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PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND
THEORETICAL PHYSICS

CONDUCTED BY

EDWARD L. NICHOLS, ERNEST MERRITT
AND FREDERICK BEDELL

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CONTENTS OF VOLUME III.

XIII. JULY–AUGUST, 1895.

PAGE

Thermal Conductivity of Copper. II. *R. W. Quick, C. D. Child, and B. S. Lanphear* 1

On Ternary Mixtures. I. *Wilder D. Bancroft* 21

On the Secular Motion of a Free Magnetic Needle. II. *L. A. Bauer* 34

A Galvanometer for Photographing Alternating Current Curves. *H. J. Hotchkiss and F. E. Millis* 49

Minor Contributions: (1) Experiments with a New Polarizing Photo-chronograph as applied to the Measurement of the Velocity of Projectiles, *A. C. Crehore and G. O. Squier*; (2) Experimental Demonstration of a Law of Fluid Pressure, *W. J. Humphreys* 63

New Books: *Hertz:* Die Principien der Mechanik. *S. P. Thompson:* Elementary Lessons in Electricity and Magnetism. *Yeo:* Steam and the Marine Steam Engine . 73

XIV. SEPTEMBER–OCTOBER, 1895.

A Study of the Polarization of the Light emitted by Incandescent Solid and Liquid Surfaces. *R. A. Millikan* 81

Alternating Currents when the Electromotive Force is of a Zigzag Wave Type. *E. C. Rimmington* 100

On Ternary Mixtures. II. *W. D. Bancroft* 114

Minor Contributions: (1) On a Simple Method of Photographically Registering the Infra-red Energy Spectrum, *Knut Ångström*; (2) On the Electrolytic Conductivity of Concentrated Sulphuric Acid, *Dr. K. E. Guthe and L. J. Briggs* 137

New Books: *Helm:* Grundzüge der Mathematischen Chemie. *Ostwald's* Klassiker der Exacten Wissenschaften. *Mach:* Popular Science Lectures. Proceedings of the Electrical Society of Cornell University. *Naber:* Standard Methods in Physics and Electricity Criticised 152

XV. NOVEMBER–DECEMBER, 1895.

Variation in Electric Conductivity of Metallic Wires in Different Dielectrics. *Fernando Sanford* 161

A Study of the Polarization of the Light emitted by Incandescent Solid and Liquid Surfaces. II. *R. A. Millikan* 177

On Ternary Mixtures. III. *W. D. Bancroft* 193

On the Changes in Length produced in Iron Wires by Magnetization. *L. T. More* . 210

Notes: Eli W. Blake; The American Association for the Advancement of Science . 226

Minor Contributions: (1) The Limits of Pitch for the Human Voice, *W. LeConte Stevens*; (2) The New Physics Laboratory at Lille, *E. L. Nichols* 230

New Books: *Hertz:* Electric Waves. *Glazebrook:* Mechanics 234

XVI. JANUARY-FEBRUARY, 1896.

PAGE

On the Photometry of Differently Colored Lights and the "Flicker" Photometer. *Frank P. Whitman* 241

The Chemical Potential of the Metals. *Wilder D. Bancroft* 250

On the Freezing-points of Dilute Aqueous Solutions. *E. H. Loomis* 270

Minor Contributions: (1) Some Questions in Regard to the Author's Method of Measuring Freezing-points of Dilute Solutions, *E. H. Loomis;* (2) A Comparison of Two Concave Rowland Gratings, *Alice H. Bruère;* (3) A New Apparatus for the Study of Color Phenomena, *Ernest R. von Nardroff;* (4) On a New Form of Water Battery, *L. W. Austin and C. B. Thwing* 293

New Books: *Daniell:* Principles of Physics. *Whetham:* Solution and Electrolysis. *S. P. Thompson:* Polyphase Motors. *Palaz:* Industrial Photometry. *Walter:* Oberflächenfarben. *Clerke:* The Herschels and Modern Astronomy . . . 311

XVII. MARCH-APRIL, 1896.

On the Viscosity of Certain Salt Solutions. *B. E. Moore* 321

Notes on the Theory of Oscillating Currents. *Charles Proteus Steinmetz* . . . 335

An Experimental Study of Induction Phenomena in Alternating Current Circuits. *F. E. Millis* 351

Demagnetization Factors for Cylindrical Rods. *C. Riborg Mann* 359

A Photographic Study of Arc Spectra. I. *Caroline Willard Baldwin* 370

Minor Contributions: (1) The Surface Tension of Liquids, *Arthur L. Foley;* (2) The Resistance of Tin-foil as changed by Electric Waves, *C. D. Child* 381

New Books: *Lamb:* Hydrodynamics; *J. J. Thomson:* Elements of the Mathematical Theory of Electricity and Magnetism; *Story-Maskelyne:* Crystallography, a Treatise on the Morphology of Crystals; *Nipher:* Electricity and Magnetism; *Stanley:* Notes on the Nebular Theory; *Glazebrook:* Mechanics and Hydrostatics; *Menschutkin:* Analytical Chemistry; *Stevens:* Elementary Mensuration; *Nichols and Franklin:* Elements of Physics, I 390

XVIII. MAY-JUNE, 1896.

Solids and Vapors. *Wilder D. Bancroft* 401

On the Heat Effect of Mixing Liquids. *C. E. Linebarger* 418

The Influence of Heat, of the Electric Current, and of Magnetization upon Young's Modulus. *Mary Chilton Noyes* 432

A Photographic Study of Arc Spectra. II. *Caroline W. Baldwin* 448

Minor Contributions: (1) A Method for the Use of Standard Candles, *C. H. Sharp;* (2) The Graphical Representation of Magnetic Theories, *H. N. Allen;* (3) On the Alternating Current Dynamo, *W. E. Goldsborough* 458

New Books: *Roscoe and Harden:* A New View of Dalton's Atomic Theory; *Loudon and McLennan:* A Laboratory Course in Experimental Physics; *Ball:* A Primer of the History of Mathematics; *Bedell and Crehore:* Étude Analytique et Graphique des Courants Alternatifs; Theorie der Wechselströme in Analytischer und Graphischer Darstellung; *Holman:* Computation Rules and Logarithms, with Tables of Other Useful Functions; *Hornby:* A Text-book of Gas Manufacture . . . 483

Volume III. *July–August, 1895.* *Number 1.*

THE

PHYSICAL REVIEW.

THERMAL CONDUCTIVITY OF COPPER.

BY R. W. QUICK, C. D. CHILD, AND B. S. LANPHEAR.

PART II.

CONDUCTIVITY AT LOW TEMPERATURES.

By R. W. Quick and B. S. Lanphear.

IN Part I. appeared an account of an investigation on conductivity of copper between the range of temperature 70° to 170°. As was there stated, many investigations have been made relative to the subject at ordinary and high temperatures, but, to the knowledge of the writers, no experiments had hitherto been made with the object of determining the absolute value of the thermal conductivity K and its dependence on temperature at temperatures below the freezing point. This fact induced the writers to extend their observations on the copper bar already described, to temperatures as low as −60° C.

I.

The Measurement of Temperature.

In dealing with low temperatures, the method employed for measuring the temperature of the bar has to be considerably modified; for the Wheatstone slide wire bridge cannot, in this case, be calibrated *directly* for temperatures of the bar by means of a mercury thermometer, as was done in the first part of this investigation. Therefore, in addition to the requirement of a means of detection of small changes of resistance, the measurement of the low temperatures of the bar involves: (1) a knowledge of the temperature coefficient of resistance of the wire on the collar through the range 0° to −60°, and (2) a knowledge of the temperature difference between the wire on the collar and the bar beneath it, if such difference exists.

(*a*) *Determination of the temperature coefficient of the wire.*

Now if the curve of resistances and temperatures of the wire be a straight line, the determination of the coefficient α would involve only a measurement of resistance of the wire corresponding to two known temperatures. Dewar and Fleming,[1] who investigated resistances of various metals from high temperatures to nearly −200° C., found that the curve of resistance and temperature of electrolytic copper wire was almost exactly a straight line, with a coefficient 0.00410. In consequence of this fact, together with the fact that experiments on the wire, conducted by the writers, at temperatures above the freezing point, seemed to give a fairly straight line, it was decided to obtain the resistance of a portion of the wire at the temperatures of melting ice and melting mercury (the latter temperature being well established), to calculate α from these observations, and by observing the temperature corresponding to a certain resistance of the wire on the collar, draw a straight line at proper pitch through the point thus located, and to use this curve in reading temperatures corresponding to any resistance. The slide wire bridge was of course easily calibrated for resistances by aid of a standard Wheatstone plug bridge.

To obtain the temperature of the wire at the freezing point of mercury, the following arrangement was used, which proved in every way successful: Referring to Fig. 6, *t* is a tube about 1 cm. long and 7 mm. in diameter, open at one end, and constructed from very thin sheet copper. On the outside of this cylindrical

---

[1] London Electrician, v. 29.

tube, and separated from it only by tissue paper to secure good insulation, a portion of the fine insulated copper wire was wound in a single layer, having its terminals joined to very heavy wires which passed through holes in the cork of a glass tube *t'* about 5 cm. long and 2 cm. in diameter, into which the small copper tube *t* was placed, as shown in the figure. The glass tube was then enclosed in a glass bottle *T*, with an air space of about 1 cm. between the two. In the copper tube was placed a small globule of pure mercury.

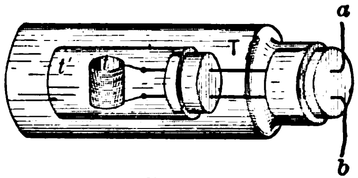

Fig. 6.

Since both the mercury and the wire were in close contact with the same good thermal conductor, and since no sudden change could affect the copper tube by virtue of the double air space, the wire was *very* nearly at the temperature of the mercury. The precise moment of solidification of the mercury was told by the cessation, under slight jars, of the gliding motion peculiar to the globule so long as a surface film existed. Likewise, in passing from the solid into the liquid, at the moment a surface film was formed, the globule which in its solid state remained motionless when subjected to slight jars, would glide off on the bottom of the tube. In order to prevent the formation of white frost on the inside of the glass, which would obscure the observations, perfectly dry air was passed for a considerable length of time into the tubes, after which the bottle was sealed with paraffin around the cork. The terminals *a* and *b* were joined to the slide-wire bridge, and the bottle was cooled by surrounding it with a cotton jacket containing carbon dioxide snow. A small aperture in the jacket directly above the top of the copper tube permitted observations on the condition of the mercury globule. An artificial light could not be used, owing to low radiant efficiency and consequent emission of sufficient heat to affect the temperature of the wire. To eliminate any error that might have arisen by simply taking the resistance when the globule solidified, the latter was alternately frozen and melted many times in succession by simply pressing tightly or loosening the cotton jacket filled with CO_2

snow; and, moreover, these changes were brought about so gradually that the readings on the slide bridge corresponding respectively to the freezing and the melting of the mercury were brought within one division of each other, — where one division is equivalent to 0.2° C.

To obtain the resistance near 0°, the bottle *T* (Fig. 6) was surrounded by melting snow, and after the mercury of the thermometer which was inserted through the two corks, so that its bulb was inside tube t', came to a stationary point, resistance and temperature were recorded. The temperature of the copper tube did not fall quite to 0°, on account of the heat conducted in by the leading-in wires. The temperature of freezing mercury was taken as $-38.6°$.

Table V. gives the data from which the coefficient α was computed.

TABLE V.

Temperature.	Bridge reading.	Resistance of wire.
−38.6	402.5	7.142
+ 1.5	667.6	8.556
	$\alpha = 0.004147$	

The coefficient thus obtained lies between the determination by Dewar and Fleming, 0.00410, and that of Cailletet and Bouty, 0.00423, both being over ranges of low temperatures. From the above value of α, and from the fact that the resistance of the coil on the collar at a temperature of 19.5° was 9.461, we have

$$R_t = 8.753\,(1 + 0.004147\,t),$$

which gives temperature in terms of resistance of the collar.

(*b*) *Determination of difference of temperature of collar and bar.*

It was found by experiment that at great temperature excesses of the bar over the air, the temperature of the wire of the collar was less than the temperature of the bar directly beneath the middle turn of the coil; and as the latter temperature is that which is required in both the statical and the absorption experiment, it was necessary to determine the correction to be applied to the temperatures obtained for the coil. This correction was arrived at under the following apparently justifiable assumption: If the collar be placed upon the bar, and the latter be heated to a certain temperature, giving a certain excess, the difference of temperature between the coil and the bar will be the same as when the bar is cooled to a temperature that gives the same excess (but of opposite sign). Three sets of observations were taken: First, when the end of the short bar containing a thermometer bulb was inserted through a board screen (viz. the end *E* of the box afterwards described, and shown in Fig. 7) and heated by an electric current to different stationary temperatures, with the collar placed upon the bar between the heated end and the thermometer; second, when the thermometer was between the heated end and the collar; and third, when the bar was heated to a uniform temperature by means of a solenoid conveying an electric current, and then allowed to cool, — in each case simultaneous readings being taken on the slide bridge to which the collar was attached, on the thermometer whose bulb was inside the metal bar, and on the thermometer which registered the temperature of the surrounding medium. From the data thus obtained, two curves were plotted with abscissæ as temperature excess of collar over air, and ordinates as temperature difference of bar and collar. The first curve was drawn from the first two sets of observations, and was used in correcting temperatures obtained from the resistance of the collar in the statical experiment; the second curve was drawn from the last set of observations, and gave the correction in case of the curve of absorption. Although the points located were quite irregularly disposed, they indicated the direction of the curve, and showed that the correction is by no means inappreciable, being at a temperature excess of 80°, between 4° and 5°.

II.

Determination of Data for the Statical Curve.

We now come to the determination of the final distribution of temperature along the bar when one end is maintained at the constant temperature of about $-70°$ C. When high temperatures are used, this experiment offers no special difficulties; but as soon as the bar becomes very cold, frost will be deposited upon it, which not only vitiates the surface, but prevents the movement of the collar. The bar must therefore be placed in an air-tight box with everything so arranged that the dew-point of the air within it may be reduced to a very low temperature, that the collar may be moved along the bar without introducing air into the box, and lastly, that a *constant* low temperature may be maintained at one end of the bar.

The box was constructed of dry wood with glass sides, and to insure imperviousness to moisture, the wood was painted on the inside with shellac and twice with asphalt varnish. The complete box is shown in Fig. 7. The front and back sides are each formed of three panes of glass. P and P' are two movable glass plates that were sealed during the experiment. B is the copper bar, one of whose ends projects about 1 cm. through the wooden end E of the box, while the other end rests on the wooden support S. r and r' are two iron rods about 8 mm. in diameter, which pass through the end E' of the box on a level with the bar, and which admit of longitudinal movement in the grooves of two wooden

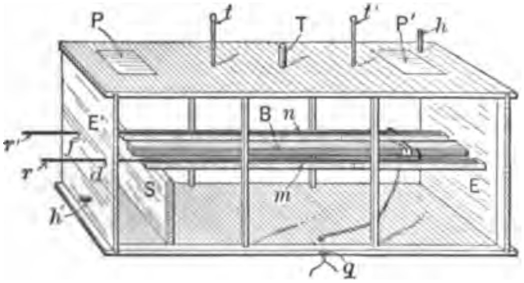

Fig. 7.

supports, *m* and *n*. The inside ends of these rods are so bent that a small torsional force applied at their protruding extremities will bring these ends in contact with the projections *c* or *c'* (Fig. 1, Part I.) of the collar. A longitudinal movement of the rods will then move the collar to any desired division on the bar, without the introduction of air, inasmuch as they pass through tightly fitting rubber tubes at *d* and *f*. The terminals of the collar were joined to a cable, and the latter was brought out of the box at *q*. A copper test tube *T*, extending into the box about 5 cm., provided means of testing the dew-point of the air within by showing whether frost was deposited on its surface when it was filled with a cooling mixture of CO_2 snow and ether. *t* and *t'* are thermometers used to determine the temperature of the air in the box. For about 24 hours immediately preceding the time of observations, air which had previously traversed a series of Y-shaped tubes filled with pumice-stone saturated with concentrated H_2SO_4, was forced into the box through *h*, and after diffusing itself through the air in the box, found its exit at *h'*. In this way the dew-point was sufficiently reduced to prevent deposition of frost on the tube *T* when filled with CO_2 snow and ether.

The end of the bar that extended through the wooden box was neatly soldered into the side of a copper box which had a capacity of about a liter. Fig. 8 is a horizontal cross-section of the cooled end of the bar and its surroundings. Around the copper box *B*, into which the cooling mixture was placed, were three wooden boxes *b*, *b'*, *b''*, having only one common side, and separated from each other by the three air spaces *a*, *a'*, *a''*, loosely filled with cotton to prevent convection currents. These boxes were provided with small slide covers for the purpose of renewing the liquid in the copper receptacle.

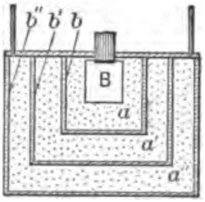

Fig. 8.

When the test for the dew-point showed that the air was sufficiently dry to begin cooling the bar, the box at the end of the bar was filled with ether, and CO_2 snow added until the liquid became saturated with the snow. The temperature of this mixture, according to Cailletet and Colardeau, is $-75°$; but since its exact temperature was not required in the experiment, no determination of it was made. According to the authority above quoted, this mixture of a *saturated* solution of carbon dioxide snow in ether undergoes scarcely any changes of temperature. The dioxide was obtained in this solid state by drawing off the liquid kept in iron cylinders under high pressure. About two quarts of snow were drawn off at each time, and this was maintained ready for use with small loss from evaporation, in a box surrounded with other boxes, much in the manner as the liquid at the end of the bar was guarded from heat.

To test the constancy of the temperature at the end of the bar, two devices were employed. A thermo-junction was placed in the

TABLE VI.

DATA FOR CURVE OF FINAL DISTRIBUTION OF TEMPERATURE ALONG THE BAR WHEN ONE END IS MAINTAINED AT A CONSTANT LOW TEMPERATURE.

Dist. in cm. from cold end.	Temp. of air in box.	Bridge readings.	Resistance from curve.	Resistance of collar.	Temp. of collar	Excess collar over air.	Excess bar over collar.	Excess bar over air.
0	14.7	378.6	7.550	6.900	−51.1	−65.7	−3.3	−69.0
5	14.6	417.5	7.751	7.900	−45.6	−60.2	−2.8	−63.0
10	14.8	453.4	7.936	7.286	−40.4	−55.2	−2.4	−57.6
15	14.9	477.6	8.061	7.411	−37.0	−51.9	−2.0	−53.9
20	15.0	498.2	8.167	7.117	−34.1	−49.1	−1.9	−51.0
25	15.1	518.4	8.272	7.662	−31.2	−46.3	−1.7	−48.0
30	15.2	543.0	8.400	7.750	−27.6	−42.9	−1.4	−44.3
35	15.4	555.1	8.466	7.816	−25.8	−41.2	−1.3	−42.5
40	15.6	570.8	8.556	7.906	−23.3	−38.9	−1.2	−40.1
45	15.7	582.7	8.627	7.977	−21.4	−37.1	−1.0	−38.1
50	15.8	594.7	8.701	8.051	−19.3	−35.1	−0.9	−36.0
55	15.9	604.1	8.753	8.103	−17.9	−33.8	−0.9	−34.7
60	15.9	611.7	8.793	8.143	−16.8	−32.7	−0.8	−33.5
65	15.9	620.5	8.833	8.183	−15.7	−31.6	−0.8	−32.4
70	15.7	627.7	8.866	8.216	−14.8	−30.5	−0.7	−31.2
75	15.7	632.3	8.888	8.238	−14.2	−29.9	−0.7	−30.6
80	15.6	637.6	8.915	8.265	−13.4	−29.0	−0.6	−29.6
85	15.9	643.7	8.948	8.298	−12.5	−28.4	−0.6	−29.0
90	15.2	639.8	8.928	8.278	−13.1	−28.3	−0.6	−28.9
95	14.9	643.3	8.947	8.297	−12.6	−27.5	−0.6	−28.1
100	15.3	646.0	8.962	8.312	−12.2	−27.5	−0.6	−28.1

cooling mixture very close to the end of the bar, and the terminals joined through keys to the slide bridge galvanometer. Also, just inside the end *E* of the wooden box, a few turns of the 0.002 in. insulated wire were wound directly on the bar, and its terminals joined to a Wheatstone plug bridge.

About three hours after the cooling mixture was placed in the receptacle *B* (Fig. 8), the bar came to a statical temperature condition, as was indicated by the slide bridge to which the collar was connected. By frequent observations of the thermo-element, and of the resistance of the fine wire directly on the bar, it was ascertained that the fluctuations of temperature at the end of the bar were not large enough to appreciably affect the distribution of temperature along the bar. In Table VI. are the observed and calculated data for the construction of the statical curve shown in Fig. 9. The second column is the average of the readings of the two thermometers that registered the temperature inside the box. Column 4 is obtained from the calibration curve of the slide bridge. Column 5, which is made up from the preceding column

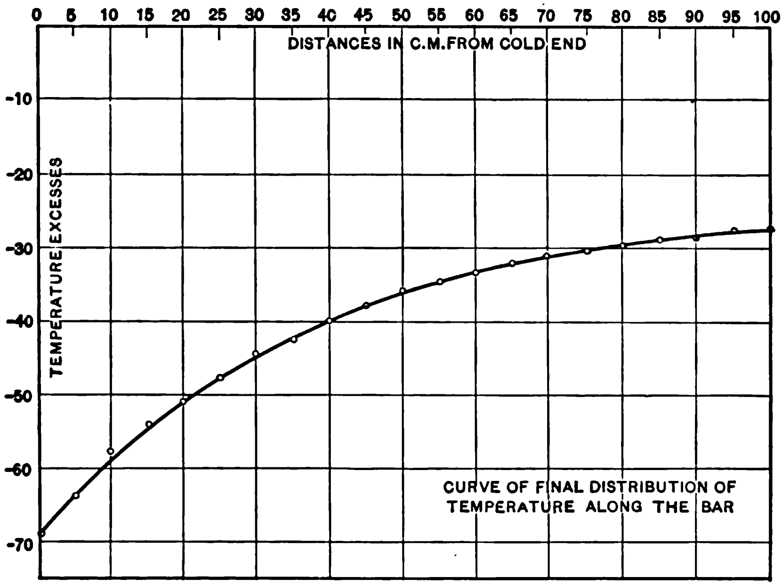

Fig. 9.

by subtracting the resistance 0.65 of the line in the room, and not subjected to temperature changes, is converted into temperatures of column 6 by the formula already obtained,

$$R_t = 8.753\,(1 + 0.004147\,t).$$

Subtracting (algebraically) the temperature of the air from numbers in column 6, gives column 7, and adding to these the temperature difference of collar and bar as obtained by curve already described, gives the last column, which, together with the corresponding distances in centimeters of column 1, gives the coördinates of the curve in Fig. 9.

III.

Cooling and Absorption Experiments.

In investigations on conductivity, it seems to have been customary to obtain the curve of cooling of a short bar of the same material and cross-section, and to use this curve in connection with the statical curve of the long bar. In the present case, experiments of cooling on the two bars, whose lengths it will be remembered were respectively about 100 cm. and 20 cm., showed that their rates of cooling at the same temperature excess were noticeably different, the surface being as nearly the same as possible. And since it is probable that the emissivity is a function of the temperature, it was necessary to obtain the rates of heat absorption of the long bar at different negative excesses. Although the method devised for obtaining the requisite observations for the absorption curve of the short bar was applicable to the long one, it was not feasible on account of the limited supply of liquid CO_2 at our disposal, and hence the rates of absorption of the long bar were obtained in an indirect manner. Now it must be nearly, if not rigorously, true that the ratio of the rates of cooling of the short and long bars at any positive excess is the same as the ratio of their rates of heat absorption at an equal negative excess,— other conditions being the same. Hence if at a certain excess, B and b are the tangents to the curve of cooling of the long and short bars respectively, and A and a are the respective tangents to the curves of absorption at an equal negative excess, we have

$$A = \frac{aB}{b}, \tag{2}$$

which gives the rates of heat absorption of the long bar in terms of obtainable quantities. Observations must hence be taken for three curves, viz., absorption curve of short bar and the cooling curves of both bars.

(*a*) *Absorption curve of short bar.*

In order to obtain observations for this curve, the bar must be cooled in a perfectly dry atmosphere, to a uniform temperature as low as the lowest temperature observed in the statical experiment; it must be removed from the cooling apparatus and placed in the *dry* atmosphere of the wooden box, so as to be under conditions similar to those of the long bar in the statical experiment; and, moreover, this must be done with the collar on the bar, not only to afford a means of ascertaining its temperature condition before being removed from the cooling chamber, but to be ready to begin observations soon after thus removed.

The above requirements were met in the following way: The collar was placed on the short bar and the latter placed in a specially constructed, tightly fitting, tin box, which is shown in Fig. 10. This box, B', which contained the bar, was soldered into another tin box, B, such that there was an air space of about 2 cm. surrounding the box B' on five sides. In the figure a portion of the outside box is broken away, showing this air chamber, with which there was no communication except through the two glass tubes t and t', each about $\frac{3}{4}$ inch in diameter, that extended through the end E of the wooden box of

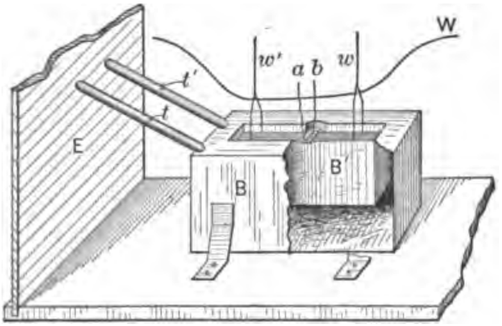

Fig. 10.

Fig. 7, from which the long bar had been removed. *a*, *b* are the terminals of the collar, and *w*, *w'* are wires passing through very small holes in the top of the wooden box and fastened respectively to two loops of small wire that passed around each end of the bar.

Table VII.

DATA FOR TIME CURVE OF ABSORPTION OF SHORT BAR.

Time.		Temp. of air.	Bridge readings.	Resistance from curve.	Resistance of collar.	Temp. of collar.	Excess collar over air.	Excess bar over collar.	Excess bar over air.
min.	sec.								
0	15	16.1	371.6	7.515	6.865	−52.0	−68.1	−4.0	−72.1
1	5	16.1	383.3	7.574	6.924	−50.4	−66.5	−3.8	−70.3
2	24	16.1	400.9	7.665	7.015	−47.9	−64.0	−3.5	−67.5
4	12	16.0	422.7	7.778	7.128	−44.8	−60.8	−3.3	−64.1
5	16	16.0	435.7	7.845	7.195	−42.9	−58.9	−3.1	−62.0
6	52	16.0	452.7	7.933	7.283	−40.5	−56.5	−2.8	−59.3
8	30	16.0	470.2	8.023	7.373	−38.0	−54.0	−2.6	−56.6
9	55	16.0	484.8	8.099	7.449	−35.9	−51.9	−2.4	−54.3
10	58	15.9	494.9	8.150	7.500	−34.5	−50.4	−2.3	−52.7
12	47	15.9	512.0	8.240	7.590	−32.0	−47.9	−2.1	−50.0
13	46	15.9	520.5	8.284	7.634	−30.8	−46.7	−2.0	−48.7
14	59	15.9	530.4	8.334	7.684	−29.5	−45.4	−1.8	−47.2
16	19	15.9	542.0	8.396	7.746	−27.8	−43.7	−1.7	−45.4
18	13	15.9	556.5	8.474	7.824	−25.6	−41.5	−1.5	−43.0
21	2	15.8	576.0	8.587	7.937	−22.5	−38.3	−1.4	−39.7
23	19	15.8	590.2	8.675	8.025	−20.0	−35.8	−1.2	−37.0
25	33	15.9	603.1	8.748	8.098	−18.0	−33.9	−1.1	−35.0
28	16	15.9	617.3	8.817	8.167	−16.1	−32.0	−1.0	−33.0
30	38	15.9	628.1	8.867	8.217	−14.7	−30.6	− .9	−31.5
32	18	15.9	635.3	8.903	8.253	−13.7	−29.6	− .9	−30.5
35	0	15.9	646.1	8.963	8.313	−12.1	−28.0	− .7	−28.7
37	13	15.9	654.7	9.010	8.360	−10.8	−26.7	− .7	−27.4
39	8	15.9	661.4	9.051	8.401	− 9.7	−25.6	− .7	−26.3
40	54	15.9	667.5	9.088	8.438	− 8.7	−24.6	− .6	−25.2
42	34	16.0	673.2	9.123	8.473	− 7.7	−23.7	− .5	−24.2

In order to cool the bar, a viscous mixture of CO_2 snow and ether was poured into one of the glass tubes till the liquid began to rise in the tubes, which easily carried off the vapor arising from

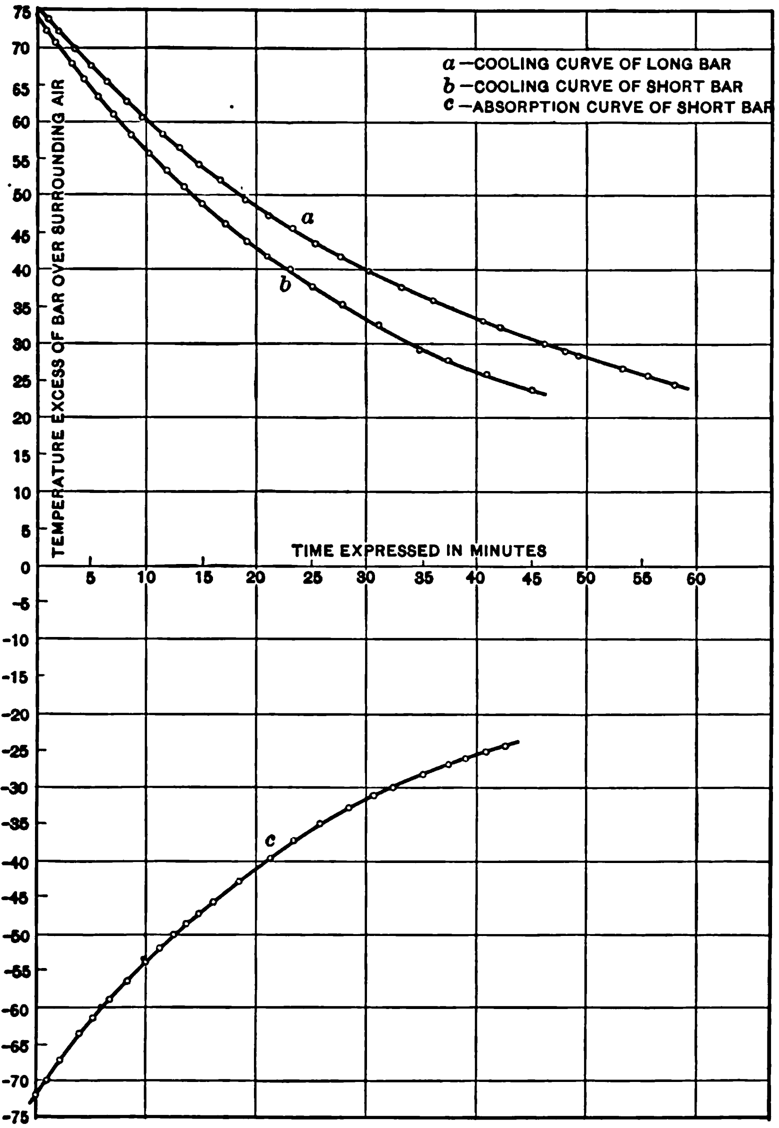

Fig. 11.

the violent ebullition of the liquid. To maintain the liquid at a low temperature, carbon dioxide snow was constantly pushed down the glass tubes (alternately) by means of a closely fitting wooden piston. When the slide bridge to which the collar was attached showed that the temperature was sufficiently low and constant, the bar was lifted out of the receptacle by means of wires *w*, *w′* (Fig. 10), and swung off out of the influence of the

Table VIII.

DATA FOR CURVES OF COOLING.

Short bar.			Long bar.		
Time.		Excess of bar over air.	Time.		Excess of bar over air.
min.	sec.		min.	sec.	
0	40	73.2	0	36	74.2
1	53	70.7	1	57	71.7
3	12	68.2	3	27	69.4
4	27	65.7	4	51	67.2
5	49	63.3	6	15	65.0
7	11	60.9	7	56	62.7
8	40	58.3	9	35	60.4
10	10	55.9	11	18	58.3
11	50	53.5	13	0	56.1
13	25	51.2	14	53	54.0
15	8	48.9	16	45	51.9
17	8	46.8	18	45	49.8
19	12	44.5	20	50	47.7
21	14	42.2	23	15	45.7
23	21	40.0	25	26	43.7
25	40	37.6	27	57	41.8
28	11	35.3	30	21	39.9
31	15	33.1	33	15	38.1
35	25	29.6	36	8	36.0
37	18	28.6	40	40	33.1
40	55	26.6	42	27	32.3
44	45	24.3	45	48	30.4
			47	43	29.3
			49	38	28.5
			53	31	26.8
			55	41	25.8
			57	53	24.8

cooling chamber by aid of the wire *W* which passed through each end of the large wooden box. Soon after, observations were begun. The air of the large wooden box had, of course, been previously thoroughly dried in the manner already described.

In Table VII. are the data, both observed and calculated, for the absorption curve of short bar. As the columns are arranged in the same manner as in Table VI., no explanation is necessary. From the first and last columns of this table, curve *c*, Fig. 11, was constructed.

(*b*) *Cooling curves of both bars.*

These observations were made according to the method which has already been described in IV., Part I., except that in this case each bar was allowed to cool within the wooden box, in order to preserve the conditions for radiation as nearly the same as possible as those for absorption. The bridge was calibrated directly for temperatures, as was described in Part I. The reason for calibrating the bridge for these observations directly for temperatures of the bar is twofold: first, in order to obtain readings on the slide bridge over the range of 20° to 100°, the resistances r and r' (Fig. 2, Part I.) had to be changed, thus, in any case, necessitating a re-calibration of the bridge; second, the temperature coefficient of the coil on the collar might be slightly different for high temperatures, and this difference would have to be determined.

In Table VIII. are given the data for the curves of cooling of both bars, from which curves *a* and *b* (Fig. 11) were constructed. The difference in the rates of cooling of the long and short bars is plainly evident, and also a slight difference in the direction of the curves of cooling and absorption of the short bar.

IV.

Deduction of Results.

It now remains to construct the curve whose area, multiplied by the product of specific heat and density, is equal to the quantity of heat absorbed per second by the bar when one of its ends was maintained at a low temperature. Table IX. contains the calculated data for this curve. Columns 2, 3, and 4 are the respective tangents to the cooling curve of short bar, absorption curve of short bar, and cooling curve of long bar. These were taken from the curves of Fig. 11 at temperature excesses of the bar, which were read from the statical curve of Fig. 9 at the different distances of column 1. The numbers of the last column are tangents to the hypothetical absorption curve of long bar, and are obtained according to formula (2); *i.e.*, by dividing the product of columns 3 and

TABLE IX.

DATA FOR CURVE OF RATES OF ABSORPTION CORRESPONDING TO DIFFERENT POINTS ALONG THE BAR WHEN UNDER THE CONDITIONS OF THE STATICAL EXPERIMENT—INTEGRATION CURVE.

Distance in cm. from cold end.	Tangent to curve of cooling of short bar. $\left(-\frac{dv}{dt}.\right)$	Tangent to curve of absorption of short bar. $\left(\frac{dv}{dt}.\right)$	Tangent to curve of cooling of long bar. $\left(-\frac{dv}{dt}.\right)$	Tangent to curve of absorption of long bar (calculated). $\left(\frac{dv}{dt}.\right)$
0	0.03355	0.03500	0.02721	0.02840
5	0.02950	0.03100	0.02400	0.02522
10	0.02773	0.02872	0.02166	0.02240
15	0.02375	0.02545	0.01914	0.02050
20	0.02180	0.02330	0.01720	0.01838
25	0.02010	0.02240	0.01548	0.01724
30	0.01890	0.02125	0.01400	0.01574
35	0.01810	0.02030	0.01300	0.01460
40	0.01700	0.01880	0.01214	0.01343
45	0.01594	0.01695	0.01146	0.01220
50	0.01533	0.01592	0.01080	0.01123
55	0.01421	0.01392	0.01030	0.01010
60	0.01328	0.01236	0.01000	0.00931
65	0.01267	0.01160	0.00944	0.00865
70	0.01200	0.01097	0.00900	0.00823
75	0.01160	0.01067	0.00853	0.00785
80	0.01110	0.01037	0.00827	0.00772
85	0.01076	0.01033	0.00796	0.00764
90	0.01053	0.01024	0.00783	0.00762
95	0.01046	0.01010	0.00780	0.00753
100	0.01024	0.00977	0.00773	0.00752

4 by column 2. From the first and last columns the curve in Fig. 12 was plotted, and its area was obtained by integration in

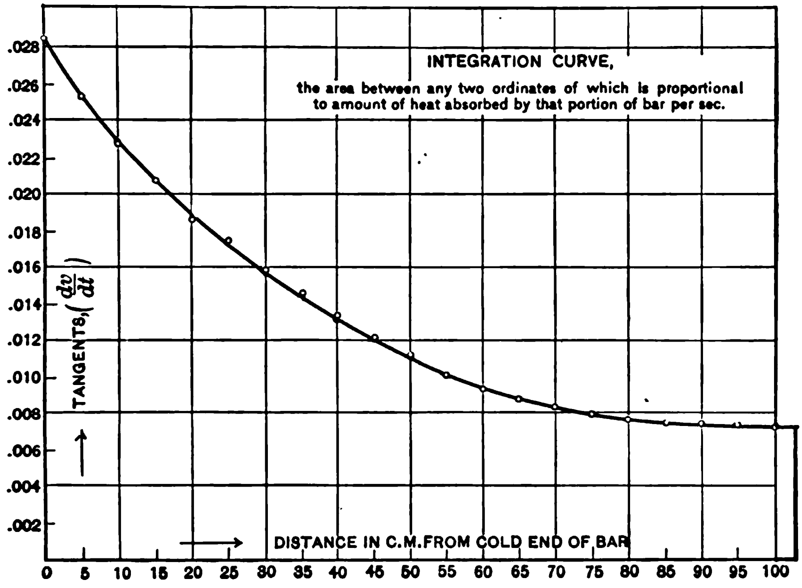

Fig. 12.

Table X.

DERIVED DATA FOR THE CURVE OF CONDUCTIVITY (K).

Distance (x) in cm. from cooled end of bar.	area, $\int_s^a \frac{dv}{dt} dx$.	Tangent to statical curve. $\frac{dv}{dx}$.	Temperature of copper.	Conductivity, K.
80	0.1692	0.125	−13.6	1.059
65	0.2917	0.217	−16.3	1.050
55	0.3855	0.289	−19.0	1.040
45	0.4952	0.372	−22.4	1.035
40	0.5575	0.422	−24.5	1.025
35	0.6255	0.475	−26.9	1.020
30	0.6999	0.542	−29.6	0.999
25	0.7812	0.605	−32.6	0.996
20	0.8701	0.690	−36.0	0.971
15	0.9676	0.785	−39.8	0.946
10	1.0748	0.873	−44.0	0.942
5	1.1939	0.986	−48.7	0.923
0	1.3273	1.095	−53.9	0.921

parts as is indicated in column 2 of Table X. In this column, to each number is added the area corresponding to the heat absorbed per second by the free end of the bar. This table is made up in the same way as the corresponding table of Part I. For the want of experimental data on the relation between specific heat and temperature over the range 0° to −60°, the same formula was used here as in the case of high temperatures, viz.: —

$$S_t = .0892(1 + 0.00073\,t).$$

Also the same variation in density was made use of, viz.: —

$$D_t = 8.862(1 - 0.000056\,t).$$ [1]

In Fig. 13 is the curve of conductivity plotted from the last two columns of Table X. and Table IV. (Part I.), and shows graphically the results of the complete investigation.

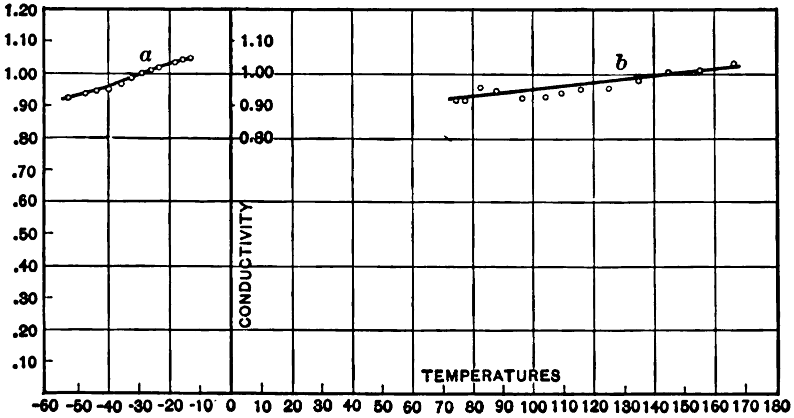

Fig. 13.

V.

Discussion of Results.

