was to be expected.

The photographic plate was exposed in the neighbourhood of the great H-lines. A movable shutter enabled me to expose different portions of the same plate without changing any adjustments of the apparatus. The resulting photographs showed no displacement of the iron-lines. The iron-lines in the two photographs met exactly (continued in an unbroken line across the double photograph), and were of the same breadth throughout their extent (see figure).

The conclusion seems to be a strong one that the electrical oscillations do not carry the atoms of metals with them—in spark-discharges. The atom is merely shaken up and caused to emit the vibrations or subsidiary ripples which appeal to our senses as light and heat, while the electrical waves pass on without conveying the atoms.

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LV. *The Greater Influence of First Quantities of Electrolytes on Volta-Electromotive Force.* By Dr. G. GORE, F.R.S.\*

IN thermochemical research, Favre and others observed that, on adding equal quantities of water in succession to a fixed amount, either of nitric or sulphuric acid, the quantity of heat evolved was greater with the first than with any succeeding dilution (Watts's 'Dictionary of Chemistry,' vol. iii. p. 310); and similar effects were noticed by J. Thomsen on diluting concentrated hydrochloric, hydrobromic, and hydriodic acids. Nicol has observed that the total contraction of volume of a saline solution increases with the proportion of dissolved salt, and that each successive equivalent weight of the salt produces less contraction. Kohlrausch and others

\* Communicated by the Author.

have also shown that very minute proportions of dissolved acids, salts, &c. exercise a relatively great influence upon the electric conduction-resistance of pure water; and I have found "that a much greater increase of electromotive force is usually caused by the first amount of substance added to the water than by the subsequent amounts" ("On a New Method and Department of Chemical Research," *Phil. Mag.* May 1890, p. 421), and have given a number of instances. According to the researches of M. Lindeck also (*Ann. Phys. Chem.* [2] vol. xxxv. pp. 311-331), whilst the first portion of zinc added to mercury increases its electromotive force in electrolytes, further additions have scarcely any effect.

In the present research I have extended the inquiry, and have not only examined the effect of adding equal quantities in succession of acids and salts to a fixed amount of water, but of water to fixed amounts of acids and salts, and of bases to acids, upon the electromotive force of a simple voltaic couple immersed in the water at ordinary atmospheric temperatures. The electromotive force was measured by the method of balance, with the aid of a suitable thermoelectric pile of iron and German silver (see *Proc. Birm. Phil. Soc.* vol. iv. p. 130; 'The Electrician,' 1884, vol. xii. p. 414), and a differential astatic galvanometer having 50 ohms' resistance in each coil.

In consequence of the following circumstances very little error or inconvenience was caused by polarization:—(1) all the measurements were made at the null-point, when no perceptible current was passing; (2) by experience in working, the null-point could be almost instantly attained; (3) the metals were only immersed during a very short period of time; (4) the positive metal was cleaned each time before immersion; (5) the platinum was washed each time, and heated to redness occasionally; and (6) to test whether the energy of the couple remained unchanged, it was occasionally balanced in distilled water by a similar freshly prepared one in distilled water.

The relatively great increase of electromotive force with a zinc-platinum couple, on adding the first unit quantity of chlorine, bromine, iodine, hydrochloric, hydrobromic, hydriodic, nitric, and sulphuric acid, and the chlorides, bromides, iodides, and sulphates of potassium and sodium, and certain other salts, to a fixed amount of water, have already been shown in the paper referred to (*Phil. Mag.* May 1890, p. 421).

The similar large effects upon a cadmium-platinum couple in the reverse process of adding the first unit quantity of water to a fixed amount of hydrochloric, sulphuric, and nitric acid are shown by the following curves. The electromotive force

of the couple in distilled water at  $20^{\circ}$  C. was  $\cdot 85$  volt. The constant difference or unit quantity of water added to each acid was  $89\cdot 1$  grains. In order to obtain more reliable results, and to make the conditions more alike, and to obtain curves more comparable with each other, each acid was so far diluted previous to adding the first unit quantity of water as to contain one equivalent weight proportion, in 100ths of a grain of absolute acid, in 18 grains of water ; for instance, the starting-point solution of hydrochloric acid contained  $\cdot 365$  grain of HCl in that amount of water.

The electromotive force of the couple in pure concentrated hydrochloric acid containing  $5\cdot 81$  grains of HCl per cubic centimetre at  $15^{\circ}\cdot 6$  was  $1\cdot 235$  volt ; in pure concentrated sulphuric acid it was  $1\cdot 278$  ; and in pure concentrated nitric acid it was  $1\cdot 477$  volt, each at  $20^{\circ}\cdot 5$  C. These electromotive forces, especially that of nitric acid, are much less accurate than those obtained with the same acids when diluted as above.

Fig. 1.

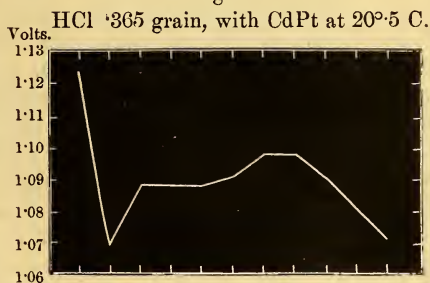


Fig. 2.

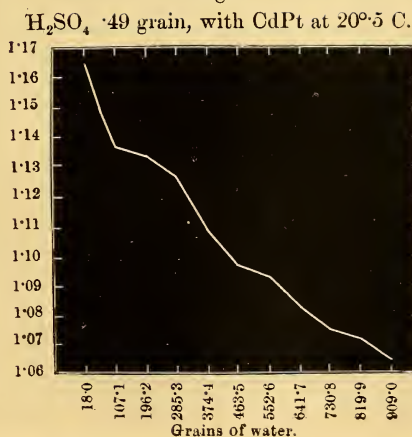
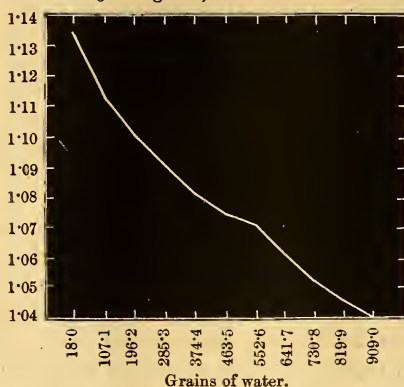




Fig. 3.

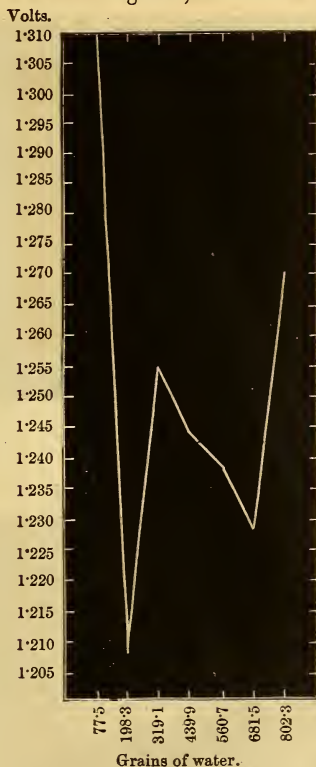
 $\text{HNO}_3$  .63 grain, with CdPt at  $21^\circ \text{C}$ .

On examining these curves, the greater effect of the first unit quantity of water added to the acid than the succeeding ones is distinctly visible in each case. On comparing them with those obtained by adding unit quantities of the same acids to water (Phil. Mag. May 1890, p. 421), we find that the greater effects of the first added unit quantities of acid were much more conspicuous than those of the first added unit quantities of water; and that whilst the first quantities of acids added to water increased the electromotive force, the first quantities of water added to acids decreased it. The less conspicuous effects produced by adding water to acids than by acids to water, were probably due to the circumstance that the acids had each been already largely diluted, about 30 to 50 times their weight, before adding the first units of water to them. In confirmation of this statement, I have found by experimental measurements that both with hydrochloric and with sulphuric acid the greater influence of the first added unit of water was more conspicuous when the acids were less diluted beforehand.

The results obtained with these three acids indicate that the greater influence of the first added unit quantity of water is not limited to water added to absolute acid, but extends to that added to acid already considerably diluted, and therefore the property under consideration is a more general one.

I have similarly examined the effect of adding successive unit quantities of water to a saturated aqueous solution of potassium chloride, containing 25.0 grains of the salt in 77.5 grains of water, upon the electromotive force of a zinc-platinum couple. The annexed curve shows the results:—

Fig. 4.—KCl 25 grains, with ZnPt at 21° C.



The greater effect of the first added unit quantity is in this case also clearly manifested.

With the object of arriving at some idea of the relative amounts of effect of the first and last unit portions of potassium chloride added to water, and to obtain a complete curve of electromotive force of that salt in water, the degrees of electromotive force with a zinc-platinum couple were measured, using five series of aqueous solutions of the salt, comprising the entire range from water to a saturated solution. In order also to show the manifest effect of an extremely minute quantity in the first addition, and not to extend the entire curve to an extraordinary length, it was found necessary to divide the entire range into five sections, and to increase the magnitude of the unit quantity to ten times its amount in each successive section; the unit quantities added, therefore, are 10,000 times larger in the last section than in the first one.

Fig. 5.—Potassium Chloride, with ZnPt at 24° C. Unit quantity = 1.

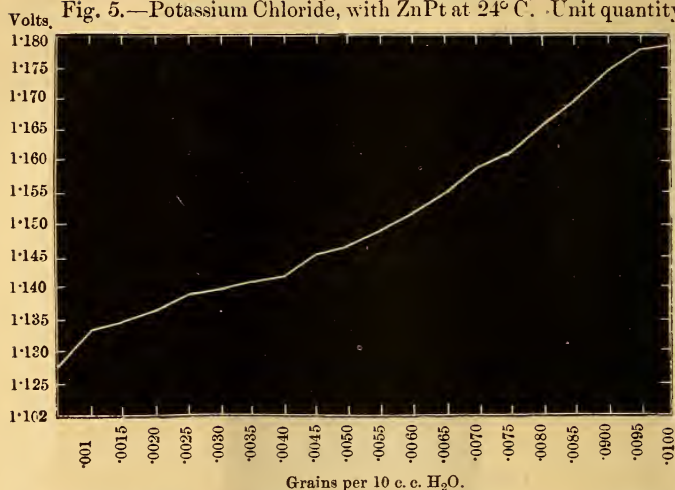


Fig. 6.—Potassium Chloride, at 23° 5 C. Unit quantity = 10.

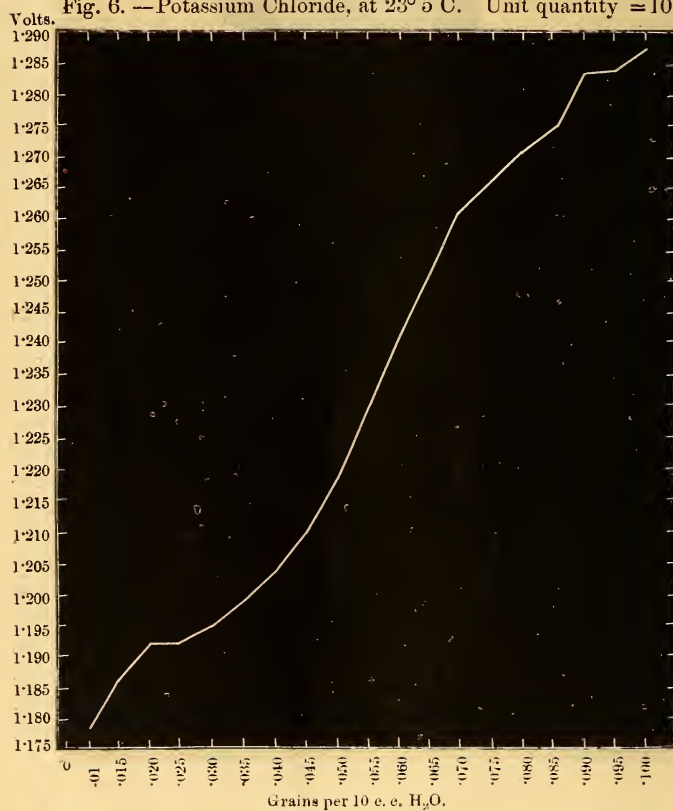


Fig. 7.

Potassium Chloride, at 15° C. Unit quantity = 100.

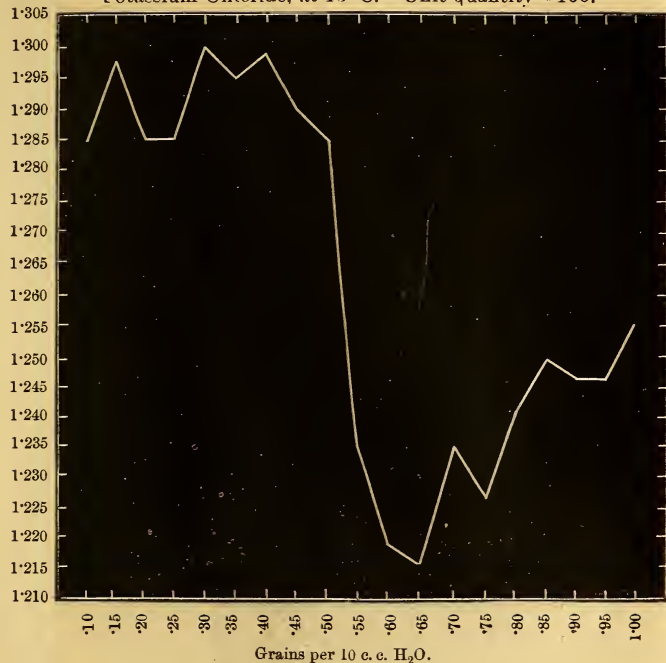


Fig. 8.

Potassium Chloride, at 21°·5 C. Unit quantity = 1000.

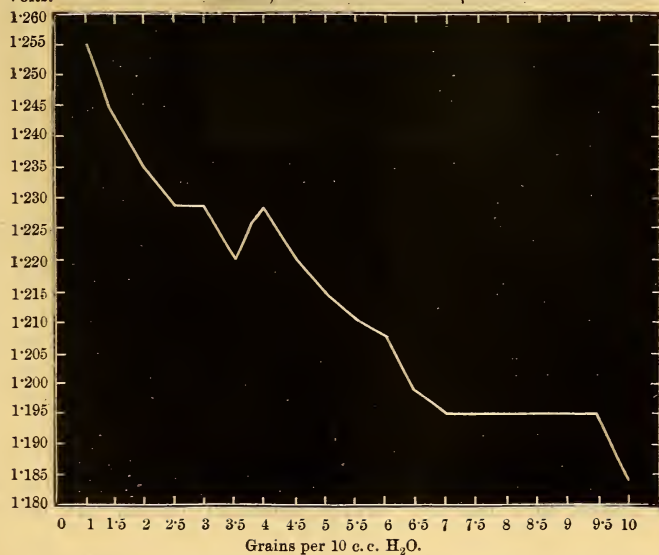
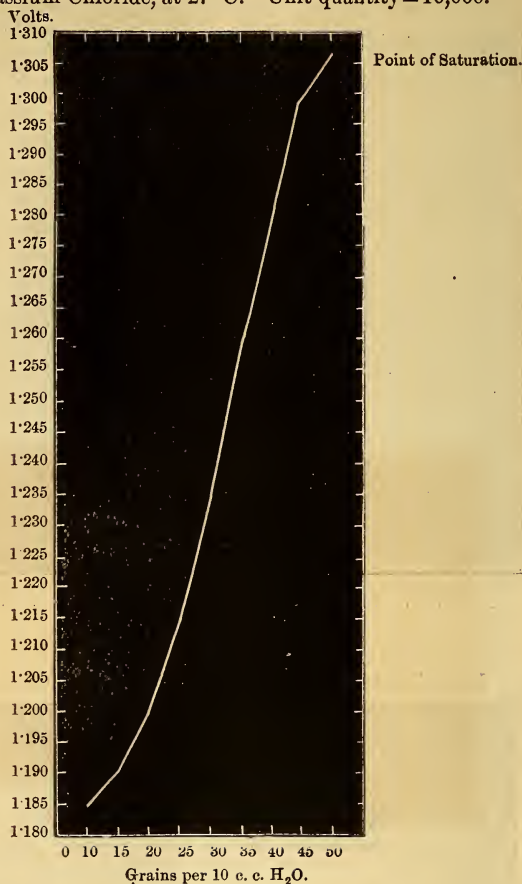




Fig. 9.

Potassium Chloride, at 27° C. Unit quantity = 10,000.



These curves and numbers show that increasing the unit quantity of salt added from .0005 grain in the first section to 5 grains or 10,000 times the amount, in the last one, only produced about 5.27 times the amount of average difference of electromotive force, and therefore the addition of the same weight (*i. e.* .0005 grain) had only about one 1897th part of the average effect upon the electromotive force in the series of strong solutions that it had in the weak ones.

In all these cases the phenomenon was produced, either by increasing the degree of dilution or that of concentration of the liquid, and not by strong chemical union. In order

therefore to ascertain whether the same effect occurred when two electrolytic substances united chemically together I made two experiments, in each of which the combined influences of dilution and strong chemical union cooperated together. I took in each experiment the same fixed quantity of the same mixture of  $\cdot 365$  grain of hydrochloric acid and 18 grains of water as before, and added to this diluted acid four unit quantities in succession of a mixture of  $\cdot 088$  grain of  $\text{NaC}_2\text{O}_3$  and 89.1 grains of water in one experiment, and  $\cdot 115$  grain of  $\text{K}_2\text{CO}_3$  and 89.1 grains of water in the other. The total quantity of alkali added in each experiment was just sufficient to neutralize two thirds of the acid. The following curves show the results :—

Fig. 10.

$\text{HCl} + \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$ ,  
with CdPt at  $19^\circ \text{C}$ .

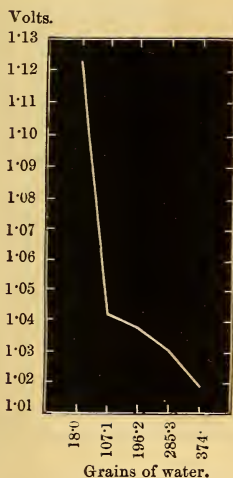


Fig. 11.

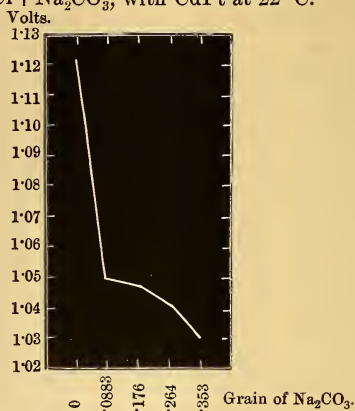
$\text{HCl} + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ ,  
with CdPt at  $19^\circ \text{C}$ .



These curves show distinctly, 1st, the greater degree of influence of the first unit quantity of substance added than that of the succeeding one, and prove the existence of the same phenomenon in cases of strong chemical union; and, 2nd, that strong chemical union *increased* the magnitude of the phenomenon.

To determine the influence upon the phenomenon of strong chemical action alone, apart from that of dilution, I made a precisely similar experiment to the last one, but employing anhydrous carbonate of sodium and omitting the unit quantities of water. The following curve represents the results :—

Fig. 12.

HCl + Na<sub>2</sub>CO<sub>3</sub>, with CdPt at 22° C.

The greater effect of the first unit quantity of the anhydrous alkali is quite conspicuous, and is about equal in magnitude to that of mixed soda and water in the immediately previous experiment. The amount of such effect, however, obtained with the first unit quantity of mixed soda and water was not equal to the united amounts of first effect of dry soda and that of water alone (see curve, fig. 1).