It is to be observed that the average value obtained for K over the range −54° to −13° is slightly higher than the average value over the range 74° to 166°, — being in the former case 0.994, and in the latter, 0.954. A curious fact is the much greater slope of

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[1] See V., Part I.

the curve over low temperatures. From these results one of two inferences may be drawn: first, that a maximum value of K exists at a temperature near 0°, since, if the curves *a* and *b* were joined, a point of inflexion must exist between $-10°$ and $+70°$; second, that owing to some error, the values of K in *a* are too great, or that the values of K in *b* are too small, thus producing the irregularity in the curve. As regards the latter inference, the authors state that the observations were not only taken with the greatest of care, but were also reduced with the utmost precaution to eliminate error. Of course, if values of K were obtained for temperatures between $-10°$ and $+70°$, a more definite conclusion could be reached. The reason those points were not obtained, thus filling in between the curves *a* and *b* (Fig. 13), may be briefly stated thus: when the excess of the temperature of the bar over air, or air over bar, is 30° or less, the slope of the curve of final distribution of temperature along the bar is so small in the case of copper, that great inaccuracies arise in the calculation of the tangents. A method for overcoming this difficulty, but which would impose conditions hard to realize, is to place the bar in an atmosphere whose temperature is maintained constant at 0°, and a temperature of about 80° kept at one end; or to maintain a temperature of about $-15°$ at one end of the bar which is placed in an atmosphere kept constant near 80°. In either case a good gradient would be obtained.

Over both ranges of temperature the results show an increase of K with increase of temperature. This is in accordance with the results of Tait, Lorenz, and Kirchoff and Hansemann, but is contrary to those of R. W. Stewart, who found a decrease of K in electrolytic copper, with increase of temperature over a range of high temperatures. His values of K were considerably greater than those hitherto obtained, a fact indicating that conductivity increases with the purity of the metal. Stewart's value of K at 0° obtained by extrapolation, coincides almost exactly with the K_0 obtained from curve *a*. It is to be hoped that further investigation will be made on electrolytic copper at temperatures near 0°, also at low temperatures, by using, perhaps, a cooling mixture whose boiling point is even lower than that of carbon dioxide snow and ether.

The authors desire to acknowledge their obligations to Dr. E. L. Nichols, who not only suggested the line of work, but who made many valuable suggestions as to details throughout the investigation.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
December, 1894.

ON TERNARY MIXTURES.

FIRST PAPER.[1]

By Wilder D. Bancroft.

FOLLOWING out the analogy between dissolved substances and gases, Nernst deduces the law that, when two dissolved substances have no common ion and do not react chemically, the influence of each on the solubility of the other is zero, within certain undefined limits. He says:[2] "Die Analogie zwischen der Auflösung und Sublimation bezw. Dissociation fester Stoffe zeigt sich nun auch deutlich ausgesprochen, was den Einfluss fremden Zusatzes betrifft. Ebenso wenig wie die Sublimationsspannung bei Gegenwart fremder indifferenter Gase sich ändert, wird die Löslichkeit eines festen Stoffes durch Zusatz eines zweiten (in nicht zu grosser Menge) beeinflusst, wofern der hinzugefügte fremde Stoff nicht chemisch auf jenen einwirkt; und ebenso wie die Dissociationsspannung im höchsten Maasse durch Zusatz eines der gasförmigen Zersetzungsproducte beeinflusst wird, so variirt entsprechend auch die Löslichkeit derjenigen Stoffe, bei welchen die Auflösung mit einem mehr oder weniger vollständigen Zerfall verbunden ist, die also bei ihrer Auflösung mehrere Molekülgattungen liefern, wenn eine dieser letzteren der Lösung hinzugefügt wird." There are several things in this statement which are open to criticism. If taken literally, the author implies a fundamental difference between solutions of liquids in liquids, and solids in liquids, a distinction which is not in accordance with the view that in dilute solutions the solute,[3] whether liquid or solid in the pure state, behaves like a gas at that temperature.

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[1] A paper presented to the American Academy of Arts and Sciences, May 9, 1894.

[2] Theor. Chemie, p. 383.

[3] There seems to me a need for a word denoting the dissolved substance. In future I shall use the word "solute," meaning the substance dissolved in the solvent. Instead of the phrase "infinitely miscible liquids," I propose "consolute" liquids.

If applied to any dissolved substance, the statement just quoted is too inaccurate to need any comment. The precipitation of salts by alcohol is a well known instance where it does not apply, and, in general, adding to a solution a substance in which the solute is practically insoluble diminishes the solubility of the latter. This is recognized by Nernst, for he has based a method for determining reacting weights upon it.[1] Even if limited to solids, the proposition cannot be admitted. We have the precipitation of lactones by potassium carbonate as an intermediate step, and the precipitation of salts by phenol as a definite case of diminished solubility without the presence of a common ion. Other cases could be cited, if necessary, and there are also examples where an increase of solubility takes place when a solid substance is added to a solution containing another solid as solute. The explanation usually offered under these circumstances is, that "double molecules" are formed, a mode of getting round the facts which is not always entirely satisfactory.

Since in the application of the gas laws to solutions there has been observed no difference between a solid and a liquid when dissolved, I am inclined to think that the general statement should be, that in all cases where a third substance, B, is added to a solution of A in S, the solubility of A undergoes a change. This variation may be large or small, positive or negative, depending on the nature of the three substances, A, B, and S. When both A and B are liquids, or even when only one of them is, the effect is so marked as to be familiar to all; when both are solids, the effect is not yet recognized by so competent an authority as Nernst.

The work of the last few years on solutions has been devoted to bringing out the analogy between the dissolved substance and gases. In the cases of changed solubility, no common ion being present, the analogy is no longer with gases, but with liquids. The added substance acts as a liquid, precipitating the solute more or less in proportion as the dissolved substance happens to be more or less soluble in it. The laws governing these displacements are entirely unknown, with the exception of Nernst's Dis-

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[1] Zeitschr. f. ph. Chem., VI. 16. 1890.

tribution Law,[1] which is only a first approximation, in that it takes no account of the changing mutual solubilities of the hypothetically non-miscible liquids. Under these circumstances it seemed to me desirable to investigate the laws governing systems composed of three substances, and the experiments which I communicate in this paper have been made on the simplest form of ternary mixtures, — that where all three substances are liquids. The subject has been very little studied, the only researches known to me being by Tuchschmidt and Follenius,[2] Berthelot and Jungfleisch,[3] Duclaux,[4] Nernst,[5] and Pfeiffer.[6] Of these, all except the first and last deal with the equilibrium between two liquid phases; the paper of Tuchschmidt and Follenius contains but one series of measurements, while Pfeiffer remarks, apropos of his own extended investigations, that "there is very little to be made out of them." In this he does himself an injustice, for, as I shall show, his results are very satisfactory and astonishingly accurate when one remembers how they were made.

The simplest case of three-liquid systems is when one has two practically non-miscible liquids, and a third with which each of the others is miscible in all proportions; for then any complication due to the mutual solubility of the two dissolved liquids is avoided. It is possible to say something *a priori* about the law which governs these saturated solutions. Let A and B be two non-miscible liquids, S the common solvent with which A and B are miscible in all proportions when taken singly, and let the quantity of S remain constant, so that we are considering the amounts of A and B, namely x and y, which will dissolve simultaneously in a fixed amount of S. It is known, experimentally, that the presence of A decreases the solubility of B, and *vice versa;* it is required to find the law governing this change of solubility. This, being a case of equilibrium, must come under the general equation of equilibrium.

$$(1) \qquad \frac{\delta F(x, y)}{\delta x} dx + \frac{\delta F(x, y)}{\delta y} dy = 0,$$

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[1] Teilungssatz.

[2] B. B., IV. 583. 1871.

[3] Ann. chim. phys., [4.], XXVI. 396. 1872.

[4] Ibid., [5.], p. 264. 1876.

[5] Zeitschr. f. ph. Chem., VI. 16. 1890.

[6] Ibid., IX. 469. 1892.

where dx and dy denote the changes in the concentrations of A and B, respectively.

This equation, though absolutely accurate, is of no value practically so long as the differential coefficients are unknown functions. In regard to them we may make two assumptions. The decrease in the solubility of A may be proportional to the amount of B added, and independent of the amounts of A and B already present in the solution. The differential equation expressing this is: —

$$adx + bdy = 0, \tag{2}$$

where a and b are proportionality factors and constants. This equation may be rejected on *a priori* grounds, because it does not show that when B is absent, the miscibility of A with S is infinite, and also because it has no similarity with the other equations representing chemical equilibrium. The second assumption is that the change in solubility may be a function of the amounts of A and B already present. This is the usual condition of chemical equilibrium, and is known as the Mass Law. Its mathematical expression is: —

$$\frac{\alpha dx}{x} + \frac{\beta dy}{y} = 0, \text{ or}$$

$$\alpha d \log x + \beta d \log y = 0, \tag{3}$$

where x and y denote the amounts of A and B in a constant quantity of S, α and β are proportionality factors, and the logarithms are natural logarithms.

If α and β are constants, this equation is integrable, and gives, when cleared of logarithms: —

$$x^{\alpha} y^{\beta} = \text{Constant}. \tag{4}$$

If we make $\frac{\alpha}{\beta} = n$, we shall have: —

$$x^{n} y = C, \tag{5}$$

where C is of course different in value from the constant in equation (4).

Before we proceed to test equation (5) experimentally, it remains to be seen in what unit x and y should be expressed. It is obvious that the nature of the unit has no effect on the general form of the equation, nor upon the exponential factor n. The only change will be in the value of the integration constant $\log C$, so that the measurements may be expressed in any form that is convenient, as chemical units,[1] for example, grams per liter, volumes, reacting volumes, or anything else. It is not even necessary that x and y be expressed in the same unit, though it would probably always be more practical. In my own experiments, x and y are expressed in cubic centimeters because they were measured directly as such, and in this way it was not necessary to make determinations of the densities of the liquids used, nor any assumptions in regard to their reacting weights. Equation (5) will not remain unchanged if the reacting weight of A or B varies, that is, if the ratio of the active mass to the actual mass changes as x or y changes. The converse of this is also true, that if the system follows the law $x^n y = C$, the common solvent remaining constant, the reacting weights of the substances A and B cannot have varied with the concentration.

I have found that the equation, $x^\alpha y^\beta =$ Constant, is the expression representing the saturated solutions of two non-miscible liquids in a constant quantity of a consolute liquid. I find, however, that in most cases the concentrations cannot be given by one curve, but involve two, so that for one set of concentrations I have the relation $x^{n_1} y = C_1$, for the other set $x^{n_2} y = C_2$. This cannot be true unless the two sets of saturated solutions correspond to different conditions. This is the case. Duclaux[2] found that a saturated solution of amylalcohol and water in ethylalcohol became turbid on adding a drop either of amylalcohol or of water. In other words, the solution was sensitive to an excess of either liquid.[3] I have confirmed this result, and it is perfectly general. It is not proper,

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[1] I have adopted the following nomenclature for molecular and atomic weights, viz. reacting and combining weights. As the reacting weight is proportional to the chemical unit experimentally, I propose that the gram molecule in the unit of volume (reacting weight in grams per liter) be called the chemical unit, or simply the unit. The object of these arbitrary changes in our chemical terms is to do away with everything involving or implying the assumption of the existence of molecules and atoms.

[2] Ann. chim. phys, [5.], VII. 264. 1876.

[3] Ostwald, Lehrbuch, I. 819.

however, to draw the conclusion that the solution is saturated in respect to both liquids. If to a given saturated solution of chloroform, water, and alcohol, for instance, one adds a drop of water or of chloroform, the solution becomes turbid; but what separates out is the same in both cases. It is analogous to a saturated solution of salt in a mixture of alcohol and water. It is indifferent whether one adds alcohol or salt to the solution. In either case, there is a precipitate; but in both cases the precipitate is salt, and the solution is saturated in respect to salt, not in respect to alcohol. It is not so easy to see what takes place in a system composed of liquids because the precipitate, being itself a liquid, dissolves part of the solution, and the new phase is not composed of pure substance. This need not trouble us, for, theoretically at any rate, the precipitate may be treated as pure liquid, and the final equilibrium looked upon as due to a subsequent reaction. One of the two curves represents, then, the set of solutions which is saturated in respect to chloroform, and not in respect to water. Whether one adds water or chloroform to these solutions, the precipitate is chloroform. The other curve represents the mixtures which are saturated in respect to water, and not in respect to chloroform. Either water or chloroform, when added to these solutions, produces a precipitate of water. These two sets of solutions are easily distinguishable qualitatively, because in the first case the new phase, containing a large percentage of chloroform, is denser than the mixture from which it separates, while in the second case the new phase, containing chiefly water, is lighter than the original solution. The point where the new phase changes from being denser to being lighter than the first phase is the point of intersection of the two curves. At this point only is the nature of the precipitate determined by the nature of the infinitely small excess added. The intersecting point represents the concentration at which, were chloroform and water solids at that temperature, both could be in equilibrium with the solution and its saturated vapor. It corresponds to the concentration of a solution containing two salts with a common ion which is in equilibrium with the two solid salts, formation of a double salt being excluded. In one respect the analogy between a system having three liquid components and one composed of two solids and a liquid does not hold. If to a saturated solution of silver bromate silver acetate is added, the precipitate is silver bromate, and, conversely, the precipitate is silver acetate if silver bromate be added to a saturated solution of silver acetate. The salt with the less concentration precipitates the one with the greater, up to a certain point. In a chloroform-water-alcohol mixture in which chloroform is present in large quantities, the precipitate is water, or the substance with the greater precipitates the one with the lesser concentration. This difference of behavior is due to the new phase being a solid in the one case and a liquid in the other. By a suitable choice of the three components, and by varying the temperature, the substance in respect to which the solution was saturated could be made to separate either as a liquid or a solid phase, and this difference could be made zero. The transition point would come when the equilibrium was between four phases, one solid, two liquid, and one gaseous.

There is no apparent theoretical reason why the two curves should not be prolonged beyond their intersection; but there is a very good practical one. Beyond the point of intersection the curves denote saturated but labile solutions, and a supersaturated system composed of liquids is almost impossible to realize. When I come to the study of ternary mixtures having one or more solid components, I hope to be able to follow one of the curves at least beyond the intersecting point; but in the present work I have made no such attempt.

I will now describe the method used in my work, and then take up the experimental data obtained. As pairs of non-miscible liquids, I have taken chloroform and water, benzol and water; and as consolute liquids, ethylalcohol, methylalcohol, and acetone. The next point was how to determine the composition of the saturated solutions. The methods of quantitative analysis are useless in this case; but the problem is solved without difficulty by quantitative synthesis. Instead of making a saturated solution and analyzing it, I measured the quantities required to make a saturated solution at the required temperature. Definite amounts of the consolute liquids were put in test tubes by means of a carefully graduated pipette; varying quantities of one of the non-miscible liquids were run in from a burette, and the second non-miscible liquid added from another burette to saturation. The test tubes were corked, warmed just above the temperature at which the final readings were made, so that there should be a single homogeneous liquid layer, and placed in a constant temperature bath. If the tube clouds, it is beyond the saturation point; if it remains clear, it is not up to it, the required value lying between the two. By making a series of experiments one can bring the limiting values very close together, and thus determine the saturation point with great accuracy. The constant temperature bath was at 20° C. No correction was made for the amounts of the three liquids evaporating off into the vapor space in the upper part of the test tubes; but by using different sized test tubes this space did not vary much, being about five cubic centimeters, so that the error due to this may be neglected.

The chloroform used (Squibb's) was treated with sodium bisulphite solution to free it from acetone, washed thoroughly with water, dried over calcium chloride and fractionated, twelve hundred grams going over within one quarter of a degree. Kahlbaum's crystallized benzol was recrystallized twice and fractionated to constant boiling point. The ethylalcohol was dried over lime and copper sulphate and fractionated. The lot used distilled within half a degree. Part of the acetone (from Eimer and Amend) was converted into the bisulphite compound, back again, dried over potassium carbonate and calcium chloride, and fractionated. Another portion was treated direct with calcium chloride and fractionated. I could detect no difference between the two lots. I tried to purify a sample of acetone from Cutler Brothers, purporting to be manufactured by Merck in Darmstadt; but it was so bad that I used none of it in my experiments. The methylalcohol (from Kahlbaum) was dried over anhydrous copper sulphate and fractionated.

The measurements in the tables are the mean of at least four determinations, and the error is probably not more than 5 per cent, except in the cases where the quantity of one component is less than 0.20 c.c., when it may easily rise to 10 per cent. The values for n are accurate to within 2 per cent without much question.

The values for log C are more untrustworthy, being much affected by a slight variation in n, while the term C is liable to even greater fluctuations, and is not given, as being too uncertain. Under the headings "Calc." are the values required by the formula to correspond with the experimental data for the other component. The figures in the column marked log C are Briggsian logarithms. As will be noticed, I have not always taken the mathematical mean of this column as the value of log C in the formula. It seemed better to take the value which best satisfied the experimental data, and to ignore numbers which were obviously faulty.

TABLE I.

x c.c. H_2O; y c.c. $CHCl_3$; 5 c.c. Alcohol. Temp. 20°.

Formula $x^{n_1}y=C_1$; $n_1=1.90$; log $C_1=1.190$.

Water.		$CHCl_3$.		
Calc.	Found.	Calc.	Found.	log C_1.
9.94	10.00	0.195	0.20-	1.195
8.99	9.00	0.24	0.24	1.192
7.98	8.00	0.30	0.30	1.193
7.14	7.00	0.385	0.37	1.174
6.00	6.00	0.515	0.515	1.190
5.97	5.00	0.73	0.73	1.191
3.97	4.00	1.12	1.13	1.197
	Average, ...			1.190

Formula $xy^{n_2}=C_2$; $n_2=1.111$; log $C_2=0.742$.

				log C_2.
3.00	3.00	1.73	1.73	0.741
1.99	2.00	2.49	2.51	0.745
1.01	1.00	4.66	4.60	0.737
0.92	0.91	5.07	5.00	0.736
0.755	0.76	5.96	6.00	0.745
0.635	0.63	7.06	7.00	0.738
0.55	0.55	8.00	8.00	0.743
0.48	0.49	8.86	9.00	0.750
0.43-	0.425	10.06	10.00	0.739
0.20	0.20-	20.00	20.00	0.742
0.127	0.125	30.24	30.00	0.738
	Average, ...			0.741

TABLE II.

x c.c. Water; y c.c. $CHCl_3$; 5 c.c. Methyl Alcohol. Temp. 20°.
Formula $x^{n_1}y=C_1$; $n_1=2.30$; log $C_1=1.291$.

Water.		$CHCl_3$.		
Calc.	Found.	Calc.	Found.	log C_1.
9.91	10.00	0.10	0.10	1.300
5.01	5.00	0.48	0.48	1.288
4.03	4.00	0.81	0.80	1.283
1.99	2.00	3.97	4.00	1.294
	Average,	. . . .	. . . .	1.291

Formula $x^{n_2}y=C_2$; $n_2=1.25$; log $C_2=1.061$.

				log C_2.
1.49	1.49	7.00	7.00	1.061
1.34	1.35	7.93	8.00	1.065
1.12	1.12	10.00	10.00	1.061
	Average,	. . . .	. . . .	1.062

TABLE III.

x c.c. Water; y c.c. Chloroform; 5 c.c. Acetone. Temp. 20°.
Formula $x^{n_1}y=C_1$; $n_1=1.415$; log $C_1=0.194$.

Water.		Chloroform.		
Calc.	Found.	Calc.	Found.	log C.
5.01	5.00	0.16	0.16	0.193
4.00	4.00	0.22	0.22	0.194
3.47	3.50	0.266	0.27	0.201
3.00	3.00	0.33	0.33	0.193
2.49	2.50	0.43	0.43	0.196
2.01	2.00	0.586	0.58	0.189
	Average,	. . . .	. . . .	0.194
	1.50		0.74	
	1.20		0.83	
	1.00		0.955	
	0.93		1.00	
	0.79		1.12	
	0.71		1.20	
	0.58		1.40	
	0.53		1.50	
	0.505		1.60	
	0.38		2.00	
	0.30-		2.50	
	0.25		3.00	
	0.21		3.50	
	0.19		4.00	
	0.16		5.00	
	0.12		10.00	

TABLE IV.

x c.c. Water; *y* c.c. Benzol; 5 c.c. Alcohol. Temp. 20°.
Formula $x^n y = C$; $n = 1.60$; $\log C = 0.554$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log *C*.
19.87	20.00	0.03	0.03	0.557
10.65	10.00	0.09	0.08	0.503
7.94	8.00	0.13	0.13	0.559
4.97	5.00	0.273	0.275	0.557
4.00	4.00	0.39	0.39	0.554
3.02	3.00	0.61	0.61	0.558
2.01	2.00	1.18	1.17	0.550
1.72	1.72	1.50	1.50	0.553
1.50	1.50	1.87	1.87	0.554
1.44	1.45	1.98	2.00	0.559
1.00	1.00	3.58	3.57	0.553
0.605	0.605	8.00	8.00	0.554
0.526	0.525	10.04	10.00	0.552
0.34	0.34	20.14	20.00	0.551
	Average, ...			0.551

TABLE V.

x c.c. Water; *y* c.c. Benzol; 5 c.c. Methyl Alcohol. Temp. 20°.
Formula $x^{n_1} y = C_1$; $n_1 = 1.48$; $\log C_1 = 0.216$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log C_1.
5.05	5.00	0.15	0.15	0.211
3.95	4.00	0.21	0.215	0.223
3.01	3.00	0.32	0.32	0.211
2.00	2.00	0.59	0.59	0.216
1.40	1.40	1.00	1.00	0.216
	Average, ...			0.215

Formula $x^{n_2} y = C_2$; $n_2 = 2.00$; $\log C_2 = 0.281$.

				log C_2.
1.13	1.13	1.50	1.50	0.282
1.00	1.00	1.91	1.90	0.279
0.80	0.80	2.99	3.00	0.283
0.69	0.69	4.01	4.00	0.280
0.49	0.49	7.96	8.00	0.283
	Average, ...			0.281

TABLE VI.

x c.c. Water; y c.c. Benzol; 5 c.c. Acetone. Temp. 20°.
Formula $x^{n_1}y = C_1$; $n_1 = 1.40$; $\log C_1 = 0.262$.

Water.		Benzol.		
Calc.	Found.	Calc.	Found.	log C_1.
7.97	8.00	0.10	0.10	0.264
7.00	7.00	0.12	0.12	0.262
5.04	5.00	0.19	0.19	0.258
4.03	4.00	0.26	0.26	0.258
2.99	3.00	0.393	0.395	0.264
2.49	2.50	0.51	0.51	0.265
2.18	2.20	0.61	0.615	0.269
2.01	2.00	0.69	0.69	0.260
	Average, ...			0.2625

Formula $xy^{n_2} = C_2$; $n_2 = 1.35$; $\log C_2 = 0.114$.

				log C_2.
1.67	1.67	0.833	0.833	0.114
1.50	1.50	0.90	0.90	0.114
1.30	1.30	1.00	1.00	0.114
1 005	1.00	1.215	1.21	0.112
0.65	0.65	1.67	1.67	0.114
0.51	0.51	2.00	2.00	0.114
0.38	0.38	2.49	2.50	0.116
0.295	0.295	3.00	3.00	0.114
0.20	0.20	4.00	4.00	0.114
0.15	0.15	4.96	5.00	0.119
	Average, ...			0.1145

There is but one exception, in the chloroform-water-acetone series. As chloroform and water behave normally with alcohol (Table I.), water and acetone with benzol (Table VI.), the disturbing effect must be due to chloroform and acetone in presence of each other. I have not yet had time to investigate mixtures of chloroform and acetone in the absence of water, to determine whether they are abnormal in respect to any other physical properties. In the other five cases the agreement between observed and calculated values is a remarkable one, well within the limits of experimental error, and this in spite of the wide range that the measurements cover. In the benzol-water-alcohol series the ratio of benzol to water varies as one to forty thousand; in the chloroform-water-alcohol series the ratio chloroform-water varies as one to twelve thousand. In the last measurement of Table I., the chloroform forms over 85 per cent by volume synthetically of the solution, so that in this instance we are well beyond the realms of the "dilute solutions," without noticing any disturbing effect due to "variations from the gas laws." The series benzol-water-alcohol is represented by a single curve; but it must not be thought that in this it forms a real exception to the other mixtures. Theoretically, there are two curves for this series; but the two happen to have the same direction, and therefore appear as one. The point where the precipitate ceases to be less dense than the original solution lies between the mixtures benzol 2.00 c.c., water 1.45 c.c., and benzol 3.57 c.c., water 1.00 c.c.

(*To be continued.*)

ON THE SECULAR MOTION OF A FREE MAGNETIC NEEDLE. II.[1]

By L. A. Bauer.

ACCORDING to the principle explained in the first part of this article, all the curves on the two plates given have been constructed. In this paper no attempt at a detailed account of material employed, or of construction formulæ, can be given. It will suffice to present in tabular form the final construction data.

With the aid of Tables I. and II. appended, the curves on Plate I. were drawn. Only a part of the material collected by the writer has been utilized thus far. The object was to give only so much as was absolutely necessary to establish the conclusions here given. To be able to do this to the best advantage, it was the aim to select such stations as would exhibit most clearly the various phases of the secular variation. To further facilitate the study, most of the stations were selected approximately in latitude 40° N., and encircling the earth. The idea was to make a first attempt with the aid of such stations to follow a secular wave around the globe. It will be seen by turning to the plate, that the points (the intersections of the broken lines) which represent the mean values (D_0 and I_0) for each station have been placed in the latitude of that station. Owing to the difference in the size of the curves, the *real* difference in longitude between the various stations could not be preserved; the points (D_0, I_0) have, however, always been placed relative to each other in the proper longitude. This plate does not exhibit everything as clearly as the author would have wished; a larger scale could have been employed to good advantage. It should be remembered, however, that these curves have been drawn for the first time, and that in the nature

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[1] A paper read before the National Academy of Sciences, Washington, April 16, 1895; concluded from page 465.

of the case this preliminary chart had to be more or less a trial one. The author hopes to be able to present, in the near future, a more complete and more comprehensive picture of the secular variation of geomagnetism.

But one more point with regard to the construction of the curves remains to be referred to. By turning to the Paris curve, it will be seen that the curve has been drawn from 1540 to 1890. For this station we possess declinations 1541–1895, but inclinations only from 1671 to 1895. How was it possible then to construct the curve from 1540 to 1671, since for this interval we possess the knowledge of but one ordinate, viz., declination? In this way. From the declination interpolation formula, it is found that the minimum value, −9°.6, or maximum easterly digression, was reached in about 1580. The secular variation curve must then have run in 1580 tangent to the declination ordinate corresponding to the value of 9°.6 E. With the aid of this fact the curve can be extended backward from 1671 to 1580. Having done this, we can scale off an approximate value of the inclination for 1580, *i.e.* for a date for which we possess no such observations. This method of deriving inclinations for periods for which no data are at hand is here given for the first time. That the values thus derived can be relied upon to within 1° to 3°, is shown from the following. The scaled value of the inclination for Paris in 1580 lies between 70° and 72°; Norman observed at London in 1576, 71°.8. This would imply a value for Paris lying between 70° and 71°. Hence the value 71°.0 ± 1°.0 cannot be far from the truth. With this value we can now extend the use of our interpolation formula, which had been established for the epoch 1671–1890. The formula gives for 1580, 71°.0; we can consequently use it without great error back to 1580. The drawing of the curve can thus be undertaken without difficulty. Between the years 1541 and 1580 we know that the easterly declination was increasing; hence the secular variation curve, 1541–1580, must have approached the tangent point (1580) from the left. This part of the curve (1541–1580) is of course determined but very roughly, as no other values of the inclination were at hand than the extrapolated ones from the formula; but the *direction* of the motion

[illegible] and that is the chief object of these investi-
[illegible] from 1541 to 1890, *i.e.* for over 350 years,
[illegible] clockwise. In precisely the same way, the
[illegible] extended from 1576 to 1540; the Rome curve
[illegible] the latter case the direction has therefore
[illegible]-nigh 400 years. For the epoch of maxi-
[illegible] viz., 11°.6 E. in about 1570, we scale off
[illegible] As the earliest reliable inclination
[illegible] at London in 1576, 71°.8 ± 1°, the
[illegible] boast of being one of the oldest that
[illegible]

[illegible] observed is that for all the stations (24) on
[illegible] throughout in the direction of the
[illegible] has now been tested for more than
[illegible] series scattered over the earth. Where
[illegible] upon, or the series covered a sufficient
[illegible] found to hold in every case. As the
[illegible] not simple geometrical ones, but are
[illegible] smaller waves, the writer does not mean
[illegible] drawn on a very large scale and, say,
[illegible] the clockwise motion will obtain through-
[illegible] loops of which the curve may be composed.
[illegible] that in every case for the larger part of the
[illegible] secular variation broadly considered, the law
[illegible] for which the curves have been drawn. The
[illegible] furthermore tested with the aid of the published
[illegible] viz., the isogonic and the isoclinic charts for the
[illegible] From these charts the data were scaled for the
[illegible] the parallels of latitude 60° N., 40° N., 20° N., 0°,
[illegible] S., with the meridians 20° apart. The secular
[illegible] for parallels of latitude 40° N., 0° and 40° S., *i.e.*
[illegible] curves, have been drawn. For about a dozen there
[illegible] as to the direction of the curve; in the rest, the
[illegible] again revealed itself. The doubtful curves were
[illegible] on the earth's surface where the data are very
[illegible] where for the interval drawn the curve is in reality
[illegible] nearly a straight line, *i.e.* the greater part of the

variation occurs in the inclination, the declination suffering very little change (see, for example, Manila curve). We believe then that we can safely draw our first conclusion, —

In consequence of the secular variation of geomagnetism, the north end of a freely suspended magnetic needle viewed from the center of suspension of the needle, moves on the whole earth in the direction of the hands of a watch.

So much care has been given the establishment of this law for two reasons: —

a. Because, knowing now that it is a law that the secular variation observes, the means are given herewith to judge somewhat as to the value of doubtful data.[1]

b. Because it is recognized that in the above law we have already one criterion, with which to decide between some of the causes of the secular variation that have been suggested. This law will doubtless play an important rôle in the next step of these investigations, — the mathematical examination and critical discussion of the possible causes.[2]

Very little can as yet be said as to the true geometric nature

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[1] This can be elucidated by the following example. In 1885, Mr. Schott, the well-known geomagnetician, drew the secular variation curve for a mean station of New England, and for the interval 1820–1885. He knew approximately when the needle had reached its maximum easterly point, and also the value of the declination for this period. He could determine then the line to which the curve would have to run tangent, prior to 1820. Although he had had an experience of over forty years in terrestrial magnetic matters in the United States, he nevertheless did not dare to extend the curve back to this tangent line for the reason that he could not tell whether the extension would have its convex side turned downwards or upwards. Inclinations had been observed at Boston in 1780, but as they appeared doubtful to him no use was made of them. When the writer laid his preliminary investigations before the A. A. A. S. in 1892, he could then say how Mr. Schott's curve ought to be extended prior to 1820, viz., the convex side must be turned downwards in order to make the direction of the motion correspond to that obtaining at the European stations. Or, if the observed inclinations for 1780 were utilized, the curve would proceed in the direction as prescribed by the law. The curve for Boston was then exhibited for the period 1780–1885, and the direction prior to 1780 also indicated with the aid of the observed declinations. In the latter part of 1894, the writer's attention was called by Professor Cleveland Abbe to a work in which he obtained an observed inclination at Boston for the year 1722, this being probably the earliest observed inclination in the United States. With these data the Boston curve has now been laid down from 1722 to 1885. It is seen that the law of the motion obtains throughout, and that consequently the observed inclinations for 1780 cannot be far from the truth.

[2] See American Journal of Science for August, 1895, and following numbers.

of the secular curve. To the great question, however, whether it consists of a single branch or of several, an answer can be attempted. It may be remarked that it would be far more astonishing if the curve were a single closed one, than if it were shown to consist of branches or loops, since the daily and annual variation curves are known to be very complex indeed. Indications of loops are shown at two stations, Rome and the Azores. At the first station, by means of the so-called compass-charts of the 14th and 15th centuries, we are able to gain some knowledge of the magnetic bearing of the needle for that epoch. On these charts the directions from port to port are laid down magnetically. By comparison with charts on which astronomical directions are given, some knowledge of the magnetic declination for the period of the compass-charts can be obtained. Thus it was found that according to the compass-charts of 1436, by Andrea Bianco, the magnetic declination at Rome ought to be about 5° E. If we now assume that the law governing the secular variation of the declination from 1508 to 1890 holds good also from 1400 to 1508, we find that in 1400 the declination ought to be 12° W., and for 1436, 7° W. Prior to 1400 the westerly declination would be increasing. The material with which Bianco's charts were constructed is doubtless older than 1436. If we make the most favorable assumption, however, that the value 5° E. refers to 1436, we find a difference of 12° between compass-charts and formula. For 1400 the difference would be even 17°, and prior to that still greater. The best plausible explanation we can give of such large discrepancies, is that a different law of the secular variation came into play, or, in other words, a loop was described prior to 1500. A similar conclusion is reached at the Azores station, by considering the observed compass-bearing of Columbus in 1492, in the vicinity of these islands. Even if we assume that the value is erroneous so far as 6°, there still remains an outstanding difference between observation and formula of 8°. The writer does not mean to say that the foregoing considerations should be regarded as sufficient proofs, but simply as indications of loops. The singular points exhibited at some of the stations drawn, *e.g.* Acapulco and station, 40° N., 40° W., are doubtless due chiefly to inaccurate data. If we compare the two curves 40° N., 60° W., and 40° N., 40° W., we find that they both observe the law of motion, and yet there is a striking difference between them. The former follows the United States type, the latter the European. Some remarkable change in the curve must have occurred between these two stations. The European type cannot change suddenly into that of the United States. The change must be a progressive one, and be made by means of loops or singular points. It is probable that the curves in this region will contain such singularities.

As to the period, nothing definite can be said as yet, and it moreover appears questionable whether there really exists a secular variation period, at the close of which the needle describes the same orbit it did before. The time interval between the epochs of maximum westerly and easterly digression of the needle can be determined for a number of stations to within about ten per cent. Thus this interval for London is, $1812-1580=232\pm 10$ years; for Paris, $1809-1580=229\pm 10$; for Rome, $1810-1570=240\pm 15$. Accordingly, we might say that this interval for western Europe is about 235 years. For the eastern part of the United States the interval appears to be on an average about 150 years. We have a proof here at once that if the secular variation period has the same length all over the earth, we cannot then regard the interval between the extreme digressions as covering half the period; for, if this were so, then the period for Europe would be about 470 years, that for the eastern United States only about 300. *We are then forced to conclude that either the period is different for various portions of the earth, or that the secular curve is not a single closed curve, but consists of loops. This is our second conclusion.*

Now let us follow a secular wave around the earth. We will begin with London, and proceed in an easterly direction. The London curve seems to be approaching the upper extreme point, *i.e.* the inclination is diminishing with a speed that has become less and less ever since about 1810, or, in other words, it is nearing a minimum value which may be reached about the middle of the next century. Paris appears somewhat nearer this phase; Rome and Berlin still nearer, where it will probably take place shortly. At Tiflis this phase has already been passed, in about 1875. At

Bombay the minimum inclination phase has long ago occurred, and in about 1880 the curve had already reached its maximum easterly digression. Irkutsk, Peking, Manila, Petropawlowsk, station 40° N., 180° E., are either nearing the maximum inclination phase or have already passed through it. It is extremely difficult to say through what phase the San Francisco curve has passed, for the reason that in the Pacific Ocean and on the western coast of the United States, secular waves of opposite phase, but of different amplitudes, seem to make their appearance, and consequently partially annihilate each other. St. Louis, Boston, Bermudas, 40° N., 60° W., have passed through their extreme lower points, and are approaching now the maximum westerly digression. The latter will take place in time in the reversed order of the stations. At station 40° N., 40° W., the maximum westerly elongation has just occurred, or will occur soon. At the Azores it took place about 1852, and the needle, as at London, is bent now upon reaching its upper extreme position. We have now followed a wave around the earth.

Our next conclusion is that the secular variation curves appear to develop themselves more and more as we go around the earth eastwardly; or, in other words, the secular wave appears to travel in the main, roughly speaking, westward. We might then conclude that by obtaining a composite of the various parts of the successive secular variation curves for stations, somewhere near a parallel of latitude, we could get the total curve. If we do this mentally, we shall find at once that the curve constructed thus is not a single looped one, as there are two regions where the needle is passing through a maximum inclination phase, and likewise two where the maximum easterly (or minimum westerly) phase is taking place.

But what does this unfolding of the secular variation curve, with eastward progression, imply? If this continuous development has been caused by a wave traveling from east to west around the earth, would it not follow that if we made an instantaneous circuit of the earth in an easterly direction with a free magnetic needle, the same phenomenon would unfold itself from station to station, as occurs at any fixed station in the lapse of time? Let us see if this be true. In 1885 we will start from a point, the latitude of which is 40° N., and longitude 0°. We will take with us a free magnetic needle, and travel with it eastwardly around the earth along the parallel, 40° N. At points distant 20° in longitude, we will observe the direction of the needle; measuring the declination and the inclination. Throughout the circuit the needle is constantly changing its direction. If we now suppose that the center of suspension of the needle is fixed, but the needle itself subject to the changes encountered during the circuit, we can construct the curve described by the north end, in a manner analogous to that which was followed in drawing the secular variation curves. We thus obtain the striking curve exhibited on Plate II., — the heavy curve on the left. The only difference from the secular variation curves is, that instead of time we now have longitude marking the various points of the curve. Instead of actually making the circuit, we can obtain the necessary data from the excellent isogonic and isoclinic charts for 1885, constructed by Professor Neumayer, director of the German Naval Observatory. The broken places correspond to the data for the points 20° distant in longitude, and lying in latitude 40° N. It will be observed that this curve also proceeds throughout in the direction of the hands of a watch; even the small loop follows this law. Furthermore, the part without the loop exhibits a great similarity to the secular variation curves for London, Paris, and Rome. Is this mere accident? Suppose we make our circuit along other latitudes, or for other epochs, — will a similar condition of things obtain? To answer this the writer has drawn first the instantaneous curves for latitudes 75° N., 70° N., 60° N., 50° N., 40° N., 20° N., 0°, 20° S., 40° S., 60° S., from data of 1885, and secondly the curves for 40° N., 0°, and 40° S., for the additional years 1780 and 1829. In every case the direction of motion was clockwise. On Plate II., these latter curves are drawn for the three years; the necessary data are given in Table III. It will be observed that although the nine curves present many irregularities and singularities, they nevertheless all unite to exhibit a hitherto unsuspected law. Before we formulate the new conclusion to be drawn, let us see what we shall get if we make the circuit in some other way than along a parallel of latitude. Of course the circuit must always be made eastwardly as the waves come, generally speaking, from the east. Likewise is it apparent that for every circuit we shall get a closed curve. At first sight it might appear more natural to make the circuit along a magnetic parallel. If we define the latter as an isoclinic, then the curve will reduce to a straight line, since along an isoclinic the inclination is constant, the declination alone varying. If we regard an equipotential line as a magnetic parallel, and make the circuit *e.g.* along the zero equipotential line or along the magnetic equator, we get the peculiar curve given on Plate II., middle figure. This curve has a large loop proceeding clockwise, and two small loops, one going anti-clockwise and the other clockwise. It will at once be seen that this curve does not present such a striking similarity to the secular variation curve. It seems then that the circuit must be made somewhere near a parallel of latitude. Is this not an indication that the secular variation is in some manner connected with the rotation of our mighty geomagnet? This matter is at present being investigated. Our next conclusion is then: —

The north end of a free magnetic needle, viewed from the center of suspension of the needle, moves clockwise in making an instantaneous easterly circuit of the earth along a parallel of latitude; or,

The north end of a free magnetic needle, whose center of suspension is fixed in space close to the earth's surface, will describe a curve as the earth rotates under it, which as viewed from the center of suspension of the needle, moves anti-clockwise.[1]

In the foregoing we have already hinted at a connection between the secular variation and the distribution of geomagnetism, in that they both observe similar laws. This connection is also revealed in another way. By turning to Plate I., it will be seen that the largest secular curves seem to occur at stations somewhere near the equator, — see Ascension and St. Helena islands. Likewise the curve for Rome is smaller than the one for Cape Town, lying in

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[1] The original formulation of this law was given in the first form. The curves are indicated then on Plate II., as proceeding clockwise. For the second form the arrows would have to be reversed. The motion is now reversed since the earth rotating from west to east is equivalent to making a *westerly* circuit of the earth with the needle.

about the same latitude south. Turning now to Plate II., it will be seen that a precisely similar condition of things prevails. Thus the largest instantaneous curve is described at the equator; likewise the curves for 40° S. are larger than those for 40° N. A connection seems to prevail also with regard to the loop in the northern hemisphere. This cannot be exhibited here, however.

Our final conclusion is then:—

The secular variation and the prevailing distribution of geomagnetism appear to be closely related.