I have found the same effect with dilute hydrochloric acid and the anhydrous carbonates of lithium, sodium, potassium, rubidium, barium, strontium, calcium, magnesium, zinc, and cadmium; with dilute sulphuric acid and the carbonates of rubidium, potassium, sodium, magnesium, zinc, and cadmium; with dilute nitric acid and the carbonates of sodium and potassium; with dilute hydrochloric, hydrobromic, and hydriodic acids, and carbonate of sodium; ditto with the carbonates of calcium and cadmium. In no case has an exception been observed.

The curves of electromotive force obtained in this research and in the one referred to (Philosophical Magazine, May 1890, p. 421) support in greater or less degree the general conclusion, that *when successive equal quantities of one electrolyte are added to a fixed and much larger quantity of another, the first added quantity has usually a much greater effect than any of the immediately succeeding ones in altering the amount of electromotive force of a voltaic couple, and consequently also in altering that of all other properties inseparably related to it.*

This conclusion is further supported by the facts already mentioned, viz., 1st, that on adding equal quantities of water

in succession to a fixed amount of either nitric, sulphuric, hydrochloric, hydrobromic, or hydriodic acid, the largest amount of heat is evolved by the first quantity added; 2nd, by the diminishing amount of contraction which usually occurs on adding successive equal portions of a salt to water; and, 3rd, by the circumstance that on adding equal quantities in succession, either of an acid or a salt, to water, the electric conduction-resistance is much more largely diminished by the first quantity added than by any of the succeeding ones.

It is evident from these considerations that the property in question, which I may term "*the greater influence of first quantities*," is a very general one of electrolytes, and that the four several phenomena mentioned are instances of it, and are probably results of one common cause. The method of examining this property by means of variations of electromotive force is very convenient, and the curves thus obtained implicitly contain more detail of information than those obtained by thermal measurements, because they represent more perfectly integrated effects.

The relatively greater increase of electric conductivity by addition of the first unit quantity of acid or salt than by any succeeding one, has been explained by the theory of dissociation; but it is also consistent with the simple mechanical view that the molecules of the first added unit of the dissolved substance have greater freedom and velocity of motion; the relatively greater electromotive force under those conditions is also consistent with this idea. The increase of electromotive force by addition of acid to water, and its decrease by addition of water to acid, admit of a very simple explanation. The degree of electromotive force depends partly upon the average velocity of the molecules of the liquid. Strong acids possess greater molecular velocity and excite greater electromotive force than water. By admixture of the acid and water heat is evolved and the average molecular velocity of each uniting substance is diminished. When we add a little water to a large amount of acid, the average molecular velocity of the mixture is less than that of the acid, first, because water has less molecular velocity than the acid, and, second, because heat is set free and molecular motion is lost. But when we add a little acid to a large quantity of water, the average molecular velocity of the mixture is greater than that of water, because the molecular velocity of the acid is so much greater than that of water that it more than compensates for the loss of motion which occurs in the form of heat during the act of mixing.



LVI. *On the Magneto-Optical Generation of Electricity.**By* PROFESSOR A. GRAY, M.A.\*

IN the October number of the Philosophical Magazine is an article describing some experiments made by Dr. Samuel Sheldon on the magnetic effect of rotation of the plane of polarization of a beam of light transmitted through a helix of wire. Several years ago I made some experiments on this subject myself without obtaining any result; and since coming to the University College of North Wales, I have resumed the investigation without obtaining any decisive indication of the effect of which I was in search. My method of proceeding was, however, quite different from that of Dr. Sheldon, and failed, I feel sure, simply through the inadequacy of my arrangements for the detection of what can never be more than an exceedingly small magnetic force. But before describing my own experiments, I wish to refer to one or two of the statements which Dr. Sheldon makes. After describing the direct experiment of the rotation of the plane of polarization of a beam of plane-polarized light by the creation of a magnetic field, he says:—

“Now if a difference of potential, under these conditions, produces such a rotation of the plane, why should not a rapid rotation of the plane under exactly the same conditions produce an inverse difference of potential between the terminals of the coil? A continuous rotation should produce a continuous current of electricity, and an oscillating of the plane an alternating current. The experiments which have been performed verify the latter supposition.”

Dr. Sheldon then proposes to produce the “continuous rotation” of the plane of polarization by rotating the polarizing prism, but abandons the idea on account of the difficulty of producing and maintaining a sufficiently high angular velocity to give any observable effect, and substitutes oscillation of the Nicol for continuous rotation. It seems to me that the notion that “a continuous rotation should produce a continuous current of electricity” involves a fallacy which it may be desirable to point out.

When a ray of plane-polarized light is subjected to the action of a magnetic field the lines of force of which are parallel to the direction of propagation of the beam, the plane of polarization changes in the medium to a twisted surface. If the medium be quite uniform, the surface has a uniform twist from one face to the other of the stratum of substance

\* Communicated by the Author.

across which the light is propagated. Calling  $\theta$  the angle which the plane of polarization of the incident light makes with that of the emergent light, and  $d$  the thickness of the medium, the twist is numerically  $\theta/d$ . The greater the intensity of the field in the medium the greater is this twist.

Now consider the inverse experiment proposed by Dr. Sheldon. The field is non-existent, to begin with; but a beam of plane-polarized light produced by a Nicol prism is passed along the axis of a helix, the ends of which are joined so that the circuit is closed. The Nicol is then set into rotation continuously in one direction. Clearly a twist will be given to the plane of polarization depending on the velocity of rotation. If  $v$  be the velocity of light, the time taken by the beam to penetrate the medium is  $d/v$ ; and if  $\omega$  be the angular velocity of the polarizing prism, the twist given will be the angle turned through in this time divided by the thickness, that is  $\omega/v$ .

But so long as  $\omega$  is constant this twist is constant, and the surface simply turns *as a whole* in the medium with angular velocity  $\omega$ . I do not think the latter motion can produce any magnetic effect whatever. A magnetic field may perhaps be, and I should say probably is, produced when the twist is created by the setting of the Nicol into rotation, and annulled when the Nicol is stopped. For a continuous current a continuous flux of magnetic induction through the coil would be necessary, and this could only be produced by increasing the twist of the surface, that is by continually increasing the angular velocity of rotation. What is to be looked for therefore is an induced current when the Nicol is started, and an opposite current when it is stopped; in the interval there will exist with constant rotation a constant field, and the current will be zero.

If Dr. Sheldon's idea were correct, continuous rotation of the Nicol prism would produce a continually increasing field-intensity within the coil, and thus as intense a field as might be named could be produced by only driving the Nicol long enough. Or, again, an action on the magnetic field which twists the plane of polarization in the direct experiment would be produced by merely rotating the substance round an axis in the direction of the magnetic force.

With regard to the oscillation experiments, it seems possible that by this method the effect looked for may be obtained, as the twist of the plane of polarization changes sign at each swing of the polarizer. But in the account of his experiments given by Dr. Sheldon, there is nothing to show that the "sizzling" in the telephone which might be produced by the moving machinery was not mistaken for the magneto-optic

effect. The proper precaution for this was of course the screening off of the light while the machinery was kept going, and the circuit &c. the same as before. If, then, the sound ceased, the inference would be that the disturbance in the telephone was caused by the motion of the beam of light.

My own experiments were made to test a conclusion I had come to, that the passage of a beam of circularly-polarized light along the axis of a solenoid, included in the circuit of a sensitive galvanometer, would, by instituting a magnetic field, cause an induced current to flow in one direction in the circuit, and the quenching of the beam by annulling the field would cause an induced current to flow in the opposite direction. I therefore produced a beam of circularly-polarized light, and tried the effect of introducing and removing a screen, by which the light was alternately cut off from the coil and allowed to pass through it. As I have stated, on neither of the two occasions on which I made these experiments did I find the introduction or the removal of the screen produce any effect. The failure, I am certain, was due to the utter inadequacy of my apparatus to detect the effect of the extremely feeble magnetic field produced. It might be possible perhaps to detect the effect looked for by improved arrangements, employing as powerful a coil and as intense a beam of light as possible, alternately cutting off and restoring the light by a rapidly rotating perforated screen, and using in the circuit of the coil a telephone instead of a galvanometer.

My conclusion that such a field would be produced I was glad to find corroborated by an investigation in Prof. J. J. Thomson's 'Applications of Dynamics to Physics and Chemistry' (p. 77), where it is shown that a circularly-polarized beam of strong sunlight ought to produce a magnetic field of intensity not greater than  $2 \times 10^{-18}$  C.G.S. units. Prof. Thomson states that this is much too small to be detected by experiment. It seems to me just possible that the above mode of experimenting might show some result; at any rate the plan may be worthy of a trial.

A similar mode of experimenting might be used, I think, to test whether the twisting of the plane of polarization of ordinary plane-polarized light produces any magnetic effect. Supposing the substance (for example, a bar of heavy glass, or a tube containing carbon disulphide) placed along the lines of force between the poles of an electromagnet with perforated pole-pieces for Faraday's magneto-optic experiment, and surrounded with a coil in circuit with a sufficiently sensitive galvanometer, any reaction on the field produced by the twisting of the plane of polarization would be shown by an induced



current in the coil, in one direction when the beam was sent along the specimen, and in the opposite direction when the beam was interrupted. If the effect were too small to be detected by a galvanometer in this way, perhaps it might be found by alternately interrupting and restoring the beam by a rapidly rotating perforated screen, and listening for sound in a telephone included in the circuit of the coil.

LVII. *On the General System of Winds on the Earth.*

By WERNER VON SIEMENS.\*

IN the May number of the *Meteorologische Zeitschrift* there is a paper by Dr. Sprung, entitled "On the Theories of the General System of Winds on the Earth," in which the calculations of the direction and strength of general currents of air set forth in my communication to the Academy, of the 4th March, 1886, "On the Conservation of Energy in the Earth's Atmosphere"†, are critically compared with Ferrel's old theory. This paper induces me to make the following observations which, however, are not directed against Dr. Sprung's objections to the strict validity of the results of my calculations, which objections are to a certain extent quite just, but against the supposition that I have attempted, like Ferrel, "to found on theoretical calculations a theory of the general system of winds on the earth." Apart from not considering myself a sufficient adept in mathematics, I may say that I consider this method altogether inappropriate. So very complicated a problem as that of the general system of winds cannot possibly be constructed *à priori* on the basis of mathematical calculations, as up to now no simple basis has been found underlying all the phenomena. In my treatment "Of the Conservation of Energy in the Earth's Atmosphere," I first sought to determine the forces which produce, maintain, and retard the motion of the air, and then to find by calculation the direction and magnitude of the general motion of the air induced by their combination. It is therefore not correct "that I sought like Ferrel to demonstrate by means of calculation an original state of atmospheric motion in order afterwards to base my further speculations thereon." Nor is it correct that I have taken no account in my calculations of the retardation of the motion of the air through friction, for

\* Translated from the *Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin*, 1890, xxx., by E. F. Bamber. Communicated by the Author.

† Phil. Mag. vol. xxi. 1886, p. 453.



the meridional flow of air, very appropriately called "main circulation" by Dr. Sprung, on which my theory of the the general system of air-currents is based, depends exactly on the balance between the upward acceleration of the air in the equatorial regions caused by the heating of the lowest strata through solar radiation, and the loss of energy which the air in motion suffers during its circulation. This main circulation has in the course of thousands of years brought about an admixture of masses of air, which without it would have rotated with the surface of the earth on which they rest. I only made use of the mathematical idea of an instantaneous frictionless admixture of the strata of air of all latitudes, to determine in a simple manner the direction and magnitude of the motion which has existed since remote antiquity. Ferrel does not start, as I do, from a main circulation which continually interchanges the strata of air rotating with the velocity due to their latitude, and thereby gradually intermixes them, but brings about this admixture through a frictionless displacement in the meridional direction of the rotating rings of air of the different latitudes in a manner not very clearly explained. We have here essentially the same basis of calculation as that underlying my idea of an admixture, and Ferrel's and my calculation are therefore the same in result as regards the direction of the currents of air; on the other hand, we differ essentially in our statements of the relative strength of the wind north and south of the 35th degree of latitude. I am quite of Dr. Sprung's opinion that neither of the two theories can be considered quite correct. I look upon mine indeed as nothing more than a first approximation to the truth. And so in my calculations I have not taken into consideration such complicating influences as the diminution of temperature towards the poles, and the non-coincidence in direction of centrifugal force and gravity. The latter fact, the effect of which is also proved by the consideration that the mass of air rotating in the higher latitudes must everywhere have a tendency to continue moving in the greatest circles, and therefore to strive to reach the equator, would bring about a diminution in the pressure of the air with approach to the poles, and would therefore essentially prejudice the result of the calculation of the admixture, if this tendency were not compensated by other forces having an opposite effect. It is not, however, these but other fundamental assumptions which determine a very great difference between the two conceptions and lead to very different results. One of them is the assumption by Ferrel that the so-called law of areas in the form of the conservation of the moment of inertia

holds good for the displacement of the air rotating with the earth's surface in a meridional direction. To this I cannot agree, but, on the contrary, must deny that the conservation of the moment of inertia comes into play in the motion of the air.

This law of areas, taken from astronomy, states that a mass which rotates freely about another describes equal areas in equal times. This is due to the acceleration of the rotating mass as it approaches and its retardation as it recedes from the centre of attraction of the fixed mass. The greater velocity acquired by acceleration results in the description of a larger arc in the unit of time, and so leads to the law of areas. According to Ferrel a quantity of air rotating in any latitude with the earth's surface cannot travel in the direction of the meridian with an invariable absolute velocity, and therefore with a constant *vis viva* as I assume it to do, but its moment of inertia must remain constant, which corresponds to a considerable change of velocity. In order that the moment of inertia may remain constant (which is the case when the linear velocity of the rotating body varies so that equal areas are described by it in equal times), a considerable amount of energy must be expended to produce the alteration in the velocity of the inert mass of air. But there is no force whatever available to perform this work. If the radius of rotation of a rotating solid body is shortened, the force which produces the shortening must overcome the centrifugal force. The sum of the products of all the centrifugal forces into the paths traversed gives the work expended in the acceleration of the rotating mass, and this exactly suffices to maintain the law of areas, that is, in this case the moment of inertia constant. But no analogous relations exist in the case of the motion of the air on the earth's surface, where no alteration in the force of attraction is caused by the tangential displacement, and no acceleration of the shifting mass by gravitation. Nor is it clear how the neighbouring air-strata can exert a pressure on those to be displaced capable of performing the considerable work of acceleration which the maintenance of the moment of inertia requires. A displacement of the whole mass of air of a rotating ring in the meridional direction cannot moreover take place, for the volume of such a ring of definite thickness varies as the cosine of the latitude, and with a polar displacement a corresponding portion of the mass of the ring must either lag behind or return to the equator. But even as regards that portion of the ring actually displaced in the polar direction, there is no physical reason for assuming a conservation of the moment of inertia in the case of currents of air; such an assumption would, on the contrary,

lead to the greatest contradictions and discontinuities. For in the assumed original condition from which both Ferrel and I start, when as yet no meridional currents existed, the air of each latitude rotated with the velocity of the ground upon which it rested, and its velocity therefore diminished with the cosine of the latitude. Now, according to Ferrel's views, this relation must not only have been reversed with the appearance of meridional currents, but instead of a diminution an increase of the velocity of the air must have occurred in a yet higher degree, if the moment of inertia of the air is supposed to remain constant. But why it must remain constant, and what forces could bring about so considerable an increase of the *vis viva* of the rotating air are equally incomprehensible\*.

Another of Ferrel's assumptions with which I cannot agree is that the uppermost strata of air can slide down inclined surfaces of equal air-pressure, for in these there is as little tendency to tangential displacement as on a level surface. That such a displacement could not in general take place follows at once from the consideration, that even if a current of air did descend, a difference of pressure would arise, with a consequent disturbance of the balance of pressure, and the immediate production of a back current. It hence follows that meridional currents of air cannot be caused by the steady increase in the temperature of the air from the poles to the equator which (disturbances excepted) is found to exist, and to this Dove agrees. Surfaces of equal pressure exist at all levels throughout such an unequally heated atmosphere which reach from the equator to the poles, and along which no spontaneous motion of the air can take place. Notwithstanding the greater rarefaction or loosening of the air through the heat of the torrid zone, the air would remain at rest, if the indifferent equilibrium were not disturbed in some portion of it. The real condition of equilibrium and of

\* I must emphatically protest against Dr. Sprung's statement, "that there is the same (certainly very excusable) error contained in my assumption of a constant velocity of rotation of the air, as in the conception of Hadley and Dove on the influence of the earth's rotation on the motion of the air." Dr. Sprung is not entitled to bring forward von Helmholtz's communication "On Atmospheric Motions" in support of this opinion, for in this mathematical inquiry von Helmholtz has considered a "hypothetical case." He says, "If we assume a rotating ring of air—the axis of which coincides with the earth's axis—to be displaced at one time to the north and at another to the south by the pressure of similar neighbouring rings, the moment of inertia must remain constant, in accordance with the well-known general mechanical principle." This is no doubt correct, for in the assumed case the pressure of the neighbouring rings performs the work of acceleration; but the point in question is just whether there are forces available to exert this displacing pressure.



relative rest of the atmosphere is that of indifferent equilibrium with the adiabatic scale of temperature appropriate to it. In other words, setting aside friction, no work is required to take a mass of air from one level to another, which means in this case that the energy expended by the expansive action of the air is balanced by the loss of heat in cooling, and inversely. The condition of relative rest of the atmosphere depends therefore on the maintenance of indifferent equilibrium, every disturbance of which makes its appearance as a storage of energy, having the tendency to re-establish it through the motion of the air. These disturbances are to be explained exclusively by the unequal heating of the strata of air by the sun's rays and their unequal cooling by radiation of heat into space. The sun's rays heat the surface of the earth, which then heats the strata of air resting on it. The excess of temperature thus brought about over the adiabatic temperature of the earth, which corresponds to the mean temperature of the whole superincumbent column of air, forms a store of energy like a bent spring, which can only be balanced again through the spreading of the excess temperature of the deepest to the overlying air-layers, and thus restoring the disturbed indifferent equilibrium. Practically, this can only be effected by air-currents. When the superheating is only local, a rising of the superheated air will occur at some locally favoured place, which will increase quickly with the height, for the upflow in the so-formed natural chimney increases with the height. This chimney differs from ordinary chimneys not only in height, but essentially, in so far that it has elastic walls, and that the pressure and density of the strata of air inside and outside diminish with the height. The velocity of the ascending air must therefore increase inversely as the density, for at each instant equal masses of air must pass through all sections of the chimney. Considering the small height of the atmosphere as compared with the earth's radius, no considerable increase of area with height takes place within it, and hence the velocity of the currents of air with up and down flow must increase and diminish absolutely with the air-pressure of the place. Through this upflow a greater portion of the sun's energy stored up in the air is therefore changed into the *vis viva* of air in motion than would be the case without such acceleration. The final results of the upflow of air limited as to space which has been overheated on the earth's surface, will be that this local air-current ascends with accelerated velocity up to the very highest regions of the air, that at the same time the strata of air surrounding the upflow descend with diminishing velocity, and



that finally the heat produced on the earth's surface, and thereby disturbing the equilibrium, is dispersed through all the overlying air-strata and so restores the indifferent equilibrium of this part of the atmosphere.

When this heating of the layers of air near to the ground is extended to a whole zone of the earth, the balancing of the indifferent equilibrium disturbed through solar radiation is effected on the same principle, although the resulting phenomena are quite different. In this case the upflow would no longer be limited as to space, but comprehend the whole torrid zone systematically, nor can it be limited as to time, but the adjustment, like the cause of the disturbance, must continue unlimited. A continuous system of currents comprehending the whole atmosphere must consequently be formed, which eventually brings about the continual transference of the extra heat of the air near to the ground in the torrid zone to the whole atmosphere at all levels and latitudes, and restores the indifferent equilibrium disturbed in the torrid zone, through continuous air-currents.

If the possible lines of currents are constructed, bearing in mind that stream-lines cannot cut one another, that the velocity of an ascending current of air must increase directly as the height and inversely as the pressure, and finally that the air must maintain its velocity unaltered unless expended in friction, mixture, or the work of compression, the system of winds proposed by me is necessarily arrived at, depending essentially on the *vis inertia* of the heated air set in accelerated motion by the equatorial upflow. This *vis inertia* not only forces the accelerated rising air along the higher strata of the atmosphere, but is also the cause of its return along the lower strata to the equator.

It would lead me beyond the scope of this communication were I to enter upon a closer discussion of this *vis inertia* of the air, and on the influence of the vapour of water, which considerably modifies it. But I may be allowed to say something on the origin of the great stores of local energy indicated by the maximum and minimum pressure of the air. The sum of the pressure of the atmosphere at every part of the earth's surface must be constant, for this sum represents the weight of the invariable total amount of air. A reduction of the pressure of the air at one part must therefore necessarily be always opposed by a simultaneous increase of pressure elsewhere. It is evidently no use to look for the originating cause of the maxima and minima in local conditions of the atmosphere. The barometer frequently gives intimation of these before any alteration takes place in the state of the

atmosphere on the earth's surface. Frequently, however, light clouds indicate an alteration already set in in the higher strata ; and so in my paper, " On the Conservation of Energy in the Earth's Atmosphere," I placed the origin of the maxima and minima in the upper strata of the atmosphere, in the temperature and velocity of which constant alterations take place, depending upon the place of ascent of the air, *i. e.* on its temperature and hygroscopic state before it ascends. If no change in the seasons took place, there would probably be great regularity in the currents in the upper strata of the atmosphere, which would bring about a certain sequence in the changes of weather not hitherto attained. We are not yet able to find out where the air comes from which flows at any moment over any portion of the earth's surface in a polar direction along the higher strata of the atmosphere, and upon the place and the season of the ascent will depend the temperature and velocity of this air. As the expenditure of heat during the ascent of the air, *i. e.* during its working expansion, depends upon the degree of its attenuation, and therefore on its elevation, nearly the same diminution of heat takes place with hot as with cold air. At all heights of the atmosphere differences of temperature must make their appearance equal in degree to those existing on the earth's surface, for any surplus of heat which the air possesses before its ascent must be retained by it after it has been rarefied and cooled through the ascent. On this account the general condition of the atmosphere will not be that of unstable equilibrium but so-called stable equilibrium, for the higher strata of the atmosphere, on account of their equatorial origin, will be warmer and lighter throughout than they should be according to the adiabatic scale of temperature of the place over which they are. The velocity of ascent of the air will increase with the quantity of heat and moisture which it contains before its ascent ; and therefore in the higher strata of the atmosphere of the mean and higher latitudes, relatively warm and light currents of air of greater velocity must intermingle with colder and slower currents. Such a current of relatively light and warm air, completely or partially occupying the upper atmosphere, disturbs on its side the indifferent equilibrium of the lower strata of the atmosphere. The lower atmosphere, relatively at rest on the boundaries of the strata, must be under too great a pressure, and must therefore expand and be carried along with the quick-flowing lighter air above it. As von Helmholtz has shown, this carrying away must go on with great energy, producing waves, and in consequence there must be an expansion and flowing up of the

lower air, which will continue until the indifferent equilibrium disturbed by the lower pressure of the upper strata of the atmosphere is again restored. When the pressure of the air of the upper strata increases beyond that due to their elevation, through cooling and condensation, in consequence of the diminution of the width of the current with increasing latitude the opposite effect will be produced, the limiting strata will sink down, condensing the lower strata of air, and thereby increasing their pressure. In both cases the disturbed indifferent equilibrium must eventually be again restored by the strata of air lying below the source of disturbance delivering by means of up-currents, or taking up by means of down-currents, as much air as is required to restore the condition of indifferent equilibrium in the whole height of the atmosphere. In order to effect this the pressure of the air of the lower strata must increase or diminish, in the first instance, until it has adjusted itself to the scale of pressure of the indifferent equilibrium of the disturbing upper air-strata. In other words, the pressure on the earth's surface must vary proportionately with the change of pressure above, by which means the sudden changes observed in the pressure of the air on the earth's surface are perfectly explained. This alteration in the condition of the lower strata of air will continue even after this adjustment has been effected so long as the cause in the upper strata of the atmosphere continues; and during that time minimum pressures of air with ascending currents, and maximum pressures with descending currents, of air must occur, and set the atmosphere for a considerable distance in whirling motion. It is only when the flow of air in the higher strata of the atmosphere has again become normal, that a mean position of the barometer and relative rest of the atmosphere on the earth's surface will again prevail.

The theory of the general system of winds may therefore be summed up in the following statements :—

1. All motions of the air depend upon disturbances of the indifferent equilibrium of the atmosphere, and tend to bring about its restoration.

2. These disturbances are caused by the superheating of the strata of air lying nearest to the earth's surface through solar heat, by unsymmetrical cooling of the upper layers of the air through radiation, and by the piling up of masses of air in motion through obstructions occurring to the current.

3. The disturbances are balanced by means of ascending currents, which possess an acceleration of such a kind that the increase of velocity of the air is proportional to the diminution of its pressure.



4. Down-currents of equal magnitude correspond to the up-currents, and in these the velocity of the air is retarded in the same proportion as that of the upflow is accelerated.

5. If the heating of the lower strata of air takes place within a limited area, a local upflow occurs reaching to the uppermost regions of the air, and presenting the appearance of whirling columns with ascending spiral currents of air inside and similarly directed descending currents outside. The result of these whirling currents is a diffusion of the surplus heat of the lower strata through which the adiabatic equilibrium is disturbed, to the whole column of air which took part in the whirling motion.

6. When the sphere of disturbance of the indifferent (or adiabatic) equilibrium is very extended, comprising for instance the whole torrid zone, the equalization of temperature can no longer be effected by local ascending whirling currents, but these must comprise the whole atmosphere. The conditions are the same as with local currents, viz. an accelerated ascent and retarded descent of the air, so that the velocity of the air due to the action of the heat is at the different latitudes approximately inversely proportional to the air-pressure prevailing there.

7. As the air of every latitude rotates with approximately the same absolute velocity in consequence of the constant meridional currents which the heat produces and maintains, the meridional combine with the terrestrial currents to form the great system of currents of air surrounding the whole earth, whose function it is to give a share of the surplus heat of the torrid zone to the whole atmosphere by transferring equatorial heat and moisture to the middle and higher latitudes and by originating local air-currents in them.

8. These latter are due to the local production of alternate increase and decrease of pressure through the disturbance of the indifferent equilibrium in the upper strata of the atmosphere.

9. The maximum and minimum air-pressures are effects of the temperature and velocity of currents of air in the higher strata of the atmosphere.

From what precedes, the investigation of the causes and effects of the disturbance of the indifferent equilibrium of the atmosphere may be considered as one of the most essential problems of meteorology, and the investigation of the geographical origin of the air-currents passing over us on their way to the poles as the most important problem in the prognostication of the weather.



LVIII. *Intelligence and Miscellaneous Articles.*

## ON PHOTOGRAPHS OF RAPIDLY MOVING OBJECTS.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

St. Petersburg, October 24, 1890.

MR. C. V. BOYS has published in the September number of the Philosophical Magazine a paper ("Notes on Photographs of Rapidly Moving Objects, and on the Oscillating Electric Spark") containing the description of a direct method for photographing a liquid jet.

I myself have already successfully used the same method in 1889, and I communicated the results of my researches to the Russian Physico-Chemical Society at the meeting on February 11, 1890. By the aid of this method I have now investigated the constitution of the jet of a pulverulent body issuing through the orifice of an ordinary glass funnel, 3 millim. in the clear, either under the influence of its own weight or aided by the pressure of compressed air; and I have the honour of sending you the results in the form of the four photographs enclosed, which may interest you. A plate or a sheet of paper sensitized with gelatino-bromide of silver was placed vertically behind the jet, which was illuminated in front by the spark of a Voss's machine. The enclosed photographs show clearly that jets of pulverulent bodies are made up of nodes and loops, and of detached drops like those of liquids. The powders used were lycopodium, emery, and sand.

I am continuing my researches with the object of determining whether the constitution of jets of pulverulent bodies may be attributed to a kind of surface-tension, or to some other cause; and, further, to examine the influence of heat on the phenomenon, and so forth,

I have the honour to be,

N. KHAMONTOFF,

*Assistant in the Physical Laboratory of the  
University of St. Petersburg.*

## ON DROPPING-MERCURY ELECTRODES. BY W. OSTWALD.

I am glad to find a perfect agreement between Mr. Brown's observations on dropping-currents and mine. For I have asserted that the current between a dropping electrode and an electrode of stationary mercury is *constant* if the latter receives the drops, but is much weaker, and decreasing, if not. Mr. Brown likewise asserts that *at the first moment* both currents are of the same strength. I have not the least doubt that this is so, for at the first

moment no real difference exists between the two cases ; but that I did not make special mention of this of course displays a want of acuteness on my part, which I regret. The chief point, a "subsequent decrease" of the current, is also observed by Mr. Brown.

Mr. Brown asserts, it is true, that the last facts can be explained as well by Helmholtz's theory as by what he calls his hypothesis, but unfortunately he has not given his explanation.

This hypothesis is said by Mr. Brown to be opposed to the theory of Helmholtz, of which he says: "It was perhaps unnecessary to disprove what had not been proved." If a theory can be proved by developing its consequences and comparing them with experiment, the theory of Helmholtz is proved by many facts. I may recall, for instance, the agreement between the electromotive force of a perfect dropping electrode and the value of the E.M.F., which the maximum surface-tension of mercury in contact with the same electrolyte reaches ; further, the fact that this *maximum* surface-tension of mercury always shows the same value, while the natural surface-tension depends to a great extent upon the nature of the electrolyte in contact with it ; further, the connexion between the currents caused by stretching the common surface and its state of polarization, &c. On the other hand, I am not aware if there exists a single fact in favour of Mr. Brown's hypothesis.

But Mr. Brown prefers his own theory because it seems to him "much simpler" than Helmholtz's theory. I must, however, confess that the assumption that mercury is negatively charged in contact with sulphuric acid is, to my mind, in no perceptible degree simpler than the assumption that it is positively charged.

Even if Helmholtz's theory were no better proved than Mr. Brown's, I should probably prefer the former. This may be attributed to national prejudice, but I cannot help it.

Leipzig, November 16, 1890.

#### VELOCITY OF SOUND AT VERY LOW TEMPERATURES.

BY M. GREELY.

A base-line of 1279 metres was accurately measured, and the interval determined between the flash of a gun at one end and the appearance of the sound-wave at the other.

The following results were obtained, where  $t$  is the temperature,  $x$  the number of observations, and  $v$  the corresponding velocity :—

$t$	= -10.9	-25.7	-37.8	-45.6
$x$	= 53	114	164	205
$v$	= 326.1	317.1	309.7	305.6 m.

The velocity diminishes therefore 0.603 metre for 1° C.—*Meteorolog. Zeitschrift*, vii. p. 6 (1890).

## ON THE ACTION OF OILS ON THE MOTIONS OF CAMPHOR ON THE SURFACE OF WATER. BY CHARLES TOMLINSON, F.R.S.

In Lord Rayleigh's paper on the above subject, read before the Royal Society on the 27th March last, and reported in 'Nature' of the 8th May, it is stated that a film of olive-oil, in two or three cases, "was incompetent to stop the camphor motions upon a surface including only a few square inches."

I have often noticed this fact as a consequence of the use of chemically-clean materials. Water, contained in a shallow glass vessel, 4 inches in diameter, on the surface of which camphor fragments were active, was touched with rape-oil delivered from the point of a penknife. The fragments continued to rotate on that part of the surface which had not been invaded by the oil film (Phil. Mag., November 1873). I had previously noticed that a drop of a volatile oil, free from oxidized products, could be spread over the whole surface of the water, without impeding the motion of the camphor fragments, which skated through and cut up the film. In the case of old volatile oils, redistillation was found to be necessary (Phil. Mag., September 1863). A similar effect was produced by a drop of creosote (or its constituent acids) on a film of a fixed oil that completely covered the surface of the water. The creosote repels the oil film, cuts it up in all directions, moving over the surface with great vigour (Phil. Mag., June 1867). So also by attention to chemical purity, a raft of mica carrying a bit of camphor will float about briskly on the surface of water night and day during a whole week and upwards (Phil. Mag., December 1869).

By attending to the chemical purity of the materials the results led to the explanation of many phenomena which had taken refuge under the vague term "molecular change," or "molecular condition," and to the discovery of other phenomena which had some influence in developing theory. I propose to apply the term *catharized* to bodies thus made chemically clean, from *καθαρός*, "pure" or "clean" (Journal of the Chemical Society, April 1869; also Phil. Trans. for 1870).

I may be allowed to add that, in arriving at the true theory of the camphor motions and their varied kindred phenomena, Professor Van der Mensbrugghe was kind enough to refer to me in his second memoir, as "le physicien qui a le mieux préparé la vraie théorie de ces phénomènes."—*Proceedings of the Royal Society*, No. 294, September 20, 1890.

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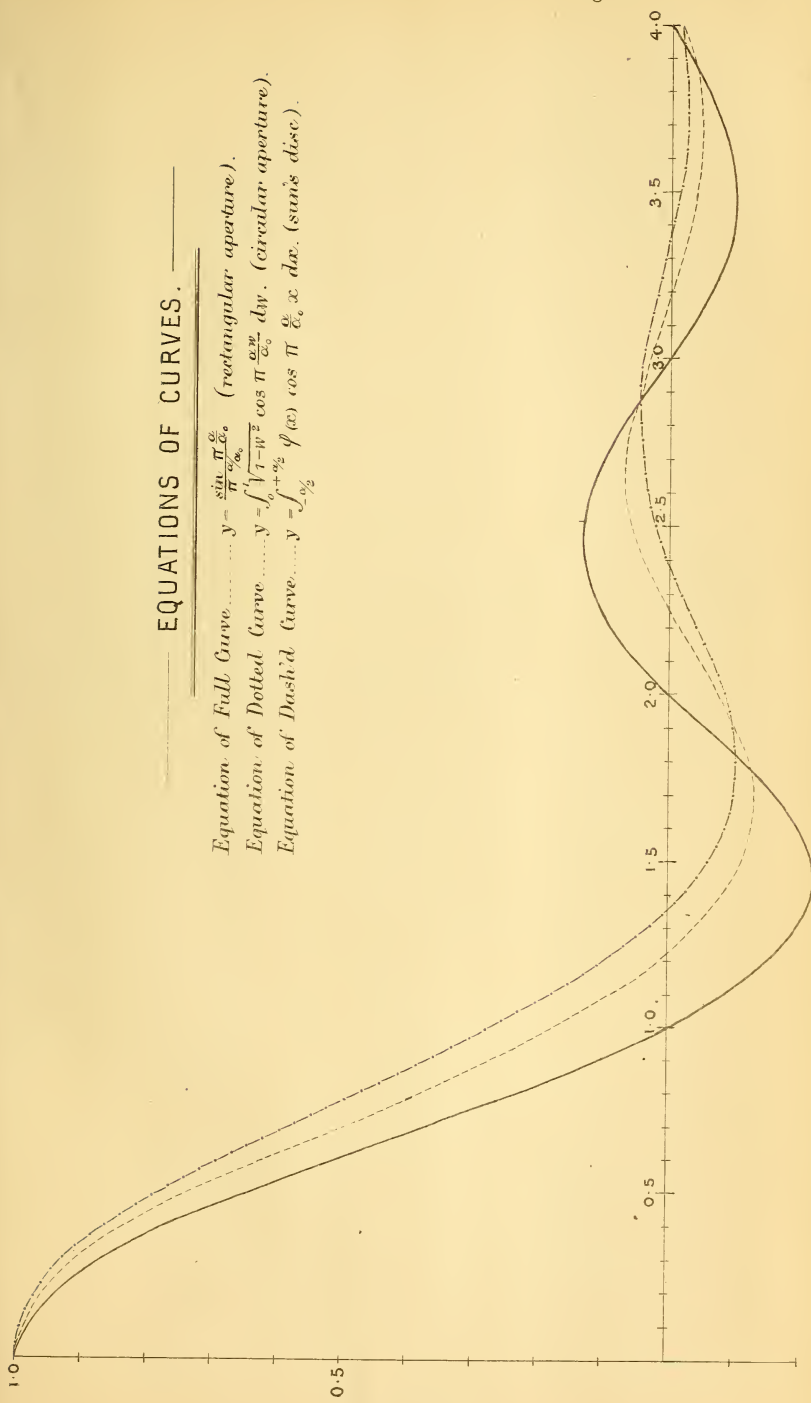
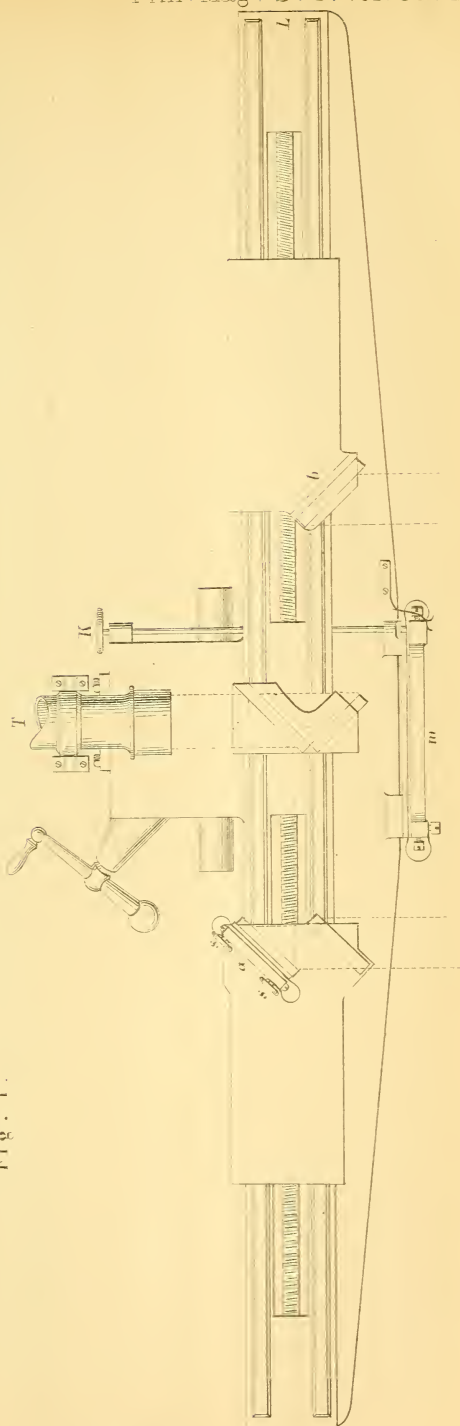