TABLE II. — (*Continued.*)

Station.	1750		1760		1780		1800		1820	
	D	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*
	°	°	°	°	°	°	°	°	°	°
Fayal Is. (Azores)	—	—	—	—	+21.25	+70.26	+24.08	+69.10	+26.13	+67.83
Berlin	+14.98	—	+16.07	—	+17.56	+71.92	+18.12	+70.33	+17.74	+69.02
Geneva[1]	—	—	—	—	—	+69.07	+21.50	+67.47	+20.59	+66.07
Basle[1]	—	—	+18.	+70.35	+20.	+68.90	+21.7	+67.61	+21.7	+66.47
Peking	—	—	—	—	—	—	—	—	—	—
Manila	—	—	—	—	—	—	− 0.18	+12.9	− 0.38	+15.0
Petropawlowsk .	—	—	—	—	− 6.3	+63.0	− 5.7	+63.4	− 4.7	+63.8
San Francisco . .	—	—	—	—	−12.6	—	−13.6	—	−14.54	—
St. Louis . . .	—	—	—	—	—	—	—	—	—	+69.86
Ascension Is. . .	+ 6.7	+11.3	+ 8.4	+10.3	+11.6	+ 8.2	+14.0	+ 5.6	+16.4	+ 3.0
St. Helena Is. . .	+ 9.77	− 9.9	+11.70	−10.5	+14.59	+12.0	+17.51	−13.5	+20.01	−15.4
Rio de Janeiro .	− 7.27	−20.41	− 7.44	−19.50	− 6.84	−17.98	− 5.42	−16.50	− 3.46	−14.66
Cape Town . . .	+19.10	−43.6	+20.5	−44.2	+23.2	−46.53	+25.4	−48.85	+27.2	−51.01
Melbourne . . .	—	—	—	—	—	—	—	—	—	—

Station.	1840		1860		1880		1890	
	D	*I*	*D*	*I*	*D*	*I*	*D*	*I*
	°	°	°	°	°	°	°	°
Fayal Is. (Azores)	+27.22	+66.57	+27.33	+65.39	+26.40	+64.38	+25.58	+63.96
Berlin	+16.43	+68.00	+14.18	+67.25	+11.0	+66.8	—	—
Geneva[1] . . .	+19.21	+64.89	+17.34	+63.91	+15.00	+63.13	+13.65	+62.81
Basle[1]	+20.2	+65.49	+18.	+64.66	+15.2	+63.99	+13.0	+63.47
Peking	+ 2.06	+55.5	+ 2.32	+56.6	+ 2.68	+56.8 ?	+ 2.9	+56.5 ?
Manila	− 0.54	+16.5	− 0.70	+17.4	− 0.78	+17.7	− 0.80	+17.6
Petropawlowsk .	− 3.4	+64.1	− 2.0	+64.2	− 0.4	+64.3	+ 0.5	+64.3
San Francisco . .	−15.42	+62.4	−16.10	+62.4	−16.51	+62.3	−16.58	+62.3
St. Louis . . .	− 8.6	+69.46	− 7.7	+69.66	− 6.4	+69.26	− 5.6	—
Ascension Is. . .	+18.8	− 0.4	+21.4	− 4.7	+22.9	− 9.3	+23.0	−11.6
St. Helena Is. . .	+22.00	−18.0	+23.41	−22.0	+24.11	−26.5	+24.21	−29.65
Rio de Janeiro .	− 1.01	−12.89	+ 1.71	−12.01	+ 4.52	−12.11	+ 5.88	−12.29
Cape Town . . .	+28.8	−53.03	+29.7	−54.89	+29.6	−56.59	+29.2	−57.39
Melbourne . . .	—	—	− 8.50	−67.09	− 8.14	−67.08	− 7.85	−67.03

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[1] These curves could not be given on Plate I. for want of space.

TABLE II.—(*Concluded.*)

Acapulco.			Bermudas.			40° N., 60° W. of Gr.			40° N., 40° W. of Gr.		
Date.	*D*	*I*	Date.	*D*	*I*	Date.	*D*	*I*	Date.	*D*	*I*
	°	°		°	°		°	°		°	°
1791.3	−7.7	+36.1	1837.5	+6.93	+65.82	1780.0	+ 8.2	+68.8	1700	+ 5.8	+73.0
1803.2	−7.8	+38.9	1873.4	+7.17	+66.43	1830.0	+12.7	+72.3	1780	+14.5	+70.0
1838.1	−8.2	+38.0	1890.4	+8.07	+64.79	1885.0	+18.0	+71.3	1830	+22.7	+70.1
1866.4	−8.4	+39.9							1842	+24.5	+70.9
1880.9	−7.9	+40.1							1885	+25.4	+68.1

Tiflis.			Bombay.			Irkutsk.			40° N., 180° E. of Gr.		
Date.	*D*	*I*	Date.	*D*	*I*	Date.	*D*	*I*	Date.	*D*	*I*
	°	°	°	°	°		°	°		°	°
1840.0	+2.55	+55.90	1846.0	0.00	+18.14	1828.5	−1.74	+68.04	1780	−12.5	+49.5
1871.0	−0.20	+55.50	1856.0	−0.32	+19.10	1870.0	−2.70	+69.80	1830	−12.4	+54.3
1875.0	−0.55	+55.45	1870.0	−0.79	+19.50	1888.0	−2.28	+70.08	1842	−12.6	+55.0
1882.0	−0.90	+55.51	1880.0	−0.96	+19.70				1885	−11.5	+53.8
1888.0	−1.23	+55.66	1890.0	−0.81	+19.80						

TABLE III.

CONSTRUCTION DATA[1] OF THE INSTANTANEOUS CURVES (PLATE II.).

Long. E. of Gr.	Latitude 40° N.						Equator.						40° S.						Zero equi-potential line.	
	1780		1829		1885		1780		1829		1885		1780		1829		1885		1885	
	D	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*
°	°	°	°	°	°	°	°	°	°	°	°	°	°	°	°	°	°	°	°	°
0	+19.8	+66.2	+22.0	+59.6	+15.6	+58.2	+16.5	+15.5	+21.3	+ 6.5	+19.0	− 8.2	+11.3	−44.3	+20.3	−47.7	+27.4	−51.0	+19.5	− 9.5
20	+15.3	+60.3	+13.6	+54.0	+ 8.0	+54.7	+18.7	+ 0.3	+20.1	−12.5	+13.3	−21.8	+22.6	−51.0	+28.5	−56.1	+31.7	−58.8	+12.0	−11.0
40	+ 8.7	+54.6	+ 4.0	+51.0	+ 0.7	+53.0	+14.5	−13.0	+12.4	−24.7	+ 7.6	−23.8	+29.2	−60.0	+30.8	−62.9	+31.2	−64.0	+ 6.0	− 7.0
60	+ 3.4	+51.2	− 3.4	+51.9	− 4.6	+54.1	+ 7.0	−23.0	+ 3.6	−26.5	+ 3.	−22.0	+27.0	−69.?	+27.7	−66.9	+27.0	−67.0	+ 1.7	− 3.0
80	+ 1.1	+51.2	− 5.6	+55.1	− 6.5	+55.3	− 0.0	−20.7	− 0.7	−21.9	0.0	−20.4	+20.5	−69.?	+22.0	−68.7	+23.0	−68.5	− 1.1	− 1.0
100	+ 2.7	+53.8	− 2.4	+57.3	− 3.0	+56.6	− 0.2	−16.3	− 0.8	−17.8	− 2.2	−17.3	+16.8	−67.?	+15.0	−69.6	+17.0	−69.2	− 3.0	+ 1.0
120	+ 0.7	+54.4	+ 1.9	+56.8	+ 3.6	+56.8	− 0.2	−16.0	− 0.8	−17.1	− 2.1	−12.8	+10.8	−67.5?	+ 5.0	−69.9	+ 5.2	−70.0	− 1.8	+ 4.0
140	− 1.8	+51.8	+ 2.0	+54.5	+ 5.3	+54.0	− 3.5	−14.5	− 4.1	−16.9	− 3.2	−12.4	− 1.3	−67.5?	− 6.6	−68.2	− 5.8	−69.5	− 2.0	+ 5.0
160	− 6.6	+48.6	− 2.9	+53.1	− 2.5	+51.8	− 9.1	−11.7	− 8.9	−12.5	− 7.3	−10.0	−12.1	−66.2	−13.4	−64.1	−12.9	−66.8	− 6.8	+ 3.0
180	−12.5	+49.5	−10.0	+54.3	−11.5	+53.8	−10.5	− 7.6	−10.8	− 3.7	− 8.7	− 2.8	−14.0	−62.7	−13.5	−59.5	−14.5	−63.2	− 8.8	+ 4.5
200	−15.6	+52.5	−15.5	+57.7	−14.8	+57.3	− 7.1	− 5.0	− 8.1	+ 3.1	− 6.6	+ 1.5	−10.9	−60.3	− 9.9	−57.1	−12.7	−60.0	− 6.7	+ 1.2
220	−15.9	+57.5	−17.6	+61.8	−17.1	+60.8	− 3.9	− 4.5	− 5.3	+ 4.3	− 3.0	+ 2.4	− 6.6	−60.5	− 7.8	−57.4	−12.2	−58.2	− 2.5	− 1.5
240	−13.3	+63.0	−16.2	+65.6	−17.6	+64.8	− 1.7	− 2.4	− 6.1	+ 4.3	− 5.2	+ 4.2	− 2.3	−62.2	−10.5	−58.1	−13.7	−56.0	− 5.6	− 4.0
260	− 7.3	+67.0	−11.2	+69.1	−12.4	+69.0	− 5.3	+ 3.3	− 8.6	+ 8.5	− 7.6	+ 8.2	− 6.8	−61.6	−15.9	−56.0	−18.0	−52.2	− 9.2	− 5.0
280	− 0.7	+68.7	− 1.5	+72.5	+ 1.8	+71.4	− 7.6	+11.5	− 8.9	+17.1	− 7.4	+15.3	−14.0	−56.0	−17.8	−50.6	−19.4	−44.5	−10.5	− 5.0
300	+ 8.2	+68.8	+11.7	+72.3	+18.0	+71.3	− 6.3	+20.0	− 4.2	+25.7	− 1.8	+23.8	−17.5	−50.5	−13.5	−44.0	−11.1	−35.4	− 4.7	− 1.0
320	+14.5	+70.0	+22.4	+70.1	+25.4	+68.1	− 0.6	+24.4	+ 5.2	+28.7	+ 9.6	+25.8	−10.5	−45.5	− 4.0	−39.8	+ 3.1	−33.8	+ 9.0	+ 3.5
340	+19.7	+69.2	+25.8	+65.6	+23.6	+63.2	+ 8.8	+24.8	+15.5	+22.4	+21.0	+12.7	+ 0.3	−42.7	+ 8.4	−41.2	+17.4	−41.5	+21.5	− 1.0
Mean	+ 1.1	+58.8	+ 1.0	+60.1	+ 0.7	+59.7	+ 0.5	− 1.9	+ 0.6	− 1.8	+ 1.0	− 3.2	+ 2.3	−59.1	+ 2.5	−57.7	+ 3.5	−57.2	+ 0.4	− 1.5

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[1] These data were obtained by scaling published isogonic and isoclinic charts. The figures as given are on the average liable to an uncertainty of at least ½°–1°. Those for 1780 were derived from Hansteen's isogonic charts of 1770 and 1787, and his isoclinic chart for 1780 as given in the Atlas to his "Magnetismus der Erde," Christiania, 1819. The mean values of the declinations obtained from the first two charts when giving double weight to the 1787 scalings, were regarded as corresponding to the epoch of the inclinations scaled from the chart 1780. The 1829 data were extracted from Erman and Petersen's "Grundlagen der Gaussischen Theorie und die Erscheinungen des Erdmagnetismus im Jahre 1829," Berlin, 1874. They are the computed results as based upon Gauss's potential theory of terrestrial magnetism. The 1885 figures were derived by scaling the excellent charts of Neumayer as given in his "Atlas des Erdmagnetismus," Gotha, 1891. Some interesting results follow from the above table, *e.g.* that the mean declination for a parallel of latitude is always plus or westerly. The discussion of these results will be given in a future paper in connection with the data from 27 charts.

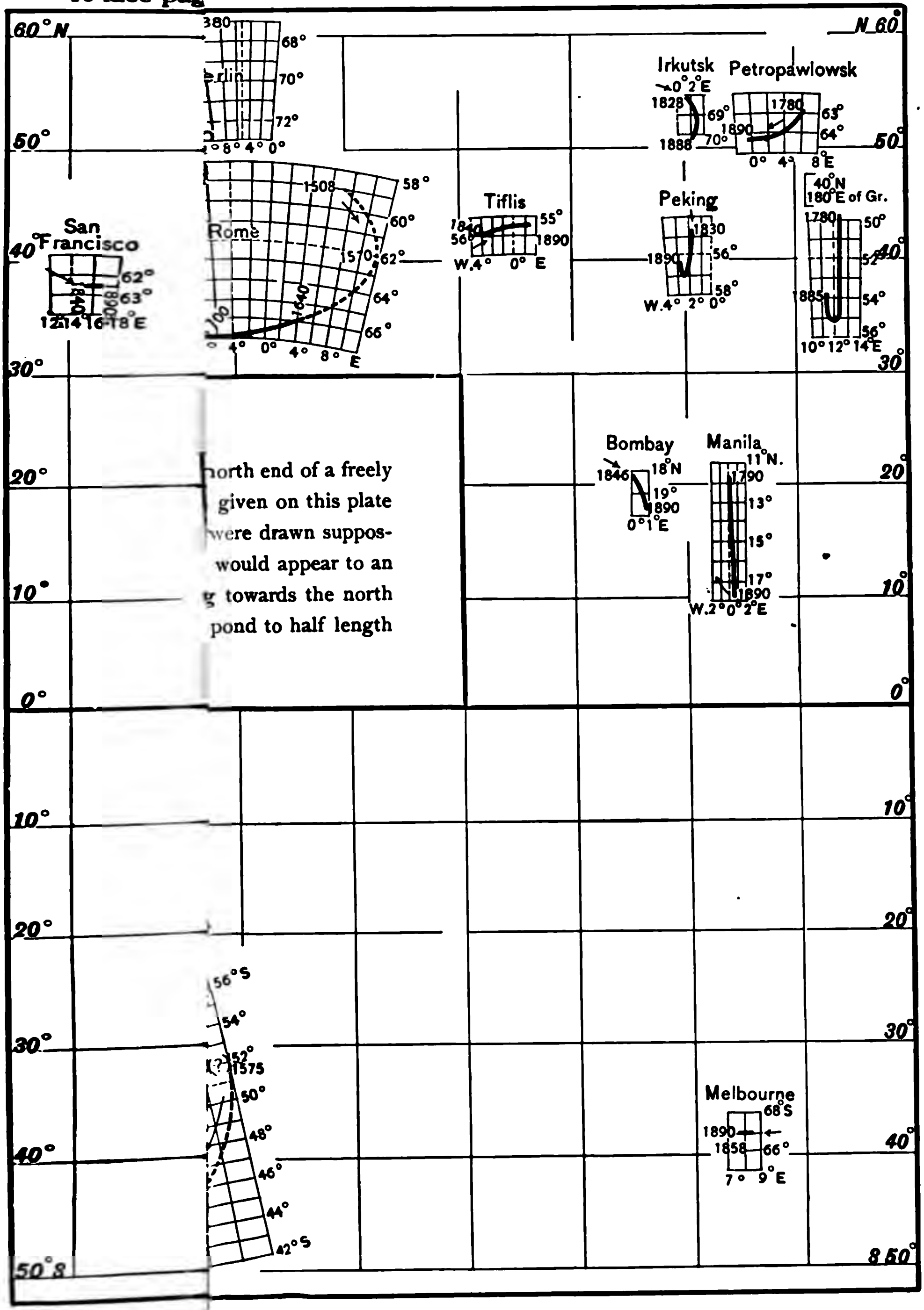

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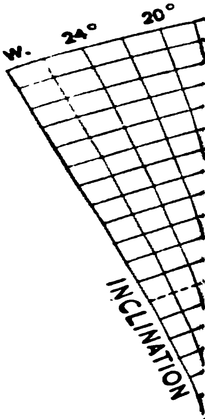
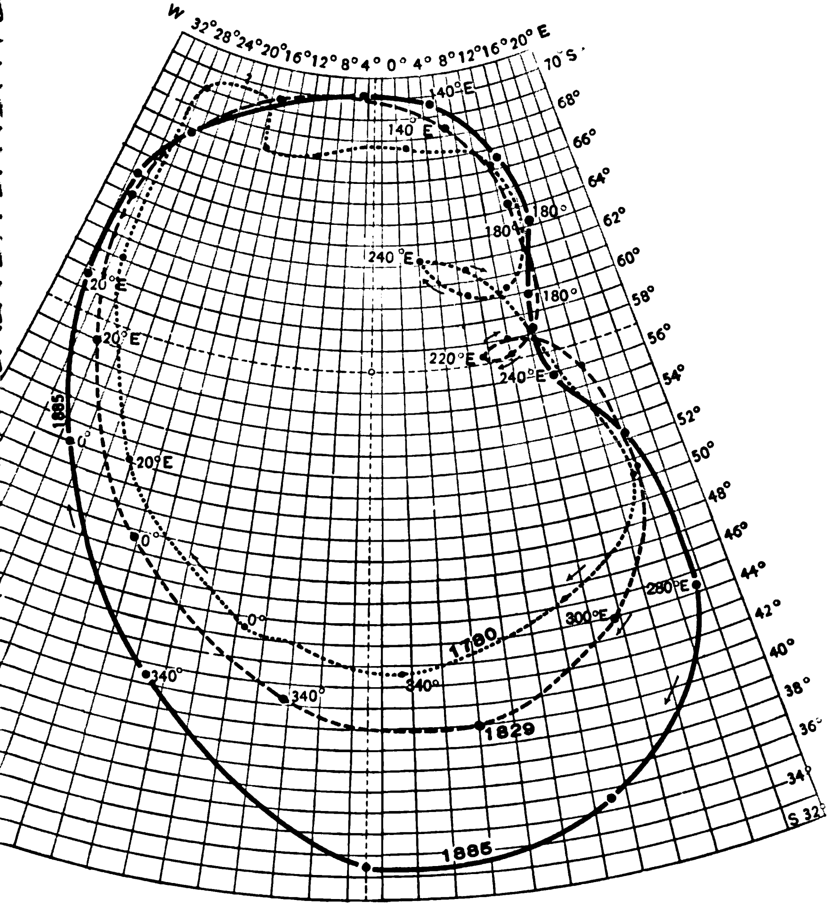
Plate 2.

IN CURVES





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Parallel of Latitude 40°S.

A GALVANOMETER FOR PHOTOGRAPHING ALTERNATING CURRENT CURVES.

By H. J. Hotchkiss and F. E. Millis.

IN the latter part of 1893 one of the writers undertook an experimental study of the extra currents corresponding to the exponential term in the common expression for the current curve produced upon closing a circuit containing an harmonic electromotive force, resistance, and self-induction; and the other, an investigation of the variations of current and armature lag in synchronous motors when the load is suddenly changed. For the experimental study of these subjects we wished an instrument which would readily and accurately record the alternating current curve from the instant of changing the conditions until the permanent form was reached. Photographing on a moving plate the spot of light reflected from a modified form of M. Blondel's oscillograph[1] seemed to lend itself best to our purpose. The modified form is essentially a galvanometer having a very small needle of soft iron, a very strong field for the directing force, and a single small coil carrying the alternating current which deflects the needle.

That the curve thus obtained might not be distorted by the inertia of the vibrating needle and mirror, both were as small as they could be conveniently made, and were mounted with their greatest dimensions in the axis of vibration. That the natural period of the needle may not affect the shape of the curve, it should be *much* less than that of the current.

We experimented with many forms of mounting for the needle, and finally succeeded in getting one sufficiently sensitive which made a little more than 3500 double vibrations per second. The frequency of the current experimented upon in the study of extra

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[1] Electrician, Lond., Vol. XXXI., March 17, 1893; page 571.

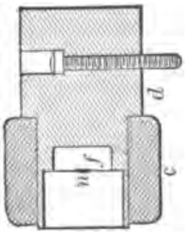

Fig. 2.

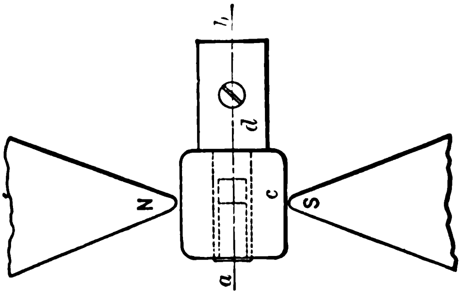

Fig. 1.

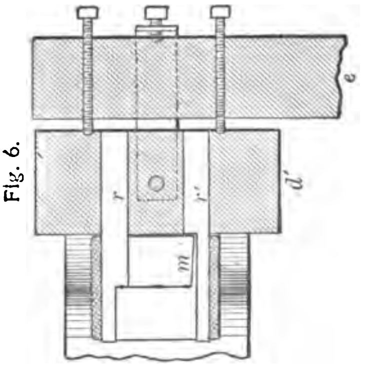

Fig. 6.

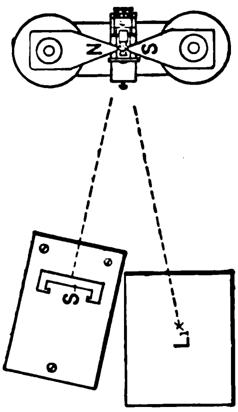

Fig. 3.

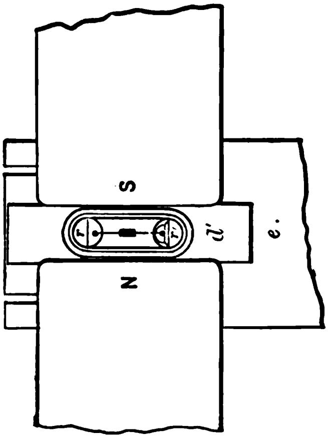

Fig. 5.

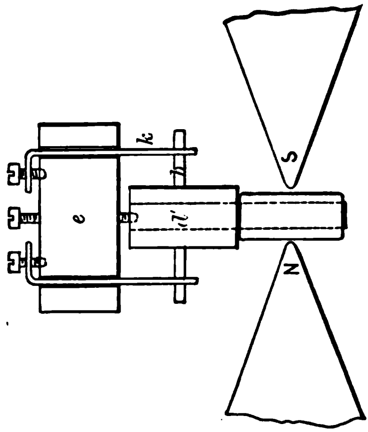

Fig. 4.

currents was 120 complete alternations per second, and it was not possible to detect the slightest distortion of the curve due to the combination of the period of the needle with that of the current.

Figures 1 and 2 show the manner of mounting the needle and its position between the poles *N*, *S*, of the electromagnet. Figure 1 is a horizontal projection, and Fig. 2 a vertical section through Fig. 1 along the line *ab*.[1] The needle *n*, and the small coil *c* around it, were supported upon a vulcanite block *d*, having a rectangular hole 6 × 15 mm. cut into one end. The latter was cut down until the walls were quite thin, in order to bring the coil close to the needle and not to separate the pole pieces too far. Within, shoulders were left, on which to mount the coarse quartz fiber *f*, to the middle of which the needle and mirror were fastened, on opposite sides, with shellac. The needle was made from a piece of soft iron such as is used for armature cores. The mirror was cut from a microscope cover-glass silvered. The dimensions of the parts are given in column I. of the table.

The small coil *c*, around the needle, contained about 480 turns of copper wire heavy enough to carry 3 or 4 amperes. With this apparatus an alternating current of 2.35 amperes gave an amplitude of about 18 mm. on the photographic plate.

A top view of the electromagnet and photographing apparatus, drawn to a scale of about one-fifteenth, is given in Fig. 3. The wrought iron cores, about 2 inches in diameter, were connected at the bottom by a large yoke piece, while the magnetizing coils, each of which contained about 970 turns of heavy wire, were excited by a current of about 10 amperes. The light from an arc lamp, *L*, passed through a vertical slit a few inches from the lamp and fell upon the mirror, from which it was reflected to a narrow horizontal slit in the slide carrier *S*. The photographic plate was allowed to drop vertically in front of the slit. No lenses were used.

The natural period of the needle was determined by mounting a very small mirror on the end of a heavy tuning-fork which was known to make 512 double vibrations per second, and then placing this fork in such position that its mirror would reflect a spot of light from the lamp to the horizontal slit in the slide carrier beside

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[1] Figures 1, 2, 4, 5, and 6 are drawn about one-half natural size.

the spot of light from the mirror on the needle. The needle was deflected by a current from a storage battery, the fork bowed, and the sensitive plate dropped. A trip was so arranged that as the plate passed the slit it broke the battery circuit. By comparing the curve from the fork with that made by the needle as it came to rest, it was found that the needle made seven times as many vibrations as the fork, or about 3580 complete vibrations per second.

Curves were taken from different sources of alternating electromotive force giving different forms, which, when compared with those taken by other methods, showed that the photographed curves could be depended upon, and were probably much more accurate than the others.

In the study of extra currents, some preliminary experiments were made in which curves were taken showing the dying out of current in a closed circuit containing resistance and self-induction when the impressed electromotive force was suddenly removed by short-circuiting the leads from the source. The curves in Figs. 7 and 8 (see Plate) are portions of two thus taken, one for direct current and the other for alternating, the resistance being 5.1 ohms, and the self-induction 0.032 henries. When superimposed they coincide quite exactly. The small sinusoidal curve in Fig. 7 is that of the tuning-fork before mentioned.

Others, not shown, were taken for increase of current when the electromotive force was suddenly impressed. Their form was the same as Fig. 7 would appear if turned over, except that the straight line ended abruptly where the curve began at the instant the electromotive force was impressed.

When taking these curves, the arc lamp was always operated so as to give as bright a spot of light as it was capable of producing. The varying brightness of the curves is probably due to the hissing of the arc.

The final results of the investigation obtained with the galvanometer described were quite satisfactory. These, however, will not be discussed here, since this article relates more especially to the galvanometer itself, using as illustrations a few of the various kinds of curves that have been photographed with it.

Fig. 7.

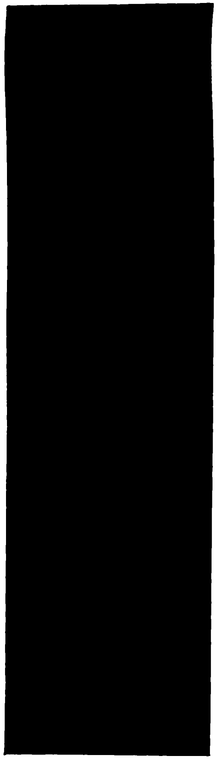

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

The galvanometer may be modified to adapt it to the particular use to be made of it. For the study of synchronous motors, new apparatus was made, with modifications, some of which were made necessary by the new conditions, and others tried with a view to improvement and to extending the range of usefulness of the galvanometer. The same electro-magnet was used, but it was necessary to use other coils having only about 1050 turns instead of 1940. Slide *S*, Fig. 3, was made a little longer in order to give the plate a higher speed as it passed the slit. The latter was two feet below the top. The average speed of the plate while passing the slit was about ten feet per second. In place of the arc lamp enclosed in a box, a light wooden box about 8½ × 10 × 12 inches, lined with asbestos paper, was used to enclose the light and support hand-fed carbons at an angle of about 30° or 35° from vertical, so as to have the maximum intensity directed horizontally toward the narrow slit in the side toward the galvanometer. When fed by hand, curves could be obtained without the variations of brightness seen in Figs. 7 and 8. A space was left between the wood and the asbestos lining, so that air could circulate.

The mode of supporting the needle was somewhat modified, as shown in Figs. 4, 5, 6; Fig. 4 being a plan, 5 an elevation, front view, and 6 a vertical section. For convenience in making, and to get the coil *c* nearer the needle laterally, the coil was supported on two ¼ inch rods *rr′*, Figs. 5 and 6, set in holes ¾ inch between centers in a piece of wood *d′*. Portions of the rods were cut away as shown. On one a shoulder was left, to which one end of the fiber *f* was fastened, the other end being attached to a spring *m*, which should give as much tension as the fiber will safely bear.

For supporting the coil in position between the pole pieces, *N S*, a standard, *e*, was fastened to a base that was clamped to the yoke piece of the magnet by a screw. The block *d′* is held against the ends of two screws through the standard by tightening the screws in the bent end of the metal strips *k*, which draw upon the rod *h*, through the block. These form a sort of universal joint, convenient for adjusting the needle so as to bring the spot of light from the mirror on the slit of the slide; also, one needle and coil could be readily removed and replaced by another in the experiments made for the purpose of comparing the behavior of needles of different dimensions and suspensions. The block d' served also to hold the binding screws for the small coil.

Several needles were made and tried. Dimensions and data for five of them are given in Table I. The mirrors for the last four were obtained by selecting from a large number of microscope cover-glasses one that had a plane surface, as shown by the interference bands that appeared when the glass was placed on a standard plane surface. The glass was .08 mm. thick.

Table I.

MEASUREMENTS OF GALVANOMETERS. DIMENSIONS IN MILLIMETERS.

Numbers.		I.	II.	III.	IV.	V.
Fiber	Material	Quartz.	Quartz.	Quartz.	Quartz.	Silk.
	Length	14.		12.	12.	12.5
	Diameter	0.14		0.015	0.057	0.035(?)
Needle	Length	2.4	Nearly like IV.	1.80	2.50	2.81
	Width	1.25		0.56	1.23	2.56
	Thickness	0 33		0.065	0.07	0.07
Mirror	Length	2.00		0.80	1.72	1.44
	Width	1.25		0.45	0.65	0.49
	Thickness	0.30		0.10-	0.10	0.10
Approximate vibration frequency with about 10 amperes in field coils		3580	3950	3450	3900	2850

After silvering by Draper's method,[1] and varnishing, the thickness was between .09 and .1 mm. It was then cut to the desired size with a small marking diamond.

In mounting the iron and mirror on the fiber, a metal plate was supported a few inches above the table, upon which was fastened one end of the fiber; the other was allowed to hang over the edge, with a lump of wax attached to keep it straight and in place. The iron was placed on the plate under the fiber. Two minute particles

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[1] Smithsonian Contributions to Knowledge, Vol. 14, Article IV., p. 3, 1865.

of dry shellac were then placed on the fiber, or close against each side, above the iron, and heat was applied by a bunsen burner beneath the plate until the shellac melted and spread as much as desired. It was then allowed to cool before putting the mirror in position upon the shellac. When the mirror was carefully adjusted, heat was again applied beneath. The mirror was lightly pressed down upon the melted shellac with a plane surface so as not to spring it, and left to cool slowly. The fiber was cut off to the required length and mounted on the supports with melted shellac. The small pieces of iron and mirror may be conveniently handled with two fine pointed glass rods by slightly wetting the end of one and touching it to the corner of the piece to be lifted; then use the dry one to remove the piece from the other, and to place it.

Figures 7–11 inclusive are full size copies of portions of a few curves photographed, the whole plate being 2½ × 8 inches. Figure 9 shows the natural vibration frequency of needle II. for comparison with Fig. 10, which is a current curve for an eight-pole alternator in the Dynamo Laboratory taken with the same needle and 7.8 amperes in the small coil (2) of 34 turns of number 18 copper wire. The plate passed the slit with the same mean speed of about 120 inches per second for both. The frequency of the alternating current was about 98, and that of the needle about 3950 per second. The straight line in Fig. 9 shows the width of spot of light that may be obtained, and that the needle remains perfectly steady while the plate falls if not deflected by current; also that the plate falls without being disturbed by friction or jar. At the end of the short, straight line the circuit from a storage battery was closed by a trip operated by the falling plate holder. When the vibrations due to inertia had nearly died out, the circuit was broken by another trip. In Fig. 10, the parts of a second curve are due to the plate being dropped twice for the same current a few minutes apart. The speed of the dynamo had changed a little.

For part of our work a much slower motion of the plate was desired. This was accomplished by an arrangement on the principle of the Atwood machine. A string hooked to the top of the plate holder passed over a pulley mounted on the top of the slide, and supported on the other side a weight which nearly counterbalanced the plate holder. A stretched rubber band started the holder and weight, which maintained quite nearly the same speed after the band ceased to act. Figure 11 shows a curve thus taken for electromotive force between two terminals of a three-phase generator on open circuit; the frequency being about 22 cycles per second. Needle IV. was used with the 300 turn coil (3) of number 28 copper wire. A tracing of a current curve for the same dynamo with the plate dropping at full speed is shown a little more than one-half size by IV., Fig. 12. The other three curves are similarly reduced.

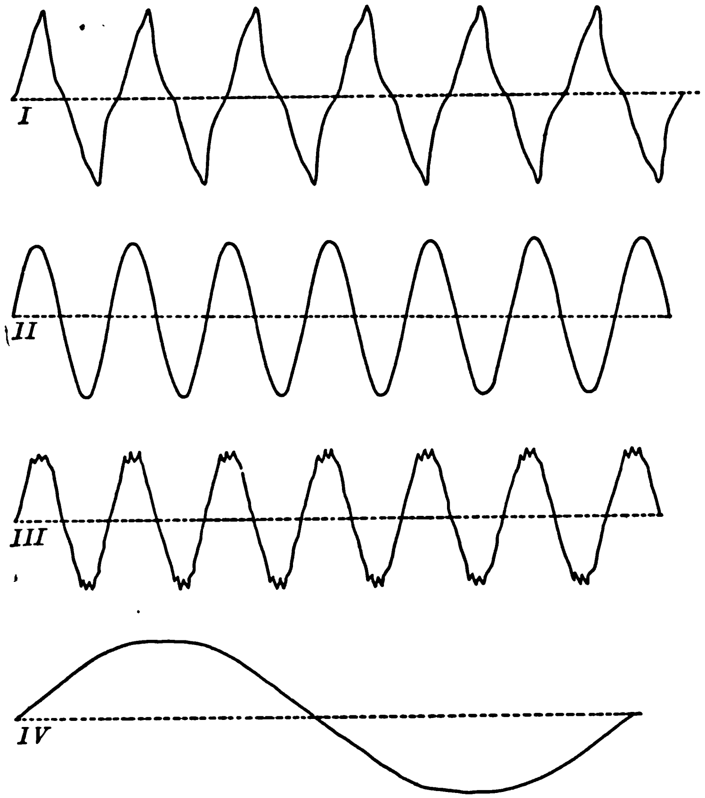

Fig. 12.

In Fig. 12, I. is a curve for current through a synchronous motor run by one of the large transformers in the laboratory.

Curve II. is for current from a small 50-volt, 10-ampere Westinghouse alternator having a smooth cored armature, it being the same one used in the experiments on extra currents.

Curve III. is for current from another alternator of the same type, except that the armature coils are laid in grooves cut in the core. The small variations, plainly noticeable by the shading of the line in the plate, cannot be represented by the tracing. The irregularities of the curve, indicated not only by change of direction of line, but by the shading, recur regularly in each cycle, being of the same number, shape, and position in the cycle; and were evidently not due to the natural period of the needle. Figure 13 is a curve for the same dynamo taken by the instantaneous contact and telephone method.

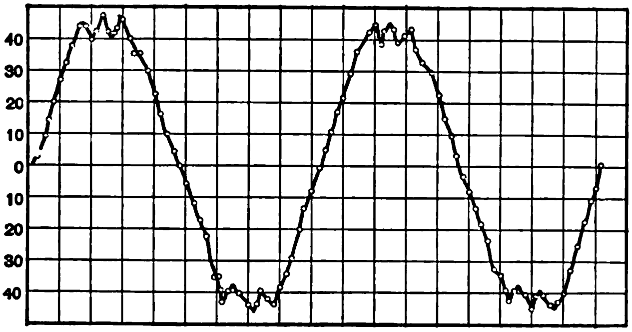

Fig. 13.

A photograph was taken the same way as Fig. 9 to try the effect on the frequency of the needle when the field was weakened; and also to show the promptness with which the needle obeyed the deflecting force. With about 12 amperes in the field coils the first throw of the spot of light was 0.55 inch; while with 1.7 amperes in field coils it was 1.3 inches. Under these same conditions the frequency was reduced from about 3900 to 2700. When a square was applied to the angle between the first throw and the axis for zero current, its variation from a right angle could not be detected near the axis. The spot of light in the first throw and return travelled about 2.6 inches, while the plate travelled $\frac{1}{23}$ inch in about $\frac{1}{2700}$ second. For taking curves the slide was usually between 12 and 18 inches from the needle.

To determine whether the deflection of the needle is proportional to current in the small coil, for constant field excitation, a calibration curve for needle III. was taken, with the result shown by line *D*, Fig. 14, which is a straight line; showing that the galvanometer may be depended upon to give ordinates proportional to current when properly adjusted. The needle should be adjusted relative to the pole-pieces until the spot of light remains at rest when the field current is suddenly made or broken.

When using different needles it was noticed that with one there was very little deflection when there was no current in the field coils, while for another the deflection, under the same conditions, was very large. This led to taking the curves shown in Fig. 14, and further explained in Table II.

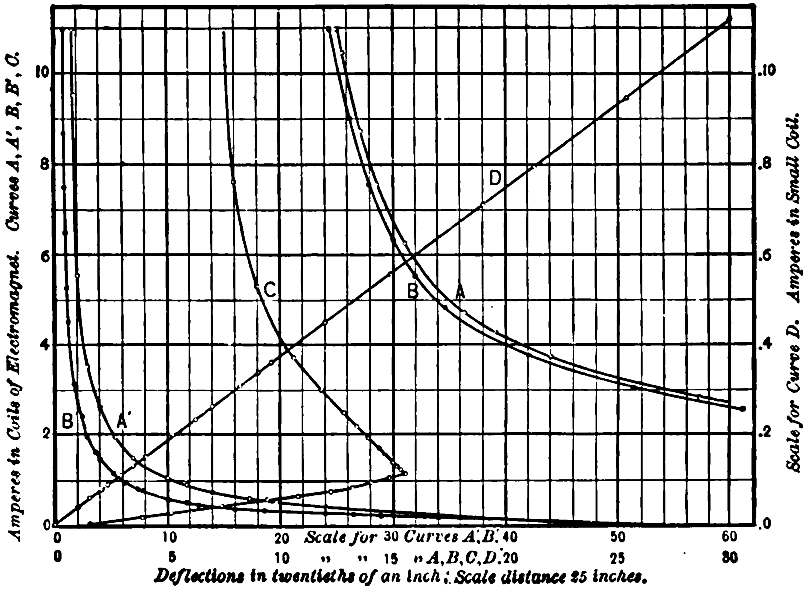

Fig. 14.

The three curves, *A*, *B*, *C*, were taken for the same current and with the same conditions, except the use of different needles. Before beginning the readings, the residual magnetism was that left after breaking the circuit when 9 or 10 amperes were flowing in the coils. The cores and pole-pieces being of wrought iron, it was quite small. The magnetizing current was then gradually increased, giving the curves as plotted.

In order to get the complete curves like *A* and *B*, so as to show the magnitude of the deflections for zero field-current relative to those for higher magnetization, the curves A', B' were taken for smaller currents in the small coil.

TABLE II.

EXPLANATION OF CURVES IN FIGURE 14.

Curve.	Needle used.	Constant current in small coil of 300 turns.
A	III.	0.5 ampere
A'	III.	0.06 "
B	V.	0.5 "
B'	V.	0.034 "
C	IV.	0.5 "
D	III.	Constant current in magnet coils=9.4 amperes.

From the curves *A*, *B*, A', B', it seems that for constant current the action and sensitiveness of the smallest needle with the fine quartz fiber is about the same as that of the comparatively large needle with the silk fiber; and that, for both, the maximum deflection corresponds to a magnetization equal to or less than the residual value. Curve *C* indicates that the coarse fiber is so stiff that a much smaller deflection in a stronger field is the maximum. Other things not yet experimented upon may have a part in determining the form of curve *C*. A study of the behavior of different needles under different conditions with comparatively low magnetic fields is in progress. If sufficient steadiness and freedom from vibration can be obtained by the use of a permanent magnet, or a small electromagnet, it would be much more convenient for a portable apparatus and would be very much more sensitive for experiments in which only small currents can be used.

For one part of the synchronous motor experiment a galvanometer giving a large deflection for small currents of comparatively slow variations was desired. For this purpose a U-shaped permanent magnet of about $\frac{7}{8}$ square inch cross-section was mounted in such a way that any one of the five needles could be readily adjusted; needle V., however, was made especially for use with this magnet. There were four small coils on the permanent magnet which could be used to increase the field if found necessary. The pole pieces were loose and rested on a block to which the needle block was fastened. Either the pointed ends or the square ends could be placed against the coil around the needle, or drawn away from it if a weaker field were desired.

In the spring of 1895 Messrs. A. Barnes and H. Zimmerman undertook[1] an experimental determination of the variations of temperature at the inner surface of the walls of an engine cylinder during a double stroke of the piston; also the variations at different depths below the surface. The use of a quick-acting galvanometer was suggested to them by one of the writers. After a preliminary trial with the large electro-magnet and needle II., they decided to adopt the method; so the one described above with needle V. and coil 3 was constructed and used for the purpose. The general method was to have the changes of temperature produce a corresponding change in the resistance of a fine wire, and thus to vary the amount of current flowing through the galvanometer. The latter was placed in shunt with the resistance. The plate was moved up and down in front of the slit by a cord connected to a reducing motion operated by the movement of the piston, so that the spot of light from the galvanometer traced out a closed curve for the complete cycle, quite like an indicator diagram.

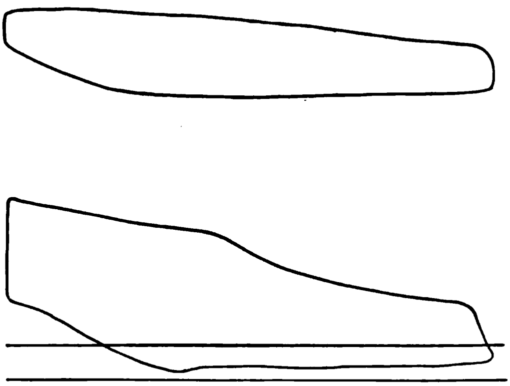

Fig. 15.

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[1] Thesis in Cornell University Library; Abstract in Sibley Journal of Engineering, June, 1895.

A tracing from one of them, and a slightly reduced copy of the indicator card taken at the same time, are shown in Fig. 15. The abscissæ for both are the same, representing parts of the stroke. The ordinates of the upper loop represent temperatures, while those of the lower are pressures. The gauge pressure was 40 pounds, and the speed 84 r.p.m.

The vertical width of the upper loop shows the range of variation of deflection, while the total deflection due to the current of 0.4 or 0.5 ampere flowing was about 5 or 6 inches; the plate was perhaps 18 inches from the galvanometer. Each 0.1 inch of change of deflection was found to represent a change of temperature of 12.5° C. The needle trembled slightly, making the finely toothed line about $\frac{1}{40}$ inch wide, the line itself being perhaps $\frac{1}{100}$ inch wide. The width of loop decreased as the speed increased, the results being quite uniform, and apparently in accord with theory. The galvanometer seemed to be quite reliable without any field excitation. For part of the work the pole pieces were turned with the square ends toward the coil, and were also drawn apart to a width of $\frac{3}{4}$ inch instead of $\frac{15}{32}$ inch, as before. The deflections were increased, but the trembling was also increased, so that there was not much gained.

The vibration due to inertia does not take place to any great extent, even with a rather weak field, if the current is continually varying without very large or sudden changes in the rate of variation; for then the condition for simple harmonic motion — that the displacement be proportional to the acceleration — does not exist, if the period of the needle differs from that of the current or its harmonics. It was found that the needles with quartz fibers were more reliable than those having silk fibers, especially for high frequencies and strong fields. For these conditions it is better to have the fiber as large as can be used without too much decrease of deflection or increase of size of the small coil.

It was found that with needles II. and IV. the spot of light was improved by placing a small lens of 10 or 12 inches focal length immediately in front of the small coil, so that the light passed through it both to and from the mirror. The lens was supported on an arm from the standard *e*, shown in Fig. 3. With the other needles no lens was used. If the mirror is plane, a real inverted image of the arc is obtained at all distances, the principle being the same as in the case of a pin-hole camera. This fact may be used to test the mirrors after they are cut and before and after mounting, to determine whether they have been sprung in mounting and whether they are suitable for use.

In the construction of the apparatus described prominent considerations were that it be inexpensive and easily made from materials, and with means, most readily obtained. Other considerations would doubtless have led to a quite different construction. It was deemed best, however, to investigate the working of the cheap and simple apparatus for special uses, before undertaking a more expensive and elaborate design for more general use.

The original plan for the synchronous motor experiment was to photograph on the same plate simultaneous records of current and lag variations by having the spots of light from two galvanometer needles thrown upon the slit in the slide. The work along this line is not yet completed; however, there does not seem to be anything to prevent the use of two or more galvanometers, or needles for obtaining simultaneous curves for current, electromotive force, etc., on the same plate.

The results thus far obtained seem to warrant a more careful study, and such modifications in design as will adapt the instrument to the many uses to which it may be applied.

Physical Laboratory of Cornell University,
May, 1895.

MINOR CONTRIBUTIONS.

EXPERIMENTS WITH A NEW POLARIZING PHOTO-CHRONOGRAPH AS APPLIED TO THE MEASUREMENT OF THE VELOCITY OF PROJECTILES.[1]

BY ALBERT CUSHING CREHORE AND GEORGE OWEN SQUIER.

IN May, 1894, a paper[2] was read at the general meeting of the American Institute of Electrical Engineers in Philadelphia describing a novel method of measuring the variations in an electric current. The point of novelty consisted in the fact that the indicator or the vibrator, which actually describes the curve representing the current, possesses no mass, and is therefore not subject to the laws of inertia. It is the application of a modification of this instrument to the measurement of the velocity of projectiles which forms the subject of this paper.

The instrument, as used for measuring current, made use of a dark band in the spectrum to indicate by its movement along the spectrum the varying values of the current. This band is obtained as follows: Instead of taking sunlight direct and analyzing it into the colors of the spectrum, it is first passed through a polarizer and then through a quartz plate to rotate the planes of polarization of the component colors in different amounts depending upon the color, and finally through an analyzer, whose office it is to extinguish only that color which is rotated to the same extent as its plane. The resulting light emerging from the analyzer is colored, due to the absence of the color which the analyzer abstracted from the white light. Upon analyzing the emergent light into the pure colors of the spectrum, the color which the analyzer abstracted is absent, and in its place is a dark band in an otherwise continuous spectrum. The motion of this band is effected by placing between the polarizer and analyzer a transparent substance surrounded by a coil of insulated wire; that substance to have the property of rotating the plane of polarization when in a magnetic field. This field is produced by the current to be measured flowing in the coil of

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[1] For a detailed account of these experiments, see the Journal of the United States Artillery, July, 1895, published at Fort Monroe, Va.

[2] "A Reliable Method of Recording Variable Current Curves," by A. C. Crehore; Transactions of the American Institute of Electrical Engineers, Vol. XI., No. 10. October, 1894; also THE PHYSICAL REVIEW, Vol. II., No. 2. 1894.

wire, and its strength is consequently proportional to this current, since no magnetic material, such as iron, is present.

It may not be evident at a glance what the relation is between an instrument which will accurately measure a variable electric current, and the measurement of the velocity of projectiles. In regard to this it may be said that any good instrument for measuring a variable current possesses the essentials of a chronograph, and a chronograph is the essential instrument for measuring the velocity of projectiles. A good current measurer must give sufficient data to construct a curve, the horizontal axis representing time, and the vertical axis current. The time interval between any two phenomena can therefore be measured by such an instrument if the phenomena referred to are capable of either interrupting the current or changing its strength in any way. The instrument referred to is therefore adapted to the measurement of the velocity of projectiles; for screens may be placed at any desired intervals along the trajectory, and the current mechanically interrupted. The instrument measures the time between these screens by indicating when the current is changed; the distance is measured on the field. The average velocity of the projectile is this distance divided by the time interval.

In the present application to the measurement of the velocity of projectiles, since it is only necessary to indicate the presence or absence of a current, the instrument may be simplified by omitting not only the quartz plate, but also the arrangement for resolving the light into a spectrum. The operation of the instrument is now as follows: White light is passed through the polarizer, and then through the transparent substance possessing the property of rotating the plane of polarization when in a magnetic field, and then through the analyzer. A lens is used to intensify the light emerging from the analyzer by bringing it to a focus on the photographic plate. The analyzer is then "crossed" and set for total extinction, so that normally no light is admitted to the plate. When a current is sent through the coil, all the planes are rotated, the blue more than the red. The effect is that light immediately emerges from the analyzer, and is recorded on the plate. The light persists as long as the current flows, but is cut off completely upon its interruption, — much more suddenly than it could be interrupted by any mechanical shutter. In fact, the office of the whole combination of polarizer, analyzer, and medium for rotating the planes of polarization is to play the part of a shutter.

The experiments with this instrument were made at the United States Artillery School, Fort Monroe, Va., between the dates of Dec. 27, 1894, and Jan. 12, 1895. The instruments used were homemade and quite hastily assembled. Many things adopted for the sake of expediency were a disadvantage in experimenting, and these things, if instruments were now manufactured for the purpose, might be avoided. The camera was made at Dartmouth College and the instrument shipped to Fort Monroe during the latter part of December, where it was installed after the 27th inst. Besides this, many things remained to be done after this time, such as running wires to the temporary proving grounds, arranging suitable supports for the novel kind of ballistic screens used, etc., etc.

The camera is shown in the views Figs. 1 and 2. [See Plate.] It consists of a rectangular box *A*, 10 × 10 × 2½ inches inside measurement. The cover *B* is removed, showing a small auxiliary dark chamber *C*, which contains the electromagnetic device *D* with armature *E* attached to the spring *F* for releasing the camera slide *G*. This slide is shown withdrawn from the grooves in which it normally slides by passing it through the opening at the top after removing the cover *H*. The narrow horizontal slit through which the light is admitted to the plate is shown at *I*. The slit is made of sheet brass, the upper jaw being stationary and parallel to a radius of the plate. The lower jaw *J* is a sector of sheet brass which slides between two guides so as to make the slit always a sector of the plate, the object being to secure a uniform exposure for every point of the plate. When the camera slide is in position, the nail at *K* rests on the top of the brass spring *F*, and the upper edge *L* of the lower part of the slide covers the slit. When the current passes through the magnet by the binding posts *M*, the slide is released. The slit is only exposed while the opening in the camera slide is passing by. The upper part of the slide *G* is capable of adjustment along the rods of the slide, and the time of exposure of the slit thus under control. When the cover *B* is in position, the space containing the release mechanism is a complete dark chamber in itself. A cap *N* in this cover *B* is removed just before the camera is to be used. The wires at *O* are for the purpose of producing on the plate reference circles by casting their shadows. The entire back of the camera is removable, and its outside face is shown at *P*. Through the back a horizontal shaft *Q* passes which revolves in the bearing *R*.

The inside of the camera is seen in Fig. 2. The slide is shown with the upper part *G* removed. The plate is mounted on the shaft at *S*.

The object of the camera slide is to prevent the exposure of the plate from extending over more than one revolution and thus spoiling the record by a second exposure.

The polarizer used was a Nicol prism the dimensions of which are 104 by 39 mm. on the side, while the diagonals of the ends measure 60 by 49 mm. The analyzer was similar to the polarizer. Between polarizer and analyzer was placed a tube 45 cm. long and 3 cm. internal diameter, made of glass and fitted with plane glass ends. This tube was filled with liquid carbon bisulphide, which has the property of rotating the plane of polarization when in a magnetic field, and only then. The tube was wound with No. 18 single cotton magnet wire from end to end in four sections. Each section had 725 turns, which made in all 2900 turns when the four coils were connected in series.

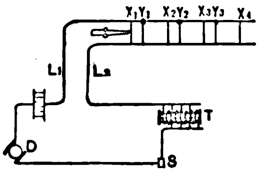


Fig. 3.

The diagram of the circuit which contained this tube is seen in Fig. 3. Current is supplied at a constant electromotive force of 110 volts by the dynamo *D*. The amount of current is regulated by a bank of resistance lamps. The tube is at *T* and a switch at *S*. Line wires L_1L_2 lead to the proving ground, where the screens $X_1X_2X_3X_4$ are erected in the path of the projectile. At $Y_1Y_2Y_3$ are placed devices for establishing the current immediately after it is broken by the preceding screen. The device to re-establish the current is a simple arrangement represented in Fig. 4. The springs *CC* are separated by a small insulating plug *D*, which is attached to a wire running across the path of the projectile. This is mechanically pulled out by the projectile, which therefore establishes the current by connecting the binding posts *BB'* together.

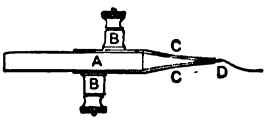


Fig. 4.

The camera shaft was coupled directly to a small electric motor operated by four cells of storage battery. A fly wheel was placed on this shaft, which served a double purpose. It was a gear wheel having fifty-six teeth. By holding the edge of a card against it, a tone is given out whose pitch depends upon the speed. It was thus that the speed was adjusted before each shot. The speed was not obtained in this way, but it is desirable to have a speed such that the plate will revolve nearly once around while the slide is passing by the slit. The note thus obtained was compared with a tuning fork in the other hand of the observer just before each shot, and the negatives show that this method gave pretty uniform results.

The record of the time is recorded on the plate itself at the time the shot is fired. A tuning fork mounted to run electrically is placed so that the shadow of one prong is brought to a distinct outline on the plate. This shadow gives a sinusoidal wave on the negative. On the average about 35 waves of the fork used can be counted on the negative. The convenience of this method proved to be very great, not only because the record of time is on the plate itself, but because it was not necessary to time the revolutions before and after firing.

The tuning fork used made 512 complete vibrations per second, and was in unison with another similar fork before it was mounted electrically. After it was mounted, it was observed to beat with the other fork, so that its vibrations afterward were calculated to be 509.46. This makes the average time of exposure of the negatives about .066 of a second. A speed which will make the plate revolve once during the exposure is thus about 12.25 revolutions per second, or about 735 per minute.

The complete arrangement of the instruments showing the electrical circuits used with the different pieces of apparatus is shown in diagram, Fig. 5, in which D is the dynamo, T the transmitter tube, S a switch to complete the transmitter circuit a moment before firing to prevent heating the coils, L_1L_2 the line wires leading to the proving ground, $X_1X_2X_3$, etc., the screens, $Y_1Y_2Y_3$, etc., the devices for restoring the current successively between the screens, and L and L' two arc lamps in series, which for convenience were lighted by the same dynamo D. F is the electrical tuning fork controlled by the cells E, and M is the motor for running the camera; and at O are the four storage cells for energizing the same. G is the gravity switch for exposing the camera and firing the gun, and C is the camera whose slide is operated by the cells I through the gravity switch at VV. The firing circuit contains the electric primer P at the gun, the line wires P_1P_2, the dry cells S', and the gravity switch terminals UU.

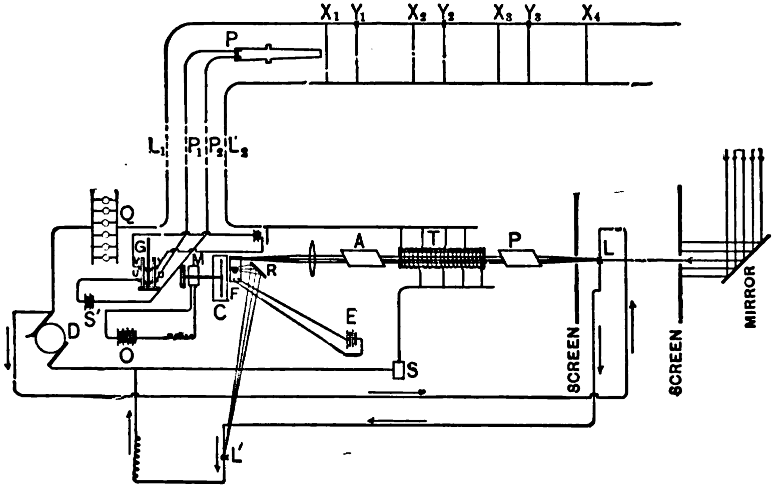


Fig. 5.

The shortness of the time of exposure was the cause of the greatest experimental difficulty; for to obtain a record of the projectile, it must be made during the particular .066 of a second when the camera is exposed. Of course a camera made in the future for this purpose can be so arranged as to avoid this difficulty. There is a certain unknown interval of time between the closing of the primer circuit, which fires the gun, and the arrival of the projectile at the muzzle, which is known as the "firing interval." There is also an unknown interval between the closing of the camera circuit and the exposure of the plate. The relation between these intervals must be determined before the camera can be used to obtain a record. It turned out that the camera circuit should be closed a short time before the primer circuit, to bring the muzzle record at the beginning of the exposure. A gravity switch was constructed with the object of keeping this position when once found constant. It consisted of a brass rod standing vertically between two uprights, and a cylindrical brass weight four inches long with a hole through its axis to permit it to fall down the rod. Near the bottom of the rod are two pairs of contacts, connected to the two uprights having projecting springs so that the falling weight will first "make" the camera circuit and then the primer circuit. The time interval between is adjustable by dropping the weight from different heights. When the proper height was found, this switch gave satisfaction.

The gun used was a 3.2-inch B. L. field rifle, No. 56, model of 1892, and the service charge of 3¾ lb. of I. K. H. powder was uniformly employed. The projectiles were common shell, so selected that each weighed 13 lb. 6 oz.

Length of bore of gun	25.2 calibers.
Travel of projectile in bore	21.81 "
Powder chamber capacity	108.9 cu. in.
Density of loading	0.95315.

For the gun two siege platforms were laid in prolongation and leveled, giving a suitable direction of fire out to sea. The firing was conducted without applying the wheel breaks, and the recoil was approximately constant at 48 ft. total, or 28 ft. on the platform and 20 ft. on the ground.

The arrangement of screens for this work possesses some interesting features. A skid 12″ × 12″ × 15′ long was placed in approximate prolongation of the axis of the bore of the gun elevated at 3 degrees, being supported by two solid upright posts. Beyond this, shifting planks were placed end to end, spiked together, and supported by scantlings set into the ground at intervals. The first shots with the gun showed that the blast was not to be feared so much as anticipated. The screens were made of two strong, upright pieces, spiked to the sides of the skid. Along the straight edge of these pieces on the side towards the gun, wire nails were driven in at close intervals, and wire wound around the nails and stretched back and forth, three times being usually sufficient. These screens were placed at various intervals, always beginning at the muzzle of the gun itself. Care was taken to place the muzzle screen at a distance in front of the muzzle equal to the length of the projectile, so that the first screen is not broken until the projectile is out of the bore of the gun.

Figure 6 is a reproduction of the first negative obtained when the circuits were arranged as in Fig. 5, the first screen being at the muzzle and the second 40.13 ft. from the first. The record of the muzzle screen appears at X_1 on the negative, the make at Y_1, and the second break at X_2. The angle between the breaks can be read with considerable accuracy. It was measured with a large spectrometer, the circle of which is graduated directly to ten minutes, and with the verniers the reading is to ten seconds. The plate is mounted horizontally on the turning table, and centered by means of the reference circles at *A* and *B* put on the plate for the purpose by the wires in the camera at *O*, Fig. 1. On this plate an average of nine readings of the angle makes it $108^\circ\, 5'.815 \pm .'444$ or $108^\circ.0969 \pm .^\circ 0074$. The probable error shows that this angle is measured with an accuracy of .0068% of the whole, or of one part in 14,630. Of course the percentage of error depends upon the whole angle measured, but 40 ft. is a smaller distance than it is customary to use with other chronographs. The tuning-fork record shows that an angle of $294^\circ.54$ subtends just 34 waves of tuning-fork, seen at the *CD*, Fig. 6. The time of one wave being $\frac{1}{509.46}$ of a second, the angular velocity of the plate is $4413^\circ.42$ per second. The velocity of the projectile is

$$v = s/t = \omega s/\theta,$$

where s is the distance between screens, θ the angle between breaks measured on the plate, and ω the angular velocity. Upon substituting the values found, the velocity is found to be 1638.5 ft. per second.

It was next attempted to obtain observations at several points along the trajectory, at regular intervals, at first fifteen-foot, then ten-foot, and lastly five-foot intervals were tried, to a distance of 45 ft. in each case. Records with all of the intervals above mentioned were successfully obtained, and in Fig. 7 is reproduced a negative taken, showing five-foot intervals beginning at the muzzle and extending to a distance of 45 ft.

It is interesting to note that when the interval between the screens is so small as 5 ft., it is necessary to place the device to establish the current before the previous screen, as the projectile moves four or five feet while the jaws of the springs are coming together. Measurements on this plate give the following angles: —

s	θ	s	θ
5	13° 49′.29	30	82° 28′.25
10	27° 19′.29	35	— —
15	40° 53′.79	40	110° 10′.46
20	54° 36′.00	45	123° 50′.88
25	68° 24′.83		

The relative velocities calculated from these angles considering the muzzle screen as the first one in each instance, are

s	*v*	*s*	*v*
2.5	1599.4	15.0	1608.3
5.0	1610.8	17.5	—
7.5	1621.7	20.0	1605.3
10.0	1619.5	22.5	1606.5
12.5	1615.7		

If the five-foot screen is taken as the first, the same angles give the following velocities: —

s	*v*	*s*	*v*
2.5	1599.4	17.5	1610.5
7.5	1637.5	20.0	—
10.0	1633.0	22.5	1606.0
12.5	1626.8	25.0	1607.3
15.0	1619.7		

These tables are exhibited graphically in Fig. 8, which shows that the velocity increases outside of the bore of the gun up to a certain maximum point at a distance of six or seven feet from the muzzle. This same effect is exhibited on all the negatives obtained with five-foot intervals, and they all compare well together. The increase is so great, about $2\frac{1}{2}\%$ of the whole, that one cannot attribute the increase to errors.

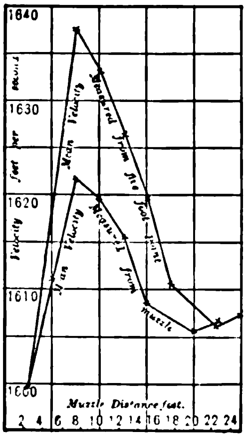
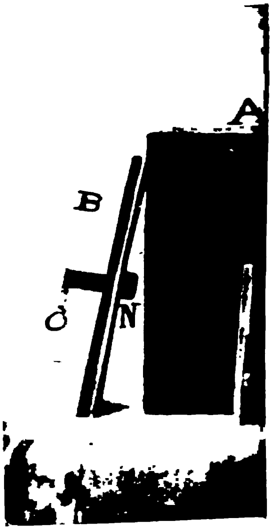


Fig. 8.

The reason why the points do not lie on a smooth curve is of course because of errors, but it is more probable that the error arises from the fact that the projectile does not strike consecutive screens exactly alike, and thus the intervals are not precisely five feet, than that they are due to the measurement of the angles on the negatives. So it appears that there is now greater accuracy in measuring the time interval than in finding the exact distance.


A
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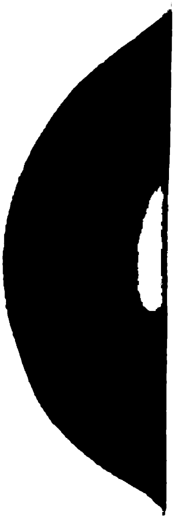
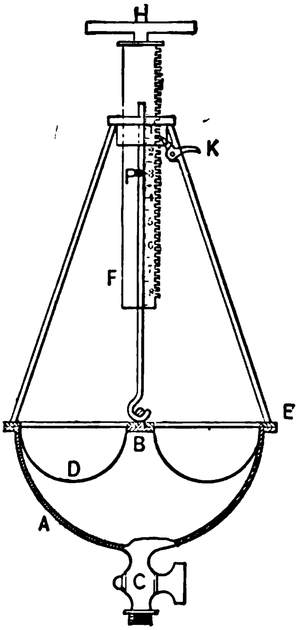


EXPERIMENTAL DEMONSTRATION OF A LAW OF FLUID PRESSURE.

By W. J. Humphreys.

IT is well known that the pressure at any point of a perfect fluid is equal in all directions, whether the fluid be at rest or in motion, and that this equality of pressure is also true of viscous fluids, provided they are at rest. Of course it can be rigidly demonstrated mathematically that this is a consequence of the inability of fluids to sustain a tangential stress, but such a demonstration is beyond the grasp of the average student when he first begins the study of physics; consequently an experimental demonstration becomes useful. The piece of apparatus here described for demonstrating this principle is easily manipulated and is well adapted to class-room work.

It would be easy to criticise several experiments suggested by elementary text-books for the demonstration of this law of fluid pressure, but I will simply say that one of the best I have seen is that of exhausting a pair of Magdeburg hemispheres, and then showing that they are held together in whatever direction they be turned. This shows that there is pressure in every direction, but does not show how much in any direction.



The piece of apparatus which I constructed for this purpose consists of a single Magdeburg hemisphere *A* (see figure), to which is connected a stopcock *C* for exhausting air, and a spring dynamometer *F* for measuring the pressure exerted. As shown in the illustration, a thin but strong rubber diaphragm *D* is made fast, by means of a metallic rim *E*, to the top of the hemisphere. To the center of this diaphragm is fastened a metallic button *B* to which is hooked the rod that communicates with the spring dynamometer. The dynamometer can be placed at any desired distance from the diaphragm and held in that position by means of the rack and catch *K*. The apparatus was so constructed that it was easy to remove an old and put on a new diaphragm, though occasion for this seldom occurred.

The experiment is performed as follows: Place the dynamometer as near the diaphragm as it will go, exhaust the air from the hemisphere by means of the stopcock to any degree desired (this can be done sufficiently well by the mouth), and then by means of the handle *H* raise the dynamometer to a suitable position and fasten it with the rack and catch. The index ***P*** will now show a certain pressure which will remain constant, no matter in what direction the rubber diaphragm be turned, up, down, or sidewise at any angle; thus experimentally demonstrating that within the limits of delicacy of the apparatus the pressure of the atmosphere — and presumably of other fluids — is at any place equal in all directions. Evidently apparatus of the same general plan could be used to demonstrate this law in the case of liquids.

I used this device in the physical lecture room of the Miller Manual Labor School, Crozet, Va., for several classes, and it always gave entire satisfaction.

Johns Hopkins University, April, 1895.

NEW BOOKS.

Die Principien der Mechanik in neuem Zusammenhange dargestellt. Von Heinrich Hertz. 8vo, pp. xxvii, 307. Leipzig, Johann Ambrosius Barth, 1894.

The work before us possesses a melancholy interest, not only as being the crowning labor of the short life of its gifted author, but as being preceded by a most sympathetic and appreciative preface by his great master Helmholtz, who was so soon to follow his favorite pupil. To have been the favorite pupil of Helmholtz was in itself no small honor, but to have justified the expectations of the master with such completeness as was the case with Hertz, was indeed extraordinary. Helmholtz, great and clear-sighted as he was in all the domains of knowledge that he touched, can hardly be said to have founded a school, for although he had many clever and appreciative pupils, few seem to have been so imbued and penetrated with the ideas of Helmholtz as to have followed in the creative work characteristic of him. The single exception is Hertz. The whole work of Hertz shows the influence of Helmholtz. The philosophical consideration of fundamental principles, the frequent introduction of metaphysical considerations, the logical and systematic deductions from the premises, and the exceedingly general nature of the principles enunciated, all bear the stamp of the master. This is true in a large degree of the present work, although the manner and matter are highly original.

In a preface of fifteen pages Helmholtz gives an account of the life of Hertz, and a review of the development of the science to which he made the greatest contributions. What Helmholtz thought of Hertz may be gathered from the following quotation: "Favored with the rarest gifts of mind and character, in his too short life he gathered a full harvest of almost unhoped-for fruits, for which during the preceding century many of the most talented of his fellow-scientists had striven in vain. In ancient classical times it would have been said that he had fallen a sacrifice to the envy of the gods. Here Nature and fate seemed to have favored in a quite uncommon manner the development of a mind which united in itself all the faculties necessary to the solution of the most difficult problems of Science. . . . I myself felt this grief deeply, for among all the pupils that I have had I might consider Hertz the one who had penetrated most deeply into my own circle of scientific thoughts, and upon whom I might place the surest hopes for their further development and enrichment."

When Hertz finished school at the age of eighteen, he chose the profession of an engineer, being, with characteristic modesty, somewhat doubtful of his success should he take up theoretical science. This doubt lasted two years, after which he began the study of physics under Helmholtz at Berlin. The latter immediately recognized his talent, and at the end of the second semester, having to propose the subject for a prize in physics, chose a subject in electrodynamics, in the hope that Hertz would interest himself in the subject and attack it with success. This subject was no less than a research intended to throw light on the critical question of action at a distance, as opposed to action from particle to particle. The various theories of Weber, Ampère, Neumann, Riemann, Grossman, and Clausius are characterized by Helmholtz as a "brilliant bouquet of hypotheses, very little 'übersichtlich' in their consequences, so that the domain of electrodynamics had at that time become a pathless desert." Weber had undertaken to remove certain difficulties in his theory by the hypothesis that electricity had a certain amount of inertia. To find out whether this was true was the problem attacked by Hertz. By means of experiments on extra-currents in double coils he showed conclusively that not more than one-twentieth of the extra-current could be due to inertia of electricity. But Hertz was not satisfied with this result. Recognizing that the induction in straight wires could be calculated with much greater accuracy than in coils with many turns, he experimented with wires forming two rectangles, and thus reduced the effect that might possibly be attributed to inertia to less than one two-hundred-and-fiftieth of the whole. Further experiments were still more convincing as to the untenability of Weber's hypotheses. It is easy to see how these experiments were the beginning of Hertz's study of electrical theory. Helmholtz, the first convert and apostle in Germany of the Faraday-Maxwell theory opposing action at a distance, considering the experimental demonstration of the existence of a magnetic effect due to the changes of dielectric polarization in an insulator (Maxwell's displacement currents), to be a crucial point in the decision between the rival theories, made it the subject of one of the great prize contests of the Berlin Academy of Sciences. The result was his now famous research on High Frequency Electrical Oscillations, and the experimental proof of the correctness of Maxwell's theory, making it highly probable that luminous vibrations are of an electromagnetic character.

After the preface by Helmholtz comes the author's preface, in which he states the object of physics to be the explanation of all natural phenomena by means of the simple laws of Mechanics. What these laws are is, however, not a matter of common agreement. It is the aim of the author to embrace all the laws of mechanics, including Newton's fundamental laws of motion, in some principle that shall be so simple as to be intrinsically probable, the truth of which shall be justified by its agreement with experience. Helmholtz had proceeded in such a manner in his work on the Principle of Least Action, starting with the assumption of Newton's laws and Hamilton's principle. The same ideas appear in the work of J. J. Thomson on the applications of Dynamics to physical phenomena. Hertz, however, proceeds in a different manner, the reason for which he explains in a long philosophical introduction. In this he discusses with great logical acumen the necessary and sufficient properties that must be possessed by any "image" that shall represent to us the true essence of the phenomena of motion, and of such images he considers in detail three, in historical order. In the first system the conceptions supposed given *a priori* are the ideas of space, time, mass, and force. Force is introduced as the cause of motion, existing before and independently of the motion. Kinematics connects the ideas of time and space, and Galileo's conception of inertia gives a relation between space, time, and mass. In Newton's laws appear all four fundamental conceptions, and the principle of d'Alembert gives the general statement of all that is predicated of them. The rest is simply deduced by logical processes. While the system here treated is perfectly logical, and is therefore a satisfactory "image," the conception of force has given rise to a number of difficulties, chiefly of a metaphysical nature, and has in recent times been the subject of vigorous attacks.

The second image treated is the far more modern one in which the notion of energy appears as a fundamental concept instead of that of force. Although this system has been frequently advocated, there exists no text-book of mechanics which follows it out completely, introducing the idea of energy before that of force. In this system the two conceptions of space and time have a simple mathematical character, while the other two, mass and energy, are introduced as given indestructible physical entities. In order to connect all four, there is needed besides the principle of conservation of energy a further principle, which may be taken as that of Hamilton. This would give as the sole result of experience needed the principle that every system of natural masses moves as if it had the task set of reaching given positions in a given time in such a manner that the mean difference between kinetic and potential energy throughout the motion should be as small as possible. This second image avoids the difficulty of the first of speaking of things of whose nature we know little or nothing, and which have also little influence on the result. For in speaking of forces we must ultimately come to speak of forces between individual molecules and atoms, of which our notions are by no means directly derived from experience. The following quotation may possibly impress others as agreeably as it did the reviewer.

"It affected almost painfully so rigorously thinking an investigator as Gustav Kirchhoff, to see atoms and their vibrations thrust into the midst of a theoretical deduction without dire necessity." Such a statement is refreshing in these days when every student, nay, almost every dynamo-tender, talks so glibly of molecules and of the ether. "The arbitrarily assumed properties of the atoms may be without influence on the final result, the latter may still be correct. Nevertheless, if the details of the deduction itself are in a large degree presumably false, the deduction is illusory. The older conception of physics leaves us here hardly any choice or mode of escaping the difficulty. On the contrary, the theory of energy and our second image of mechanics possess the advantage that there appear in the statement of the problem only things directly appreciable by experience, parameters, or arbitrary co-ordinates of the bodies considered; that the discussions proceed with the help of these quantities in finite and complete form, and that the final result can be immediately translated back into terms comprehensible by experience."

Hertz does not, however, adopt this second, or energy-image, partly because, like any other, the principle of Hamilton is not of perfect universality, partly because the principle does not possess the simplicity of enunciation requisite for a fundamental principle, as well as for more or less metaphysical reasons. The third image, to which the present work is devoted, differs from the others in that it contains but three fundamental conceptions instead of four. These are space, time, and mass. The fact that these three were sufficient was made prominent by Kirchhoff in his philosophical treatment of mechanics in his celebrated text-book. In order to fill the apparent gap without introducing a new conception, Hertz supposes that in addition to the masses that are perceived by our senses, there act certain "concealed" masses, which are recognizable only by the effect that they produce on ordinary bodies. Such bodies are the ether, Lord Kelvin's and Maxwell's vortical fluid, and the matter treated by Helmholtz in his work on "Cyclic Systems." This hypothesis has the advantage not only of eliminating all mysterious forces from mechanics, but also of preventing their entrance at all. In carrying out this principle, Hertz makes the further supposition that the connections between parts that act upon each other are rigid, thus returning to the idea that preceded that of action at a distance. Unfortunately, as Helmholtz remarks, Hertz does not give examples to explain how he conceived such intermediate members between bodies not in contact, and it will probably require a large expenditure of physical imagination in order to explain even the simplest cases of physical forces. Physicists of such extraordinary intuitional powers as Maxwell and Kelvin would probably have no difficulty in so doing. It is comforting to know that Helmholtz himself obtained more satisfaction by the ordinary methods of considering the facts as represented by the differential equations of physics.

The first half of the body of the book, treating of kinematics, concerns itself merely with definitions and terminology. This is very carefully worked out, and although appearing very abstruse, is found, when the idea of the author is once seized, to be of considerable simplicity. Ideas generally considered as applicable to the motion of a point are generalized in such a manner as to apply to systems composed of any number of material points. The length of a displacement of a system is defined as the quadratic mean (square root of mean square) of the displacements of all its mass-points, every particle of mass m being supposed in taking the mean to consist of m separate mass-points. It is easily shown that the distance or displacement between two positions of a system is always less than the sum of the distances of the two from a third, and that consequently it is possible to represent three such distances by the sides of a triangle. Any displacement may thus be considered as the resultant of two others, and may be represented by a single vector. This vector does not, of course, give us the position of each point of the system, but it has a definite relation to the configuration of the system. We may, by means of the triangle, define the difference in direction between two displacements. In particular we may define the amount and direction of infinitesimal displacements, and proceeding from one configuration to another we may consider the path of a system. The path is defined as straight if its direction is constant, which will be easily seen to involve the condition that the paths of every particle of the system are straight in the ordinary sense. If the path is not straight, we may define its curvature as the rate of change of direction per unit length of path traversed. An element of a path is straighter than another if its curvature is less. A straightest element of path is one that is straighter than all other possible elements having the same position and the same direction. A path all of whose elements are straightest elements is called a straightest path.

These definitions being premised, we may state the fundamental principle enunciated by Hertz, the consequences of which are elucidated in the second half of the book treating of dynamics.

Every free system persists in its state of rest or of uniform motion in a straightest path.

Systema omne liberum perseverare in statu suo quiescendi vel movendi uniformiter in directissimam.

This law, which is merely a generalization of Newton's first law by the changes necessary in substituting the word "system" for "material point," contains in itself all three laws. From these are immediately deduced the integral of energy, and Hamilton's principle. As all the definitions have been free from reference to any particular system of co-ordinates, the equations of motion are obtained in generalized co-ordinates in the form given by Lagrange. The motion of systems under geometrical constraint is then treated, and finally the motion of systems under the action of forces. Force does not here appear as a fundamental notion, but simply as a sort of analytic expression for the amount of deviation of a system from the straightest path, accompanied by an equal and opposite deviation of another system. This conception is after all not different from that of Kirchhoff, but the enunciation of it is here extremely precise and lucid.

The aim and general method of the work before us have now been described. There follows a treatment of the important case of cyclic systems, following Helmholtz, concealed cyclic motions, illustrating the fundamental supposition, and finally treatment of discontinuous motions. Whether the method of deducing the fundamental equations employed by our author is preferable to the usual methods may be considered doubtful — it seems to be merely a question whether we shall take a little more or less for granted. The present reviewer must confess that he feels rather content to be satisfied with the representation of the physical facts by the equations than with an attempt to reconcile them with a simple principle, and to confine his flight far below the upper air of metaphysics; and he is glad to be supported by the opinion of Helmholtz already quoted. However this may appear to others, the work of Hertz shows that it is not without reason that in German universities natural science finds its place in the *philosophical* faculty, and we can but admire the clear insight and the logical exposition of a system, which evince the treatment of a most difficult subject by a master mind.

Arthur G. Webster.

Elementary Lessons in Electricity and Magnetism (New Edition). By Silvanus P. Thompson, F.R.S. 8vo, pp. xv+628. Macmillan & Co., 1895.

An elementary text-book in science which has lived fourteen years, and which has had a sale of a number of thousand copies each year, must be a remarkable book, deserving the attention of all teachers. The book before us is no less than this, and in a completely revised edition will be welcomed by all who are interested in technical education. This book has no doubt been used as the first step in the electrical instruction of a majority of American technical graduates who are now employed in the electrical industries, and numberless men holding responsible offices will remember with interest their study of "Thompson's Lessons" during one of the terms of their sophomore year at college.

The new edition of this book bids fair to be as useful as the old. It has been brought fairly up to date, and on the whole has been made to conform very well to our present methods of scientific thought. The book has more and possibly better competitors for the attention of students and teachers than formerly, but none are so clear and satisfactory for the reader. There are one or two text-books that probably make a better foundation for the sophomore lectures and laboratory practice in electricity and magnetism which are presented to the students of our technical schools (Chapter XVI. of the revised Daniell's Physics, for instance) ; but, while these give a better preparation for the advanced work of the technical student, they are, as a general rule, too heavy for the less strongly prepared general student or the undirected reader. The reviewer is not a teacher of physics, but he feels safe in saying that Thompson's Lessons has no real rival as a text-book in the general course in college, or for a place in the hands of the general reader who wishes to obtain a knowledge of electricity and magnetism.

For elementary course instruction, the additions which have been incorporated in the new edition relating to dynamo calculations, working of alternators, theory of transformers, etc., are of questionable utility, but for the general reader these articles must be of considerable interest, and may possibly be useful. It is always possible for a reviewer to find defects in a book, especially if he is inclined to resort to special pleading, but the defects in the book before us are amply compensated by virtues. It is unfortunate that the author's proof reading was not more carefully done, especially with a view to bringing the phraseology of the old portions of the book into harmony with the more modern forms of the new. Many slips in spelling might also have been corrected; but the most prominent fault of the book is to be found in its definitions, which may sometimes be misleading to an inexperienced student. This is particularly unfortunate in a beginner's book, as a young student is readily led into error or thrown into perplexity by statements which are perfectly plain to a more experienced reader. The use of the erroneous term "virtual" instead of the formally adopted term "effective," when referring to alternating volts and amperes, must be strongly criticised. Alternating current phenomena are such a stumbling-block to the average student throughout his studies, that it is especially desirable to avoid any artificial addition, however small, to the difficulties which may be caused by a double use of terms, and it is to be hoped that the word "virtual" will be replaced in the plates by "effective" for the benefit of future reprints.

The mechanical execution of the book is carried out in the excellent style for which the publishers are justly noted.

DUGALD C. JACKSON.

Steam and the Marine Steam Engine. By JOHN YEO. 8vo, pp. xiv+196. Macmillan & Co., 1894.

This work is professedly intended for naval officers and for students of engineering in the earlier part of their training.

With this end in view, the size of the book has been kept within small limits, and the evident purpose has been to give, in plain, readable style, the salient features of modern marine engineering practice.

Judged from this standpoint, the work seems to have been conscientiously done, and the selections from the broad field of engineering practice have generally been made with care and judgment. The treatment of propulsion and resistance is, however, exceptionally brief, the latter being dismissed with less than one page, presumably on account of its less vital connection with the main subject in hand.

The illustrations are numerous and excellent, and the make-up of the book is in the usual good style of the publishers.

On the whole, there seems to be little to criticise adversely, and much to commend, when viewed from the standpoint of the author's avowed purpose. Viewed more broadly, however, the extent of the field of usefulness for such works may be fairly called in question. No book of 200 octavo pages can satisfactorily present even the leading features of so broad a subject as that here dealt with; and, while such works may serve as an introduction to more extended study, or for those who only wish a general outline of the subject, they must be laid aside early in the *student's* course to give place to sources of more extended and exact information.

W. F. DURAND.

Volume III. *September–October, 1895.* *Number 2.*

THE

PHYSICAL REVIEW.

A STUDY OF THE POLARIZATION OF THE LIGHT EMITTED BY INCANDESCENT SOLID AND LIQUID SURFACES.[1]

BY R. A. MILLIKAN.

I.

Introductory.

IN spite of the prodigious activity of physicists during the first three quarters of this century in attacking the problems of reflection, refraction, and polarization in all their different phases, both from the side of experiment and that of mathematical theory, the problem of polarization of light by emission seems to have received comparatively little attention. Although the fact that incandescent solids and liquids emit, at oblique angles of emergence, partially polarized light, was discovered more than seventy years ago, it does not appear even to-day to be very generally known. Few, even of the more complete text-books on physics, make any mention of the fact. Verdet, in his *Optique*, published in 1870, devotes a short paragraph to "Polarization by Emission," in which he says that "there exists upon the subject but a small number of experiments, due mainly to Arago." The summary of these experiments, which he subjoins, reveals none whatever that are quantitative. Since the time of Verdet, no one, so

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[1] A paper presented to the New York Academy of Sciences, April, 1895.

far as I am able to discover, has made any careful or elaborate study of the phenomenon with a view to ascertaining its generality, verifying or disproving Arago's assumption as to its cause, or classifying different substances with reference to their power of producing the phenomenon in greater or less degree.

Since even a hasty examination reveals the fact that different substances emit light of widely different percentages of polarization, it appears that a study of the relations of different bodies in this respect ought either to add something to our knowledge of the optical properties of the substances considered, or else, if this particular property is deducible from the already known properties, as Arago assumed it to be, its relation to these properties ought to be definitely proved. This investigation has therefore been undertaken for the purpose, first, of making a somewhat wide range of qualitative experiments upon the nature and generality of the phenomenon; and, secondly, of subjecting Arago's explanation of the cause to the test of comparison with carefully determined experimental quantities.

II.

Historical Review.

The simple facts of polarization of light by emission can best be observed, and in fact were first noticed, upon platinum. If a sheet of that metal be heated to incandescence in the flame of a Bunsen burner, and the emitted light examined by means of a Nicol prism, or any other instrument adapted to the detection of partially polarized light, it will be observed that when the experimenter is viewing the surface normally the emitted light exhibits no trace whatever of polarization, but as the instrument is inclined so as to receive rays emerging obliquely from the surface, the light begins to show evidences of polarization in a plane perpendicular to the plane defined by the normal and the emerging ray. If this plane be called the plane of emission, and the angle included between these two directions *the angle of emission*, the complete phenomenon may be roughly described by saying that the polarization increases as the angle of emission increases, and becomes, in the case of platinum, exceedingly strong as the emission angle approaches ninety degrees.