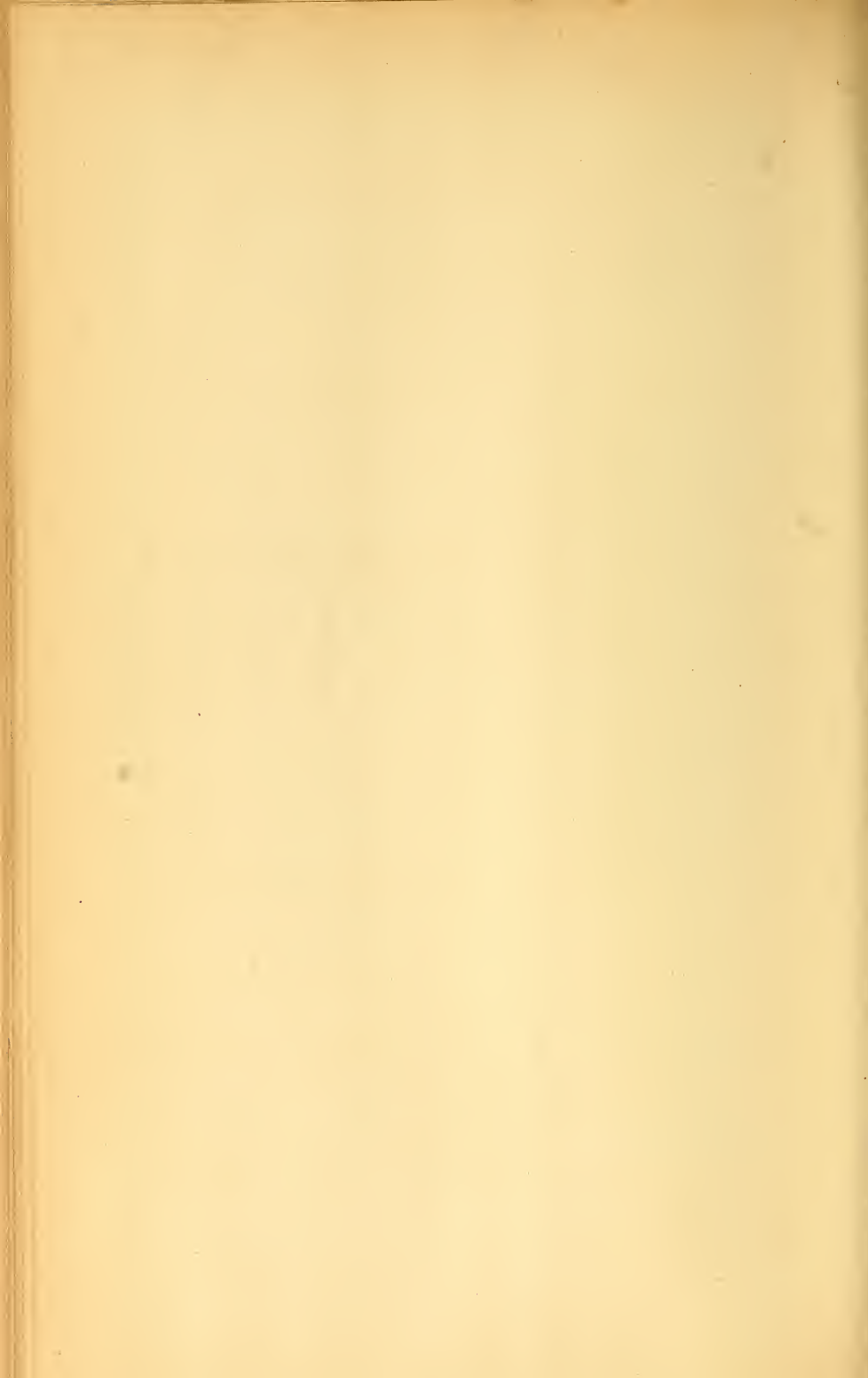


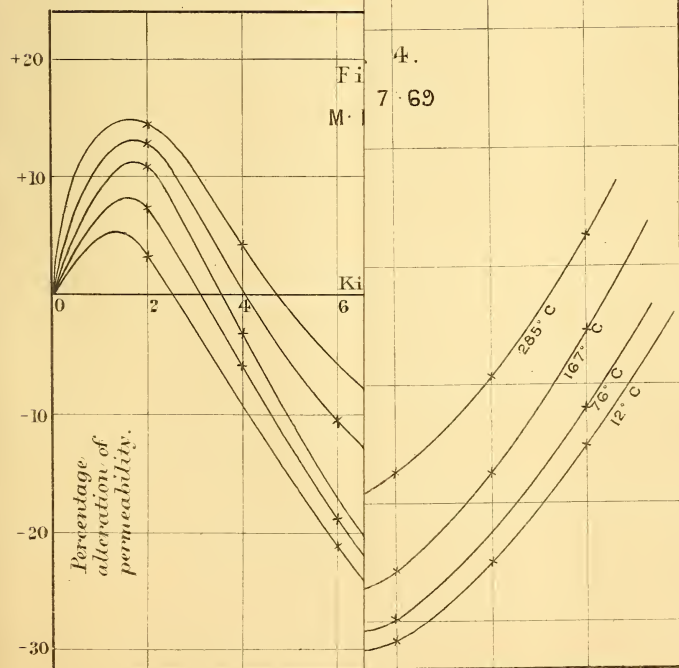
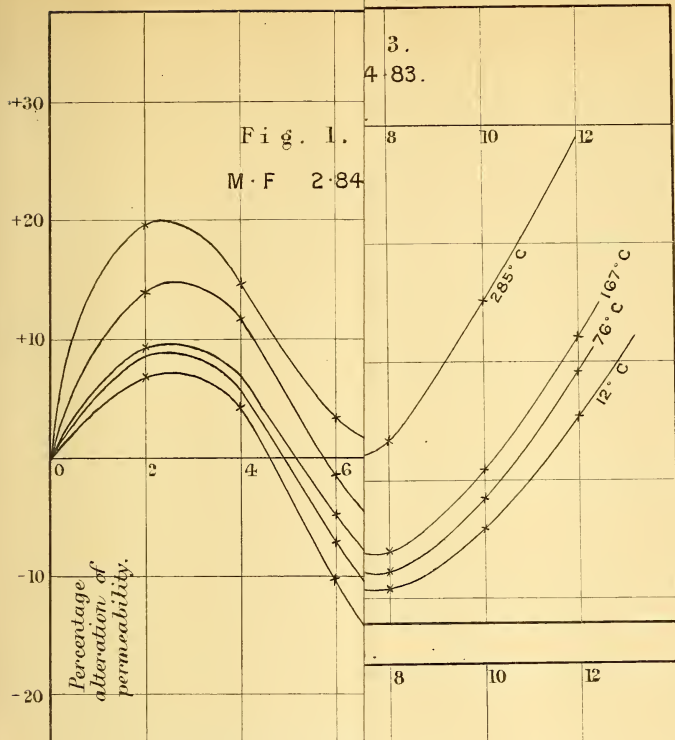


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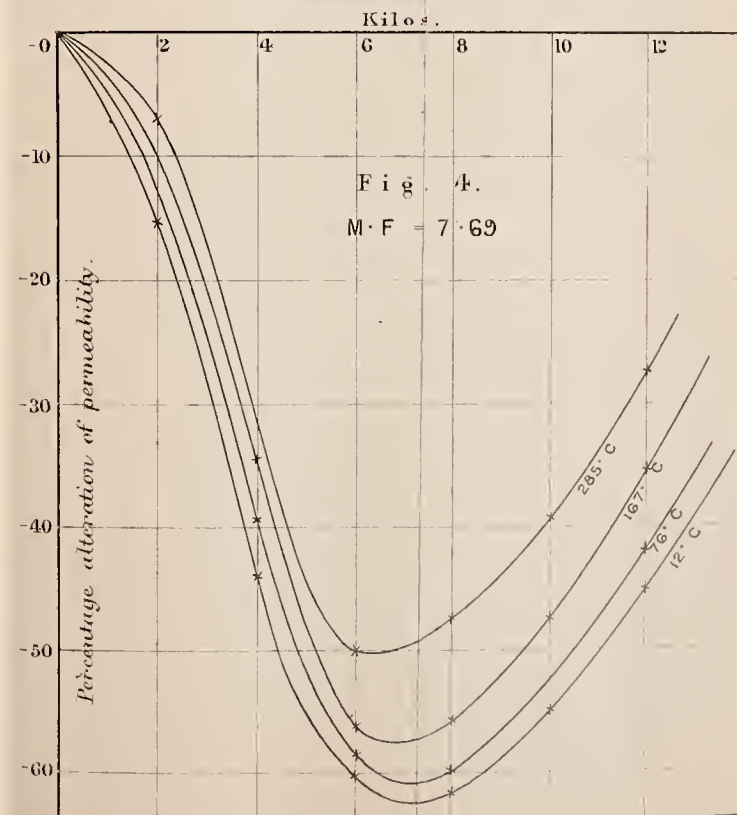
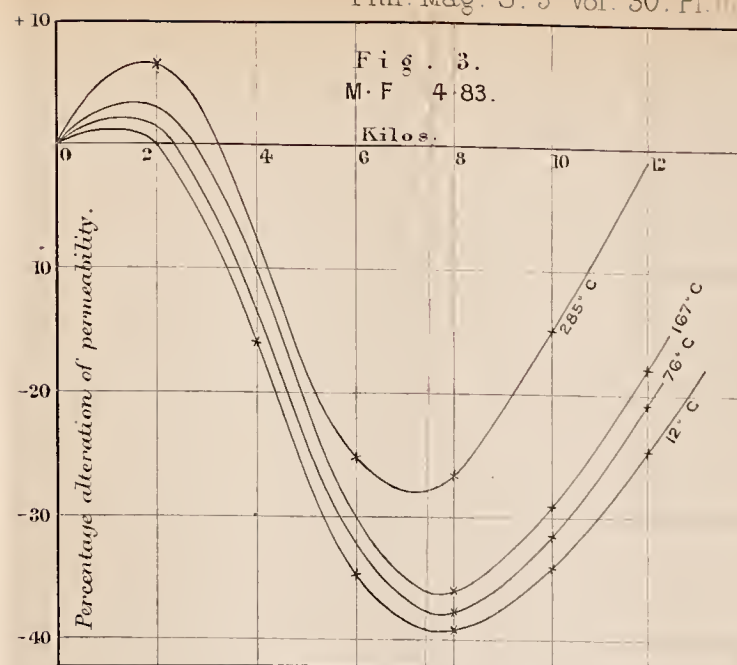
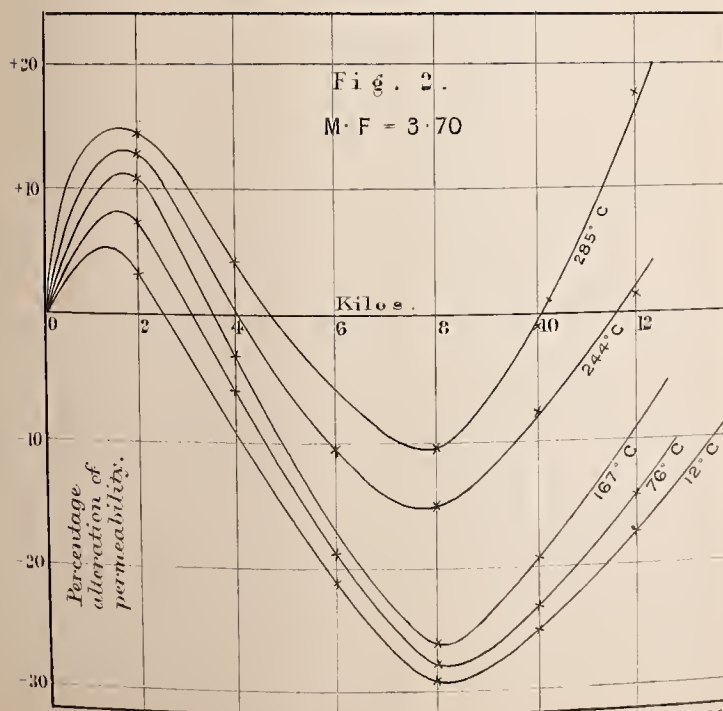
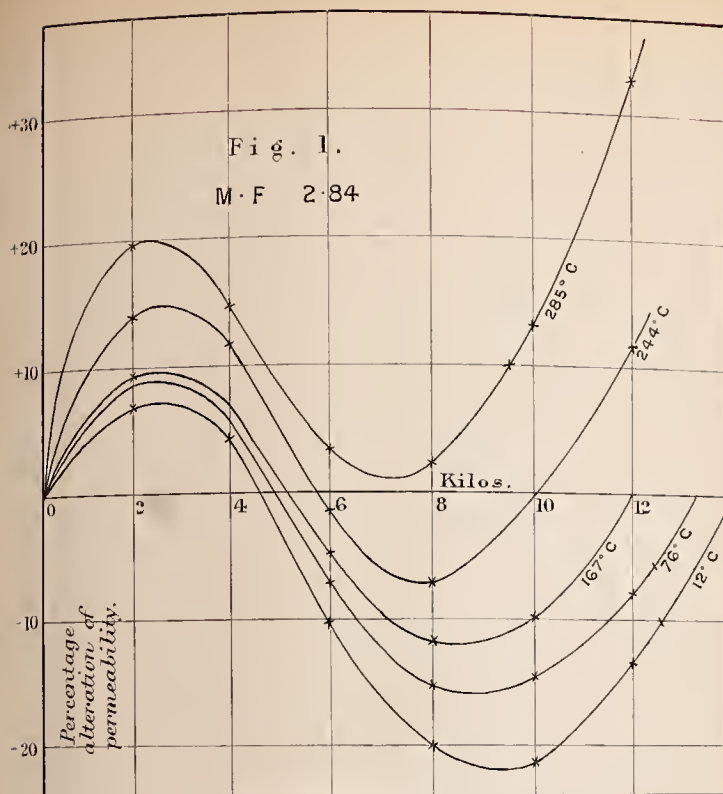
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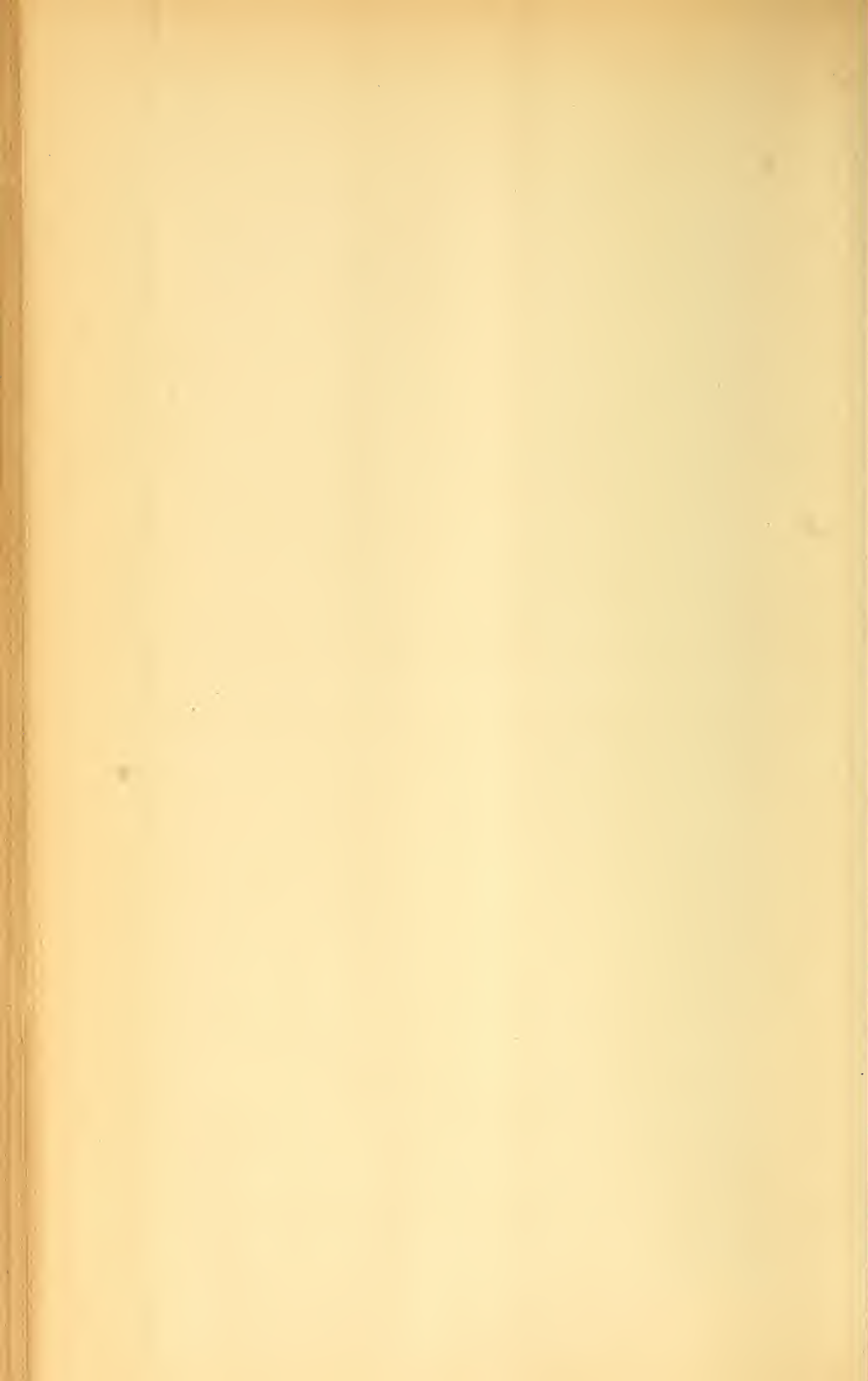


Fig. 6.  
M·F 15·32.

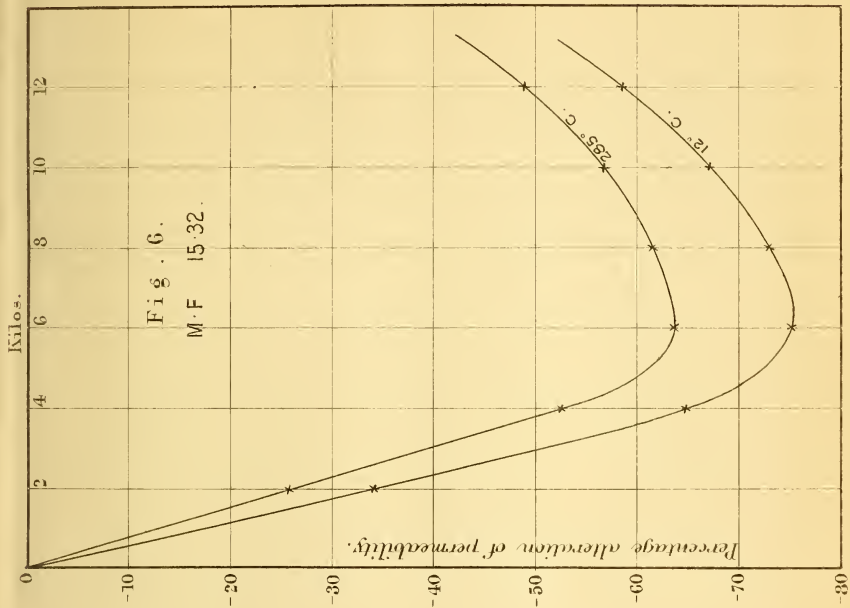


Fig. 5.  
M·F 10·40

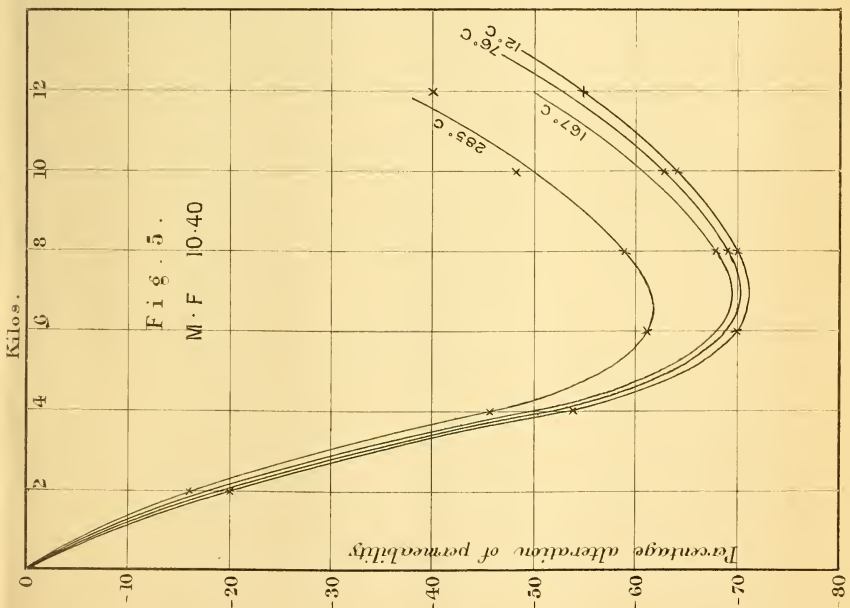






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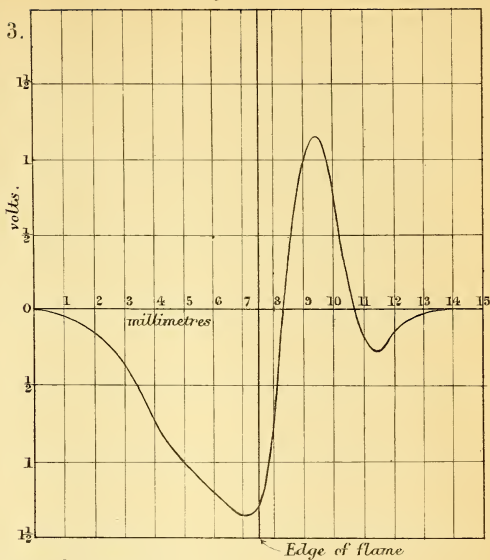


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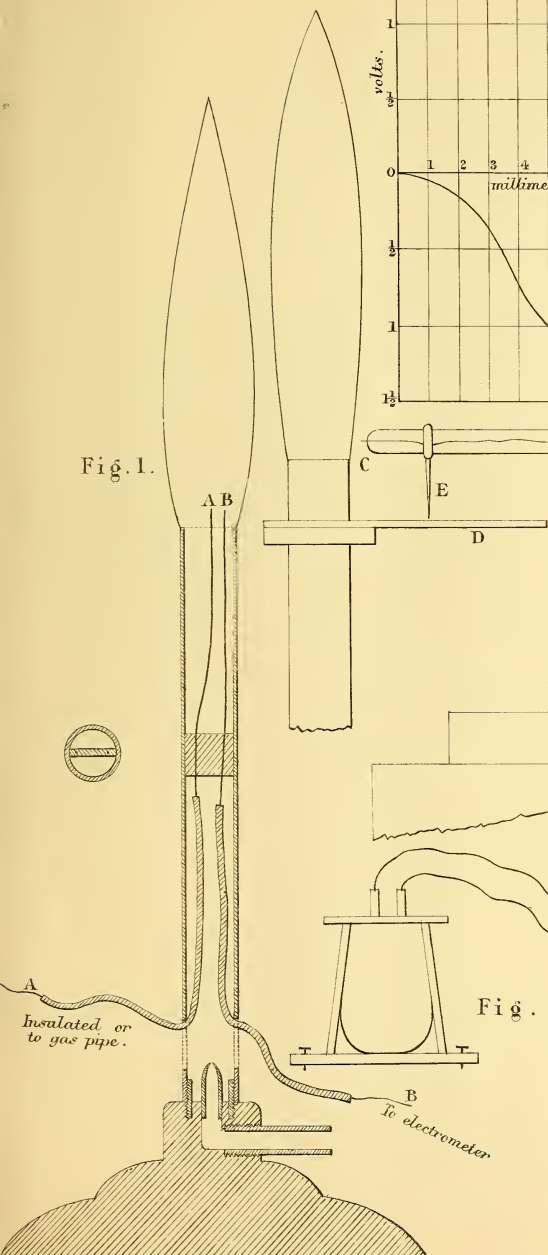


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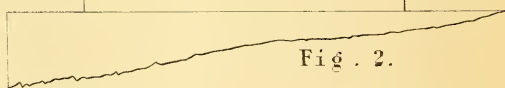
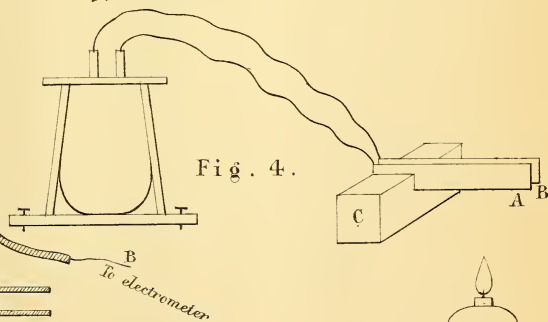


Fig. 4.





P

D

C

B

A

Fig. 6.

P





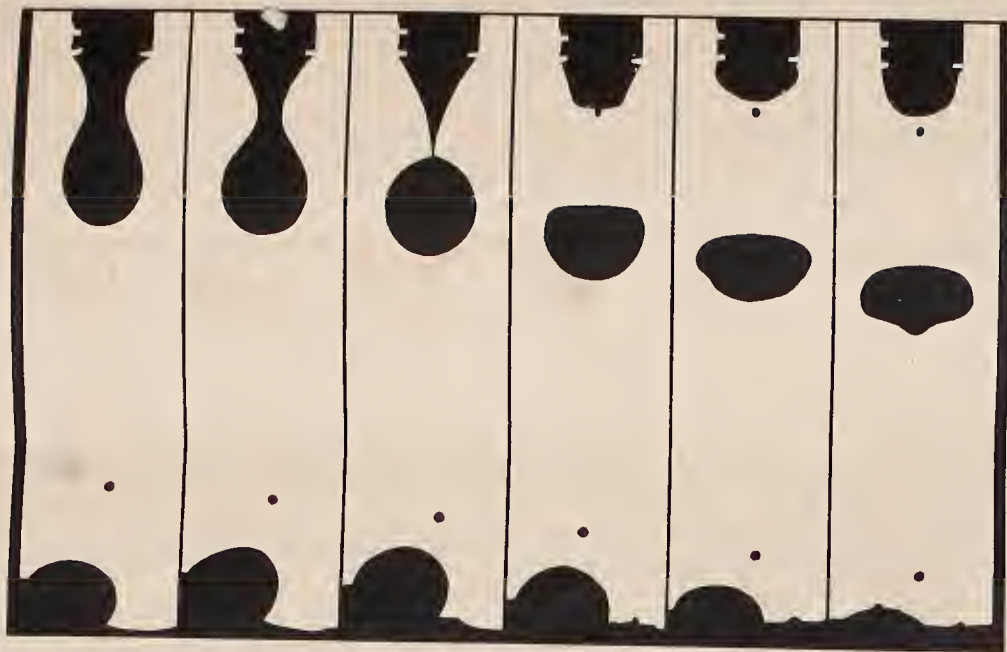


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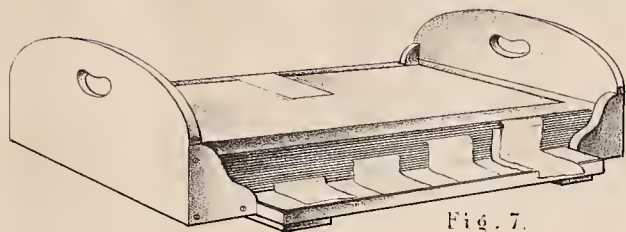


Fig. 7.



Fig. 4.

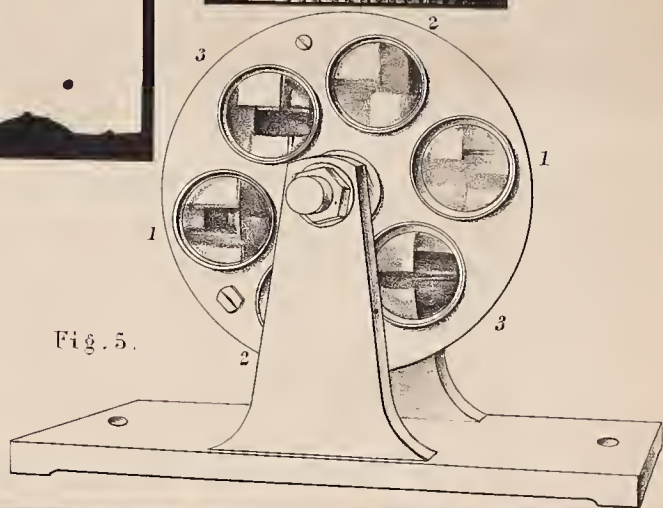


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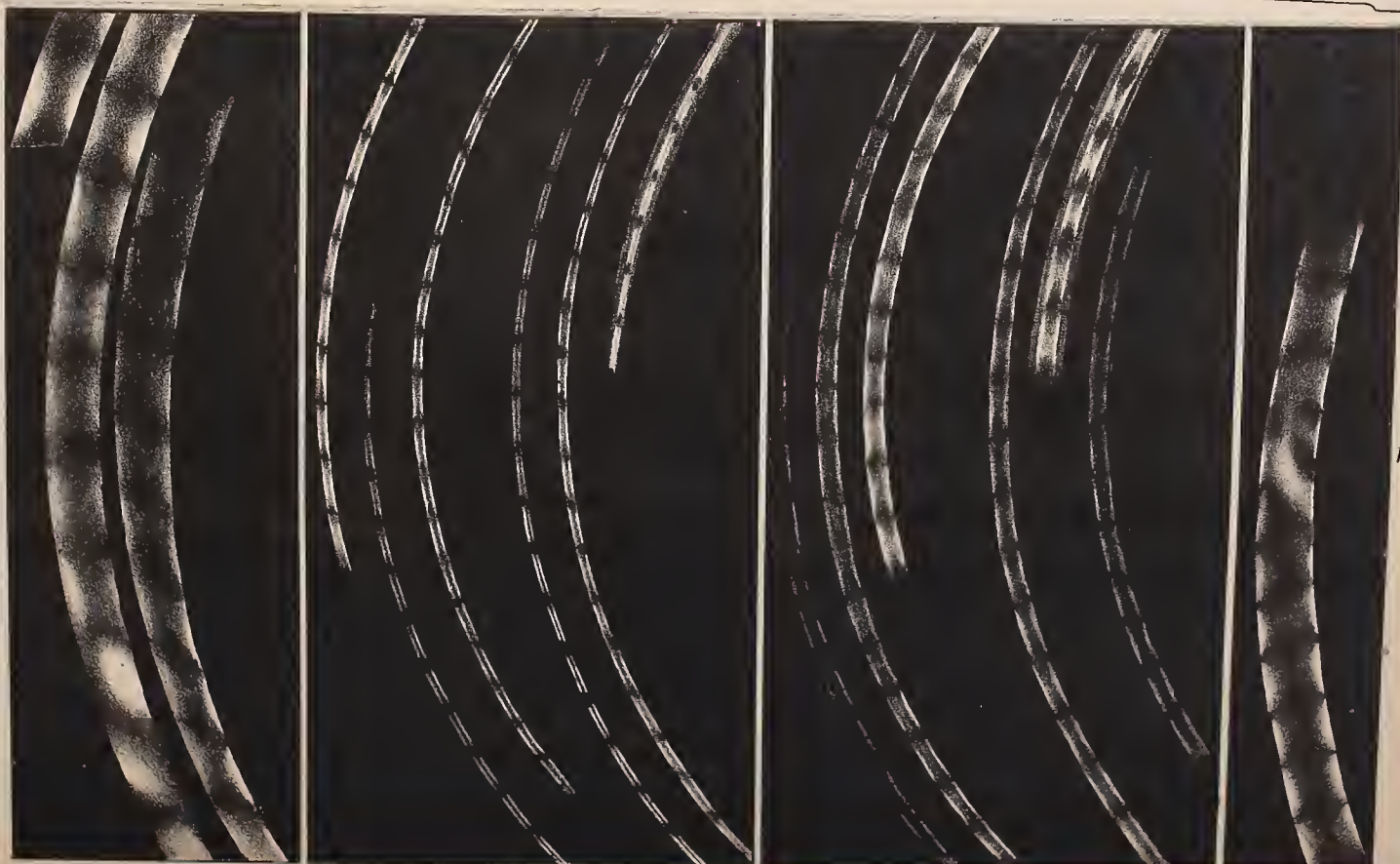
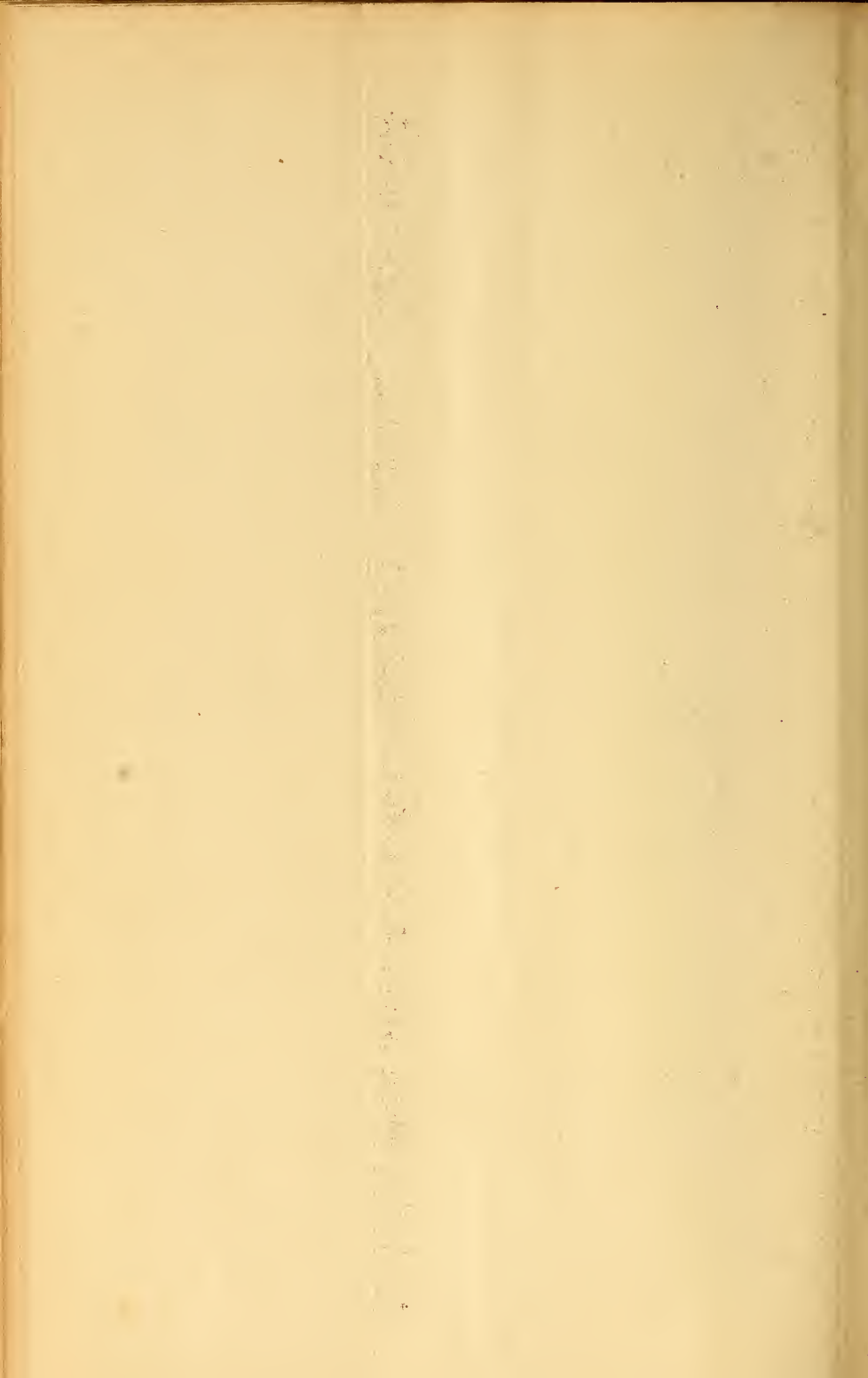
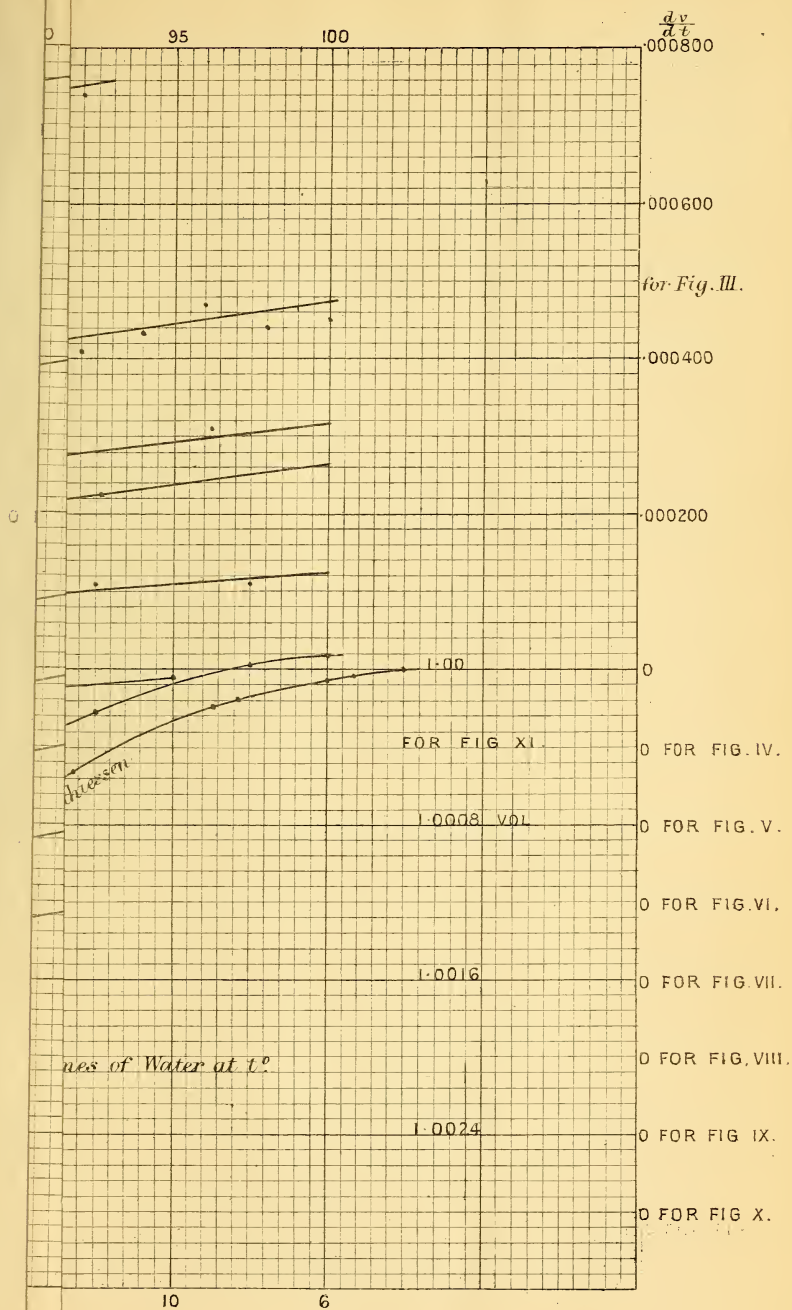