The announcement of this fact, and the consequent overthrow of the common belief that light coming immediately from self-luminous bodies is always natural, was made first in 1824 by Arago. In a report made in that year to the Royal Academy of Sciences (see *Annales de Chemie et de Physique* (1) 27, p. 89) he announced that he had some time before made a series of experiments upon the light which emanates from incandescent bodies. "He found that if the bodies are solid or liquid this light is partially polarized by refraction when the rays observed form with the emitting surface an angle of a small number of degrees. As for the light of an ignited gas it presented under no inclination traces of sensible polarization." From these experiments he drew the conclusion "that a considerable portion of the light which enables us to see incandescent bodies is produced in the interior and at depths which are not yet completely determined." "Even when the surface of a solid or liquid was not well polished," Arago still found that he "was able to detect evident traces of polarization." The substances upon which he experimented and from the observation of which he drew his conclusion were only four in number, viz. — solids, wrought iron and platinum; liquids, molten iron and glass (see *Astronomie Populairc*, II., p. 103). He made *no* quantitative measurements, nor even used an instrument which was capable of indicating roughly *amounts* of polarization. His polariscope consisted of a single quartz crystal cut perpendicularly to the optical axis, and a crystal of Iceland spar. The latter produced a double image of an opening in a diaphragm placed just beyond the crystal of quartz. The two images were of course colored when the light was polarized and uncolored when it was natural.

Arago applied the results of his experiment to the determination of the character of the sun's surface. Being unable to detect any trace of polarization in the light emitted by the outer edge of the sun's disk, he drew the well-known conclusion that the surface of the sun can be neither liquid nor solid, but must be gaseous.

After the discovery of the polarization of heat, and the construction of an instrument by Melloni for its detection and measurement, Provostaye and Desain examined the heat rays emitted by luminous platinum and found that they, like the light rays, were polarized in the plane perpendicular to the plane of emergence. Their experiments were few in number and confined entirely to platinum. In 1866 Magnus extended this method of experiment to obscure heat rays, making quantitative measurements upon the heat emitted at the temperature of 100° C., and at an angle of 35°. His experiments embraced the following list of substances: Paraffine, glycerine, white wax, melted calophony, rubol, black glass, transparent glass, quicksilver, aluminium, copper, and tin. For these substances he found a polarization at 35° ranging from .5 per cent to 27 per cent. He drew the conclusion that obscure heat, like light, must undergo refraction in emerging from the surface of the radiating body.

Verdet, in the paragraph upon polarization by emission previously referred to, while stating that little has been done in the investigation of the subject, gives the same explanation of the phenomenon as that first offered by Arago. He says that "it is due to the fact that it is not alone the surface molecules which radiate light; those of the interior layers also radiate, at least to a certain depth; and the rays emitted by the interior molecules undergo refraction at the surface." Since the time of Verdet, I believe no one has made any experiments upon the subject except Violle, who has a brief note in the *Comptes Rendus* of 1887, Vol. 105, p. 111, in which he states that, while making some other experiments upon molten silver, he took occasion to measure the percentages of polarization in the light emitted by that substance at various incidences. He plotted the curve of these percentages and found that it was very well represented by the empirical formula $p_e = (1 - \cos i)\left(1 + \cos 75^\circ + \frac{i}{5}\right)$, where p_e represents the ratio of a polarized light to the whole light in the emitted beam, and i the angle of incidence.

Assuming, then, the phenomenon to be due to refraction, he argues that the equality of the amounts of polarization in the reflected and refracted beams would require that $ep_e = pr_r$, where e is the proportion of the whole light emitted, r the proportion reflected, p_e the proportion of polarized light in the emitted beam, and p_r the proportion of polarized light in the reflected beam. Then, since the whole light is either emitted or reflected, $e + r = 1$, and the formula $r = \frac{p_e}{p_e + p_r}$ immediately follows. Taking the experimental values which have been determined for p_r by reflection at ordinary temperatures, he finds that his own results for p_e, when substituted in this formula, give a uniformly high reflecting power for molten silver; a result which agrees with the known properties of ordinary polished silver. This forms the nearest approach to a verification of Arago's assumption which has yet been given.

Such is the extent of the work which has thus far been done upon polarization by emission.

III.

Discussion of Arago's Explanation.

The explanation of Arago and Verdet is as yet the only one which has been offered to account for the phenomenon. This explanation does not rest upon careful experimental proof, and, furthermore, there seems to be considerable reason for doubting its correctness. According to that explanation the light which comes to the eye from the *surface* particles is *natural* light; but mixed with this unpolarized light is a quantity of light which has worked its way up from uncertain depths, has undergone reflection and refraction at the surface, and is consequently polarized upon emergence. Aside from the intrinsic difficulty of this conception, the first experiments which were made in this research upon platinum seemed to be inconsistent with such an explanation; for, when a well polished platinum strip was heated to incandescence by means of an electric current and the glowing surface examined by means of a double Wollaston prism, the polarization was found to be so nearly complete for angles in the neighborhood of grazing emergence that one of the images almost disappeared. But, since platinum is known to be altogether opaque, except in the case of exceedingly thin laminæ, it would seem as though the surface molecules must play a considerable part in the luminosity of the glowing metal; so that, even if the assumption were made that the laws of reflection and refraction would require complete extinction of the ray polarized parallel to the plane of emergence, there still ought to be a considerable amount of light emitted in this plane from the surface molecules; at least, a sufficient quantity to prevent so nearly complete extinction as experiment showed to exist for angles of 88 or 89 degrees.

The only apparent method of reconciling the facts with Arago's explanation was to assume that the opacity of the platinum was greatly diminished by an increase in its temperature. And yet, such experiments as were made to determine whether or not this was the case, gave only negative results. The thinnest sheet of platinum which was capable of being heated to incandescence without melting, was placed in the focus of a powerful beam of light from an arc lantern, the beam having been first polarized by transmission through a Nicol. The plane of the glowing platinum being perpendicular to the beam, the light emerging normally on the other side of the platinum was examined by means of a delicate polariscope. No trace of polarization was detected. Neither could the outlines of the focus be distinguished on the side of the platinum away from the lantern. The sheet of platinum employed was evidently just as opaque as at a lower temperature.

This difficulty of accounting for the extreme polarization noticed at large angles of emergence appeared to be considerably diminished if another cause for the phenomenon were assumed than that given by Arago.

According to the conclusions of Fresnel, Cauchy, Stokes, Mascart and most of the advocates of the elastic solid theory of light, the direction of vibration of the ether particles in plane polarized light is perpendicular to the plane of polarization. It would follow that the light emitted at large angles by platinum vibrates mainly in the direction of the normal to the surface. It is not unnatural to suppose that at the boundary between very dense and very rare media, like platinum and air, there may be less resistance to vibration in a direction away from the surface than in a direction parallel to the surface, and therefore that the light emitted is composed mainly of vibrations in a direction normal to the surface. If this were the case, the light emitted normally would be unpolarized, while that emitted at oblique angles would be polarized in the plane perpendicular to the plane of emission. Furthermore, the polarization would increase with the angle and might be very great at large angles, in case the difference in density between the two media were very great — conclusions all of which are in accordance with the facts. In view, then, of the inability to account, by Arago's assumption, for the extreme polarization at large angles of emergence, and in view of the plausibility of the other explanation, the following qualitative experiments were made in order to determine with more certainty the nature of the phenomenon.

IV.

Qualitative Experiments.

The object of this part of the research was: —

(1) To make certain that the property of polarization is due to the incandescent body itself, and is not caused by the refraction of the light as it passes through the layers of air of varying density which rest upon the luminous surface; and,

(2) To make observations upon as wide a range of substances as could be made to emit light without combustion, in order to ascertain whether any substance could be found which does not possess the characteristic, and also in order to determine in a general way the relations of different bodies with reference to this property.

For these purposes two instruments were employed; the first, a polariscope similar to that of Arago, save that the simple quartz crystal was replaced by a bi-quartz plate, and the crystal of calcspar by a double Wollaston prism. This is the same instrument which was afterwards used by Arago in his polarimeter, and it has an advantage over the first form in that the two colors to be compared are brought into immediate juxtaposition. It is delicate to the extent of detecting a polarization of about 3 per cent (as was shown by succeeding experiments), when white light is under examination. When the light to be tested is monochromatic, as was the case in some of the following experiments, the second form of polariscope was found to be preferable.

In this instrument the bi-quartz is replaced by a cube of glass which has been subjected to strain in cooling. A Nicol also takes the place of the Wollaston prism of the first polariscope. The glass being in the state of strain, is doubly refracting and exhibits with polarized light the familiar dark or light cross which is characteristic of doubly refracting crystals, when cut perpendicularly to the optic axis and viewed by convergent light. With this instrument a polarization of two or three per cent could be easily detected, and it had the further advantage of indicating immediately the azimuth of the plane of polarization. Also, by careful observation of the distinctness of different parts of the figure it was possible, after a small amount of practice, to estimate with considerable correctness the *degree* of polarization.

1. In all experiments which have been previously performed upon this subject, the white-hot body has been in immediate contact with the air. The emitted light was therefore obliged to pass through layers of air of varying density before it reached the eye of the observer. That the light might thus suffer a large number of refractions between the incandescent body and the eye, and so be endowed with the property in question, seemed entirely possible. It was therefore necessary to make some experiment in order to determine whether or not this was the entire or partial cause of the phenomenon. For this purpose the contrivance shown in Fig. 1 was employed. A strip of platinum foil *A* about 4 cm. in length and 5 mm. in width was attached to the platinum and copper wires *B* and *C*. The former was sealed into the glass tube *G*, and the latter was passed through the cork *F* which closed the other end of the tube.

The instrument was first sealed with wax and then connected with the air pump by means of the small tube *D*, and with a strong electric current by means of the wires *B* and *C*. Care was taken to place the platinum strip as near the axis of the tube as possible, in order that light emitted by it might pass normally through the sides of the tube. Otherwise polarization would have been caused by the passage of the beam through the glass itself. The tube being exhausted until the gauge showed a pressure of only four millimeters, the current was turned on and the glowing strip examined by means of the bi-quartz polariscope. The emitted light was still found to be polarized for oblique angles of emergence and did not appear to have undergone any change in intensity. In order, however, to ascertain whether or not the effect of the air was altogether negligible, more delicate experiments were necessary. These will be hereafter described.

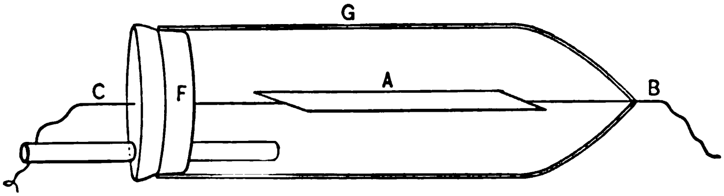

Fig. 1.

2. Having thus proved that the phenomenon is inherent in the body itself, experiments were made upon the following substances with results as indicated : —

Solids. — *Metallic.*

Platinum (polished). — Polarization very strong near grazing emergence, but falling off rapidly as the angle diminishes. Scarcely perceptible at ten degrees.

Silver. — Polarization strong, larger for small incidences than in the case of platinum.

Gold. — Polarization strong; similar to platinum, but apparently less for large angles.

Copper. — Polarization weak, probably due to roughening of surface through oxidization.

Brass. — Polarization weak — (oxidization).

Iron. — Polarization weak — (oxidization).

Solids. — *Non-metallic — transparent.*

Glass. — Polarization weak; imperceptible except at large angles of emergence.

Mica. — Polarization weaker than in glass. Surface roughened by heat.

SOLIDS. — *Non-metallic — opaque.*

Porcelain. — Polarization similar to that produced by glass.

Black Glass. — Polarization similar to that produced by transparent glass.

LIQUIDS.

Molten Silver, " Gold } Polarization similar to that in solid state.

" Iron. — Polarization strong; almost as strong as in molten gold.

" Bronze. — Polarization strong; almost as strong as in molten gold.

Lead. — Polarization weaker than for preceding metals. (Difficult to get a clear surface.)

Zinc. — Polarization weaker than for preceding metals.

From these experiments it will be seen, (1) that the metals show uniformly high percentages of polarization so long as the surface is non-diffusing; (2) that none of the non-metallic substances used produce strong polarization at any angle; (3) that the transparency or opacity of a substance has apparently little effect upon its power of producing polarization in the emitted light; and (4) that any cause which interferes with the perfect smoothness and regularity of the surface destroys in large measure the polarization.

V.

Instrument employed for Quantitative Experiments.

In order to accomplish the second and main object of the research, it became necessary to devise some means of making accurate determinations of the relations of the *constants* of the partially polarized beam. The instrument which has been most employed for such work by previous investigators is the polarimeter of Arago. This is an instrument simple enough in principle, but difficult in construction. Moreover, it does not possess a very high degree of accuracy, owing to the fact that its use depends upon the detection, by means of a bi-quartz polariscope, of the exact point at which all polarization disappears from a beam of light.

Both because of this difficulty of construction and because my own experiments with the bi-quartz polariscope made me distrustful of the accuracy with which the point of no polarization could be determined, another form of instrument was devised for these experiments which is greatly superior to the Arago polarimeter in simplicity, and is probably more than equal to it in accuracy. The credit of the first conception and use of this method of measuring the constants of partially polarized light is due to Cornu. Violle also used a similar instrument in his determinations upon silver.

In view of the exceeding naturalness and simplicity, as well as the accuracy of the method, it is surprising that it was not earlier discovered and has not been more generally employed. Cornu's description of his instrument was published in '82 in the *Ass'n Française pour l'Avancement des Sciences, Comptes Rendus;* but so far as I can discover, no reference was made to it at the time in any of the scientific journals, nor has it taken its place among other polarimeters in any of the text-books on optics. The instrument as constructed and used for the purposes of these experiments was as follows. A rectangular opening *O*, 1 mm. in width and 2.5 mm. in length, was made in a diaphragm *H* which stood a short distance in front of the double Wollaston prism *A*. The prism was rotated until the extraordinary image of the opening was to the left of the ordinary; the distance of the screen from the prism was then adjusted until the opposite edges of the two images exactly coincided. A Nicol prism *B*, capable of rotating about its axis and furnished with a graduated circle and vernier for reading azimuth to a tenth of a degree, constituted the only other essential part of the instrument. A small telescope *C* was used for viewing the images of the rectangular opening *O*. The instrument was mounted upon a support *G*, furnished with a horizontal axis at *F*, about which the upper portion of the appa-

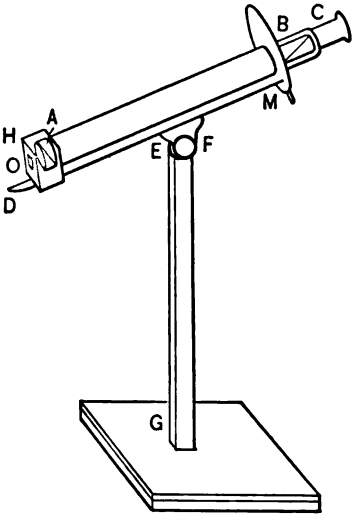

Fig. 2.

ratus could be revolved. The axis of the tube bearing the double prism and Nicol could thus be inclined so as to make any desired angle with the vertical. Since the two images furnished by the double prism consist of light polarized in planes at right angles to each other, the rotation of the Nicol will evidently extinguish each of them in turn. There will be four extinctions in the course of a complete revolution of the Nicol, and between any two extinctions there is a point for which the images, as seen through the Nicol, have exactly equal intensities. If now a partially polarized beam is under examination, and if, the plane of polarization of this beam being known, the principal sections of the prism are set parallel and perpendicular to this plane, that position of the Nicol which equalizes the two images, evidently defines the relation between their original intensities, which is also the relation between the constants of the partially polarized beam.

If we let a and b represent the original amplitudes of vibration in the two images, then the intensities of these images are represented by a^2 and b^2 respectively. The proportion of polarization is evidently the difference between these intensities divided by their sum. If w is the angle which the transmitting plane of the Nicol makes with the direction of vibration of the more intense of the two beams, say a^2, then the intensities of the two images as seen through the Nicol will be by the law of Malus,

$$a^2 \cos^2 w \text{ and } b^2 \sin^2 w. \tag{1}$$

Hence for the position of equality we have,

$$a^2 \cos^2 w = b^2 \sin^2 w \tag{2}$$

or

$$\frac{a^2}{b^2} = \frac{\sin^2 w}{\cos^2 w}. \tag{3}$$

If we call the degree of polarization in the original beam p, we have

$$p = \frac{a^2 - b^2}{a^2 + b^2}; \tag{4}$$

or, from (3),

$$p=\frac{\sin^2 w-\cos^2 w}{\sin^2 w+\cos^2 w}=-\frac{\cos^2 w-\sin^2 w}{1}=-\cos 2w. \qquad (5)$$

Hence, when the position of the Nicol which produces equality in the images has been found, the amount of polarization is immediately given by (5).

Cornu, in discussing the instrument, shows in addition, that, when the principal sections of the partially polarized beam are not known, the degree of polarization may still be found by taking one set of readings in any position whatever of the axes of the double prism, and then rotating the whole instrument through an angle of 90° and taking a second set of readings. The degree of polarization can then easily be shown to be given by the formula

$$p=\sin(w_2-w_1).$$

In this work, however, we are not concerned with this last formula, since the principal sections were always known.

VI.

Adjustment of the Instrument.

Since the series of experiments here considered were all made upon horizontal surfaces, and since the polarization of the emitted light is always in a plane normal to the surface, but one adjustment of the instrument was necessary, viz. that of bringing the principal sections of the double prism into coincidence with the horizontal and vertical directions.

This adjustment was effected in the following way. The axis of the tube bearing the prism and Nicol was first set, by measurement, parallel to the cross-piece *DM* of the supporting frame. The base *G* was then carefully leveled by means of a common level. The leveling of *DM* then brought the axis of the tube into coincidence with the horizontal line. The telescope was then focussed upon a very fine line of light reflected from the edge of a carefully leveled sheet of white paper placed just in front of the rectangular opening *O*. Since the line joining the two images produced by a crystal of calc-spar is always parallel to the optical axis of the crystal, it follows, that, when the two images of the horizontal line of light form with each other an unbroken line, the principal sections of the crystal have the desired directions, and the adjustment is perfect. The line of light used in this case was so narrow that the adjustment could be made with great accuracy. This done, the crystal was permanently fastened in position. Thereafter, it was only necessary, before each observation, to level the base of the instrument *G*, in order to bring the principal sections of the crystal into the desired positions.

In order to set the axis of the tube at any desired angle with the vertical, the cross-piece *DM*, parallel to this axis, was leveled, and the angle *DEG*, between the movable arm and the vertical support, was measured by means of a protractor. The zero position being thus determined, any desired inclination could be secured by giving to the angle *DEG* the proper value.

VII.

Degree of Accuracy of the Instrument.

The great sensitiveness of the eye in detecting slight differences in the intensities of images of the same color when brought into close proximity has often been the subject of remark. Cornu claims that the position of equality can be determined with a precision that reaches $\frac{1}{10}$ of a degree. My own observations would not lead me to attribute to the instrument so high a degree of accuracy. Furthermore, these observations are subject to the objection which attaches to all photometric experiments, that the sensitiveness of the eye varies greatly with the physical and mental condition of the observer. At times the extreme difference in my readings for a given set of conditions would be as high as $2\frac{1}{2}$ degrees. Usually, however, the extreme difference was not more than $1\frac{1}{2}$ degrees. For the sake of testing the probable accuracy of the results which are to be given later, several sets of observations were made upon the unpolarized light of a gas flame. The following illustrate about the average course of the readings. The zero of the instrument not being known, the positions of equality on each side of the positions of extinction were determined:—

Left.	Right.
50.5	39.2
50.0	39.1
50.0	38.7
50.4	38.8
51.3	40.0
50.0	40.0
51.0	40.0
51.1	39.9
50.2	39.2
49.5	39.0
50.4	39.37

$$\underbrace{50.4 \qquad 39.37}_{2w = 89.77}$$

$$w = 44.88$$

Since the light from a gas flame is unpolarized, the value of w should have been 45°. The difference is not large, but is slightly greater than the maximum error ascribed to the instrument by Cornu. The above is about an average set of readings. The extreme difference is 1°.8, a difference perhaps slightly greater than that usually found.

A second slight error may sometimes arise in the use of this instrument from the fact that the two images produced by the double prism do not correspond to exactly the same points on the luminous surface. Hence, in order that the results may be correct, it is necessary that the adjoining portions of the incandescent surface be exactly alike. In none of the experiments here recorded were the portions of the luminous surface producing the two images more than 3 mm. apart. Care was always taken to direct the instrument toward a portion of the surface which appeared to be entirely uniform. This error may, I think, be safely disregarded in all of the following cases except one, which will be mentioned later.

A third remark which should be made upon the accuracy of the instrument is that observations for large amounts of polarization are less subject to error than those made upon small amounts. For, since the intensities of the two images compared are proportional to $\sin^2 w$ and $\cos^2 w$, the change in intensity of one of them will be very rapid when w is in the neighborhood either of zero or of 90°. When, however, w is near 45°, the change in intensity corresponding to a small change of angle is comparatively small. Hence, when the polarization is large, and w consequently either large or small, the position of equality can be determined with considerably greater accuracy than when the polarization is weak and w in the vicinity of 45°.

The results obtained for large angles may therefore be considered more trustworthy than the results for small angles.

VIII.

Measurement of the Air Effect.

In the qualitative experiments previously described it was ascertained that the amount of polarization was at least not greatly affected by the contact of the air with the heated surface. Before proceeding to careful quantitative measurements it was necessary to determine whether or not its effect upon the phenomenon is altogether negligible. This could be easily done by means of the polarimeter.

The sealed glass tube containing the platinum strip was again connected with the air-pump, and the air exhausted until the pressure was about 4 mm. The current was turned on, the polarimeter arranged so as to receive the light emitted from the glowing surface at an angle of about 80°, and the Nicol turned until the images were brought into equality. The stop-cock was then suddenly turned and the air admitted. No change whatever could be perceived in the equality of the images. The experiment was repeated a number of times and in a variety of ways, but always with the same result. The conclusion was, that, if the air has any effect whatever upon the proportion of polarization in the beam, that effect is so slight as to be *altogether negligible;* a result exceedingly fortunate for the purposes of this investigation, since, had it been necessary to work upon substances in a vacuum, the following experiments would have been much more difficult, if not altogether impossible.

IX.

Experiments upon Uranium Glass.

The chief difficulties which beset the investigation of polarization by emission are, 1st, the difficulty of obtaining a perfectly *definite* and *regular* incandescent surface with which to work, and 2d, the difficulty of ascertaining with certainty the optical constants of *any* bodies at the temperature of incandescence.

The similarity between a body emitting light by incandescence and a body emitting light by fluorescence was first suggested to me by Professor Rood. According to Tait, the phenomenon of fluorescence is confined mainly to the surface layers. Whatever the cause, then, of polarization by emission, the light coming from a fluorescent surface ought to be polarized in the same way as the light coming from glowing platinum.

Experiment showed this conclusion to be entirely correct. The polarization seen in uranium glass was similar in every respect to that observed in incandescent porcelain, being scarcely discernible at any angle less than 50°, but becoming quite marked between 85° and 90°, and evidently reaching a maximum at grazing emergence.

That this polarization was not due to diffusing particles on the surface was certain for three reasons: 1. The surface was *not* a diffusing surface except to an exceedingly small extent. 2. The light which exhibited the phenomenon of polarization was the characteristic yellowish-green light which uranium emits, and not the blue light which fell upon the surface. 3. The reflecting particles on the surface would have produced a polarization *in* the diffusing plane, *i.e.* in the plane defined by the direction of the beam which entered the instrument and the direction of the incident beam, which was in this case normal to the surface. As a matter of fact, the polarization was perpendicular to this plane.

Here, then, was an instance of polarization by emission in which the surface was perfectly definite and at the same time the optical constants of the substance could be easily and accurately determined.

Accordingly, a careful series of observations was made with the polarimeter. The experiments were all conducted in a well-darkened room, and care was taken not to allow any light to enter the instrument except that emitted by the uranium glass. In order to make the determination of the angles of emission convenient, the light from the lantern was thrown vertically down upon the surface of the uranium glass by means of total reflection in a right-angled prism. The cube of glass was carefully leveled so that the emitting surface was always horizontal. The arrangement of apparatus is shown in Fig. 3.

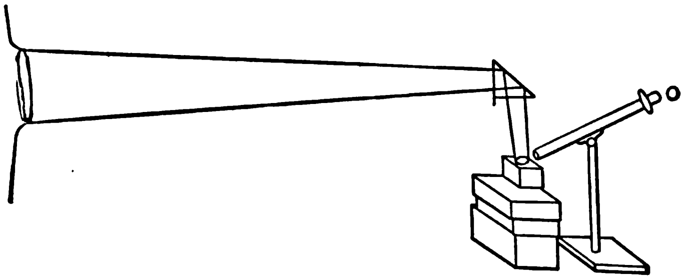

Fig. 3.

Ten readings were taken for every angle of emergence. The results are given in full.

87°.5		85°		80°		75°	
Left.	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**
40.5	29.8	42.3	30.7	43.0	32.0	44.5	34.5
39.5	29.9	43.0	31.2	43.3	32.5	45.0	35.0
39.8	28.5	42.5	30.5	43.8	32.3	44.3	35.0
40.0	29.0	41.7	30.9	44.0	32.6	44.5	33.5
39.0	28.9	40.9	31.0	43.3	32.3	44.5	34.4
39.76	29.22	42.1	30.86	43.48	32.34	44.56	34.5
$2w$ = 68°.98 p = 0 .358		$2w$ = 72°.86 p = 0 .293		$2w$ = 75°.82 p = 0 .245		$2w$ = 79°.06 p = 0 .191	

70°		65°		50°			
Left.	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**		
45.5	35.0	47.0	37.0	49.1	38.2		
46.4	36.4	47.2	36.3	48.9	38.2		
46.5	36.5	47.5	37.5	49.0	38.9		
47.0	35.0	48.0	37.0	50.0	39.3		
46.3	36.2	47.4	36.0	49.3	39.0		
46.34	35.8	47.62	36.8	49.26	38.52		
$2w = 82^\circ.1$ $p = 0.139$		$2w = 84^\circ.4$ $p = 0.098$		$2w = 87^\circ.78$ $p = 0.039$			

The chief difficulty encountered in making these determinations was the lack of perfect uniformity in the emitting surface. The uranium glass, being rendered self-luminous by the beam from the lantern, could not have entire uniformity over its surface unless the illuminating beam was uniform in intensity, which was not the case. The images corresponded to points on the surface not more than 2 mm. apart, and yet it was found that the equality of the images could be sometimes disturbed by directing the instrument toward a new portion of the field. As great care as possible was taken to direct the polarimeter toward such portions of the field as appeared to have a uniform illumination, and it is not thought that the error due to this cause could have been great.

Phosphorescent bodies were also examined for polarization, but the light emitted by such bodies is so weak that no definite results were obtained.

[*To be continued.*]

ALTERNATING CURRENTS WHEN THE ELECTROMOTIVE FORCE IS OF A ZIGZAG WAVE TYPE.

By E. C. Rimington.

ALTHOUGH no alternate-current dynamo will give an electromotive force of a zigzag form, still with some commercial machines, the electromotive force may be nearer to this type than to a sine curve, so that it is useful to investigate the current in the limiting case of a pure zigzag electromotive force.

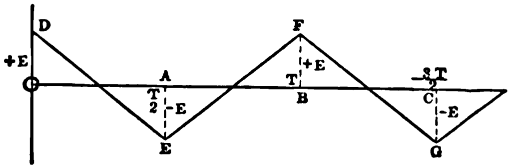

Fig. 1.

Figure 1 represents a wave of this type. It is composed of the broken straight lines *DE*, *EF*, *FG*, all of equal length and equally inclined to the horizontal axis. *OB* will represent the periodic time *T*, and *OD* the maximum value of the electromotive force or *E*.

The equation to these lines will be

$$e = \pm E\left(1 - \frac{4}{T}t\right),$$

the plus sign being employed when they slope downwards, as *DE* and *FG*, and the minus sign when they slope upwards, as *EF*.

The time t must always be reckoned from a point of maximum or minimum electromotive force, such as *O*, *A*, *B*, or *C*, and must be between the limits *O* and $\frac{T}{2}$.

Of course an electromotive force of this form could be expressed as a function of time continuously reckoned onwards from some zero point by means of a Fourier sine series, and the current equation obtained as a sum of terms, of which one is contributed by each of the terms in the Fourier series. This method does not lead to satisfactory results, and the better one to follow in this case is what may be called the "piecemeal" method. The manner in which it is to be carried out may be sketched shortly thus. We must presuppose some initial condition. The one here taken is that the electromotive force has been acting steadily, and the current has attained a steady value. Obtain now the current equation for the portion of the electromotive force zigzag *DE*, and assuming the initial current at *D* to be $\frac{E}{R}$, find the final current at *E*, *i.e.* the current when time equals $\frac{T}{2}$. This will be the initial current for the second half period or the portion *EF*; we can thus find the final current or current corresponding to point *F*. By a similar way of procedure, the current at the end of each half period can be found, and it will be seen that a single law is followed so that the current at the end of any half-period (*i.e.* when the electromotive force is a maximum or a minimum), after an indefinitely long time has elapsed, can be found, and this will be independent of the assumed initial condition. Remembering that the current at the end of a half period is obviously the same as the initial current of the next half period, we can now obtain the current equation for any time *t*, during a half period, *t* being reckoned from its commencement. This is the method of treatment that will be employed in the following. Many of the steps in the mathematical working are omitted on account of length, but enough have been put in to make clear the method employed.

Suppose that the electromotive force $+E$ has been acting before the time denoted by the point *O* in the diagram, and that the current has the steady value $\frac{E}{R}$. Let *R* be the resistance and *L* the self-inductance of the circuit. Then the current equation is

$$e=CR+L\frac{dC}{dt},$$

and consequently for the portion such as *DE* on the diagram,

$$E\left(1-\frac{4}{T}t\right)=CR+L\frac{dC}{dt}.$$

This is an equation of the well-known type

$$\frac{dy}{dx}+Py=Q,$$

where P and Q are functions of x only. Its solution is

$$y=e^{-\int Pdx}\left\{\int e^{\int Pdx}Qdx+k\right\},$$

where k is a constant and $e=2.718\cdots$.

Hence

$$C=e^{-\frac{R}{L}t}\left\{\frac{E}{L}\int e^{\frac{R}{L}t}\left(1-\frac{4}{T}t\right)dt+k\right\}$$

$$=\frac{E}{R}\left\{1-\frac{4}{T}\left(t-\frac{L}{R}\right)\right\}+ke^{-\frac{R}{L}t}, \qquad (1)$$

when the electromotive force is diminishing.

And similarly

$$C=-\frac{E}{R}\left\{1-\frac{4}{T}\left(t-\frac{L}{R}\right)\right\}+k'e^{-\frac{R}{L}t}, \qquad (2)$$

when the electromotive force is increasing.

Now consider the portion of electromotive force wave represented by DE.

When $t=0$, $C=\frac{E}{R}$ by assumption. Hence, substituting these values in (1),

$$k=-\frac{4EL}{R^2T}.$$

Call, for shortness, $\frac{RT}{2L}=n$, or $n=$ the half-period $\left(\frac{T}{2}\right)$ divided by the time constant of the circuit $\left(\frac{L}{R}\right)$.

Then we may write

$$C=\frac{E}{R}\left(1-\frac{4}{T}t+\frac{2}{n}-\frac{2}{n}e^{-\frac{R}{L}t}\right).$$

Again, when $t=\frac{T}{2}$,

$$C_{\frac{T}{2}}=\frac{E}{R}\left\{\frac{2}{n}(1-e^{-n})-1\right\}=-\frac{E}{R}\left\{1-\frac{2}{n}(1-e^{-n})\right\}.$$

Now the current at the end of the first half-period is obviously the same thing as the current at the beginning of the second half-period. Hence, making $t=0$ in equation (2), we have

$$\frac{E}{R}\left\{\frac{2}{n}(1-e^{-n})-1\right\}=-\frac{E}{R}\left(1+\frac{2}{n}\right)+k',$$

or
$$k'=\frac{E}{R}\cdot\frac{2}{n}(2-e^{-n}).$$

Substituting this value in (2), and making $t=\frac{T}{2}$, gives the current at the end of the second half-period; or

$$C_{\frac{T}{2}}=\frac{E}{R}\left\{1-\frac{2}{n}(1-e^{-n})^2\right\}=\frac{E}{R}\left\{1-\frac{2}{n}(1-e^{-n})(1-e^{-n})\right\}.$$

Proceeding in a similar manner for the third half-period, it will be found that

$$k=-\frac{E}{R}\cdot\frac{2}{n}\{1+(1-e^{-n})^2\};$$

and
$$C_{\frac{T}{2}}=-\frac{E}{R}\left[1-\frac{2}{n}\{(1-e^{-n})\{1-e^{-n}(1-e^{-n})\}\}\right].$$

In the same way the current at the end of the fourth half-period is

$$C_{\frac{T}{2}}=\frac{E}{R}\left[1-\frac{2}{n}[(1-e^{-n})\{1-e^{-n}(1-e^{-n}\overline{1-e^{-n}})\}]\right]$$
$$=\frac{E}{R}\left\{1-\frac{2}{n}(1-e^{-n})(1-e^{-n}+e^{-2n}-e^{-3n})\right\},$$

and so on. Hence the current at the end of a half-period after the zigzag electromotive force has been acting for a considerable period of time will be

$$C_{\frac{T}{2}}=\pm\frac{E}{R}\left\{1-\frac{2}{n}(1-e^{-n})(1-e^{-n}+e^{-2n}-e^{-3n}+e^{-4n}-,\text{ etc.})\right\}.$$

[illegible] etc. is a geometrical pro- [illegible] $-\epsilon^{-n}$, and this is fractional;

[illegible]

$$\frac{E}{R}\left(1-\frac{2}{n}\cdot\frac{1-\epsilon^{-n}}{1+\epsilon^{-n}}\right)=\pm\frac{E}{R}\left[1-\frac{\tanh\frac{n}{2}}{\frac{n}{2}}\right], \qquad (3)$$

[illegible] obtained from the fact that

$$\frac{1-\epsilon^{n}}{1+\epsilon^{n}}=-\tanh n.$$

[illegible] during the half-period under consideration [illegible] has been increasing, and the − sign if [illegible]

[illegible] and making $t=0$, we have, by the aid of (3),

$$\frac{E}{R}\left(1-\frac{2}{n}\cdot\frac{1-\epsilon^{-n}}{1+\epsilon^{-n}}\right)=\frac{E}{R}\left(1+\frac{2}{n}\right)+k;$$

$$[illegible]\left(1+\frac{1-\epsilon^{-n}}{1+\epsilon^{-n}}\right)=-\frac{E}{R}\cdot\frac{4}{n}\cdot\frac{1}{1+\epsilon^{-n}}$$

[illegible] becomes

$$=\frac{E}{R}\left\{1+\frac{2}{n}-\frac{4}{T}t-\frac{4}{n}\cdot\frac{\epsilon^{-\frac{R}{L}t}}{1+\epsilon^{-n}}\right\}.$$

[illegible] become

$$\frac{E}{R}\left\{1+\frac{2}{n}-\frac{4}{T}\cdot t-\frac{4}{n}\cdot\frac{\epsilon^{-\frac{R}{L}t}}{1+\epsilon^{-n}}\right\}.$$

[illegible] we may write

$$i=\frac{E}{R}\left\{1+\frac{2}{n}-\frac{4}{T}t-\frac{4}{n}\cdot\frac{\epsilon^{-\frac{R}{L}t}}{1+\epsilon^{-n}}\right\}$$

$$=\frac{E}{R}\left\{1+\frac{2}{n}(1-y)-\frac{4}{n}\cdot\frac{\cosh y-\sinh y}{1+\cosh n-\sinh n}\right\}; \qquad (4)$$

[illegible]

$$n=\frac{\frac{P}{2}}{\frac{L}{R}}=\frac{RT}{2L} \text{ and } y=\frac{R}{L}t.$$

[illegible] cosh n − sinh n.

The + sign is to be taken when t is reckoned from the time of a + maximum of electromotive force, and the − sign when reckoned from a − maximum.

To find the time at which the current is a maximum or minimum, and its value.

Differentiating (4) with respect to time, and equating to zero, gives

$$-\frac{4}{T}+\frac{4R}{Ln}\cdot\frac{e^{-\frac{Rt}{L}}}{1+e^{-n}}=0;$$

or,

$$t=\frac{L}{R}\log_e\frac{2}{1+e^{-n}}. \tag{5}$$

If t be reckoned from a maximum of electromotive force, the current will be a maximum; if from a minimum of electromotive force, a minimum. The term $\frac{L}{R}\log_e\frac{2}{1+e^{-n}}$ evidently represents the time lag of the maximum and minimum values of the current, behind those of the electromotive force, respectively.

Substituting the above value for t in equation (4), we obtain

$$C_{\max.}=\frac{E}{R}\left\{1+\frac{2}{n}-\frac{2}{n}\log_e\frac{2}{1+e^{-n}}-\frac{4}{n(1+e^{-n})}\cdot\frac{1}{e^{\log_e\frac{2}{1+e^{-n}}}}\right\}$$

$$=\frac{E}{R}\left\{1-\frac{2}{n}\log_e\frac{2}{1+e^{-n}}\right\}. \tag{6}$$

$\dfrac{R}{1-\frac{2}{n}\log_e\frac{2}{1+e^{-n}}}$ may be called the impedance of the circuit, and is a function of R, L, and T. Thus we have the maximum current equal to the maximum electromotive force divided by the impedance, in an analogous manner to the case of a sine function electromotive force, in which the impedance $=R\sqrt{1+4\frac{\pi^2L^2}{T^2R^2}}$, and is a function of R, L, and T.

Again, from equation (4),

$$\frac{dC}{dt}=\frac{E}{R}\left(\frac{4R}{Ln}\cdot\frac{e^{-\frac{Rt}{L}}}{1+e^{-n}}-\frac{4}{T}\right);$$

and

$$\frac{d^2C}{dt^2}=-\frac{4ER}{nL^2}\cdot\frac{e^{-\frac{Rt}{L}}}{1+e^{-n}}$$

Now these values apply to a half-period, during which the electromotive force is diminishing, since the + sign has been taken in (4). The current increases until

$$t=\frac{L}{R}\log_e\frac{2}{1+e^{-n}},$$

and then decreases. Hence $\frac{dC}{dt}$ is first positive and then becomes negative; $\frac{d^2C}{dt^2}$ is always negative. This means that the rate of change of current is greatest when $t=0$ and $t=\frac{T}{2}$; that is, at the times when the electromotive force has its maxima and minima.

From equation (4) it is seen that the current is zero when

$$\frac{4}{T}t+\frac{4}{n}\cdot\frac{1}{1+e^{-n}}\,e^{-\frac{R}{L}t}=1+\frac{2}{n},$$

but unfortunately this equation does not admit of a general solution.

To find the virtual current.

By the virtual current is meant the square root of the mean square value. It is found by squaring equation (4), multiplying by dt, integrating between the limits $\frac{T}{2}$ and 0, then dividing by $\frac{T}{2}$, and taking the square root.

Squaring (4) gives

$$\frac{E^2}{R^2}\left[\left(1+\frac{2}{n}\right)^2+\frac{16}{T^2}t^2-\frac{8}{T}\left(1+\frac{2}{n}\right)t+\frac{16}{n^2}\cdot\frac{e^{-\frac{2R}{L}t}}{(1+e^{-n})^2}\right.$$
$$\left.-\frac{8}{n}\left(1+\frac{2}{n}\right)\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}+\frac{32}{nT}\cdot\frac{1}{1+e^{-n}}\cdot te^{-\frac{R}{L}t}\right].$$

Multiplying by dt and integrating between limits $\frac{T}{2}$ and 0, we have

$$\frac{E^2}{R^2}\left[\left(1+\frac{2}{n}\right)^2\frac{T}{2}+\frac{16}{T^2}\cdot\frac{T^3}{24}-\frac{8}{T}\left(1+\frac{2}{n}\right)\frac{T^2}{8}-\frac{16}{n^2}\cdot\frac{L}{2R}\cdot\frac{e^{-2n}-1}{(1+e^{-n})^2}\right.$$
$$\left.+\frac{8}{n}\left(1+\frac{2}{n}\right)\cdot\frac{e^{-n}-1}{1+e^{-n}}\cdot\frac{L}{R}-\frac{32}{nT}\cdot\frac{L}{R}\cdot\frac{1}{1+e^{-n}}\left\{\frac{T}{2}e^{-n}-\frac{L}{R}\left(1-e^{-n}\right)\right\}\right].$$

Dividing by $\frac{T}{2}$ and simplifying, this becomes

$$\frac{E^2}{R^2}\left\{\frac{1}{3}-\frac{4}{n^2}+\frac{8}{n^3}\cdot\frac{1-e^{-n}}{1+e^{-n}}\right\}=\frac{E^2}{R^2}\left\{\frac{1}{3}-\left(\frac{2}{n}\right)^2\left[1-\frac{\tanh\frac{n}{2}}{\frac{n}{2}}\right]\right\}.$$

Hence the virtual current is

$$C_v=\frac{E}{R}\sqrt{\frac{1}{3}-\left(\frac{2}{n}\right)^2\left(1-\frac{2}{n}\cdot\frac{1-e^{-n}}{1+e^{-n}}\right)}=\frac{E}{R}\sqrt{\frac{1}{3}-\left(\frac{2}{n}\right)^2\left[1-\frac{\tanh\frac{n}{2}}{\frac{n}{2}}\right]}. \quad (7)$$

As an example, take a circuit whose resistance $R=1$ ohm, self-inductance $L=.01$ henry, in which the maximum electromotive force, or $E=20$ volts, and the frequency = 100, or periodic time $T=.01$ second. Then $n=\frac{RT}{2L}=\frac{1}{2}$

Equation (4) then becomes

$$C=\pm 100\left(1-.8y-.995936\cdot\frac{1}{e^y}\right),$$

where $y=\frac{R}{L}t=100t$; or

$$C=\pm 100\{1-.8y-.995936\,(\cosh y-\sinh y)\}.$$

The latter is the more convenient form for the purposes of calculation, as a very good set of tables of values of cosh θ and sinh θ for values of θ from .01 to 4 at intervals of .01 has been published by the Physical Society of London, the working out being due to Mr. Blakesley.