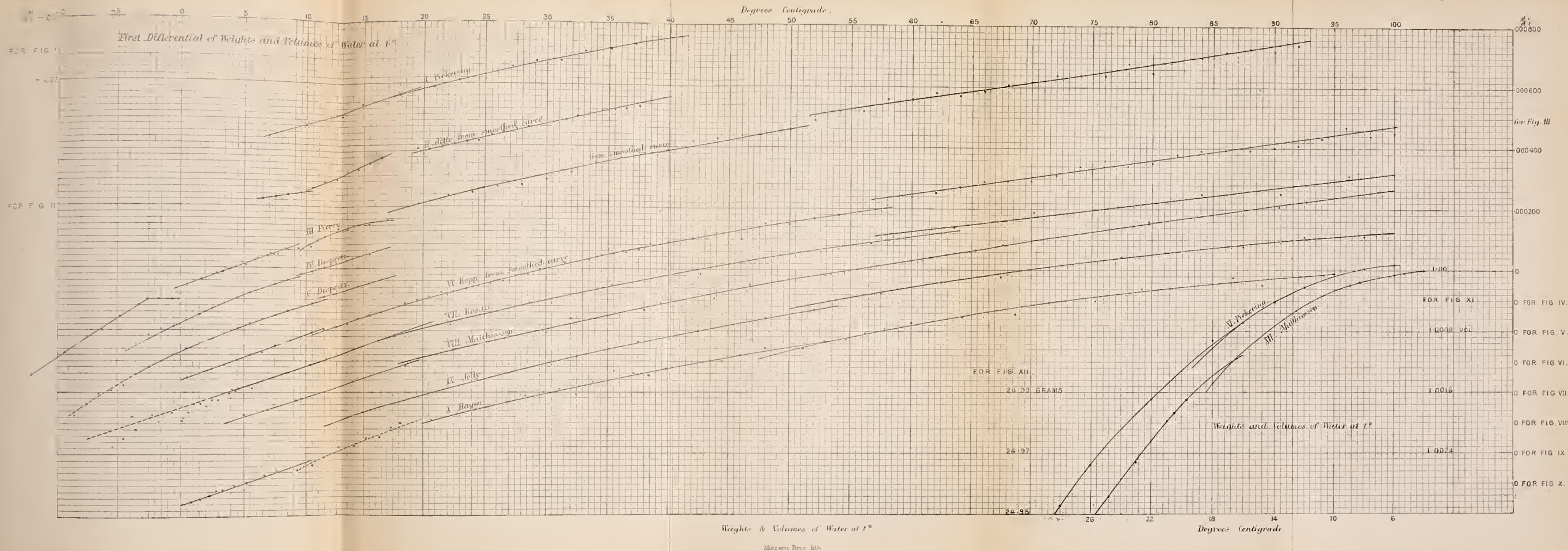
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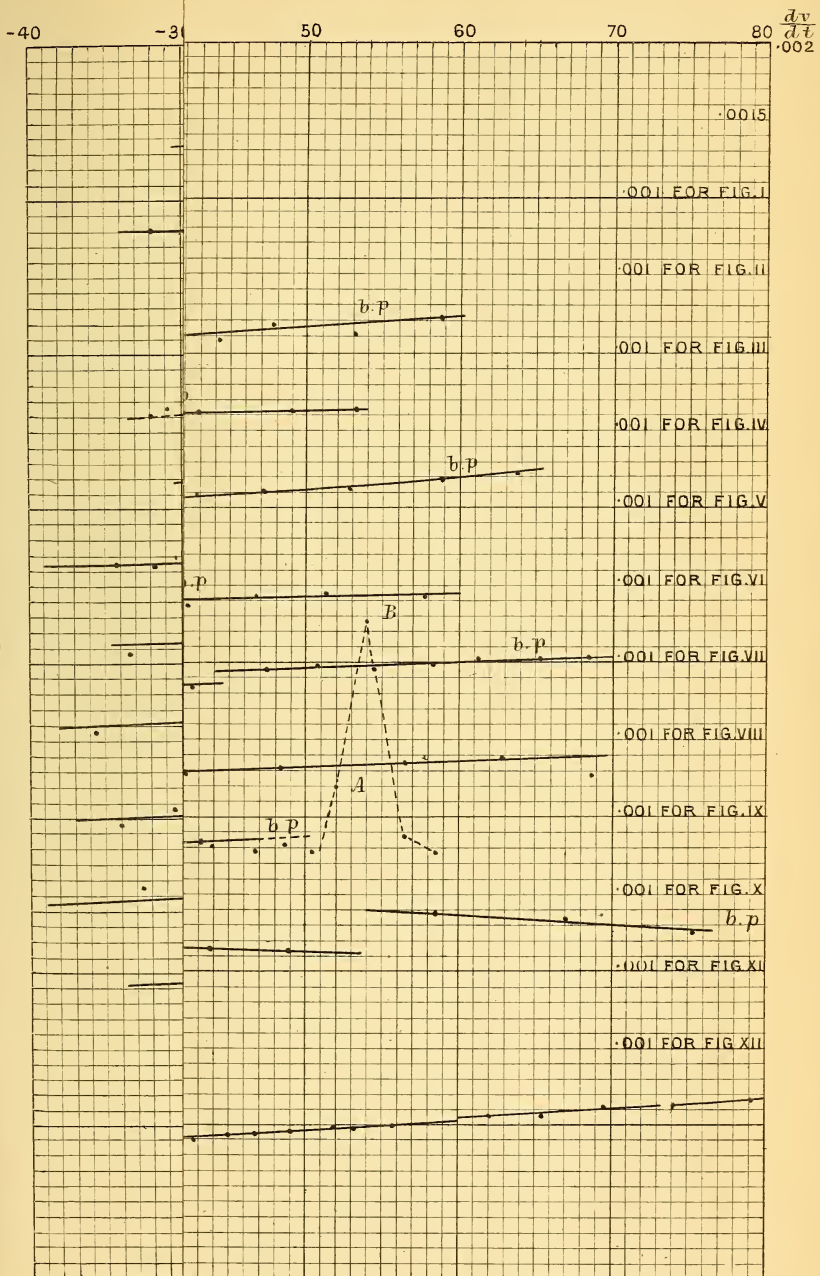






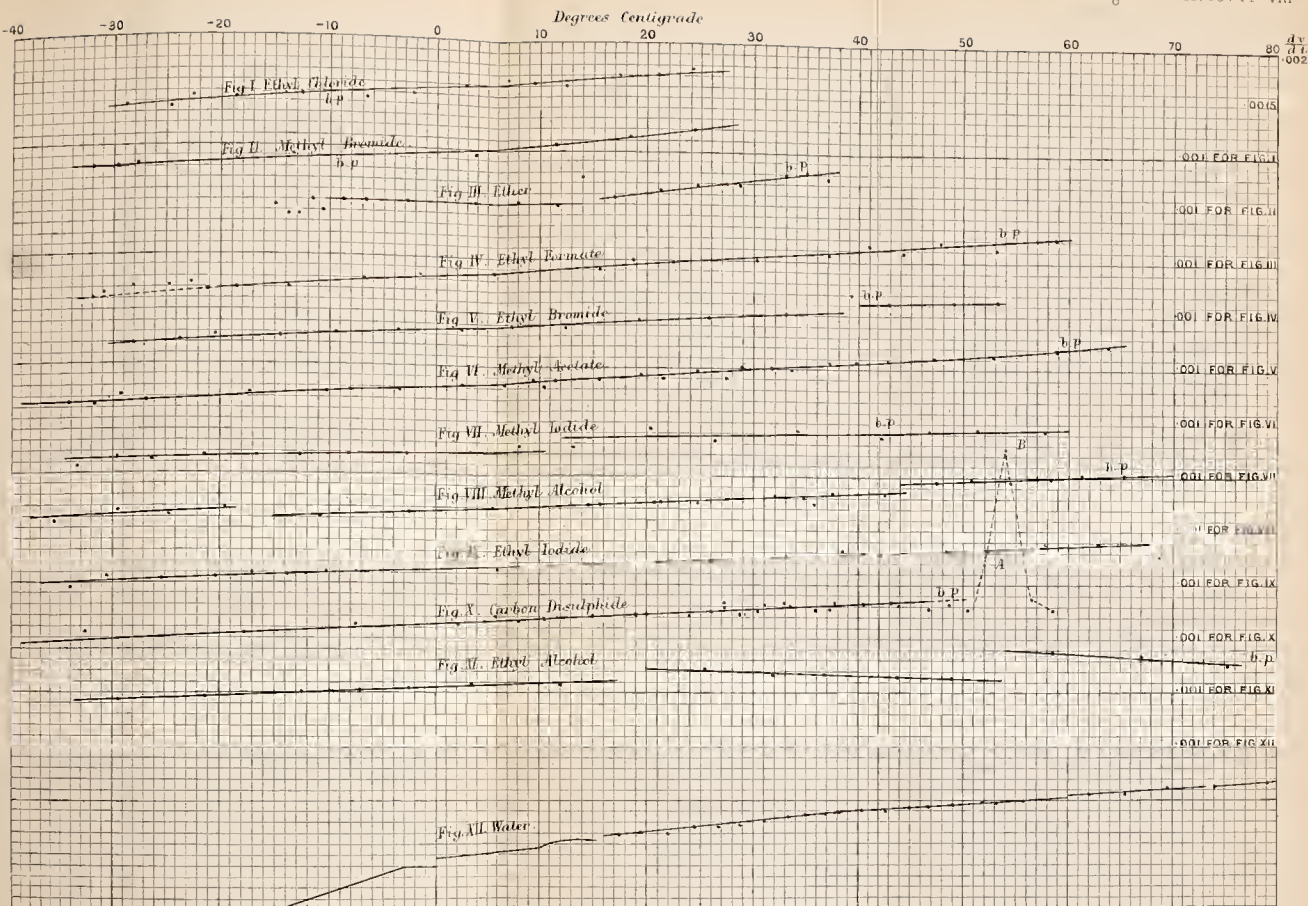










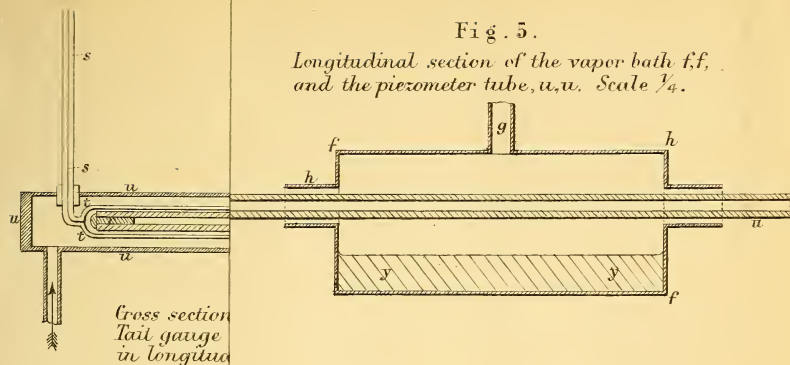


First differential of the volumes of various liquids at 1°



Fig. 5.

Longitudinal section of the vapor bath f,f, and the piezometer tube, u,u. Scale  $\frac{1}{4}$ .



Longitudinal section of the stuffing box with the screw removed showing the gland K,K, and the ring r,r. Scale  $\frac{1}{4}$ .

Fig. 2.

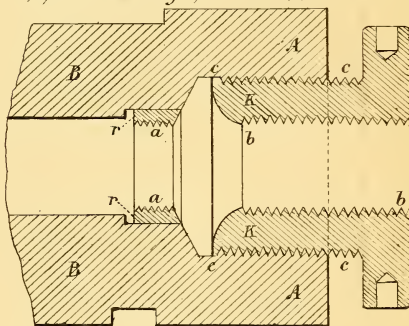
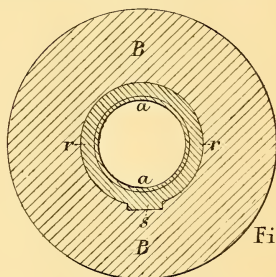


Fig 2a.

Cross section through the ring.



Longitudinal section of the compressor, showing the steel screw S,S,T,T, the ratchet L,R, etc. Scale

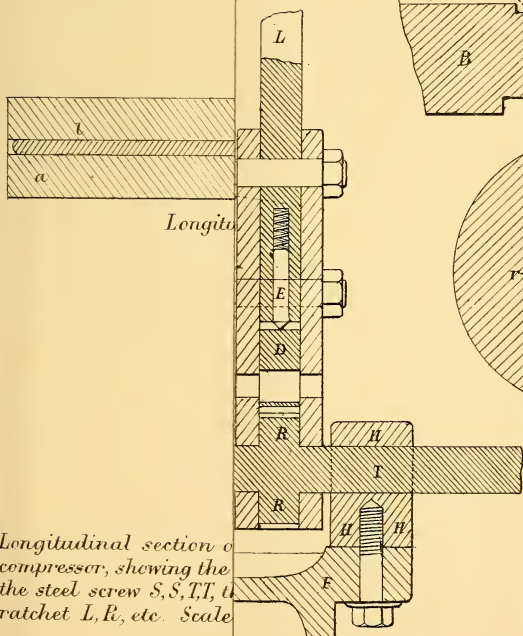
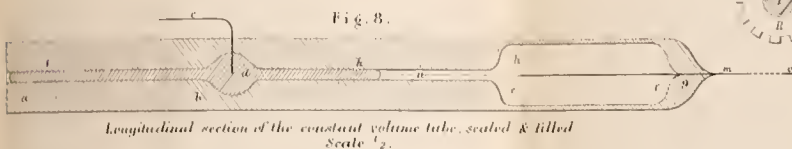
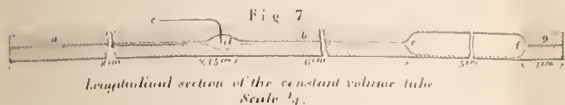
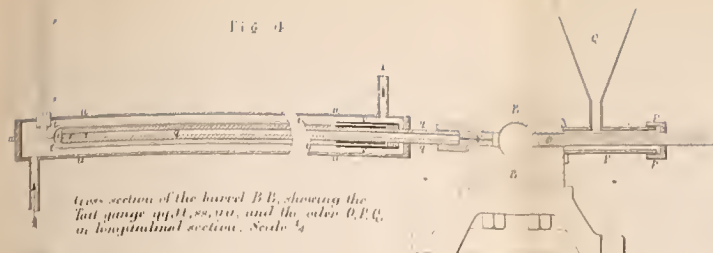


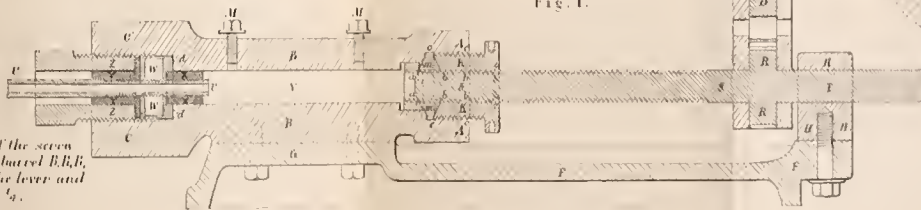




Fig. 4



Longitudinal section of the screw compressor, showing the barrel B B, the steel screw S, S, T, the lever and catch L, etc. Scale  $\frac{1}{4}$ .



Side view of the lever L, L, the ratchet wheel R, R, and the click D, all in place. Scale  $\frac{1}{4}$ .

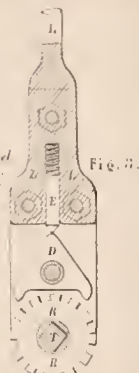
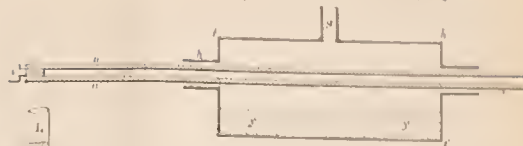


Fig. 1.

Fig. 5

Longitudinal section of the vapor bath C I and the parameter tube u, u. Scale  $\frac{1}{4}$ .



Longitudinal section of the stuffing box with the screw removed showing the gland K, K, and the ring r, r. Scale  $\frac{1}{4}$ .

Fig. 2.

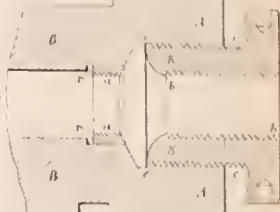
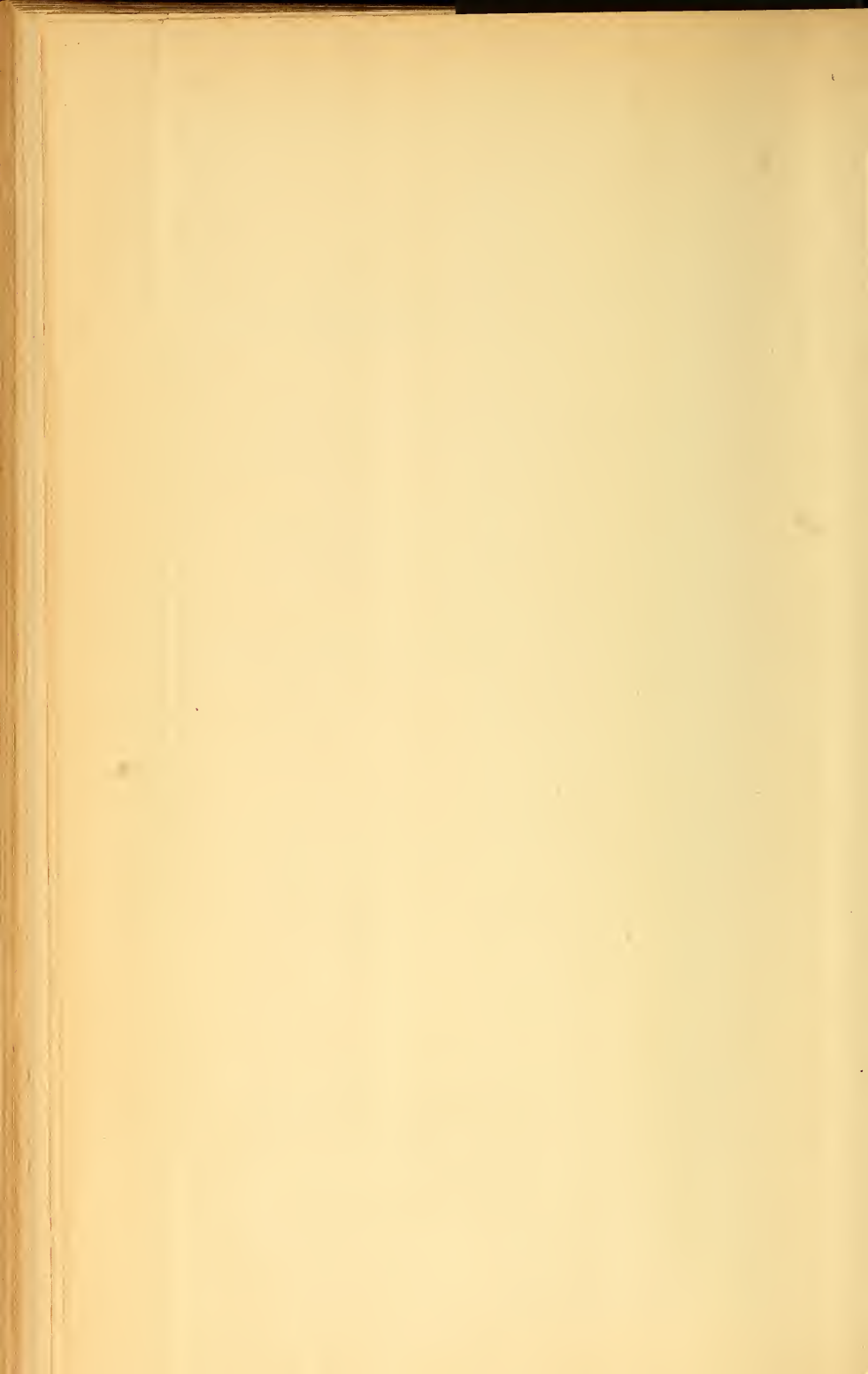


Fig. 2a



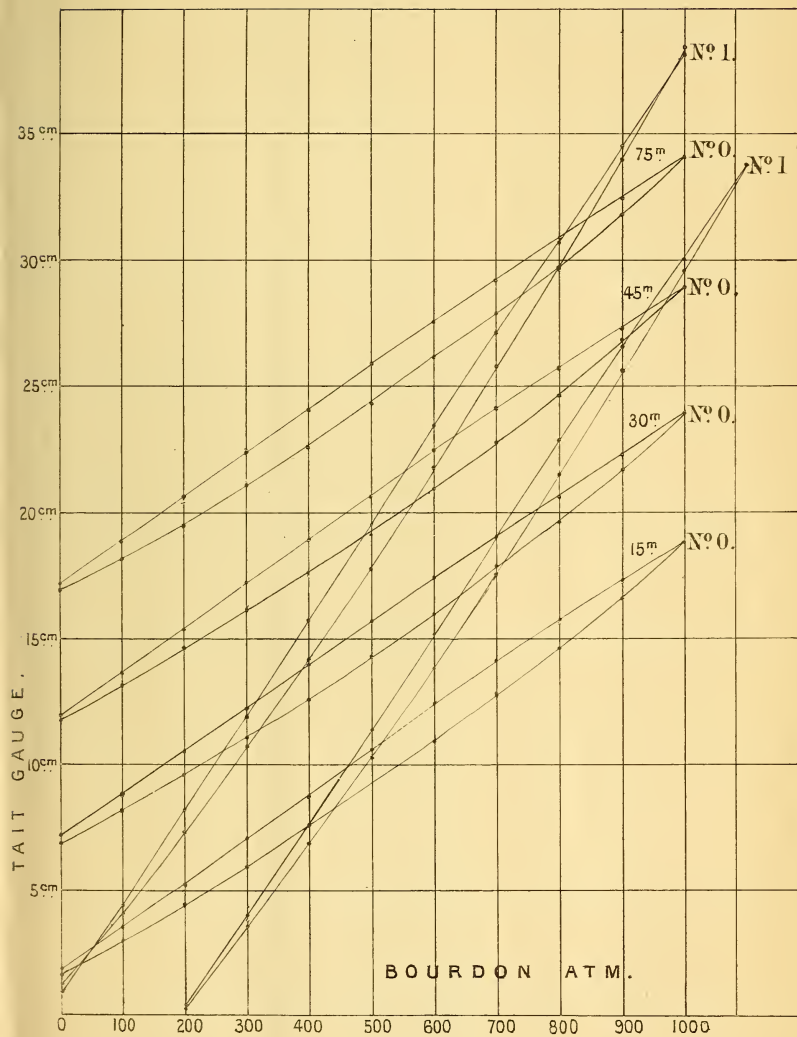
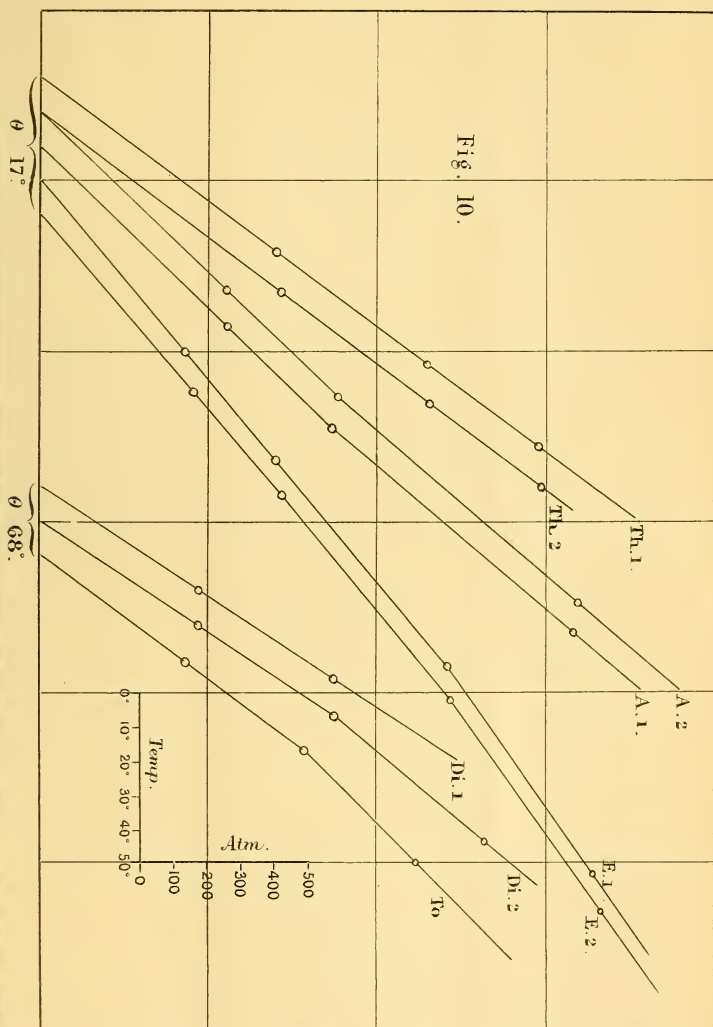


Fig. 6.  
Bow-shaped cycles, obtained in comparing  
the Tait with the Bourdon gauge.

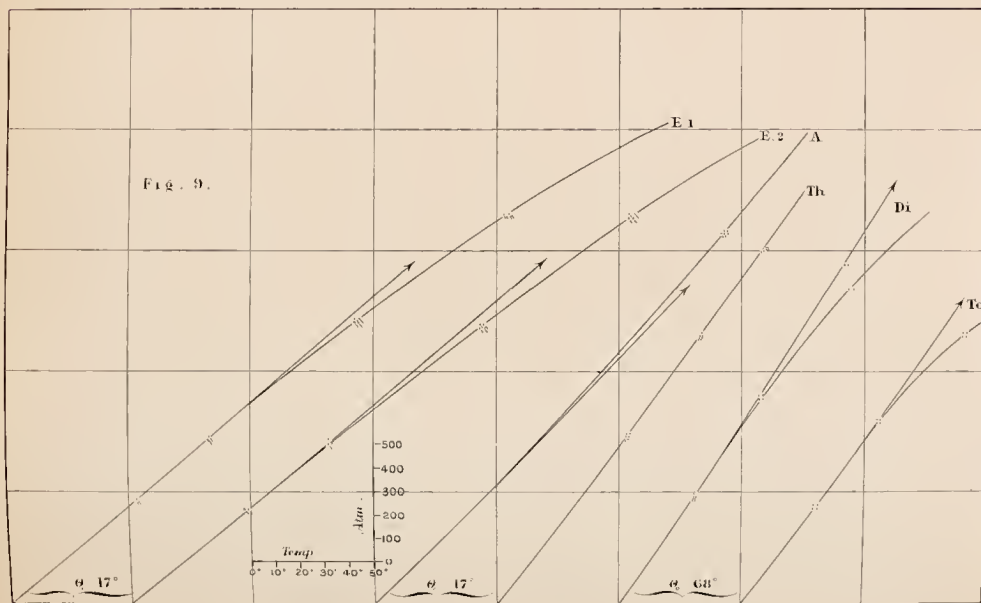
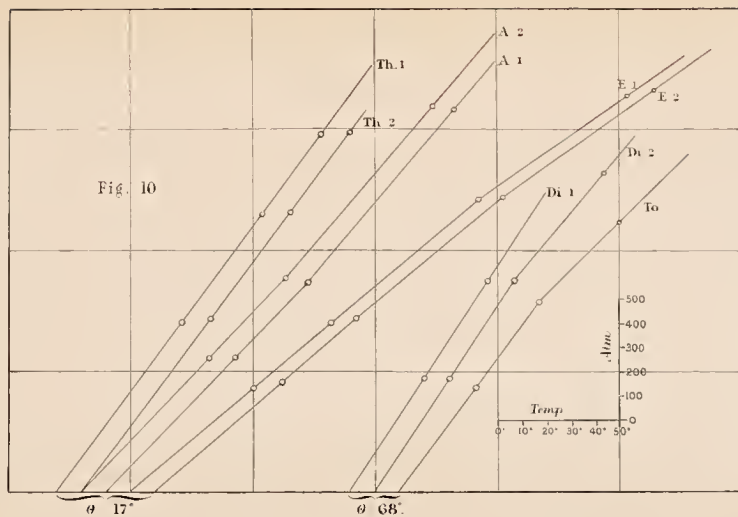




Fig. 10.







Charts showing the isometries corresponding to tables 8 and 10 respectively.





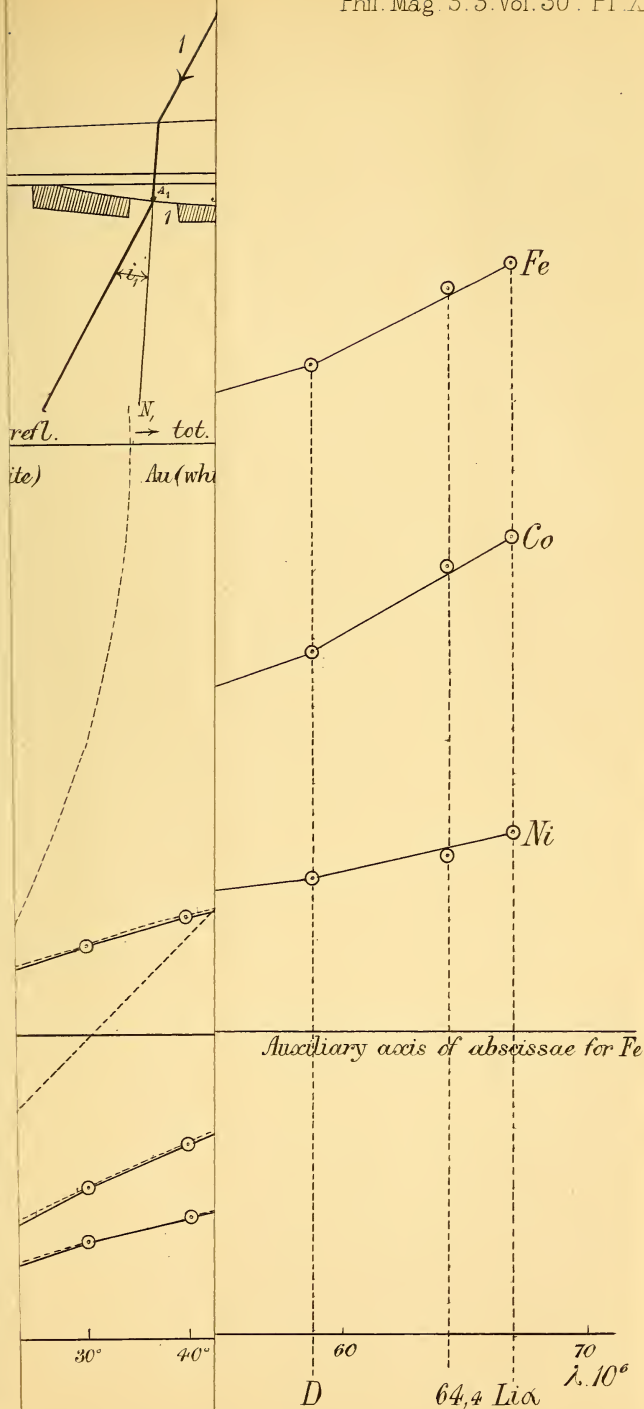




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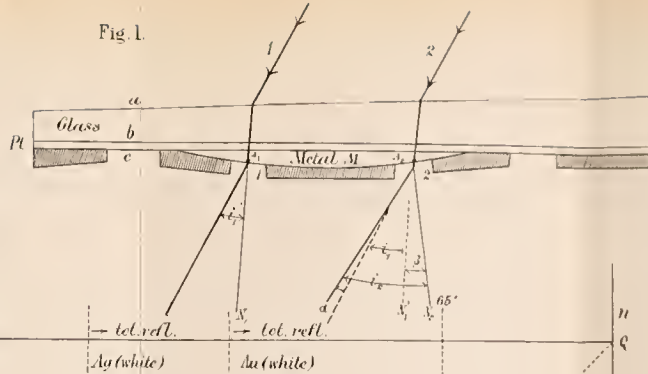


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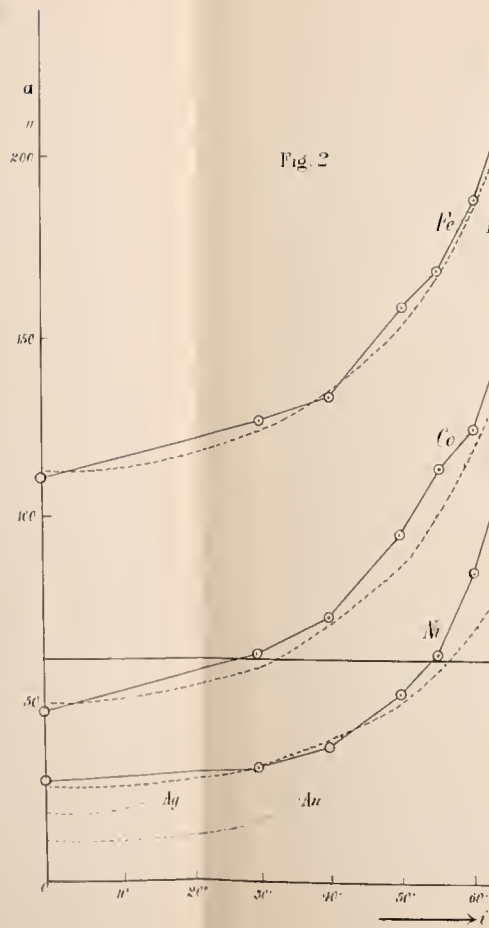


Fig. 3

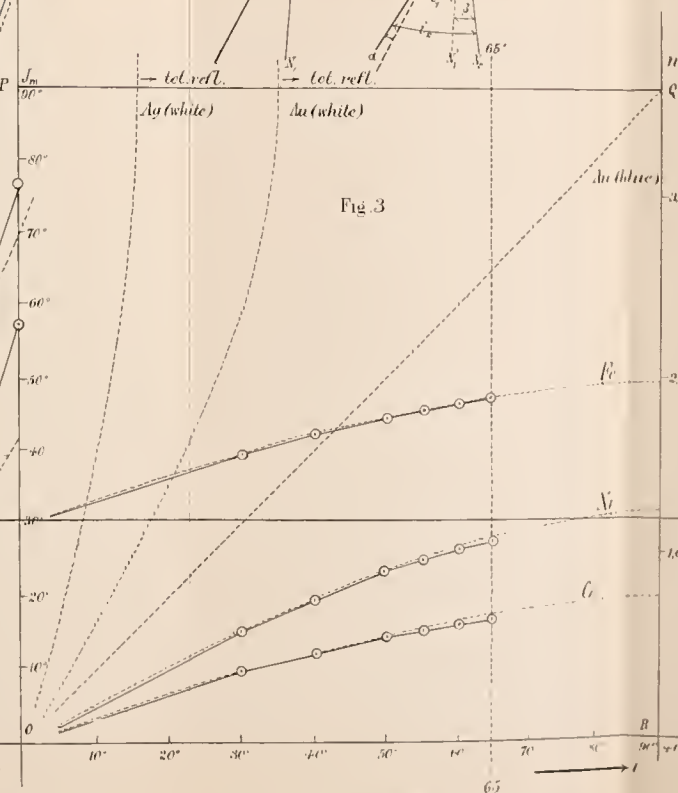
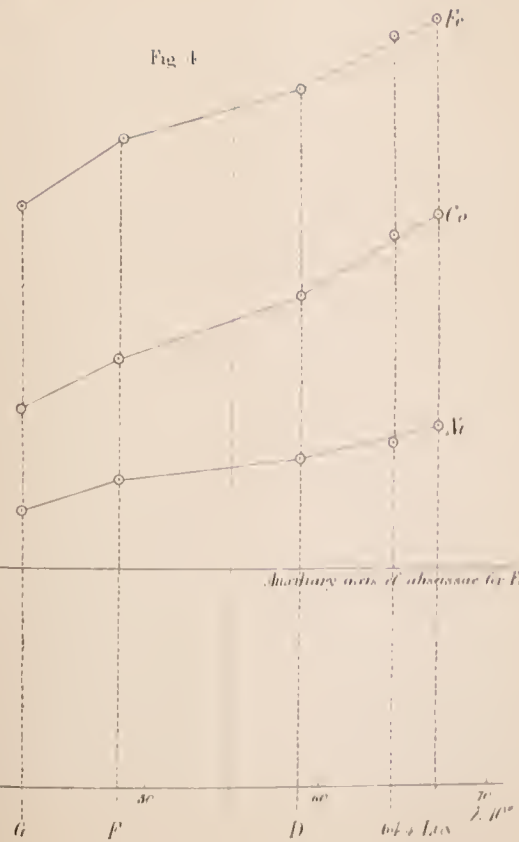
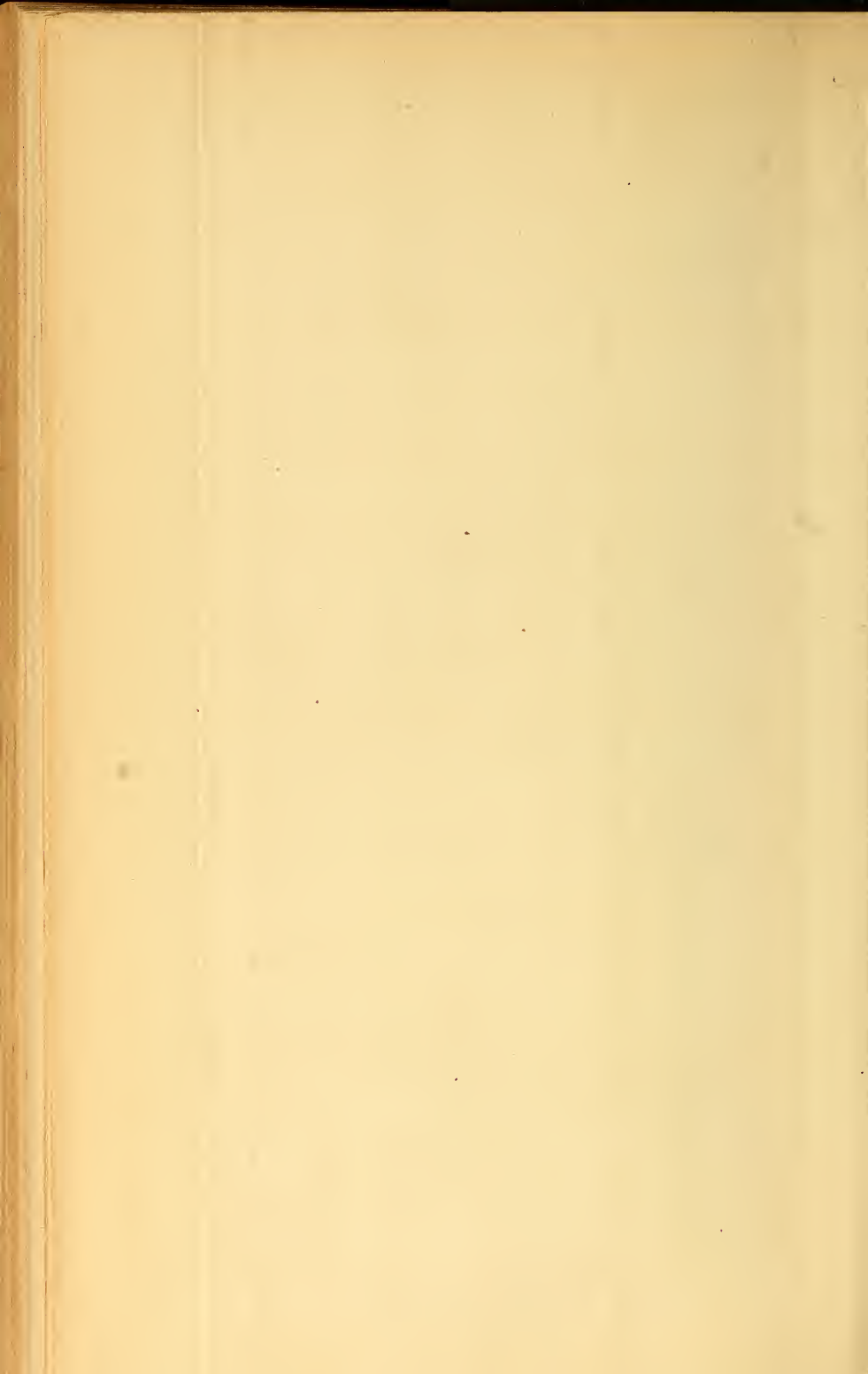


Fig. 4







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- Page 156, line 16, read square of the wave-length.  
 — 158, lines 21, 22, and 23, read  $n'\nabla^2u$ ,  $n'\nabla^2v$ ,  $n'\nabla^2w$ .  
 — — line 24, read  $n'$  for  $n$ .