From equation (5) it is found that the value of y for maximum current is .2191, and the maximum current from (6) is 2.474 amperes.

The following table has been worked out for values of y differing by .05, for a half-period, during which the electromotive force diminishes from +20 to −20. Obviously for the next half-period, during which the electromotive force will increase from

-20 to $+20$, the values of the current will be the same with their signs changed, as will be seen from equation (4).

t	y	Current in amperes.	Remarks.
0.0	0.0	+0.406	Rate of increase a maximum.
0.0005	0.05	+1.264	
0.001	0.1	+1.884	
0.0015	0.15	+2.279	
0.002	0.2	+2.460	
0.002191	0.2191	+2.474	Maximum current.
0.0025	0.25	+2.436	
0.003	0.3	+2.219	
0.0035	0.35	+1.818	
0.004	0.4	+1.240	
0.0045	0.45	+0.496	
0.005	0.5	−0.406	Rate of decrease a maximum.

The maximum current = 2.474. The virtual current = 1.798 from equation (7).

With a sine function electromotive force having a maximum value of 20 volts,

the maximum current = 3.145,
the virtual current = 2.223.

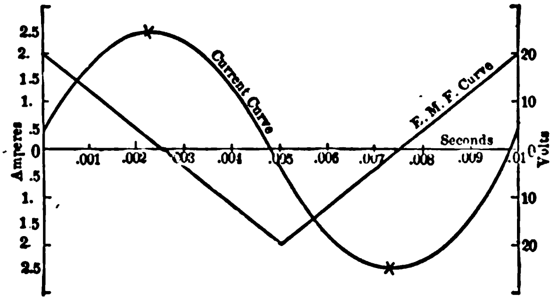

Fig. 2.

E. M. F. and current curves for one complete period. $E = 20$ volts; $R = 1$ ohm; $L = .01$ heavy; $T = .01$ sec.; frequency = 100; max. current = 2.478; virtual current = 1.8.

Figure 2 shows these results plotted as a curve, the scale of volts being one-tenth that of amperes. The points of maximum and minimum current are marked with crosses. It will be noticed that in this particular circuit the current curve is not very unlike a sine curve in appearance. With less self-inductance, however, it will become more pointed, as evidently in the limiting case of no self-inductance, it must coincide in shape with the curve of electromotive force.

To find the mean power.

The electromotive force at any instant when decreasing is

$$e=E\left(1-\frac{4}{T}t\right),$$

and the corresponding current

$$C=\frac{E}{R}\left(1+\frac{2}{n}-\frac{4}{T}t-\frac{4}{n}\cdot\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}\right).$$

Hence the power at any instant is

$$P=eC=\frac{E^2}{R}\left(1-\frac{4}{T}t\right)\left(1+\frac{2}{n}-\frac{4}{T}t-\frac{4}{n}\cdot\frac{e^{-\frac{R}{L}t}}{1+e^{-n}}\right).$$

Multiplying by dt, and integrating between limits $\frac{T}{2}$ and 0 gives

$$\int_0^{\frac{T}{2}}Pdt=\frac{E^2}{R}\left\{-\frac{T}{2}+\frac{2}{3}T+\frac{4}{n}\cdot\frac{L}{R}\cdot\frac{e^{-n}-1}{1+e^{-n}}\right.$$
$$\left.-\frac{16}{n}\cdot\frac{L}{RT}\left\{\frac{T}{2}e^{-n}-\frac{L}{R}(1-e^{-n})\right\}\right\}.$$

Now mean power or

$$P=\frac{\int^{\frac{T}{2}}Pdt}{\frac{T}{2}}=\frac{E^2}{R}\left\{\frac{1}{3}-\frac{4}{n^2}+\frac{8}{n^3}\cdot\frac{1-e^{-n}}{1+e^{-n}}\right\}$$

$$=\frac{E^2}{R}\left\{\frac{1}{3}-\left(\frac{2}{n}\right)^2\left[1-\frac{\tanh\frac{n}{2}}{\frac{n}{2}}\right]\right\}. \qquad (8)$$

This result is, of course, equal to the virtual current squared and multiplied by R.

We may also write P_m in the form

$$P_m = EC_{max.} \cdot \frac{\frac{1}{3} - \left(\frac{2}{n}\right)^2 \left(1 - \frac{2}{n} \cdot \tanh \frac{n}{2}\right)}{1 - \frac{2}{n} \log_e \frac{2}{1 + e^{-n}}}$$

Again, since $e = E\left(1 - \frac{4}{T}t\right)$, the virtual electromotive force, or

$$E_v = \sqrt{\frac{\int_0^{\frac{T}{2}} e^2 dt}{\frac{T}{2}}} = \frac{E}{\sqrt{3}}; \text{ and } C_v = \frac{E}{R}\sqrt{\frac{1}{3} - \left(\frac{2}{n}\right)^2 \left(1 - \frac{2}{n} \tanh \frac{n}{2}\right)}.$$

Hence P_m may be written

$$P_m = E_v C_v \sqrt{1 - 3\left(\frac{2}{n}\right)^2 \left(1 - \frac{2}{n} \tanh \frac{n}{2}\right)}.$$

It is interesting to consider the other limit of wave-type of an alternating dynamo, viz. the rectangular wave-type as shown in Fig. 3. This is the case of a constant electromotive force periodically reversed, and its investigation is considerably simpler than the foregoing one. It can, however, be treated in a précisely similar manner, and the results obtained are that the current at the end of a half-period reckoned from the instant of reversal of electromotive force is

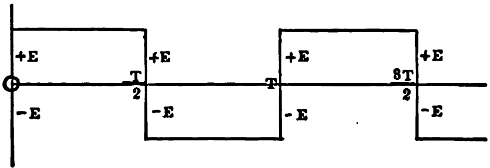

Fig. 3.

$$C_{\frac{T}{2}} = \pm \frac{E}{R} \cdot \frac{1 - e^{-n}}{1 + e^{-n}} = \pm \frac{E}{R} \tanh \frac{n}{2} \tag{9}$$

Here n has the same meaning as before, viz. $\frac{\frac{T}{2}}{\frac{L}{R}}$; the + sign is to be taken when the reversal has been from a negative value of the electromotive force to a positive one, and *vice versâ.*

We also obtain

$$C = \pm \frac{E}{R}\left(1 - \frac{2}{1+e^{-n}} \cdot e^{-\frac{R}{L}t}\right)$$

$$= \pm \frac{E}{R}\left\{1 - \frac{2(\cosh y - \sinh y)}{1 + \cosh n - \sinh n}\right\}, \qquad (10)$$

where y, as before, equals $\frac{R}{L}t$.

The current is zero when

$$\frac{2}{1+e^{-n}} e^{-\frac{R}{L}t} = 1,$$

or when

$$t = \frac{L}{R} \log_e \frac{2}{1+e^{-n}},$$

the same value of t that made the current a maximum or minimum in the case of the zigzag electromotive force. There is no mathematical maximum or minimum for the current, but obviously from (10) it is greatest or least when $t = \frac{T}{2}$, that is, at the moments of reversal, or,

$$C_{\text{max.}} = C_{\frac{T}{2}} = \frac{E}{R} \cdot \frac{1-e^{-n}}{1+e^{-n}} = \frac{E}{R} \tanh \frac{n}{2}.$$

The virtual current, or

$$C_v = \frac{E}{R}\sqrt{\left\{1 - \frac{2}{n} \cdot \frac{1-e^{-n}}{1+e^{-n}}\right\}} = \frac{E}{R}\sqrt{1 - \frac{\tanh \frac{n}{2}}{\frac{n}{2}}} \qquad (11)$$

The formula given in (11) has been published by Mr. Kennelly in the *Electrical World,* Nov. 11, 1893, page 397, where, however, it is misprinted as $\frac{E}{R}\sqrt{\frac{\tanh \frac{n}{2}}{1 - \frac{n}{2}}}$.

The mean power or P_m will obviously be

$$P_m = C_v^2 R = \frac{E^2}{R}\left[1 - \frac{\tanh \frac{n}{2}}{\frac{n}{2}}\right].$$

The following table has been calculated from equation (10) for the same circuit as considered previously. With numerical values substituted, (10) becomes

$$c = \pm 20\{1 - 1.24492(\cosh y - \sinh y)\},$$

and

$$y = \frac{R}{L}t = 100\,t.$$

t	y	Current in amperes.	Remarks.
0.0	0.0	−4.898	Current a minimum.
0.0005	0.05	−3.684	
0.001	0.1	−2.528	
0.0015	0.15	−1.430	
0.002	0.2	−0.3850	
0.002191	0.2191	0.0	Current zero.
0.0025	0.25	+0.6082	
0.003	0.3	+1.555	
0.0035	0.35	+2.454	
0.004	0.4	+3.310	
0.0045	0.45	+4.124	
0.005	0.5	+4.898	Current a maximum.

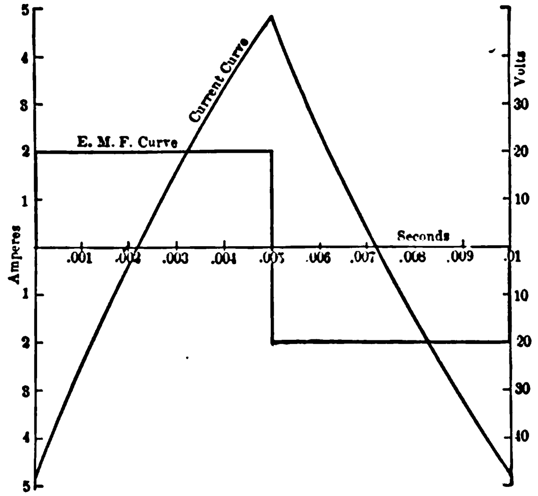

Fig. 4.

E. M. F. and current curves for one complete period. $E = 20$ volts: $R = 1$ ohm: $L = .01$ heavy; $T = .01$ sec.; frequency = 100; max. current = 4.898; virtual current = 2.851.

The maximum current = 4.898,
the virtual current = 2.851 from (11).

For the zigzag electromotive force the values were

maximum current = 2.474,
virtual current = 1.798.

For a sine electromotive force

maximum current = 3.145,
virtual current = 2.223.

Figure 4 gives the above results plotted on the same scale as in Fig. 2, the scale of volts being one-tenth those of the amperes.

It will be seen that with a sinusoidal electromotive force, the maximum and virtual currents have values which lie between those of the two extreme cases of rectangular and zigzag electromotive forces.

ON TERNARY MIXTURES. II.

BY WILDER D. BANCROFT.

THE formula $x^{\alpha}y^{\beta}$ = Constant, which was found to express the condition for equilibrium in a saturated ternary solution,[1] is not wholly satisfactory, since it contains no term expressing the variation of the consolute liquid in case one of the non-miscible liquids is kept constant, and also because a change in the units in which x and y are expressed or a change in the amount of the consolute liquid taken affects the constant of the formula. This can be remedied by the following reasoning. According to Gibbs and to experiment, the absolute mass of a phase has no effect on the equilibrium. Therefore increasing the quantities of x and y m-fold involves increasing the quantity of the consolute liquid m-fold if the solutions are to remain at the saturation point. This would increase the value of the constant $m^{\alpha+\beta}$ times. If then x and y denote the values in cubic centimeters of the non-miscible liquids A and B, z the corresponding value for the consolute liquid S, we have as equation of equilibrium for saturated solutions the expression:—

I. $$\frac{x^{\alpha}y^{\beta}}{z^{\alpha+\beta}} = C.$$

If, as was done, z is kept constant, this simplifies to formula (4), which I will renumber I*a*.:—

I*a*. $$x^{\alpha}y^{\beta} = C_1.$$

If y is constant, x and z varying, we have:—

I*b*. $$\frac{x^{\alpha}}{z^{\alpha+\beta}} = C_2.$$

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[1] PHYSICAL REVIEW, Vol. III., No. 1.

And if x is constant, y and z varying, we have:—

$$\text{I}c. \qquad \frac{y^{\beta}}{z^{\alpha+\beta}}=C_3.$$

In Equation I., the value of C is a function of the nature of the units in which x, y, and z are expressed; but independent of the size. Thus grams and kilograms give the same result, cubic centimeters and liters; but the weight constant is different from the volume constant, and the constants for reacting weights or reacting volumes would have still other values. C is also dependent on the absolute value of the exponential factors α and β. We can, however, eliminate this effect by writing

$$(6) \qquad C=K^{\alpha+\beta},$$

in which case K remains entirely unchanged, when we substitute $\frac{\alpha}{\beta}=n$. In Table VII. I give in the first two columns the values for log C according to the general formula $\frac{x^n y}{z^{n+1}}=C$, when x, y, and z are expressed in volumes. Since $z=5$ in all these measurements, Table VII. gives the constants of the preceding tables less the corresponding values of $(n+1)$ log 5. It would have been better to calculate the integration constant using the rational exponents α and β; but only their ratio can be determined by a study of equilibrium in one liquid layer, and the case of two liquid layers will form the subject of a separate communication. In columns three and four are the corresponding values of K_1 and K_2 according to Equation (6). They are the constants of the preceding two columns divided by the appropriate values of $n+1$.

TABLE VII.

Mixtures.	log C_1.	log C_2.	log K_1.	log K_2.
H_2O, $CHCl_3$, C_2H_5OH . . .	$\bar{1}.163$	$\bar{1}.266$	$\bar{1}.711$	$\bar{1}.652$
H_2O, $CHCl_3$, CH_3OH . . .	$\bar{2}.984$	$\bar{1}.489$	$\bar{1}.692$	$\bar{1}.773$
H_2O, $CHCl_3$, CH_3COCH_3 . .	$\bar{2}.506$	....	$\bar{1}.381$	....
H_2O, C_6H_6, C_2H_5OH . . .	$\bar{2}.737$	$\bar{2}.737$	$\bar{1}.514$	$\bar{1}.514$
H_2O, C_6H_6, CH_3OH . . .	$\bar{2}.482$	$\bar{2}.184$	$\bar{1}.388$	$\bar{1}.395$
H_2O, C_6H_6, CH_3COCH_3 . . .	$\bar{2}.584$	$\bar{2}.471$	$\bar{1}.410$	$\bar{1}.349$

The values given under x and y in Tables I.–VI. are amounts of the liquids A and B in a given quantity of S, — in this case 5 c.c. A glance at the tables will show that these figures are very far from expressing volume concentrations, *i.e.* quantity of substance in a given volume of the solution. As most theoretical generalizations in chemistry are expressed in volume concentrations, it will be necessary to see what effect such a change would have on general Formula I. If there is no contraction or expansion on mixing, the volume of the solution will be the sum of the component volumes, or $V=x+y+z$, and the volume concentrations will be $\frac{x}{x+y+z}$, $\frac{y}{x+y+z}$, $\frac{z}{x+y+z}$, respectively. This simple case may be said never to occur, and the volume of the solution is an at present unknown function of the component volumes represented by the expression $V=F(x, y, z)$. While the knowledge of the form of this function is necessary to enable us to calculate the volume concentrations of a given solution from our experimental data, it is superfluous in the present discussion. We have (from Formula I.): —

$$\alpha \log x+\beta \log y-(\alpha+\beta) \log z=\log C.$$

Now $$\alpha \log V+\beta \log V-(\alpha+\beta) \log V=0;$$

$$\therefore \alpha \log \frac{x}{V}+\beta \log \frac{y}{V}-(\alpha+\beta) \log \frac{z}{V}=\log C;$$

or $\frac{x^\alpha y^\beta}{z^{\alpha+\beta}}=C$, if x, y, and z denote volume concentrations instead of having their previous significance. Since α, β, and C remain unchanged, we find that Equation I. represents the series of saturated solutions obtained at constant temperature with any two non-miscible liquids, and a third liquid miscible in all proportions with each of the other two, provided no chemical reaction takes place, and provided the reacting weights of the liquids remain unchanged. It is immaterial whether x, y, and z denote volume concentrations, or concentrations of two of the substances in a constant quantity of the third.

As has been said, volume concentrations are generally looked upon as the only scientific way of expressing data. This is perfectly natural when we remember that our theoretical ideas have been formed almost entirely upon a study of the gaseous state. It is not a necessary method, and in this particular case it is decidedly disadvantageous, practically to use volume concentrations. It involves a determination of the density of each solution, increasing the work and bringing in a new source of error. When expressed in volume concentrations, all three components vary, and while it is a simple matter to plot three variables in a plane,[1] I know of no way in which this can be done for the logarithms of these variables. By the method which I have followed, one constituent can be kept constant, no density determinations are necessary, and there are only two variables. The formula being hyperbolic, by plotting the data on logarithmic coördinates one gets a straight line, any variation from which is easily seen, while the constants of the curve can be determined from the diagram with more speed and accuracy than by substituting the experimental values in an equation and solving for two unknown quantities.

The next case to be considered is when we have two partially miscible liquids, and a third miscible in all proportions with each of the others. Formula I. cannot apply here, because it was deduced for two non-miscible liquids, and this condition is no longer fulfilled. There are two ways of treating a problem like this. One is to change the conditions of the experiment until they agree with the formula; the other is to change the formula till it conforms to the conditions of the experiment. I have done both. I will suppose, for the sake of clearness, that the two partially miscible liquids are ether and water. Saturated solutions of water in ether are absolutely non-miscible at the temperature for which they are saturated, being thus an improvement over benzol and water, which are slightly miscible theoretically. If x and y in Equation I*a* mean quantities of saturated water and saturated ether solutions, instead of pure water and pure ether, the conditions are satisfied for which this formula was deduced, and the equation must apply. I have found that it did, and the experimental proof is given in Tables IX. and XI.

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[1] Gibbs, Thermodynamische Studien, p. 141; Roozeboom, Zeitschr. f. ph. Chem., XII. 369. 1893.

This being settled, we can attack the second part of the problem. Let X denote cubic centimeters of saturated solution of ether in water, Y cubic centimeters of saturated solution of water in ether which saturate a given quantity of a consolute liquid. It is found experimentally that

$$(7) \qquad X^{\alpha} Y^{\beta} = \text{Constant},$$

or, if we set $\frac{\alpha}{\beta} = n$, we shall have

$$(8) \qquad X^{n} Y = C.$$

If s_1 is the solubility of ether in water, s_2 the solubility of water in ether, both expressed in volumes per cubic centimeter of the solvent synthetically, we shall have, if no contraction or expansion takes place in forming the saturated solutions of water in ether and ether in water:—

$$(9) \qquad X = A + s_1 A\,; \quad Y = B + s_2 B\,;$$

$$(10) \qquad (A + s_1 A)^{n} (B + s_2 B) = C\,;$$

where A = c.c. water in X, B = c.c. ether in Y. As we must assume some contraction or expansion, let the ratio of the actual volume to the sum of the component volumes be σ_1 in the saturated solution of ether in water, and σ_2 in the saturated solution of water in ether. We have then:—

$$(11) \qquad X = \sigma_1 (A + s_1 A)\,; \quad Y = \sigma_2 (B + s_2 B)\,;$$

$$(12) \qquad \{\sigma_1 (A + s_1 A)\}^{n} \{\sigma_2 (B + s_2 B)\} = C_1\,;$$

which can be rewritten:—

$$(13) \qquad (A + s_1 A)^{n} (B + s_2 B) = \frac{C_1}{\sigma_1{}^{n} \sigma_2}.$$

If x and y denote cubic centimeters of pure water and pure ether dissolved in a given quantity of the consolute liquid, we have:—

$$(14) \qquad x = A + s_2 B\,; \quad y = B + s_1 A.$$

Solving for A and B:—

$$(15) \qquad A = \frac{x - s_2 y}{1 - s_1 s_2}; \quad B = \frac{y - s_1 x}{1 - s_1 s_2}.$$

Substituting these values in (13): —

$$(16)\qquad \left\{\frac{1+s_1}{1-s_1s_2}(x-s_2y)\right\}^n\left\{\frac{1+s_2}{1-s_1s_2}(y-s_1x)\right\}=\frac{C_1}{\sigma_1{}^n\sigma_2}.$$

Since σ_1, σ_2, s_1, s_2, are constants for constant temperature, we can simplify equation (16) into: —

$$(17)\qquad (x-s_2y)^n(y-s_1x)=C_2,$$

where the relation between C_1 and C_2 is

$$(18)\qquad \frac{C_1}{C_2}=\frac{\sigma_1{}^n\sigma_2(1+s_1)\ (1+s_2)}{(1-s_1s_2)^{n+1}}.$$

Eliminating the effect due to the arbitrary quantity of consolute liquid used, we have: —

$$(19)\qquad \frac{(x-s_2y)^n(y-s_1x)}{z^{n+1}}=C_3;$$

where $C_3=\frac{C_2}{z^{n+1}}$. Reverting to the most general form, so as to make the equation correspond in form to Equation I.,

$$\text{II.}\qquad \frac{(x-s_2y)^\alpha(y-s_1x)^\beta}{z^{\alpha+\beta}}=C.$$

Equation II. is more general than Equation I., the latter being merely a special case of the former, where the terms representing the mutual solubilities are so small that they can be neglected.

In testing these equations I took, as pairs of partially miscible liquids, ether and water, ethylacetate and water. The ether was distilled over sodium, the ethylacetate dried with calcium chloride and fractionated, the boiling point rising a full degree for a liter distilled off. I think, however, that no essential error was introduced in this way, and that, for my purposes, it was sufficiently pure. The solubilities were determined volumetrically. In all cases I took 10 c.c. of the solvent in a test tube and ran in the solute from a burette till the solution clouded. One can determine this point to 0.01 c.c without difficulty. In Table VIII. I give the solubilities at 20° expressed in cubic centimeters of solute in 10 c.c. of solvent. The solubilities of ether and ethylacetate in water decrease with increasing temperature; the solubilities of water in ether and ethylacetate increase with increasing temperature. This behavior is well known for ether; but I have not found it stated anywhere for ethylacetate.

TABLE VIII.

Solute.	Solvent.	Solubility.
Ether	Water	1.03-4[1]
Water	Ether	0.08
Ethylacetate	Water	0.926
Water	Ethylacetate	0.294

It will be remembered that, when two liquids were practically non-miscible, the series of saturated solutions formed by these with a consolute liquid were expressed by two curves of the same general form, but having different constants; and it was found that these two curves represented, the one the series of solutions out of which liquid *B* is precipitated on addition of either *A* or *B*; the other, the converse series, when the solution was saturated in respect to *A* but sensitive to an excess of either *A* or *B*. When the liquids *A* and *B* are partially miscible, the case becomes apparently more complicated, for we have four curves instead of two. These refer to four distinct sets of equilibrium, there being the following four series of saturated solutions.

1. The solution is saturated in respect to *B*. Excess of *A* produces no precipitate.
2. The solution is saturated in respect to *B*. Excess of *A* or *B* produces a precipitate of *B*.
3. The solution is saturated in respect to *A*. Excess of *A* or *B* produces a precipitate of *A*.
4. The solution is saturated in respect to *A*. Excess of *B* produces no precipitate.

Series 2 and 3 correspond to the two series observed with two non-miscible liquids. In these two series the consolute liquid is the solvent, whereas in series 1 and 4 we have, in addition, *A* and

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[1] Schuncke finds 1.04-5, Zeitschr. f. ph. Chem., XIV. 334. 1894.

B respectively as solvents. In Tables IX.–XIII. I give the measurements made with ether and water, ethylacetate and water with the consolute liquids alcohol, methylalcohol, and acetone. In Tables IX. and XI. the experiments were made with saturated solutions; in Tables X., XII., and XIII., with pure liquids. The first method has the advantage that the readings obtained are final, involving no correction and no knowledge of the mutual solubilities. On the other hand, it is necessary to keep the solutions in the burettes at the same temperature as that at which one makes the determinations, a very difficult thing to do usually, so that the second method is to be preferred. The exponential factors are the same according to both methods, as I have already shown. The integration constants are different, standing to each other in the relation given in Equation (18). It would have been well if I had determined the densities of the saturated solutions so that they could be recalculated into cubic centimeters of the pure liquids; but I shall have to make an extended series of density determinations in connection with the equilibrium between two liquid phases, and I have postponed these others till then. The measurements in Tables IX.–XIII. are about as accurate as those in Tables I.–VI., with the exception of the solutions when water is part solvent. The precipitate in these cases is lighter than the solution, consists of a few drops only, and is very difficult to distinguish from air bubbles, especially in the ether solutions, where the clouding at best is very slight. For this reason the first series in each table must be considered as very doubtful as the absolute measurements go. The determination of the saturation point for these cases depended on the light, the state of my eyes, and the mood which I happened to be in on the days when the measurements were made. So difficult are the determinations sometimes, that I give no results for ether-water-acetone because I obtained different measurements every day. The agreement between the observed and the theoretical values is no test of the absolute accuracy of either; but merely shows that the solutions follow the same general law, the constants, exponential, and integration, varying with the degree of cloudiness which the observer takes as denoting the point of saturation. The values of n are not so accurate as in the first set of tables, because the curves cover a more limited extent, and therefore the variations are smaller, and because when the value of n is large, say over 2, a very slight change in the direction of the logarithmic curve produces a very large corresponding change in n. The amounts of ethylacetate and water which dissolve in 5 c.c. of alcohol, methylalcohol, or acetone were so large that I was forced to work with one cubic centimeter of these liquids as solvent.

TABLE IX.

X c.c. Sat. Water; Y c.c. Sat. Ether; 5 c.c. Alcohol. Temp. 20°.

Formula $XY^{n_1} = C_1$; $n_1 = 2.60$; $\log C_1 = 1.994$.

Sat. Water.		**Sat. Ether.**		**log C_1.**
Calc.	**Found.**	**Calc.**	**Found.**	
49.89	50.00	1.30	1.30	1.995
24.89	25.00	1.70	1.70	1.996
10.02	10.00	2.41	2.41	1.993
Average, ...				1.995

Formula $X^{n_2}Y = C_2$; $n_2 = 1.49$; $\log C_2 = 1.867$.

				log C_2.
9.04	9.00	2.79	2.77	1.864
7.96	8.00	3.33	3.35	1.870
7.72	7.70	3.52	3.50	1.865
6.00	6.00	5.10	5.10	1.867
Average, ...				1.867

Formula $XY = C_3$; $\log C_3 = 1.493$.

				log C_3.
5.19	5.21	5.97	6.00	1.495
4.45	4.45	7.00	7.00	1.493
3.99	4.00	7.78	7.80	1.494
3.89	3.87	8.03	8.00	1.491
3.11	3.10	10.05	10.00	1.491
2.08	2.08	14.95	15.00	1.495
1.78	1.77	17.58	17.50	1.491
Average, ...				1.493

TABLE IX. (*continued*).

Formula $X^{n_4}Y = C_4$; $n_4 = 1.73$; $\log C_4 = 1.665$.

Sat. Water.		Sat. Ether.		log C_4.
Calc.	Found.	Calc.	Found.	
1.62	1.61	20.28	20.00	1.661
1.43	1.43	24.95	25.00	1.673
1.09	1.10	39.27	40.00	1.666
0.96	0.95	50.47	50.00	1.659
Average, ...				1.665

TABLE X.

x c.c. Water; y c.c. Ether; 1 c.c. Methyl Alcohol. Temp. 20°.

Formula $(x - 0.008y)(y - 0.103x)^{n_1} = C_1$; $n_1 = 1.50$; $\log C_1 = \bar{1}.502$

Water.		Ether.		log C_1.
Calc.	Found.	Calc.	Found.	
10.05	10.00	1.13	1.13	$\bar{1}.500$
9.00	9.00	1.04	1.04	$\bar{1}.502$
7.03	7.00	0.85	0.85	$\bar{1}.500$
4.97	5.00	0.68	0.68	$\bar{1}.505$
4.00	4.00	0.60	0.60	$\bar{1}.502$
				$\bar{1}.502$

Formula $(x - 0.008y)^{n_2}(y - 0.103x) = C_2$; $n_2 = 1.13$; $\log C_2 = \bar{1}.928$.

				log C_2.
2.95	3.00	0.555	0.56	$\bar{1}.936$
2.50	2.50	0.56	0.56	$\bar{1}.928$
2.03	2.00	0.60	0.59	$\bar{1}.920$
1.80	1.80	0.63	0.63	$\bar{1}.929$
1.50	1.50	0.70	0.70	$\bar{1}.929$
				$\bar{1}.928$

TABLE X. (*continued*).

Formula $(x - 0.008y)^{n_3}(y - 0.103x) = C_3$; $n_3 = 2.04$; $\log C_3 = 0.045$.

Water.		Ether.		$\log C_3$.
Calc.	Found.	Calc.	Found.	
1.20	1.20	0.90	0.90	0.047
1.00	1.00	1.23	1.23	0.045
0.90	0.89	1.53	1.50	0.035
0.83	0.83	1.79	1.80	0.047
0.78	0.78	2.00	2.00	0.046
0.64	0.64	3.01	3.00	0.043
0.57	0.57	3.99	4.00	0.047
0.52	0.52	5.00	5.00	0.045
0.47	0.47	6.89	7.00	0.053
				0.045

Formula $(x - 0.008y)^{n_4}(y - 0.103x) = C_4$; $n_4 = 4.4$; $\log C_4 = \bar{1}.057$.

				$\log C_4$.
0.44	0.44	10.30	10.00	$\bar{1}.044$
0.45	0.45	11.62	12.00	$\bar{1}.071$
0.45	0.45	15.04	15.00	$\bar{1}.056$
				$\bar{1}.057$

TABLE XI.

X c.c. Sat. Water; Y c.c. Sat. Ethylacetate; 1 c.c. Alcohol. Temp. 20°.
Formula $XY^{n_1} = C_1$; $n_1 = 2.86$; $\log C_1 = \bar{1}.280$.

Sat. Water.		Sat. Ethylacetate.		$\log C_1$.
Calc.	Found.	Calc.	Found.	
10.05	10.00	0.25	0.25	$\bar{1}.278$
8.07	8.00	0.27	0.27	$\bar{1}.276$
7.11	7.00	0.28	0.28	$\bar{1}.263$
5.97	6.00	0.30	0.30	$\bar{1}.282$
4.97	5.00	0.32	0.32	$\bar{1}.283$
3.94	4.00	0.34	0.35 –	$\bar{1}.286$
Average,				$\bar{1}.278$

Table XI. (*continued*).

Formula $X^{n_2}Y = C_2$; $n_2 = 1.80$; $\log C_2 = 0.549$.

Sat. Water.		Sat. Ethylacetate.		log C_2.
Calc.	Found.	Calc.	Found.	
3.00	3.00	0.49	0.49	0.549
2.50	2.50	0.68	0.68	0.548
2.00	2.00	1.02	1.02	0.550
Average,				0.549

Formula $X^{n_3}Y = C_3$; $n_3 = 1.36$; $\log C_3 = 0.433$.

				log C_3.
1.45	1.50	1.56	1.59	0.445
1.25	1.25	2.00	2.00	0.433
1.06	1.06	2.51	2.50	0.432
1.00	1.00	2.71	2.72	0.434
0.93	0.92	3.04	3.00	0.428
0.75	0.75	4.00	4.00	0.432
Average,				0.434

Formula $X^{n_4}Y = C_4$; $n_4 = 1.765$; $\log C_4 = 0.372$.

				log C_4.
0.65	0.65	5.02	5.00	0.369
0.59	0.59	5.98	6.00	0.373
0.54	0.54	7.00	7.00	0.372
0.50	0.50	8.00	8.00	0.372
0.44	0.44	9.96	10.00	0.370
Average,				0.371

TABLE XII.

x c.c. Water; y c.c. Ethylacetate; 1 c.c. Methyl Alcohol. Temp. 20°.

Formula $(x - 0.029y)(y - 0.093x)^{n_1} = C_1$; $n_1 = 1.20$; $\log C_1 = 0.002$.

Water.		Ethylacetate.		
Calc.	**Found.**	**Calc.**	**Found.**	**log C_1.**
9.92	10.00	1.08	1.08	0.006
6.96	7.00	0.85	0.85	0.005
5.08	5.00	0.72	0.72	$\bar{1}.995$
3.96	4.00	0.69	0.69	0.006
3.01	3.00	0.68	0.68	0.000
2.51	2.50	0.70	0.70	0.001
Average, ...				0.002

Formula $(x - 0.029y)^{n_2}(y - 0.093x) = C_2$; $n_2 = 2.78$; $\log C_2 = 0.631$.

				log C_2.
2.03	2.00	0.83	0.82	0.637
1.80	1.80	1.04	1.04	0.630
1.72	1.70	1.19	1.15	0.617
1.49	1.50	1.63	1.69	0.644
1.41	1.41	1.99	2.00	0.633
Average, ...				0.632

Formula $(x - 0.029y)^{n_3}(y - 0.093x) = C_3$; $n_3 = 2.00$; $\log C_3 = 0.550$.

				log C_3.
1.29	1.29	2.51	2.50	0.549
1.20	1.20	2.99	3.00	0.551
1.07	1.07	4.03	4.00	0.547
1.00	1.00	4.88	4.90	0.552
Average, ...				0.550

Formula $(x - 0.029y)^{n_4}(y - 0.093x) = C_4$; $n_4 = 7.00$; $\log C_4 = 0.078$.

				log C_4.
0.97	0.97	6.00	6.00	0.078
0.98	0.98	7.02	7.00	0.076
1.00	1.00	7.61	8.00	0.100
1.03	1.03	9.98	10.00	0.079
Average, ...				0.083

TABLE XIII.

x c.c. Water; y c.c. Ethylacetate; 1 c.c. Acetone. Temp. 20°.

Formula $(x - 0.029y)(y - 0.093x)^{n_1} = C_1$; $n_1 = 1.54$; $\log C_1 = \bar{1}.364$.

Water.		Ethylacetate.		
Calc.	Found.	Calc.	Found.	log C_1.
10.12	10.00	1.02	1.01	$\bar{1}.359$
6.99	7.00	0.76	0.76	$\bar{1}.365$
5.01	5.00	0.60	0.60	$\bar{1}.363$
3.00	3.00	0.47	0.47	$\bar{1}.364$
2.00	2.00	0.43	0.43	$\bar{1}.365$
Average,				$\bar{1}.363$

Formula $(x - 0.029y)^{n_2}(y - 0.093x) = C_2$; $n_2 = 1.16$; $\log C_2 = \bar{1}.721$.

				log C_2.
1.50	1.50	0.47	0.47	$\bar{1}.721$
1.00	1.00	0.63	0.63	$\bar{1}.721$
Average,				$\bar{1}.721$

Formula $(x - 0.029y)(y - 0.093x)^{n_3} = C_3$; $n_3 = 1.26$; $\log C_3 = \bar{1}.653$.

				log C_3.
0.79	0.80	0.74	0.74	$\bar{1}.656$
0.69	0.69	0.80	0.80	$\bar{1}.652$
0.51	0.51	1.00	1.00	$\bar{1}.652$
0.31	0.31	1.50	1.50	$\bar{1}.653$
Average,				$\bar{1}.653$

Formula $(x - 0.029y)^{n_4}(y - 0.093x) = C_4$; $n_4 = 3.00$; $\log C_4 = \bar{2}.135$.

				log C_4.
0.25	0.25	2.01	2.00	$\bar{2}.134$
0.25 –	0.25	2.48	2.50	$\bar{2}.138$
0.286	0.285	3.01	3.00	$\bar{2}.134$
0.29	0.29	5.00	5.00	$\bar{2}.135$
Average,				$\bar{2}.135$

In this set of tables, as in the first set, the amount of one non-miscible liquid which will dissolve in the consolute liquid decreases as the quantity of the other non-miscible liquid increases. In this case, however, the non-miscible liquids are saturated solutions, and it does not follow that the quantity of one pure liquid decreases as the other increases. There comes a point where the rate of increase of one component in the solution in which it is solute is greater than its rate of decrease in the solution in which it is solvent. If we take the general equation (17),

$$(x-s_2y)^n(y-s_1x)=C_2,$$

it is obvious that as x increases y will first decrease, pass through a minimum, and then increase. If the same equation expressed the two equilibria, the point where y was a minimum would be the point where the solution is no longer sensitive to an excess of x. In general, the equilibrium for this second stage is given by a second equation, and all we can say in our present knowledge is that at the intersection of these two curves y should have a minimum value. This does not seem to hold in Table XII., where the amount of ethylacetate soluble in 1 c.c. methylalcohol in presence of 2.50 c.c. water is more than will dissolve when either three or four cubic centimeters of water are added. I am inclined to attribute this to experimental error, as I do not see how there can be two saturated solutions of the same substance in the same solvent. Such a case would be entirely new, and would involve such consequences that it is not to be assumed on the strength of a variation of two one-hundredths of a cubic centimeter in measurements where the probable error is known to be very large. I propose to repeat these measurements on a larger scale, so as to determine what the facts really are. There are also one or two things in respect to the ether-water-methylalcohol curve which need to be gone into more closely. In Table XIV. I give the values for log C when cleared of the term for z, and the values for log K when the effect of the exponential factor has been eliminated. Both log C and log K are calculated for x, y, and z, being expressed in cubic centimeters. A discussion of these values is not possible at present, and in any case they should be reduced to reacting volumes or reacting weights before a rational treatment could be thought of.

TABLE XIV.

Mixtures.	log C_1.	log C_2.	log C_3.	log C_4.	log K_1.	log K_2.	log K_3.	log K_4.
S. H_2O, S. Ether, Alcohol	$\bar{1}.478$	0.126	0.095	$\bar{1}.757$	$\bar{1}.855$	0.051	0.047	$\bar{1}.911$
H_2O, Ether, Methylalcohol	$\bar{1}.502$	$\bar{1}.928$	0.045	$\bar{1}.057$	$\bar{1}.801$	$\bar{1}.966$	0.015	$\bar{1}.825$
S. H_2O, S. Et. Ac., Alcohol	$\bar{1}.280$	0.549	0.433	0.372	$\bar{1}.814$	0.196	0.182	0.134
H_2O, Et. Ac., CH_3OH	0.002	0.631	0.550	0.078	0.001	0.167	0.183	0.001
H_2O, Et. Ac., Acetone	$\bar{1}.364$	$\bar{1}.721$	$\bar{1}.653$	2.135	$\bar{1}.749$	$\bar{1}.871$	$\bar{1}.894$	$\bar{1}.534$

The measurements already communicated would be sufficient by themselves to establish the general law governing this class of equilibria; but I have in addition experiments by other investigators which give the same result. In 1871 Tuchschmidt and Follenius[1] noticed that carbon bisulphide was not infinitely miscible with aqueous alcohol, and they made a series of experiments to determine the saturation points when carbon bisulphide was added to alcohol of known strengths. They expressed their results by means of a complex empirical formula. This is not necessary, as the general equation for two non-miscible liquids cover the case entirely. In Table XV. the first column gives the number of cubic centimeters of carbon bisulphide which will dissolve in ten cubic centimeters of aqueous alcohol of the percentage composition by weight given in column two. In column three is the strength of alcohol as required by the formula.

TABLE XV.

$x =$ g. H_2O; $y =$ c.c. CS_2. Temp. 17°.

Formula $xy^n = C$; $n = \frac{6}{5}$; $\log C = 1.345$.

	Per cent Alcohol.		
y.	Calc.	Found.	log C.
18.20	98.8	98.5	1.457
13.20	98.0	98.15	1.318
10.00	97.0	96.95	1.345
7.00	95.0	93.54	1.456
5.00	91.5	91.37	1.350
3.00	84.3	84.12	1.324
2.00	74.0	76.02	1.310
0.20	—	48.4	—
Average,			1.366

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[1] B. B., IV. 583. 1871.

When one considers that the carbon bisulphide was evidently determined very roughly, the agreement is an excellent one. Here, too, we find the existence of two curves. The last measurement lies on the second curve when water is the precipitate, and not carbon bisulphide. As only one point on this curve was measured, it is impossible to determine the constants even approximately. The object of this investigation by Tuchschmidt and Follenius was to obtain a method for determining the strength of aqueous alcohol quickly and easily. Owing to the unpleasant properties of carbon bisulphide, their choice of liquids was bad, though the method seems to me a good one. If one were to make a complete table for benzol or chloroform and aqueous alcohol at zero degrees, the rest would be simplicity itself. One would take ten cubic centimeters of the alcohol to be tested and run in chloroform from a burette till saturated, when a glance at the table would give the percentage composition of the alcohol. The method would be quicker than any except with a hydrometer, and more accurate than that. An idea of the accuracy is given by the fact that at 20°, 5 c.c. of 96 per cent alcohol require about 20 c.c. chloroform, while the same amount of 97.5 per cent alcohol requires about 30 c.c. for saturation. For a weaker alcohol the change for each per cent is much less; but the measurements can be made more accurately.