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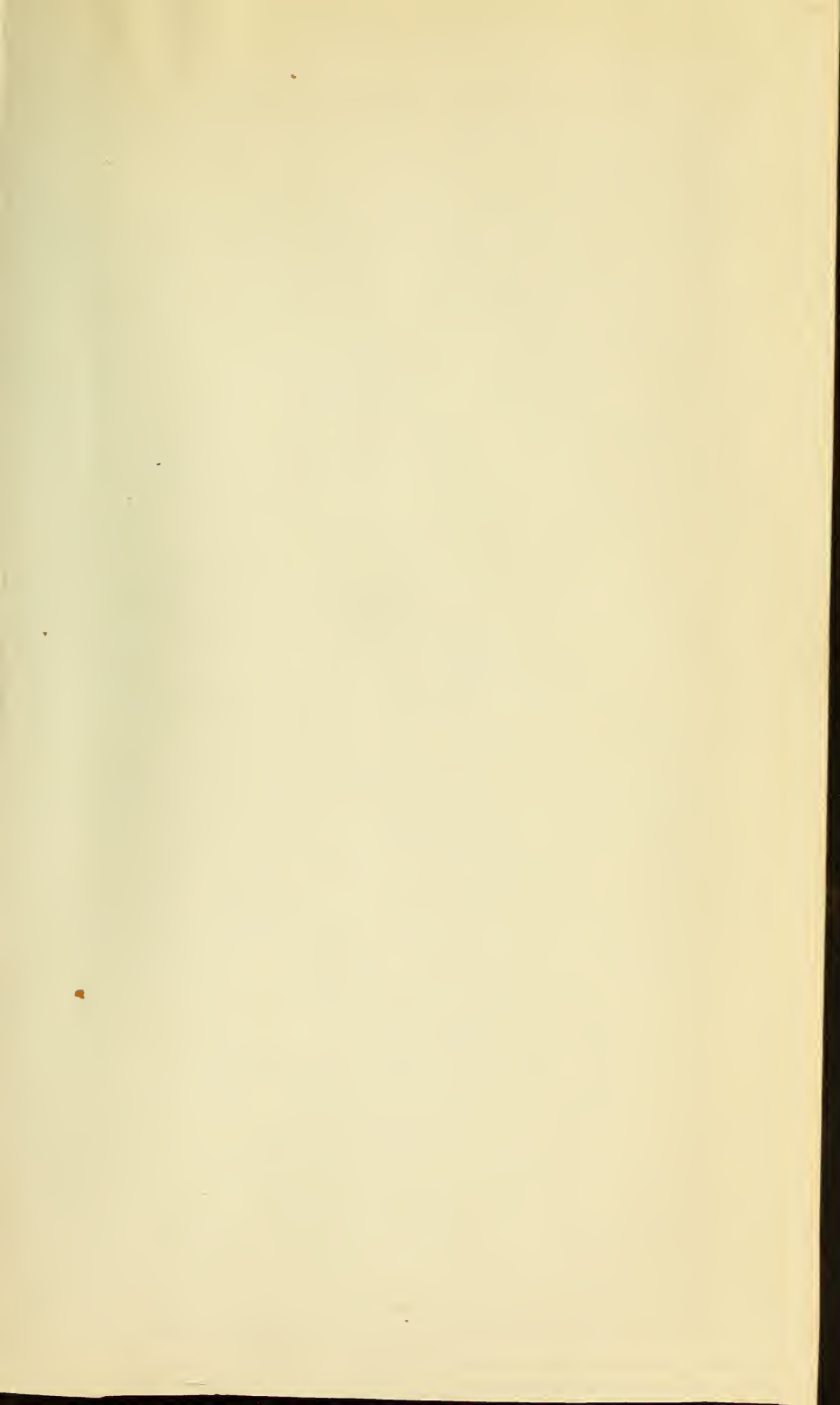
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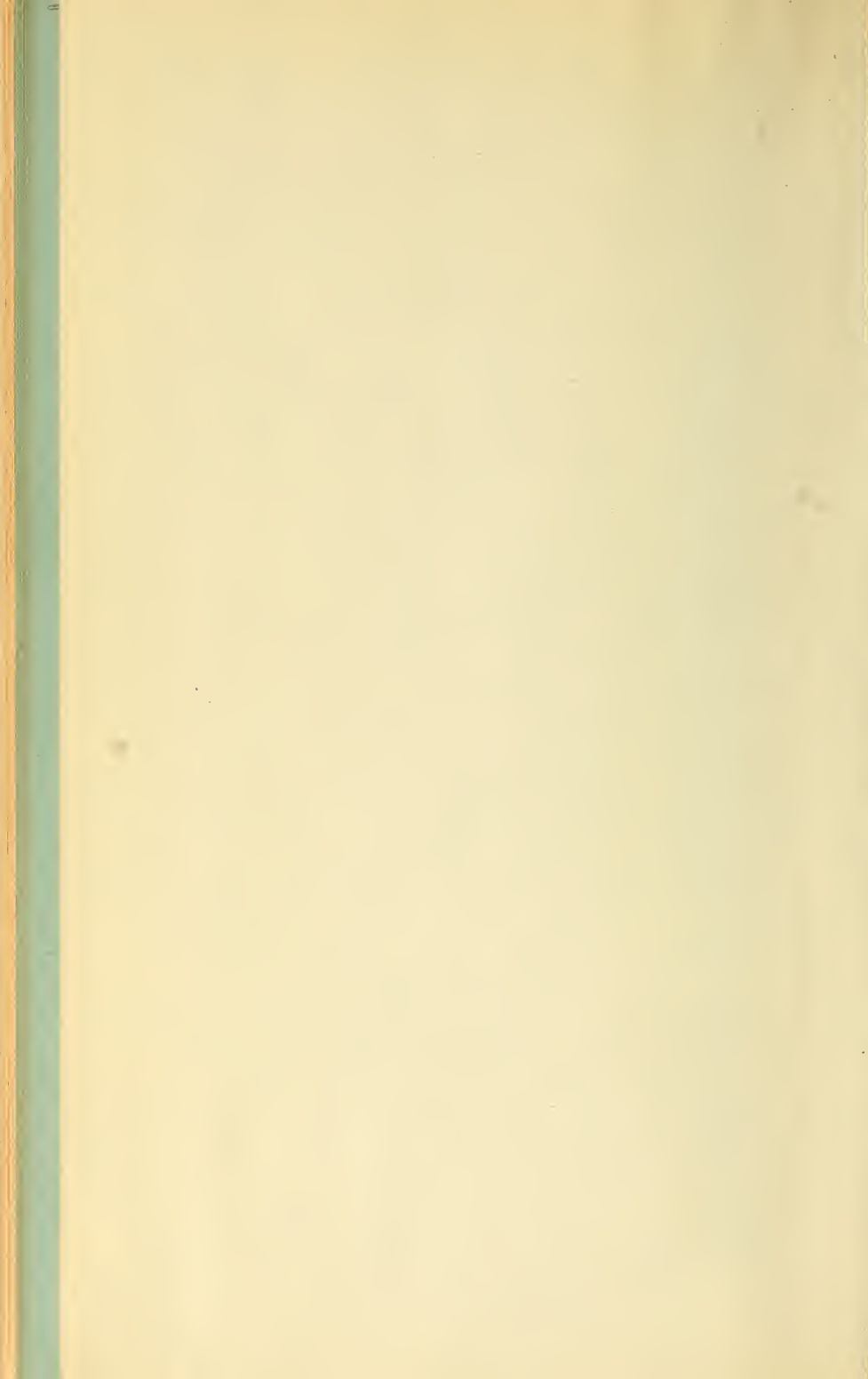
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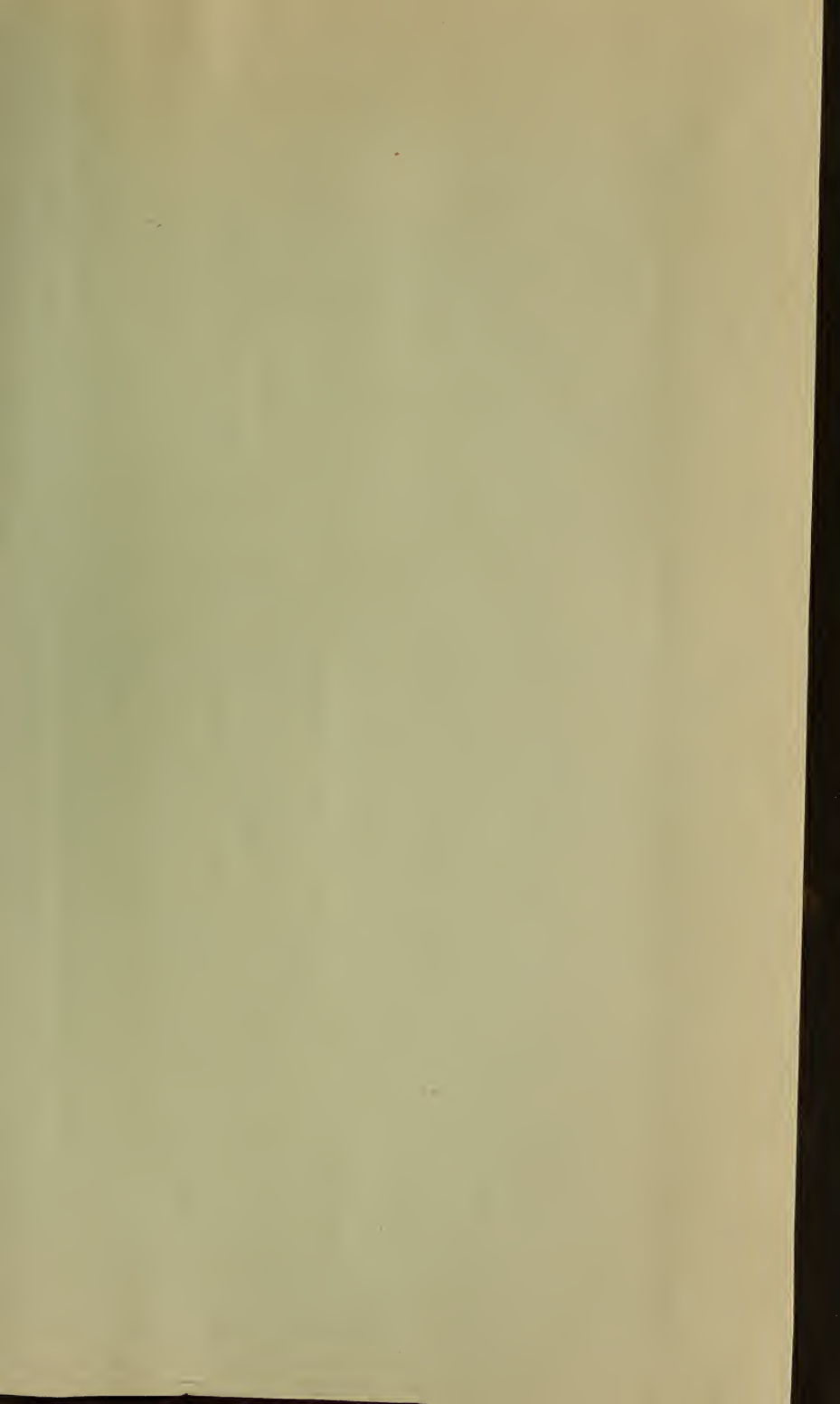
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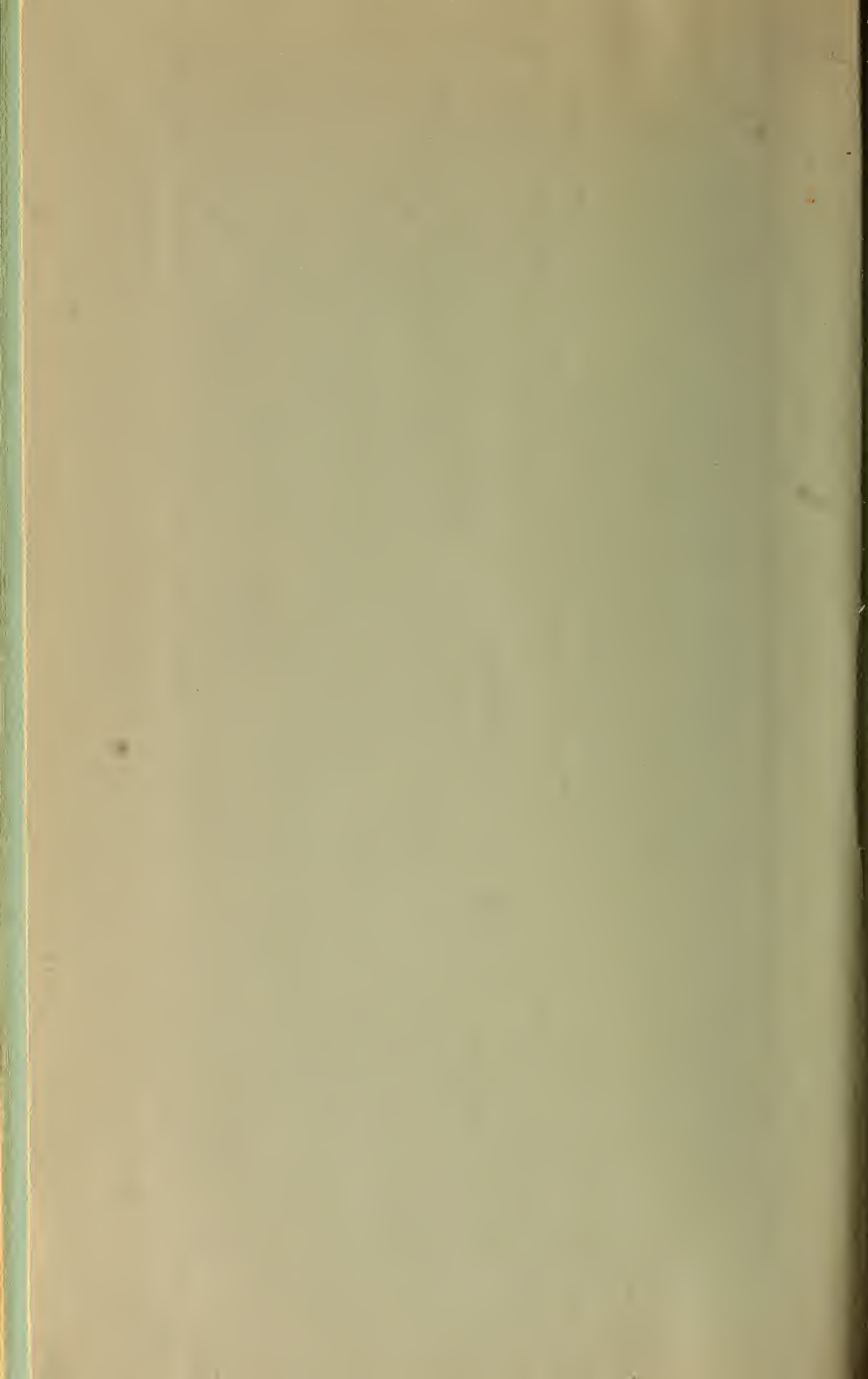
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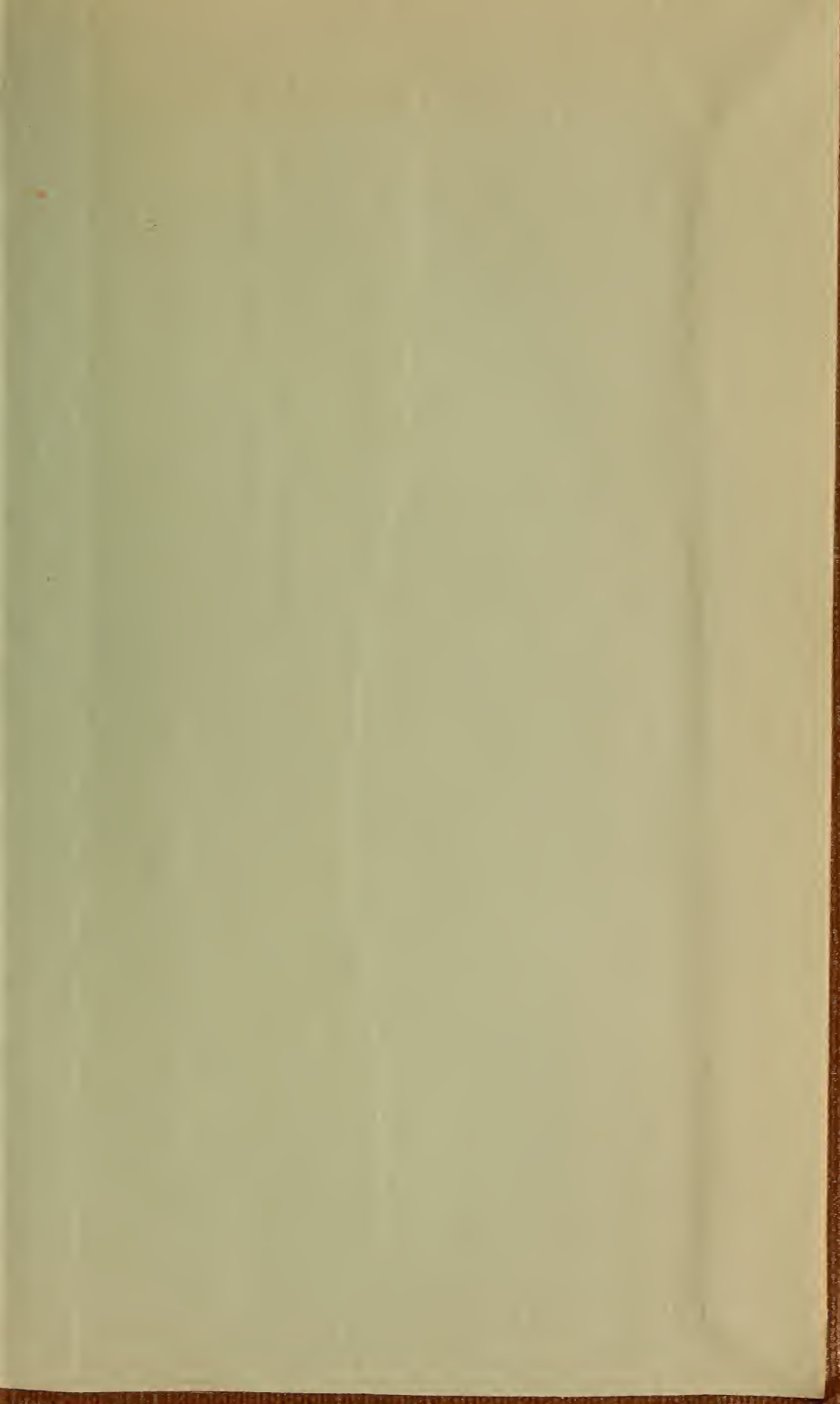












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