I will now take up the measurements of Pfeiffer[1] on the miscibility of various esters with alcohol and water. The measurements were not made under the most favorable circumstances. A known amount of the ester was poured into a beaker, a definite quantity of alcohol added, and water run in till the saturation point was reached. Nothing was done to prevent evaporation, nothing, so far as is mentioned, to keep a constant temperature, and there was no means of warming the solution above the final temperature in order to insure that equilibrium had been reached. The necessity of this last had already been pointed out by Duclaux,[2] who found that, on cooling a solution below its saturation point, it clouded at once; but on warming, the equilibrium was

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[1] Zeitschr. f. ph. Chem., IX. 469. 1892.

[2] Ann. chim. phys., [5.], VII. 264. 1876.

reached much more slowly. Given these untoward conditions, the comparative accuracy of the measurements is remarkable. While Pfeiffer has given us series upon series of valuable measurements, showing the increase of miscibility of esters and water in presence of alcohol, he has curiously enough omitted all determinations of the miscibility of water and esters when no alcohol is present. This is still more remarkable if one considers the uselessness of comparing the effect of equal quantities of alcohol on ethylacetate and water, amylacetate and water, without allowing for the fact that ethylacetate is roughly forty times as soluble in water as amylacetate. As these solubilities had to be known at any rate approximately, in order to apply Equation II. to Pfeiffer's experimental data, I have determined several myself. Through the courtesy of Mr. Dunlap of the organic laboratory, I received small quantities of ethylbutyrate, ethylisovalerate, and isoamylacetate. I dried them over calcium chloride and fractionated. The change of boiling point of the portions used was four degrees for the ethylisovalerate and two degrees for each of the others. The amounts at my disposal made it not worth while to attempt further purification. In Table XVI. I give the solubilities in cubic centimeters of the solute in ten cubic centimeters of the solvent at 20°. For purposes of comparison I have also inserted in this table the values for ethylacetate from Table VIII.

TABLE XVI.

Solute.	Solvent.	Solubility.
Ethylacetate	Water	0.926
Water	Ethylacetate	0.294
Isoamylacetate	Water	0.02
Water	Isoamylacetate	0.12
Ethylbutyrate	Water	0.08
Water	Ethylbutyrate	0.04-5
Ethylisovalerate	Water	0.02 –
Water	Ethylisovalerate	0.04 +

For these four esters I have found that the solubility in water decreases with increasing temperature, while the solubility of water in the ester increases with increasing temperature, both observations being made at 20°. As there is no obvious reason why these four esters should all be abnormal, it is more than likely that this behavior is characteristic of all esters at ordinary temperatures. As it is improbable that the solubility of the esters in water can continue to decrease indefinitely with increasing temperature, there must be some point where it reaches a minimum, and it is quite possible that a determination of this temperature for different esters might give interesting results. The experiments could be made with great ease, as the amount of saponification during the time necessary for a measurement would be very small.

Quite recently, de Hemptinne[1] has determined the solubilities of several esters in water at 25°. His measurements are given in grams of the solute per liter of solution. I have reduced his measurements to cubic centimeters of solute in ten cubic centimeters of solvent by dividing by the densities as far as I could get them out of Landolt and Börnstein's tables and Roscoe and Schorlemmer's text-book, disregarding the difference between a liter of solution and a liter of solvent. The results which I give in Table XVII. are only rough approximations, but quite sufficient for my purpose. The figures in the second column are the densities used in recalculating de Hemptinne's figures.

TABLE XVII.

Solute.	Solubility.	Density.
Isobutylacetate	0.07	0.88
Amylacetate	0.02−	0.88
Methylbutyrate	0.115	0.94
Ethylbutyrate	0.08−	0.898
Amylbutyrate	0.006	0.85
Propylpropionate	0.06+	0.88
Amylpropionate	0.01+	0.88
Ethylvalerate	0.03	0.86

De Hemptinne did not measure the solubility of water in the esters, and I have not been able to find any data on the subject

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[1] Zeitschr. f. ph. Chem., XIII. 561. 1894.

beyond the few measurements which I have made myself. In considering Pfeiffer's results, this is not very serious, because he worked always with three cubic centimeters of esters, adding alcohol in varying quantities, and water to saturation. As the solubility of water in the different esters can be rarely more than one per cent, the error in calculating the amount of water required to saturate will in no case be more than a tenth of a cubic centimeter, and will rarely exceed two or three hundredths. The solubilities of esters in water, which have not been determined by de Hemptinne or myself, have been filled in as best I could by analogy, remembering that increase of carbon means decrease of solubility, and that among isomeric esters the one with the smaller acid radical was rather the less soluble. In deciding where between two limits an unknown solubility should be put, I have taken the figure which satisfied the experimental data best. The solubilities thus obtained lay no claim to being accurate; but they are not very far out, probably in no case more than 100 per cent, and this rough approximation is better than treating the esters and water as absolutely non-miscible. In Table XVIII. I give the solubilities which I have used in calculating Pfeiffer's results, expressed in cubic centimeters of the ester in ten cubic centimeters of water.

Table XVIII.

Solute.	Solubility.	Solute.	Solubility.
Methylvalerate	0.20	Propylacetate	0.30
Ethylvalerate	0.03	Butylacetate	0.07
Methylbutyrate	0.12	Amylacetate	0.02
Ethylbutyrate	0.08	Propylformiate	0.40
Propylbutyrate	0.02	Butylformiate	0.10
Ethylpropionate	0.30	Amylformiate	0.05
Propylpropionate	0.065		

Starting, as Pfeiffer did, with a constant quantity of ester, his results necessarily lie almost entirely along the curve representing the equilibrium when addition of water or ester produces a precipitate of ester. In a few cases there are a few measurements, never more than two, on the curve where water or ester produces a precipitate of water. There are not enough of these measurements to enable me to determine the direction of this second curve, and in the tables I have therefore given no calculated values in these cases. The point where, according to Pfeiffer, infinite miscibility occurs is the beginning of the curve where the solution is saturated in regard to ester; but water produces no precipitate. The corresponding curve where the solution is saturated in respect to water, while addition of ester produces no precipitate, did not come within the scope of Pfeiffer's investigations at all. It will be noticed that in the last measurements of each series the amount of water required to saturate is very generally greater than the theoretical quantity. I attribute this variation entirely to experimental error. When one is working with one hundred cubic centimeters of solution or more, it becomes almost impossible to determine the first appearance of clouding with great accuracy. In Tables XIX. to XXXI. I give Pfeiffer's results, with the values for the water calculated according to the formula at the top of each table. It is only fair to Herr Pfeiffer to say that, if I had arranged the exponential factors so that z should have been raised to the first power only, the differences between the observed and the calculated values would have been less than they now are. I felt, however, that, as the water was the thing I was calculating, I would make its exponential factor unity instead of that of the alcohol.

[*To be continued.*]

TABLE XIX.

$y = 3$ c.c. Methylvalerate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x(y - 0.02\,x)^{0.37}/z^{1.37} = C$; $\log C = \bar{1}.807$.

	x.		
z.	Calc.	Found.	log C.
3	—	1.66	—
6	5.04	5.06	$\bar{1}.809$
9	8.88	9.03	$\bar{1}.815$
12	13.28	13.40	$\bar{1}.809$
15	18.34	18.41	$\bar{1}.809$
18	23.90	24.00	$\bar{1}.809$
21	30.09	30.09	$\bar{1}.807$
24	36.80	36.72	$\bar{1}.806$
27	44.35	44.15	$\bar{1}.805$
30	52.80	52.37	$\bar{1}.803$
33	62.60	62.25	$\bar{1}.804$
36	74.25	74.15	$\bar{1}.806$
39	91.45	91.45	$\bar{1}.807$
42	—	∞	$\bar{1}.807$

TABLE XX.

$y = 3$ c.c. Ethylvalerate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.003)^{0.40}/z^{1.40} = C$; $\log C = \bar{1}.682$.

	x.		
z.	Calc.	Found.	log C.
3	—	1.42	—
6	3.81	4.14	$\bar{1}.718$
9	6.73	7.18	$\bar{1}.710$
12	10.07	10.51	$\bar{1}.701$
15	13.81	14.13	$\bar{1}.692$
18	17.80	18.09	$\bar{1}.688$
21	22.15	22.40	$\bar{1}.687$
24	26.80	26.83	$\bar{1}.683$
27	31.65	31.70	$\bar{1}.683$
30	36.70	36.62	$\bar{1}.681$
33	42.15	41.81	$\bar{1}.678$

TABLE XX (*continued*).

z.	Calc.	Found.	log C.
36	47.65	48.00	$\bar{1}.685$
39	53.40	53.13	$\bar{1}.679$
42	59.40	58.35	$\bar{1}.674$
45	65.55	63.60	$\bar{1}.668$
48	71.90	69.97	$\bar{1}.670$
51	78.50	76.90	$\bar{1}.672$
54	83.25	84.25	$\bar{1}.688$
57	92.40	90.53	$\bar{1}.673$
60	99.50	98.60	$\bar{1}.678$
63	106.80	105.20	$\bar{1}.675$
66	114.70	112.80	$\bar{1}.674$
69	122.40	121.90	$\bar{1}.680$
72	130.40	131.00	$\bar{1}.684$
75	138.90	140.20	$\bar{1}.687$
78	148.00	158.70	$\bar{1}.712$
81	157.50	180.00	$\bar{1}.740$
			$\bar{1}.687$

TABLE XXI.

$y = 3$ c.c. Methylbutyrate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.012)^{0.52}/z^{1.52} = C$; $\log C = \bar{1}.888$.

	x.		
z.	Calc.	Found.	log C.
3	2.33	2.34	$\bar{1}.889$
6	6.75	6.96	$\bar{1}.902$
9	12.67	12.62	$\bar{1}.886$
12	19.90	19.45	$\bar{1}.878$
15	28.38	28.13	$\bar{1}.884$
18	38.76	38.80	$\bar{1}.889$
21	50.85	55.64	$\bar{1}.927$
24	—	∞	$\bar{1}.892$

MINOR CONTRIBUTIONS.

On a Simple Method of Photographically Registering the Infra-Red Energy Spectrum.[1]

By Knut Ångström.

UP to the present time it has been possible to photograph directly only an extremely small part of the infra-red spectrum, and the spectro-bolometric method is still the only one which affords us a means of obtaining a more intimate knowledge of the distribution and intensity of the longer wave-lengths. It is also to be noted that this method gives a means of comparing the different parts of the spectrum *quantitatively*, which is scarcely possible by photography. The investigation of the infra-red spectrum with the aid of the spectro-bolometer is nevertheless so tedious, and, with the apparatus which has heretofore been commonly used, occupies so much time, that we might safely predict that unless the method is further developed, it will be possible to continue investigation in this field only very slowly.

In a communication to the British Association on August 11, 1894, Professor Langley, who was the first to develop the spectro-bolometric method, has so perfected this method that the work can now be carried out in the infra-red almost as easily, and with almost as great accuracy, as in other regions of the spectrum. This is made possible partly by such refinement in the construction of the optical parts of the instrument as has heretofore never been reached; partly, also, by substituting for the observer a photographic plate. As the result of the optical improvements, such sharpness and dispersive powers were gained that the instrument not only shows both of the *D* lines, but also the nickel line in the solar spectrum lying between the two. Through the possibility of recording the indications of the spectro-bolometer by photographic methods the labor of the observer is of course lightened in the highest degree.

The principle of the new method is briefly the following: —

The telescope and scale of the galvanometer are replaced by the photographic plate, upon which falls a beam of light reflected from the mirror of the galvanometer. The telescope of the spectro-bolometer is driven by

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[1] A paper presented to the Royal Society of Sciences of Upsala, April 10, 1895.

accurate clock-work, which also gives to the photographic plate a vertical movement. The motor is constructed with such accuracy that the two movements, viz. that of the telescope and that of the plate, are as nearly as possible synchronous. For each minute of arc through which the bolometer wire is moved, the photographic plate moves one centimeter.

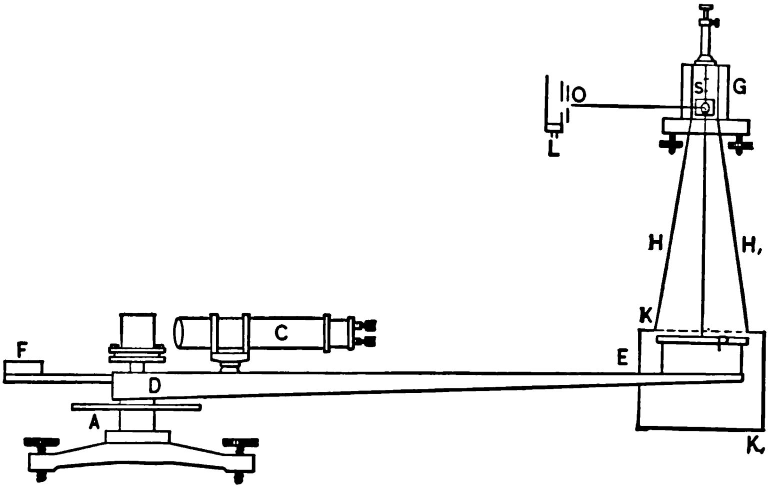

Fig. 1.

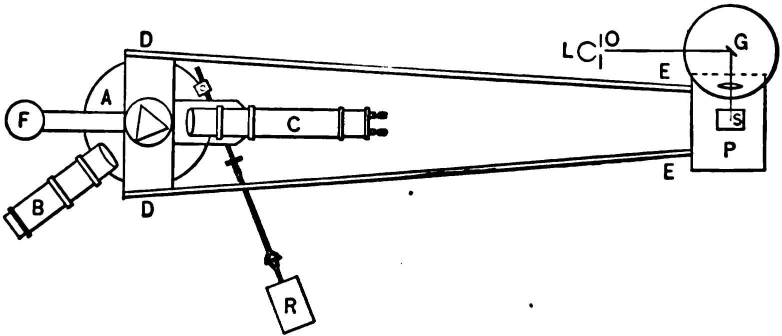

Fig. 2.

With the instrument constructed by Langley it appears that the extreme limits of sensitiveness and sharpness which are possible with the methods and apparatus at our disposal, have been reached. Such an instrument, however, can only be obtained by a richly endowed laboratory. For that reason I have undertaken the problem of simplifying the photographic method of registration, and shall describe below an apparatus which seems to offer a satisfactory solution.

The essential difference between this instrument and that of Langley consists in the fact that the photographic plate is rigidly fastened to the bolometer tube, so that both can be moved at the same time. The beam of light reflected from the mirror of the galvanometer is then thrown upon the moving plate. The movement of the spot of light resulting from a rotation of the galvanometer mirror, must, however, take place in a direction at right angles to the motion of the plate. In order to accomplish this, the apparatus is arranged as shown in Figs. 1 and 2.

The light horizontal arm *DE* is fastened to the rather solidly built support *A* of the telescope, so that the former may be rotated with the tube *C* of the bolometer. The photographic plate with its holder is placed in a horizontal position at the end of this arm. Almost vertically above the plate stands the galvanometer *G* which is used with the bolometer. The light from the source *L* passes through a slit *O* and falls upon the mirror of the galvanometer at an angle of 45 degrees. After reflection the beam is brought into a vertical direction by means of the mirror *S*, and the image of the slit falls upon the photographic plate *P*. When the galvanometer mirror is rotated, this image moves in the direction of the bolometer arm (in the plane of the drawing in Fig. 2). If the arm is rotated, however, the beam of light describes a line perpendicular to the first direction. If the tube, and with it the arm *DE*, is rotated, the bolometer wire passes through the different portions of the spectrum, and the galvanometer gives for each position the corresponding intensity of the radiation. The position of the spot of light upon the plate is thus determined at each instant by the position of the arm and the position of the galvanometer mirror. In the curve which the spot of light describes under these circumstances, distances perpendicular to the arm are therefore proportional to the angular position in the spectrum, while distances in the direction of the arm are proportional to the intensity corresponding to this position. Since the photographic plate and the bolometer wire are rigidly connected, the movements are here of necessity absolutely synchronous.

Between the galvanometer mirror and the mirror *S* a lens is placed which throws a sharp image of the slit *O* upon the plate. The latter is surrounded by a small box KK_1 in order to cut out stray light, and for the same reason a conical pasteboard tube HH_1 is placed upon the box. One side of the box is formed of two parts, which can be taken off in order to make it easier to remove the plate. Between them is a horizontal opening four centimeters wide to allow a free movement of the arm. The upper cover has a very narrow slit extending in the direction of the bolometer arm, by means of which the image (whose length is perpendicular to the opening of this slit) is limited practically to a point.

With this arrangement, a means of moving the telescope with extreme accuracy is entirely unnecessary. The only requirement is that the movement of the bolometer tube should take place rather uniformly, and without jerks. I have used with good results a very simple clock-work for this purpose, the movement being damped by an air cushion. By varying the adjustment of the latter the rapidity of the motion could be regulated. The most rapid rotation which I have used was ten minutes of arc per minute. In this case the length of the arm, and therefore the distance from the axis of the spectrometer, was two meters. A rotation of the bolometer tube through an angle of one degree thus caused the image to describe an arc on the photographic plate 3.48 cm. long; or, in other words, each minute of arc corresponded to the movement of the plate of 0.58 mm. If it is desired to have the movement of the plate greater, this can of course be accomplished by lengthening the arm. In connection with the apparatus at my disposal the motion of the plate mentioned above was, however, sufficiently great. For the preliminary investigation of many questions, also, a greater dispersion of the spectrum is hardly necessary.

I shall take this occasion to mention also another solution of the problem of photographically registering the indications of a bolometer, although I have not yet tested the method. Figure 3 indicates the arrangement. The ray of light proceeds from the galvanometer mirror G to the mirror S, making an angle of 45° with the latter. It is here reflected in a vertical direction, and then by means of mirror S_2, whose plane is perpendicular to the plane of the first mirror S_1, again reflected in a horizontal direction and projected upon the photographic plate. The last mirror is fastened upon the bolometer tube T above the axis of the spectrometer. On rotating the tube, the spot of light moves upon the plate in a horizontal direction, while if the galvanometer mirror rotates, the motion of the spot of light is in a vertical direction. This arrangement has the advantage that the movement can more easily be made much greater. For example, if the distance between S_2 and P is five meters, the spot of light will move 2.9 mm. in a horizontal direction for a rotation of the theodolite of one minute.

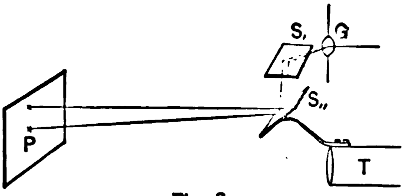

Fig. 3.

Up to the present time I have had an opportunity of testing the first method only in the case of the radiation from gas flames. I have, however, been able to convince myself of the practicability of the method. In addition to the two large maxima first discovered by Julius, and whose origin was more carefully investigated by myself, the photographic record of the spectrum of the Bunsen flame shows very clearly the two small maxima lying nearer to the visible portion of the spectrum. The latter maxima have been given by Paschen in the radiation of the oxyhydrogen flame and the Bunsen flame. For the case of a rock salt prism with a refracting angle of 60°, the positions of these four maxima as indicated by their angular deviation from the *D* line are as follows: —

1° 25′ 12″	corresponding to	$\lambda = 1.48\,\mu$;
1° 34′ 32″	corresponding to	$\lambda = 1.96\,\mu$;
1° 45′ 35″	corresponding to	$\lambda = 2.80\,\mu$;
2° 6′ 0″	corresponding to	$\lambda = 4.34\,\mu$.

In this brief preliminary note I have merely wished to show the possibility of obtaining a photographic registration of bolometer indications with comparatively simple apparatus; and that it is possible to construct an instrument which shall at least bear the same relation to that of Langley as does the direct-vision spectroscope to the larger instruments of its class.

ON THE ELECTROLYTIC CONDUCTIVITY OF CONCENTRATED SULPHURIC ACID.

BY DR. K. E. GUTHE AND L. J. BRIGGS.

IT is a well-known fact that the specific conductivity as well as the molecular conductivity of sulphuric acid is a minimum for a concentration corresponding closely to the hydrate $H_2SO_4 + H_2O$. The investigations of F. Kohlrausch, Bouty, and Ostwald have shown, moreover, that this minimum becomes less pronounced, the higher the temperature is. Seemingly this acid forms an exception to the rule that the water of crystallization has no influence upon the conductivity of electrolytes. Our experiments were undertaken in order to provide more data for solutions of this acid at a concentration near 84.5 per cent (corresponding to the hydrate), with reference to the changes produced by temperature.

Similar work has been done by Miss Klaassen[1], but since her work may include errors of even more than 2 per cent we have repeated part of it. The conclusions drawn from our experiments are new.

Experiments as to the conductivity of the hydrate in the solid state have to our knowledge not been published before.

Our arrangement differs in some points from the usual one. As the source of electricity we used an alternating current, produced by a two-phase dynamo designed by Professor Carhart and represented in the accompanying cut. The field is formed by a revolving electromagnet excited by

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[1] Proc. of Cambr. Phil. Soc., Vol. VII., p. 137.

an independent current from the storage battery which can be varied at will. In our experiments we used, of course, the sinusoidal current from only one pair of terminals. The bridge was formed by an ordinary slide wire bridge of manganin wire, lengthened by additional strictly non-inductive resistances of the same metal (each of 26 ohms' resistance = 6360 cm. of the bridge). Instead of a telephone we took a very sensitive electrodynamometer, the stationary coils of which were connected in parallel with the bridge.

Since we used for the determination of temperature a calibrated ordinary thermometer, which could not be read more accurately than to one-twentieth of a degree, we arranged the conditions so that the errors of observation would not exceed 0.1 per cent. For this purpose we sent only 0.8 ampere through the field of the generator. Since this current can easily be increased to 16 or more amperes, one can apply this arrangement for the measurement of conductivity of bad conductors just as well. The objection to the use of alternating currents for such a purpose raised by M. Wildermann[1] cannot be applied here. The time spent for one observation is very short, and not longer than that necessary for the determination by telephone.

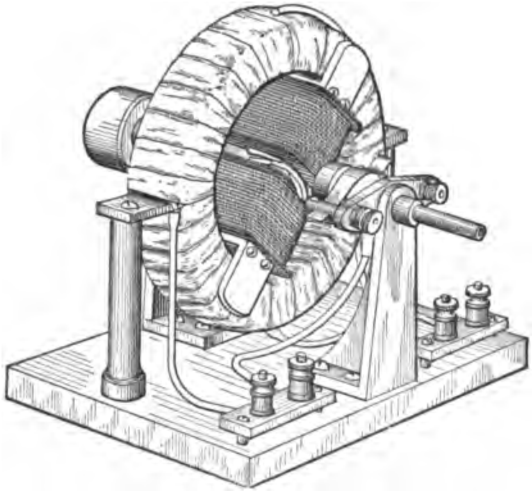

Fig. 1.

The specific gravity in each case was determined by a delicate Mohr's balance, and from this value the concentration obtained. All calculations necessary were based upon the data given in Landolt and Boernstein's Tabellen (2d ed.).

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[1] Zeitschr. f. phys. Chemie, 14, p. 247, 1894.

The vessel was of the common U form, and its capacity repeatedly determined from its resistance when filled with a concentrated NaCl solution. The acid, which we obtained through the kindness of Mr. F. W. Edwards of the Chemical Laboratory, was Baker & Adamson's strictly chemically pure H_2SO_4 of 1.84 spec. grav.

We give in the following tables the data of a number of our solutions sufficient to show the results obtained. In the first column the temperature is given; in the second, the actual resistance of the liquid; in the third, the specific conductivity. These values have to be multiplied by 10^{-12}. In the fourth column we find the molecular volume or molecular domain, *i.e.* the volume occupied by $\frac{1}{2}$ gram-equivalent of H_2SO_4 expressed in cubic centimeters; finally, in the fifth column the molecular conductivity, the product of molecular volume into specific conductivity.

TABLE I.

97 % H_2SO_4. Sp. Gr. = 1.841 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
2°.8 C.	433.0 ohms	67.45×10^{-12}	27.29	1.83×10^{-12}
8°.0	370.0	78.93	27.36	2.16
12°.9	321.0	90.98	27.43	2.50
22°.5	248.0	117.80	27.56	3.25
29°.0	212.5	137.41	27.65	3.80
17°.5	282.0	103.61	27.50	2.85

TABLE II.

93.05 % H_2SO_4. Sp. Gr. = 1.834 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
2°.5 C.	426.0 ohms	68.56×10^{-12}	28.56	1.96×13^{-12}
6°.4	377.0	76.47	28.61	2.22
12°.1	317.0	92.13	28.69	2.64
16°.7	278.0	105.06	28.76	3.02
21°.4	243.0	120.20	28.83	3.46
28°.3	202.8	144.00	28.94	4.17

TABLE III.

91 % H_2SO_4. Sp. Gr. = 1.825 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.6 C.	470.0 ohms	62.14×10^{-12}	29.31	1.82×10^{-12}
6°.4	385.0	75.85	29.40	2.23
12°.3	320.0	91.27	29.48	2.69
17°.0	279.0	104.7	29.55	3.09
22°.9	237.0	123.2	29.64	3.65
28°.8	202.0	144.6	29.73	4.30
23°.2	233.0	125.4	29.65	3.72

TABLE IV.

88.6 % H_2SO_4. Sp. Gr. = 1.812 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
1°.0 C.	505.0 ohms.	57.83×10^{-12}	30.33	1.75×10^{-12}
6°.0	422.0	69.21	30.41	2.10
11°.0	352.0	82.97	30.49	2.53
17°.0	293.0	99.67	30.58	3.05
21°.8	253.0	115.4	30.66	3.54
29°.2	204.6	142.6	30.77	4.39

TABLE V.

86.55 % H_2SO_4. Sp. Gr. = 1.798 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	552.0 ohms.	51.51×10^{-12}	31.26	1.61×10^{-12}
3°.8	480.0	59.24	31.32	1.85
8°.9	390.5	72.82	31.41	2.29
14°.6	319.7	88.95	31.53	2.80
19°.1	277.0	102.66	31.59	3.24
23°.3	242.0	117.51	31.65	3.72
29°.3	205.0	138.72	31.75	4.40

TABLE VI.

85.7% H_2SO_4. Sp. Gr. = 1.790 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	572.0 ohms.	49.72×10^{-12}	31.71	1.58×10^{-12}
8°.0	421.0	67.55	31.85	2.15
15°.5	319.0	89.11	31.98	2.85
23°.0	249.0	114.21	32.10	3.67

TABLE VII.

84.5% H_2SO_4. Sp. Gr. = 1.780 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	591.0 ohms.	48.12×10^{-12}	32.34	1.56×10^{-12}
5°.9	468.0	60.76	32.44	1.97
11°.8	367.0	77.49	32.54	2.52
17°.4	301.5	94.32	32.64	3.08
24°.0	242.5	117.27	32.75	3.84
30°.5	199.0	142.90	32.86	4.70

TABLE VIII.

80.75% H_2SO_4. Sp. Gr. = 1.741 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	487.0 ohms.	58.39×10^{-12}	34.60	2.02×10^{-12}
6°.0	404.0	70.39	34.71	2.44
10°.0	345.0	82.43	34.78	2 87
15°.5	286.0	99.43	34.88	3.47
20°.0	248.0	114.70	34.97	4.01
24°.9	214.0	132.89	35.06	4.66
30°.3	184.0	154.55	35.16	5.43

TABLE IX.

78.6% H_2SO_4. Sp. Gr. = 1.717 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	417.0 ohms.	68.20×10^{-12}	36.02	2.45×10^{-12}
5°.8	342.3	83.05	36.13	3.00
10°.7	289.0	98.39	36.22	3.56
14°.8	253.0	112.40	36.30	4.08
20°.1	216.0	131.66	36.40	4.79
24°.4	193.0	147.34	36.48	5.37
29°.8	167.0	170.28	36.53	6.23

TABLE X.

76.2% H_2SO_4. Sp. Gr. = 1.689 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	349.0 ohms	81.48×10^{-12}	37.80	3.08×10^{-12}
5°.7	297.0	95.75	37.92	3.63
10°.0	256.5	110.87	38.00	4.21
14°.9	221.0	128.67	38.10	4.90
19°.7	193.0	147.34	38.20	5.63
24°.3	170.0	167.28	38.29	6.41
29°.0	151.0	188.33	38.39	7.23

TABLE XI.

73.88% H_2SO_4. Sp. Gr. = 1.663 at 15° C.

Temp.	Res.	Sp. cond.	Mol. vol.	Mol. cond.
0°.0 C.	295.0 ohms	96.40×10^{-12}	39.57	3.81×10^{-12}
5°.3	252.0	112.84	39.69	4.48
10°.8	214.8	132.39	39.80	5.27
15°.3	189.0	150.46	39.90	6.00
19°.3	168.5	168.77	39.99	6.75
24°.1	150.0	189.58	40.09	7.60
30°.5	129.0	220.45	40.22	8.87

From the tables we platted for each solution the temperatures and the molecular conductivity, and determined from the curves the molecular conductivity of each at the temperatures 0°, 10°, 18°, 25°. By calculation we found, moreover, the molecular volume for each solution at those temperatures. The following table gives the results.

No.	0°		10°	
	Mol. vol.	Mol. cond.	Mol. vol.	Mol. cond.
1	27.25	1.66×10^{-12}	27.39	2.29×10^{-12}
2	28.52	1.80	28.67	2.48
3	29.30	1.78	29.46	2.50
4	30.31	1.69	30.48	2.44
5	31.26	1.61	31.43	2.39
6	31.71	1.58	31.89	2.33
7	32.34	1.56	32.50	2.35
8	34.60	2.02	34.78	2.87
9	36.02	2.46	36.21	3.49
10	37.80	3.08	38.00	4.21
11	39.57	3.82	39.79	5.14

No.	18°		25°	
	Mol. vol.	Mol. cond.	Mol. vol.	Mol. cond.
1	27.50	2.88×10^{-12}	27.59	3.46×10^{-12}
2	28.78	3.14	28.88	3.83
3	29.57	3.19	29.67	3.88
4	30.60	3.15	30.72	3.90
5	31.58	3.14	31.67	3.92
6	32.03	3.12	32.14	3.90
7	32.65	3.14	32.77	3.97
8	34.93	3.77	35.06	4.68
9	36.36	4.51	36.49	5.47
10	38.16	5.37	38.31	6.51
11	39.97	6.47	40.11	7.77

Platting four curves, for 0°, 10°, 18°, and 25° respectively, taking the percentages of the solution as abscissae and the molecular conductivities as ordinates, we find that the minimum does not correspond to the same concentration, as was given by Bouty.[1] But in platting the molecular volume,

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[1] Comptes Rendus, 108, p. 394, 1889.

instead of the percentage, we find that all four curves show a minimum of conductivity for the same molecular volume, *i.e.* 32.1. *Thus it is not the concentration but the molecular volume which determines the conductivity of the acid.*

The latter four curves are shown in Fig. 2. There is a very slight discrepancy between the fourth and fifth solutions, owing to the fact that the first four solutions were taken from a different bottle from that for the rest. But it is so small, in fact, as not to influence the result in the least.

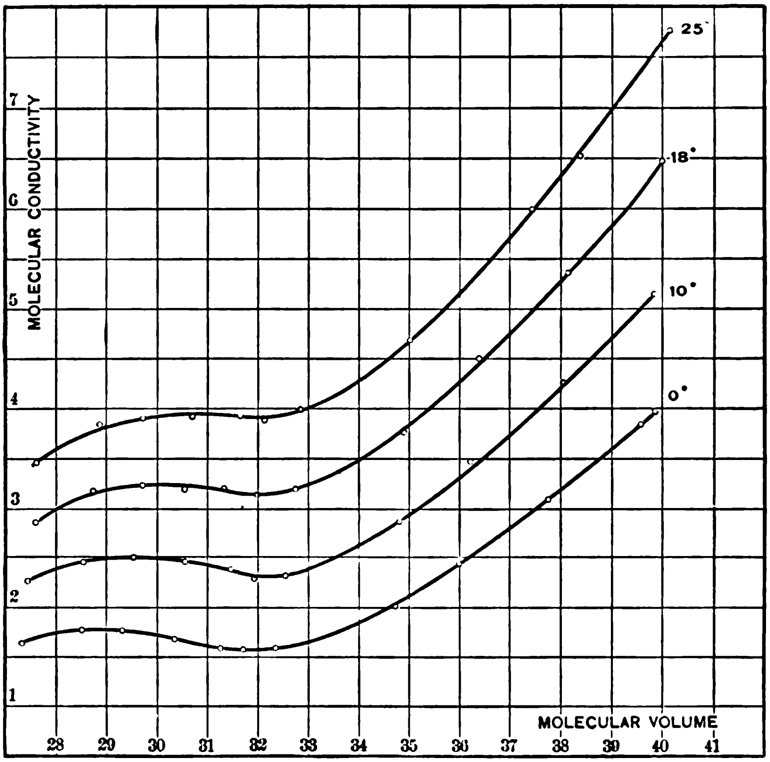

Fig. 2.

Temperature coefficient.

In the following we give the first temperature coefficient for the different solutions worked out for the formula: —

$$\mu_x = \mu_{18}\{1 + \alpha(t_x - t_{18}) + \beta(t_x - t_{18})^2\}.$$

It is apparent that the temperature coefficient is the larger, the smaller the conductivity, a result already found by F. Kohlrausch and others. As to the second coefficient, we could not obtain regular values, due to the degree of accuracy in our method. It surely becomes smaller with increasing dilution, and varies from 0.00039 to 0.00016, and is always positive.

No.	1	2	3	4	5	6
a	0.0271	0.0291	0.0294	0.0315	0.0326	0.0338

No.	7	8	9	10	11	
a	0.0346	0.0321	0.0295	0.0290	0.0273	

Electrolytic Properties of the Crystallized Hydrate of Sulphuric Acid.

Since we obtained from one of the solutions crystals of $H_2SO_4 + H_2O$, we thought it worth while to determine its conductivity, since that has to our knowledge not been done before. From the experiments of W. Kohlrausch, Bouty, Poincaré and Graetz we know that the electrolytes conduct electricity when in a solid state and that the conductivity of some increases very rapidly near the melting-point. In some cases it becomes at this temperature equal to the conductivity of the liquid, while in other cases there seems to be a sudden change with liquefaction. Though these experiments are of the greatest importance for our knowledge of the molecular structure of the salts, they do not agree satisfactorily for the salts investigated, which all melt at a high temperature.[1]

Our measurements were taken without difficulty, the crystals melting at 7°.5 C., and the electrolytic properties are very characteristic. W. Kohlrausch[2] found that the conductivity of the crystallized acid $SO_3 + H_2SO_4$ was extremely small, and varied according to the way in which they crystallized. He attributed the remaining conductivity to enclosed liquid particles.

The salt $H_2O + H_2SO_4$ shows entirely different properties. We crystallized the same repeatedly, and obtained in some cases microscopical crystals (after having undercooled the liquid), in other cases crystals 2 to 4 cm. long. The resistance was always the same at the same temperature, showing clearly that the conductivity is not due to enclosed liquid particles, but is characteristic for the solid acid.

[1] Graetz, Wied. Ann., Vol. 40, p. 18, 1890.

[2] Wied. Ann., Vol. 17, p. 80, 1882.

In the following table is given one series of observations, in which we calculated only the specific conductivity. The second table gives the measurements of the same solution in the liquid state.

CRYSTALS.

Temp.	Res.	Sp. cond.
−20°.0 C.	34000 ohms	0.846×10^{-12}
−15°.0	25000	1.147
− 8°.0	16200	1.755
∓ 0°.0	8200	3.47
5°.0	3530	8.06
7°.2	1514	18.78
7°.5	1000	28.44

LIQUID.

Temp.	Res.	Sp. cond.
0°.0 C.	585 ohms	48.61×10^{-12}
4°.8	481	59.12
9°.5	402	70.74
11°.0	376	75.63

Platting the temperature and the specific conductivity, we see that the latter increases first slowly, but more rapidly the higher the temperature. Between 0° and 7°.5 this increase is enormous, but the conductivity of the crystallized acid does not reach that of the liquid. It reaches only the value 28.44 at 7°.5 while that conductivity of the liquid is 65.4. The last point for the crystals has been computed from the curve drawn with the resistances and the temperature as coördinates.

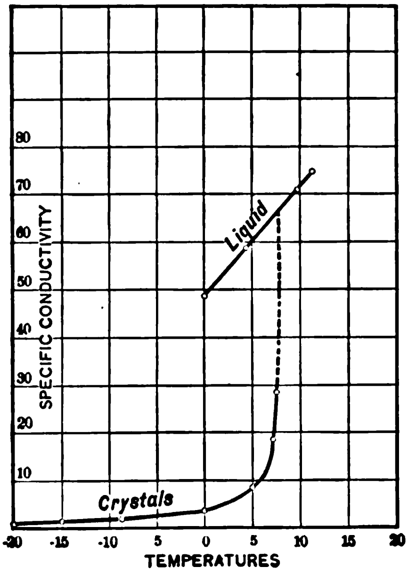

Fig. 3.

This increase of the conductivity, while the change from the solid to the liquid state takes place, seems to stand in a certain relation to the energy taken up by the acid during liquefaction. In the curves the dotted line represents this increase.

This result does not agree with Fonssereau's,[1] who found the conductivity of the solid salts at the melting-point a thousand times smaller than that of the liquid. It agrees much better with Graetz's observations, though there is a slight sudden increase at the melting-point, while he finds no such step. In fact, a difference of only 1° C. would be sufficient to make one curve reach the other.

The sudden change of the temperature coefficient is very characteristic, and we see also that such a change does not take place when we undercool the solution.

[1] Comptes Rendus, 98, p. 1325, 1889.

PHYSICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.

NEW BOOKS.

Grundzüge der Mathematischen Chemie, Energetik der Chemischen Erscheinungen. Von G. HELM. Leipzig, W. Engelmann, 1894.

At a time like the present, when both physics and chemistry are obscured by so many unnecessary hypotheses, every attempt to show the power and simplicity of general methods is very welcome. Although the general methods may themselves rest on certain assumptions, the fact that these assumptions are few, simple, and easily kept in mind is a great advantage. For one of the greatest difficulties the student has to encounter is that of remembering, often, indeed, of discovering, the hypotheses upon which the correctness of a theoretical result depends. The usefulness of thermodynamic, or energetic, methods has nowhere been greater than in the borderland between physics and chemistry. We are, however, inclined to think that pure physics may profit quite as much as physical chemistry from greater attention to the part which energy and its transformations play in natural phenomena, and that the greater advances in this direction made by physical chemistry are due rather to freedom from a long history of special hypotheses than to any intrinsic difference between the two fields.

The work before us is an attempt to give a concise and consistent treatment, based, as far as possible, only on the two laws of thermodynamics, of some of the recent advances in theoretical chemistry. It is divided into four parts, which treat *Energy*, *Entropy*, *Chemical Intensity*, and *The Degree of Freedom of Chemical Phenomena.*

Part I. contains a very good treatment of the law of the conservation of energy as applied to thermo-chemistry; in other words, of the proposition that the variation of the internal energy of a system depends only on the initial and final states of the system. We have two faults to find with Part I. The first is the failure to define temperature carefully. A satisfactory treatment of temperature must of course be left till the second law has been introduced, but we feel, especially at p. 14, that the meaning of "Celsius temperature" needs a precise definition. The second fault is a lack of clearness in the definition of molecular weight. It is, in our opinion, altogether a mistake to say (p. 15) that by the "law" of Avogadro the gas constant R in the equation $pv = RT$ is the same for one-gram molecule for all gases. This so-called law is simply our only definition of the molecular weights of gases, and our chemical molecular symbols are not independent of it, but deduced from it. The mere fact that our molecular weights so obtained are in general very simply related to the compositions of the gases in question, does not make us the less dependent on the fundamental definition in originally finding them.

Part II., headed *Entropy*, treats the second law of thermodynamics, and applies it to several problems, especially such as come under the head of Clapeynon's equation. This part seems to us the least satisfactory in the book, and we doubt whether the student who is not already familiar with the equation

$$\int\frac{dQ}{T}=0$$

will make much out of what is here given on that subject. The greatest care and precision are necessary if the meaning of entropy and of the expression $\int\frac{dQ}{T}$ is to be understood, and this precision of statement is often lacking. One wishes that the meaning of reversibility might be as well set forth as in that delightful book of M. Duhem, the *Introduction à la Mécanique Chimique.* It is perhaps carping to object to the statement that the efficiency of an irreversible engine is always less than that of a reversible one, but we have never seen a satisfying proof of that proposition. M. Bertrand's remark seems just when he says in Chapter XII. of his *Thermodynamique,* "Je serai très bref sur les cycles irréversibles; les démonstrations et les énoncés mêmes de leurs propriétés me paraissent jusqu'ici manquer de rigeur et de précision." There is, to be sure, an air of originality about the whole treatment, and this in itself is attractive, but the result seems to us less clear and simple than more ordinary methods. After this unsatisfactory section on entropy comes a short but very good introduction to free energy, the thermodynamic potential, and Gibbs's potentials, here called "chemical intensities." Most of the rest of Part II. is given up to applications of the foregoing principles to cases of equilibrium between two phases, — evaporation, allotropic changes, etc., — and to the theory of the reversible galvanic cell. In this last the author again fails to discuss reversibility, the question of the irreversible Joule heat not being mentioned. There follows an interesting paragraph on the relation of chemical intensity and electromotive force, and Part II. closes with a few pages on the conductivity of electrolytes.

Part III. begins with a section on the general properties of the chemical intensity, in which Gibbs is followed. The remainder of this most interesting division of the book considers a number of subjects by means of the chemical intensity. Among them are chemical equilibrium, osmotic pressure, and diffusion, which may serve to indicate the wide range covered by Gibbs's theory.

Part IV. deals with the phase rule, of course from Gibbs's standpoint.

Throughout the work numerical examples are introduced very judiciously to illustrate the theoretical results obtained.

To the student who is not already familiar with the elements of thermodynamics, and to some degree with free energy or the thermodynamic potential, the book will be hard reading. But the more advanced student will find it very useful as a short statement of a theory which he would otherwise have to dig out of many scattered and often obscure papers. The general impression left in the reader's mind is that so good a book ought to have been better written; but the faults are faults of detail, while the merits are those of unity and generality. We cordially recommend this work to all who are interested in physical chemistry, and we hope that this first example may find imitators in America, as it is sure to do in Europe.

EDGAR BUCKINGHAM.

BRYN MAWR, May 7th, 1895.

Ostwald's Klassiker der Exacten Wissenschaften.[1] 8vo. In Leinen Gebunden. Leipzig, Wilhelm Engelmann, 1894.

It is often difficult to realize that knowledge regarding many of the familiar facts of to-day has in many cases had a slow and laborious growth. Conceptions which we at the present time accept without a thought as to their origin have startled the scientific world at their announcement, and have set at work many a patient observer who, by his labors, has contributed no unimportant share to the world's present store of knowledge.

In a most charming series of little volumes, entitled *Ostwald's Klassiker der Exacten Wissenschaften*, Professor Ostwald of Leipzig has republished the original papers of early investigators along different scientific lines, and has thus brought these truly classic pieces of scientific literature within the reach of all. The interest felt in these papers is increased when one realizes that from these as a germ much of the present science has grown. Throughout this series of works the groping of the investigator

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[1] No. 52. Über die Kräfte der Electricität bei der Muskelbewegung. Aloisius Galvani, 1791.

No. 56. Die Gesetze der Ueberkältung und Gefrierpunktserniedrigung. Sir Charles Blagden, 1788.

No. 57. Abhandlungen über Thermometrie, von Fahrenheit, Réaumur, and Celsius. 1724-1730-1733-1742.

No. 59. Otto von Guericke's neue Magdeburgische Versuche über den leeren Raum. 1672.

is always apparent. If the reader occasionally marvels that a wrong conclusion was drawn from facts observed, or that phenomena apparently so patent escaped detection, he is quite as frequently delighted at the originality of the ideas, and the brilliancy of the conceptions, which seem now almost to have come by intuition. In all, there have been up to the present time about sixty of these little volumes published. The four mentioned below may serve to give some idea of the value of the series.

In No. 52 is contained the account by Galvani of his experiments with electricity in producing the muscular contractions in a frog's legs. At first statical electricity alone was employed, and the effects of insulators and conductors, of positive and negative electricity, were carefully investigated. Galvani's next step was to examine the effects produced by atmospheric electricity. A pointed rod, carefully insulated from the roof, was placed upon the house, and securely grounded by being connected with the water in a well. The prepared frog's legs were placed across a break in this rod, and violent contractions were observed whenever a flash of lightning was seen. That Galvani was aware of the danger attending this experiment, and of the fatal result to Richmann of a precisely similar experiment in 1753, is evident from his remark that "a careful and intelligent arrangement in this experiment must be observed." Galvani's later and more important experiments consisted in effecting the muscular contractions by the difference of potential produced by the contact of two different metals. These contractions occurred whenever the metal hook, which passed through the spinal column of the frog, touched the metal plate upon which the frog's legs rested. These phenomena Galvani attributed to the electricity resident in the frog. "It is easy, however," he says, "to be deceived by experiment, and to imagine that to be seen and found, which one wishes to see and find." Reil of Halle, and later Volta, argued that "the seat of the irritation is in the metals, that of the irritability is in the organism." Thus early began the discussion as to the seat of the electromotive force, which even to-day is not settled.

No. 56 of the *Klassiker* contains an account of two important researches carried on by Sir Charles Blagden, about the year 1788. The first is on the supercooling of water; the second is the more famous one on the depression of the freezing-point of liquids due to dissolved substances. Both researches are models of logical experimentation, and are, for their time, very accurate. In the first, the author repeated earlier experiments on supercooling, and studied the effects of various substances — salts and gases in solution, substances in suspension, etc. — in increasing or decreasing the amount of possible supercooling. The second paper contains the record of experiments which established the law that the depression of the freezing-point is proportional to the amount of the dissolved substance. Blagden's work remained unnoticed, and the same law was rediscovered by Rüdorff after a lapse of nearly eighty years. The history of these investigations, carried out first by Blagden, later by Rüdorff, Coppet, and Raoult, forms one of the most interesting chapters of modern chemistry, and leads up to the important generalizations of van't Hoff, regarding the nature of dissolved substances.

No. 57 of this series contains the original papers in which Fahrenheit, Réaumur, and Celsius published their discoveries regarding the proper construction and calibration of thermometers. Fahrenheit, according to his own statement, was led to construct a thermometer through the announcement by Amontons that water always boils at the same temperature. Wishing himself to observe this "beautiful phenomenon," Fahrenheit constructed the first mercury thermometer, and fixed thereto the arbitrary scale which now bears his name, and which contained three fixed points. For the zero of this scale he chose the point of "most intense cold," which was the temperature obtained by mixing water, ice, and sal ammoniac or common salt. The second fixed point was determined as the temperature of melting ice, which was 32 on Fahrenheit's arbitrary scale, and the third as the temperature of a healthy person, which temperature fell at 96. That the temperature of boiling water fell at 212, was purely accidental. It is strange indeed that Fahrenheit nowhere speaks of the proportions of his freezing mixture, whereby his zero was determined, and also equally strange that he should not have chosen the boiling-point of water as one fixed point, inasmuch as his attention had been especially directed to the constancy of this temperature.

Réaumur, who appears to have been ignorant of Fahrenheit's work, thought mercury to have a coefficient of expansion too small to permit of its use in a thermometer, and so chose alcohol as his thermometric substance. To obtain a sufficiently high sensibility he was obliged to use a bulb four and one-half inches in diameter, although, as he himself foresaw, so large a bulb could not indicate rapid changes of temperature. The principle employed by Réaumur in graduating his scale was radically different from that used by Fahrenheit. Réaumur assumed that only one fixed point was necessary, and chose for this the temperature of melting ice. He then determined the volume of the bulb, and so graduated his tube that each division or degree represented one one-thousandth of the entire volume of the alcohol in the bulb, when at the temperature of melting ice. As the alcohol expanded when heated, the actual increase in volume was then read off on the stem. Under these circumstances, the temperature of boiling water was indicated by the point 80 on his thermometer, although it is clearly evident that the temperature of the thermometer was not that of the boiling water in which it was placed.

Celsius, whose work followed closely upon that of Réaumur, chose the two fixed points now used — the melting-point of ice, and the boiling-point of water — and divides this interval into one hundred equal parts. He, however, mentions the fact, also referred to by Fahrenheit, that the temperature of boiling water varies with the pressure of the air, and suggests a constant barometric height at which this temperature should be taken. An important feature of Celsius' work was the introduction of the 100-degree scale, although such a scale had in all probability been suggested by du Crest in France. It is worthy of notice that Celsius, in his original paper, called the temperature of boiling water 0, and that of melting ice 100. Not until this paper appeared in the eleventh volume of the Proceedings of the Swedish Academy, do we find these figures reversed, and the scale given in the familiar form in which it is universally used.

Otto von Guericke, in the fifty-ninth volume of this series, writes of the properties and pressure of the atmosphere, and later describes the air pump devised by him, and gives the details of his many experiments with this remarkable piece of apparatus. After demonstrating the impossibility of exhausting the air from a barrel, owing to the porosity of the wood, von Guericke substituted a thin copper sphere for the barrel, only to find the sphere crushed by the pressure of the air. Later followed the construction of the large hemispheres, which, when exhausted, twenty-four horses were not able to pull apart. That the air has weight, he proved by weighing a receiver filled with air, and then empty, and noticing the diminished weight in the latter case. The pressure of the air due to its own weight, he argued, must diminish as one ascends a mountain, and he proved this to be so. The abhorrence which nature was supposed to possess toward a vacuum he showed to be identical with the atmospheric pressure. Furthermore, he argued, this pressure of the air could be balanced by an equal pressure, and proved his statement by exhausting the air from the upper end of a long closed tube, the lower end of which was open, and under the surface of water. The water rose in the tube, until, as he explained, the pressures at the surface of the water in the reservoir, outside and inside the tube, were equal. In his study of this column of water, von Guericke noticed its rise and fall with the varying pressure of the air, and placed within the tube a little floating figure, whose finger pointed to a scale on the outside of the tube, indicating the atmospheric pressure. On one occasion, as the figure sank far below his usual position, indeed, even below the scale on the tube, von Guericke announced to his friends that a storm was approaching. In less than two hours the storm broke, and thus was fulfilled probably the first weather prediction based upon meteorological instruments. Von Guericke's original air pump, as well as the colossal Magdeburg hemispheres, are now guarded as among the most valued treasures in the Berlin Physical Laboratory.

BENJ. W. SNOW.

Popular Scientific Lectures. By ERNST MACH, translated by THOMAS J. MCCORMACK. 8vo, pp. 313. Chicago, The Open Court Publishing Co., 1895.

This work is a translation of a series of lectures delivered by Professor Mach of Prague at various times between 1864 and 1894. The name Popular Scientific Lecture often conveys to the scientist the idea of dilettanteism, and the practice is condemned, and rightly, too, if the lecturer only brings before his audience a mass of details, interesting in themselves, but leaving in the minds of the hearers no one central idea. When done well, however, as in the present case, nothing but praise is the lecturer's due, and scientific inquiry is distinctly advanced. The book easily divides itself into two parts, the first seven lectures dealing with explanations of simple phenomena, and the last five lectures dealing with questions of a more philosophical and educational nature.

The first group of seven lectures belongs to the earlier period of Professor Mach's career. The first requisite of a lecture is that it shall impart information, but more important is it that the information so imparted shall cause the listener to think. The lecturer must choose from the mass of illustrations at hand those most explanatory, and must confine himself to a single line of thought. Judged in this way, these lectures are admirable. Professor Mach takes a few common, every-day phenomena, and in simple language leads his audience from the fact itself to the larger concepts that lie behind it, without their ever feeling that they are beyond their depth. Perhaps the best of all the group is the first one of this volume on "The Forms of Liquids." To the unthinking, he says, the most noticeable property of liquids is their want of form; but a discussion of the raindrop and the soap-film, in a simple and elementary but masterly way, leads to a very different conclusion. Then follow two lectures on Acoustics: viz. "The Fibers of Corti" and the "Causes of Harmony." Three lectures on Optics, under the headings "The Velocity of Light," "Why has Man Two Eyes?" and "On Symmetry," treat in a very elementary manner of some of our commonest observations, the simple explanation of which is not always easy even to one who has studied them. Mach shows that the pleasing effects of symmetry are due to the repetition of sensations; where symmetry does not produce such repetition, as in the passage from a major to a minor scale in music, this agreeableness is not experienced. The lecture on "The Fundamental Concepts of Electrostatics" is a good example of the possibility of putting in simple, untechnical language such difficult ideas as those contained in the measurement of current, electromotive force, capacity, etc., and in a manner, too, suited to the most non-mathematical person.

Perhaps the chief interest to a reader of this volume will lie in the last half of it. The lecture on "The Conservation of Energy" deals historically with the part which the principle of the impossibility of perpetual motion has played in the subject of mechanics, and the proof of the principle of the conservation of energy as derived from that subject. His statement of the results to be deduced from the fact that heat has a mechanical equivalent will repay careful reading. It does not follow that heat is not a substance, he says, and the idea that heat is a quantity is due entirely to historical connection. There is no doubt that much of the subject matter of dynamics has yet to be recast; the laws of Newton are not yet in their best possible form. The chapters on "The Economical Nature of Physical Inquiry," "Transformation and Adaptation in Scientific Thought," and "On the Principle of Comparison in Physics," treat in a clear and thoughtful way of those broader aspects and methods common to all scientific inquiry. The last address, "On Instruction in the Classics and the Sciences," is a forcible plea for the study of mathematics and the sciences; but it is a pity to see a man of the stamp of Professor Mach put forward some of the arguments which he does against the study of the classics. That much is to be said for a more general study of the sciences is true, but that this end should be gained by crying down the value and power of a classical education is to be deplored. His plea for less work in the preparatory schools, and a restriction of the number of subjects studied, is one that appeals strongly to us in this country also. "A single philological, a single historical, a single mathematical, a single scientific branch, pursued as common subjects of instruction for all pupils, are sufficient to accomplish all that is necessary for the intellectual development" (p. 290).

The translator deserves praise for the general excellence of his rendering in spite of a few evident traces of its being a translation. The publisher's work is all that could be desired.

A. Stanley Mackenzie.

Proceedings of the Electrical Society of Cornell University. Vol. II., 1894–5. 8vo, pp. 122. Ithaca, Andrus & Church, 1895.

The second volume of the Proceedings of the Electrical Society of Cornell University includes the following papers: Difference of Electrical Potential between Substances in Contact; Metals for Magnet Cores; Fuse Wire; Lightning Arresters; Mechanical Equipment of Power Stations; Some Points in Connection with the Modern Theory of Primary Batteries; A Method of Reducing Hysteresis Losses in Armature and C^2R Losses in the Field; Electricity and Mining; Electrical Resonance and Some Allied Phenomena; Alternating Current Motors; Metallic Conduction and the Influences which affect it.

Standard Methods in Physics and Electricity criticised, and a Test for Electric Meters proposed. By H. A. NABER. 8vo, pp. 114. London, George Tucker, 1894.

The volume before us is principally devoted to presenting the advantages of the Naber gas voltameter, for which the author makes the most extravagant claims. The useful applications claimed for the instrument extend to almost all branches of scientific and technical electricity, from the accurate measurement of current and electromotive force, both direct and alternating, to the determination of the form of an alternating current curve. Frequent references throughout the book to authorities show on the part of the author an extensive acquaintance with the literature of electricity. It is to be regretted that so little appreciation is shown of the value, in fact the necessity, of experiment. In spite of the claims made for the voltameter in question, no quantitative tests of its action are cited. Most readers will I think join with the reviewer in postponing a serious consideration of the contents of the book until the author's claims have received some experimental verification.

E. M.

Volume III. November–December, 1895. Number 3.

THE

PHYSICAL REVIEW.

VARIATION IN ELECTRICAL CONDUCTIVITY OF METALLIC WIRES IN DIFFERENT DIELECTRICS.

By Fernando Sanford.

IN a paper published in 1892, entitled "Some Observations upon the Conductivity of a Copper Wire in Various Dielectrics,"[1] I called attention to the fact that, with the copper wire used by me in the experiments referred to, the conductivity varied in different liquid and gaseous dielectrics by an amount approximating in some cases to 0.2 of one per cent of its air resistance at the same temperature.

In a later paper, entitled "A Necessary Modification of Ohm's Law,"[2] I referred to a similar observation made upon the conductivity of a silver wire.

The apparatus used in the experiments referred to in the above-mentioned articles consisted of a copper tube 120 cm. in length and 2.5 cm. in internal diameter, closed at the ends with copper plugs provided with stopcocks. To the inside end of one end plug was connected a copper wire 1 mm. in diameter, which was stretched lengthwise through the center of the tube, and passed out through an insulating plug in the center of the other end plug. The resistance of the wire and tube was measured at various tem-

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[1] Leland Stanford Jr. University Publications. Studies in Electricity, No. I.

[2] Phil. Mag., January, 1893, Vol. 35, p. 65.

peratures when the tube contained air, and again when the tube contained other liquid and gaseous dielectrics. A side tube midway between the ends of the long tube served to admit a thermometer, by means of which the temperature of the dielectric inside the tube and near the wire was measured.

Some fifteen different liquid and gaseous dielectrics were used, and, in general, the conductivity of the wire was found to vary from its air conductivity at the same temperature by an amount which was different for each dielectric used, and which was constant for any particular dielectric.

The accuracy of the observation was attacked upon both theoretical and experimental grounds (see especially *The Electrician*, London, of January 13, 1893, and Professor Henry S. Carhart in the Physical Review, Vol. I., p. 321), and though it had been verified by me with several different wires, and though I had collected considerable material bearing upon the nature of the phenomenon, I have thought best to publish nothing further upon the subject until the observation had been verified by some one outside of my own laboratory.

I have recently received a memoir by Professor Grimaldi and Dr. Platania, of the University of Catania,[1] giving the results of a long and very careful series of experiments upon the resistance of a copper wire in air and petroleum. These researches have been conducted with greater refinement and more delicate apparatus than have any previous experiments upon the same subject with which I am acquainted. The results show a degree of concordance quite remarkable, when the difficulties of the determinations are taken into account. In every case the resistance of the wire in petroleum was found to be less than in air. This difference in resistance was, however, when reckoned as a percentage of the whole resistance of the wire, only about one-twelfth as great as in the case of the wire with which the phenomenon was first dis-

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[1] Sulla Resistenza Elettrica dei Metalli nei diversi Dielettrici. Memoria del Dott. Giovan Pietro Grimaldi, Professore di Fisica nella Regia Università di Catania, e Dott. Giovanni Platania, Assistente al Gabinetto di Fisica della stessa Università. Parte I. Ricerche sulla variazione di resistenza del rame nel petrolio. See also, Dal Bollettino mensile dell' Accademia Gioenia di Scienze Naturali in Catania Fascicolo XXXVIII., seduta del mese Dicembre 1894. Also Nuovo Cimento July 1895.

covered by me; but the total variation in resistance amounted, taking the mean of all the determinations, to 0.00002 ohm, while in the same dielectric with the wire originally used by me it amounted to 0.00006 ohm. The wire used by Signors Grimaldi and Platania was 304 mm. in length, and 0.22 mm. in diameter. Its variation in resistance per unit length was accordingly greater than in the wire used by me, while the corresponding surface exposed was less than one-fourth as great.

The intelligence and care shown in the published work of Signors Grimaldi and Platania, and the remarkable uniformity of their results, make it improbable that the existence of the phenomenon will again be questioned.

The method and apparatus used in the following experiments were practically the same which I described in my former papers. The wires whose conductivities were to be measured were stretched lengthwise through the tube used in the earlier experiments, and were sometimes soldered and sometimes connected by means of a binding screw to the inner end of one plug, and were carried through the insulating plug at the other end of the tube. The resistance of the wire and tube was at first measured by means of a Hartmann & Braun resistance box and bridge, with bridge arms of 1 : 1000, the comparison coils being divided to tenths of an ohm. Later, a Nalder Brothers resistance box and bridge, with arms of 1 : 10000 was used, the comparison coils being divided to tenths of an ohm. The galvanometer used gave a noticeable deflection for a change in resistance of 0.00002 ohm, and later for 0.00001 ohm.

The temperature of the interior of the tube was measured by a standard thermometer graduated to 0.1°, inserted into the side tube with its bulb in contact with the wire, and read through a telescope which enabled the observer to estimate to 0.01° with a fair degree of accuracy.

The wire first used had with the tube a resistance of 0.0335 ohm at 18° C., and a temperature variation of 0.000014 ohm for one-tenth of a degree centigrade. By reversing the current it was possible, even with the least sensitive galvanometer used, to estimate the resistance accurately to 2 in the fifth decimal place; and with the galvanometer used later, an error of 1 in the fifth decimal place would not be made, even without reversing the current. This, while not the highest attainable accuracy in resistance measurement, is sufficiently accurate for the work, since the temperature of the wire could not be known with certainty to a greater accuracy than 0.1°. Had the measurements been made at a temperature differing greatly from the room temperature, or had the wire been perceptibly heated by the current, even this degree of accuracy would be improbable, since what was really observed was the temperature of the thermometer in the tube near the wire, and the small wires used would almost certainly change in temperature more rapidly than the thermometer. To guard against a possible error of this kind, the measurements were all made at the room temperature, which very rarely varied so much as 10° in twenty-four hours. The measurements were also made at all hours of the day, and sometimes late at night, in order that approximately the same number might be made with rising as with falling temperature.

To guard against the error due to heating of the wire by the current, the resistance of the wire at the same apparent temperature was observed for a wide range of current strength, and the current strength was kept far below the point where the resistance of the wire seemed to increase. The zero method of measurement was used throughout, and the current was passed through the wire only long enough to enable the galvanometer deflection to be read. In the first work, in order to secure a constant current strength, a battery of thirty-two silver chloride cells with high internal resistance was used with 100 ohms additional resistance in the battery circuit. Later, one Edison-Lalande cell was used with a resistance of from 50 to 100 ohms in the battery circuit.

That temperature fluctuations did not cause serious error may be seen from the data published with the first mentioned paper. The curve shown in Fig. 3 of that paper is reproduced here as Fig. 1. It represents the resistance of the wire in air, and in the gasoline burning gas used in the laboratory. There are twenty-six measurements made with the tube filled with air. These were made at irregular intervals for six days, the tube having been in the meantime filled with burning gas, and seventeen measurements made on three successive days with the wire in this dielectric. The tube and wire were neither disconnected nor moved in changing the dielectric. The gas was admitted through one of the end stopcocks, which was attached by a rubber tube to a gas cock in the laboratory, and was removed by blowing air through the tube with a bellows.

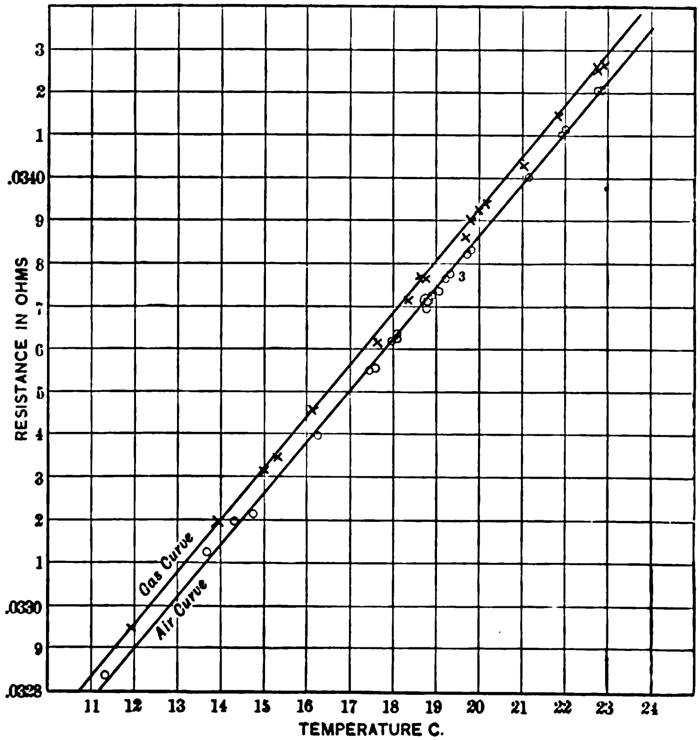

Fig. 1.

Of the twenty-six points platted for the air measurements, nineteen were made before the tube was filled with the gas, and seven were made after the gas had been removed. The greatest distance of any single air point from the curve corresponds to a resistance of 0.00002 ohm, or a temperature variation of 0.14°. In the seventeen measurements made with the tube filled with the burning gas, the greatest distance of any point from the curve corresponds to a difference in resistance of 0.000025 ohm, or a temperature variation of 0.15°, while only one point in the seventeen is more than 0.00001 ohm from the curve.

The average difference in the resistance of the wire and tube with the dielectrics named was 0.000058 ohm, corresponding to a temperature difference of 0.41°, while the nearest approach of any gas point to the air curve represents a difference in resistance of 0.00005 ohm, corresponding to a temperature difference of 0.36°.

That the temperature of the wire can be known with sufficient accuracy when the above precautions are taken is shown by the data published in the article by Professor Carhart, of which mention has already been made. In the investigation reported by Professor Carhart, a tube and wire combination similar to the one above described was heated up to 30° C. by warm water, and a series of resistance measurements was made while the temperature was falling to 20° C. Even with this arrangement, and with a thermometer reading only to half degrees, and a wire whose resistance varied by 0.000018 ohm for one-tenth of a degree, the different measurements show a very uniform decrease of resistance for the estimated decrease of temperature.

I lay special stress upon this point, because in the editorial article in *The Electrician*, previously referred to, the writer charges that it is "a great assumption to suppose that the temperature of the wire is the same as that of the dielectric," and says: "The wire is, of course, being heated by the current, and a slight change of temperature would necessarily result from change of emissivity, owing to the different thermal properties of the various dielectrics used." This explanation would hardly have been offered had the author read with any care the article which he was criticising, since it would make it necessary to assume from the data there given that the temperature of the wire in petroleum was 0.43 of a degree *less* than in air, while in petroleum containing a little wood alcohol its temperature with the same current through it as before was 0.5 of a degree *greater* than in air. As a matter of fact, increasing the current strength fourfold did not alter the apparent resistance of the wire at the same temperature. In the very careful provisions made for maintaining the wire at constant temperature by Signors Grimaldi and Platania, this possibility of error was still further eliminated, so that it is certain that, whatever else may be the cause of the phenomenon, it is not due to a temperature variation of the wire.

The following table gives the change in resistance observed in the above-mentioned wire in eight different dielectrics, and the temperature change necessary to account for such variation in resistance upon the hypothesis advanced by *The Electrician.*

Dielectric.	Resistance change.	Equivalent temperature change.
Petroleum	−0.00006 ohm	−0.43 degree
CS_2 and turpentine	−0.00003 ohm	−0.2 degree
Wood alcohol and benzine . .	+0.00005 ohm	+0.36 degree
Absolute alcohol	+0.00006 ohm	+0.43 degree
Wood alcohol and petroleum .	+0.000075 ohm	+0.53 degree
Laboratory burning gas . . .	+0.000058 ohm	+0.4 degree
Chloroform vapor	+0.00005 ohm	+0.36 degree
Ether vapor	+0.000083 ohm	+0.6 degree

Following the publication of my first paper upon this subject, a number of measurements were made with a silver wire 1.1 mm. in diameter, using as dielectrics air, petroleum, wood alcohol, absolute alcohol, ether vapor, chloroform vapor, laboratory burning gas, and a mixture of wood alcohol and petroleum. While the same phenomenon was observed as with the copper wire previously used, the variation in resistance was not so great. The most important difference, however, was in the different order of arrangement of the dielectrics with reference to their influence upon the conductivity of the wire. While the copper wire had shown a lower resistance in petroleum than in air, the resistance of the silver wire was very slightly increased in petroleum; and whereas the resistance of the copper wire had been greater in sulphuric ether vapor than in any other dielectric used, the resistance of the silver wire was less in the ether vapor than in any of the other dielectrics. The following table will show the results of the measurements made upon the silver wire: —

DIAMETER OF WIRE, 1.1 MM.; RESISTANCE OF WIRE AND TUBE AT 18° C., 0.02705 OHM; TEMPERATURE VARIATION FOR 0.1 DEGREE, 0.000009 OHM.

Dielectric.	Resistance change.	Equivalent temperature change.
Petroleum	+0.00002 ohm	+0.2 degree
Absolute alcohol	+0.00003 ohm	+0.3 degree
Wood alcohol	+0.000045 ohm	+0.5 degree
Wood alcohol and petroleum	+0.000046 ohm	+0.5 degree
Ether vapor	−0.000025 ohm	−0.3 degree
Chloroform vapor	+0.000025 ohm	+0.3 degree
Laboratory burning gas	Uncertain. Resistance slightly greater than in air	

The results hitherto mentioned have been referred to in previous publications. Those which follow were made under practically the same conditions, except that the temperature of the room was more constant, and rarely varied so much as five degrees in twenty-four hours. The time used in making a single set of comparison measurements varied from one to two weeks, during which time several measurements were usually made each day. Care was taken, as before, that approximately the same number of measurements should be made with rising as with falling temperatures.

The copper wire already mentioned will hereafter be referred to as C_1. Its diameter, as before stated, was approximately 1 mm. In order to observe any possible effect of an increase of surface of the wire, the same tube was provided with a copper wire, of 1.27 mm. in diameter, hereafter designated as C. The resistance of this wire and tube when the tube was filled with air at 20° C., was 0.02618 ohm. The resistance when the tube was filled with the mixture of air and gasoline vapor used as burning gas in the laboratory was 0.02626 ohm, showing an increase in resistance of 0.00008 ohm.

With the wire C_1, which was of the same length in the tube, the resistances in these two media at the same temperature was respectively 0.03375 ohm, and 0.03381 ohm, showing a change in resistance in the burning gas of 0.00006 ohm. This showed that while the surface of the wire had been increased about 60 per cent, the difference in resistance had been increased about 30 per cent. As this is the greatest variation observed in any wire with the change in dielectric, I give in Fig. 2 the curves representing the resistance of the wire in the two media. The data upon which the figure is based are given below. The only change made in the apparatus when the gas was introduced was the opening and closing of the stopcocks in the end plugs, as the tube was already attached to the gas cock in the laboratory.

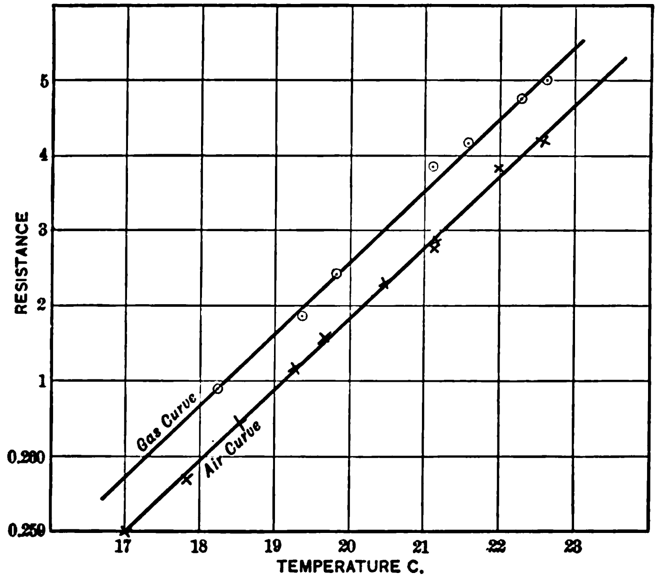

Fig. 2.

In order to determine whether all the dielectric in the tube was concerned in the resistance change, or only a thin layer of it in contact with the wire, the wire was withdrawn from the tube, and its surface was very thinly coated with paraffine oil, after which it was replaced in the tube, and a second set of measurements was made with the same dielectrics as before. These measurements gave exactly the same resistance in the two dielectrics. This, together with the fact, mentioned in my first paper, that after the tube had contained a liquid dielectric the wire frequently required a considerable time before it returned to its air resistance, has led me to believe that the phenomenon is due to a very thin film of the dielectric adhering to the surface of the wire, and possibly absorbed to some extent by the wire. It was especially noticed that after the tube had contained ether vapor it required a long time, frequently several days, to return to its previous air resistance. In one case, the wire continued to show an augmented resistance, apparently due to ether vapor, after air had been drawn through the tube by a filter pump for more than twenty-four hours, and it returned to its air resistance only after the tube had been filled with alcohol for some time and was then emptied and dried. It was also noticed that during all this time the odor of the ether could be detected in the tube.

COPPER WIRE C_2, 1.27 MM. IN DIAMETER.

Date.	**Hour.**	**Dielectric.**	**Temperature.**	**Resistance.**
Nov. 4	12.30	Air	21.1−	0.02629
Nov. 4	3.30	Air	22.6	0.02642
Nov. 4	5.45	Air	22.0	0.02638−
Nov. 5	10.30	Air	18.5	0.02604−
Nov. 5	11.45	Air	19.25	0.02612
Nov. 5	5.10	Air	20.5	0.02623
Nov. 7	10.00	Air	17.0	0.02590
Nov. 7	11.15	Air	17.8	0.02597
Nov. 7	2.00	Air	19.7	0.02616−
Nov. 7	5.00	Air	21.1	0.02628+
Nov. 7	5.10	Burning gas	21.1	0.02639
Nov. 8	8.45	Burning gas	18.2	0.02609
Nov. 8	11.00	Burning gas	19.8−	0.02624
Nov. 8	1.45	Burning gas	21.6	0.02642−
Nov. 8	3.20	Burning gas	22.3	0.02647
Nov. 8	5.00	Burning gas	22.7	0.02650
Nov. 9	9.10	Burning gas	19.3	0.02619+

In order to observe whether any effect would be produced by increasing the surface of a given wire, another wire, C_3, 1.27 mm. in diameter, was cut from the same spool as C_2, and was hammered flat to increase its surface. This wire was placed in the tube, and its resistance was measured in the two dielectrics which had been used with C_2, but no increased resistance could be observed in the gas. The wire had been much hardened by hammering, but what change had been produced in its surface is not known.

The next wire used was 1.66 mm. in diameter, and is designated C_4. Instead of giving an increased difference of resistance corresponding to its increase of surface, its resistance change in burning gas was less than that of either C_1 or C_2. Its resistance in air at 18° was 0.01915 ohm, and in burning gas at the same temperature it was 0.01917 ohm, showing a difference of only 0.00002 ohm. The same wire was tested in absolute alcohol and in petroleum poured in after the alcohol had been drawn off, in both of which dielectrics it gave a smaller difference of resistance than did C_1. In alcohol this difference amounted to about 0.00004 ohm, and in petroleum with trace of alcohol to about 0.00005 ohm.

Another copper wire, C_5, 1.27 mm. in diameter, was cut from the same spool as C_2, and was amalgamated upon the surface by immersing it a short time in a solution of mercuric chloride. Its resistance at 20° was 0.02640 ohm in air, and 0.02646 ohm in ether vapor. In freeing the tube from ether vapor, one of the contacts was loosened, and the apparatus was disconnected and remained standing unused from Feb. 9 to March 6. It was then reconnected, and measurements were made with air, burning gas, petroleum, and a mixture of wood alcohol and petroleum. By the time these measurements were undertaken the surface of the wire had become blackened, instead of showing the bright mercury surface, and the resistance of the wire had appreciably increased. All of the following measurements made with this wire showed much more than the usual irregularity, but in the case of air and petroleum this irregularity was not great enough to bring any point made with the wire in one dielectric upon the curve made with the wire in the other dielectric. The resistances at 20° were as follows: In air, 0.02660; in petroleum, 0.02656. In the case of burning gas and the mixture of wood alcohol and petroleum, the irregularity was so great that some of the points fell upon one side of the air line, and some upon the other, and the measurements were accordingly rejected.

The apparatus was next fitted with a copper wire, C_6, about 0.35 mm. in diameter, and its resistance was measured in air, burning gas, and petroleum. In this wire, a change of temperature of 0.1° corresponded to a change in resistance of 0.00008 ohm, so that any resistance change in the different media was masked by possible temperature differences. The mean of fifteen measurements in air, and five in burning gas, seemed to indicate an increase in resistance in the gas of about 0.00001 ohm, but this was probably purely accidental. In petroleum, no difference could be observed. Evidently, the detection of the resistance changes in such fine wires requires a more delicate means of measuring temperature than was afforded by my apparatus. That this difference in resistance may still be considerable in much finer wires than any used by me is shown in the work of Signors Grimaldi and Platania, where a wire only 0.22 mm. in diameter gave a difference in resistance per unit length as great as my wire C_1.

Silver Wires.

The measurements made with the silver wire referred to in my paper in the *Philosophical Magazine* have already been mentioned. The actual resistances observed at the same temperature in the various dielectrics used are given below. These numbers are the mean of three series of measurements, but not all the dielectrics were used in each series.

SILVER WIRE, S_1, 1.1 MM. IN DIAMETER.

Dielectric.	Resistance.	Dielectric.	Resistance.
Air	0.02722 ohm	Ether vapor . . .	0.02719– ohm
Petroleum	0.02724– ohm	Chloroform vapor .	0.02725– ohm
Wood alcohol . . .	0.02727– ohm	Wood alcohol and petroleum . . .	0.02727– ohm
Absolute alcohol . .	0.02725 ohm		

After the above measurements were made, the wire was removed from the tube, and was coated electrolytically with copper from a bath of copper sulphate. The copper coating, while adherent to the silver, was very rough and porous, and it was very difficult to remove any adhering liquid from it. The measurements made with it were more irregular than those which had been made with the wire before coating it with copper, but there was no possibility of confounding the air curve with the curve made when either of the other dielectrics was used. The resistances at 20° in the dielectrics used were as follows: —

SILVER WIRE, S_2, S_1, COATED ELECTROLYTICALLY WITH COPPER.

Dielectric.	Resistance.	Dielectric.	Resistance.
Air	0.02561	Petroleum and wood alcohol	0.02564
Petroleum	0.02562+	Ether vapor	0.02559

It will be seen that not only the arrangement of the dielectrics with regard to their influence upon the conductivity of the wire is the same as before the wire was copper-plated, but that the absolute difference in resistance is almost the same as before. This result was entirely unlooked for on my part.

The following table is intended to show the resistances at corresponding temperatures in the dielectrics used of all the wires above mentioned: —

RESISTANCES.

Dielectrics.	C_1	C_2	C_3	C_4	C_5
Air	0.03375	0.02618	0.02842	0.01915	0.02640+
Petroleum	0.03369	—	—	?	—
Wood alcohol. . .	0.03376	—	—	—	—
Benzine	0.03377	—	—	—	—
Wood alcohol and benzine	0.03380	—	—	—	—
Absolute alcohol . .	0.03381	—	—	0.01919	—
Wood alcohol and petroleum . . .	0.03382	—	—	—	—
Alcohol vapor. . .	0.03377(?)	—	—	—	—
Chloroform vapor. .	0.03380+	—	—	—	—
Burning gas . . .	0.03381	0.02626	0.02842	0.01917	—
Ether vapor . . .	0.03383	—	—	—	0.02646

RESISTANCES (*continued*).

Dielectric.	C_5 second series.	C_6	S_1	S_2
Air	0.02660	0.17715	0.02722	0.02561
Petroleum	0.02656	0.17715	0.02724–	0.02562+
Wood alcohol. . .	—	—	0.02727–	—
Absolute alcohol . .	—	—	0.02725	—
Wood alcohol and petroleum . . .	?	—	0.02727	0.02564
Alcohol vapor. . .	—	—	—	—
Chloroform vapor. .	—	—	0.02725–	—
Burning gas . . .	?	0.17716	—	—
Ether vapor . . .	—	—	0.02719–	0.02559

Thus far I have offered no explanation of the above-mentioned phenomenon. The only hypothesis which I am able to advance, while it would suggest the probability of a difference in resistance in different dielectrics, would hardly account for the irregularity observed in different wires. It will be noticed, however, that while the irregularity in quantitative results is very great, the variations in resistance with wires of the same material are always in the same direction. This is true of the copper wire before and after having its surface amalgamated, and of the silver wire before and after being copper-plated. In the results already referred to, which have been published by Signors Grimaldi and Platania, the variation observed between the air and petroleum resistances of the copper wires used, while less than some of the variations observed by me, were in the same direction. Since the hammering of a wire or the oiling of its surface may produce such a marked change in the degree to which its conductivity is affected by different dielectrics, it is not strange that different observers, working with different samples of wire, should get very different results; and there is, accordingly, nothing contradictory in Professor Carhart's results and my own.

The only explanation which I am able to offer is based upon the assumption that the passage of a current through a metallic conductor is accomplished by means of disruptive discharges from molecule to molecule through the intervening ether. These discharges would, like the discharge of a Leyden jar, be of an oscillatory character, although the discharge in one direction would be of much greater intensity than in the opposite; and their rate of oscillation would be affected by the elasticity and density of the intervening ether. While I am not aware that the rate of oscillation of a condenser discharge has been observed to vary in different dielectrics, it is known that the capacity of a condenser does so vary, and this would necessitate a variation in the rate of oscillation of its discharge. In the case of the outer layer of molecules of a wire, the surrounding dielectric would influence the rate of oscillatory discharge between contiguous molecules. If the dielectric should penetrate for some distance into the wire, the rate of discharge of a correspondingly great number of layers of molecules would be affected. That gases, at least, frequently do penetrate for some distance into metals is well known. In the case of some of the dielectrics used by me, something of this character seemed to take place. This was especially noticeable in the case already referred to of the sulphuric ether vapor and the copper wire. If, however, the dielectric should penetrate to a definite depth into the wire, the difference in resistance should be more marked in fine wires than in coarse ones, since a larger proportion of the molecules would have their rate of discharge influenced by the surrounding dielectric. My own results are too irregular to enable me to decide whether this is the case or not, but the variation in resistance observed in the fine wire used by Signors Grimaldi and Platania was much greater in proportion to the cross-section of the wire than in any of the wires used by me.

It seems probable that after a current has been once established in a wire, all the molecules in a given cross-section will receive their charges at the same time, and part with them at the same time. This would necessitate the same rate of discharge for both external and internal molecules. It might, nevertheless, occur that the hastening or retarding of the rate of discharge of the external molecules would affect the rate of all the molecules of the wire.

One conclusion which seems necessarily to follow from this hypothesis concerning conductivity is that the variation in resistance in different dielectrics should be greater for alternating than for direct currents. I have not, however, been able to verify this conclusion, owing to the difficulty experienced in measuring resistance accurately by means of alternating currents.

In my first paper, I published the results of some attempts to find a relation between the effect of the different dielectrics upon the conductivity of the copper wire surrounded by them and their refractive index for light. In this attempt I was unsuccessful, but scarcely more so than have been the other attempts to establish a relation between the refractive index and the specific inductive capacity. Aside from the general discrepancy observed between the values of these two properties of dielectrics, it seems probable that neither Fresnel's nor MacCullagh's theory of the propagation of light in material bodies will give a complete explanation of the phenomenon, and that the refractive index of a substance will not alone enable one to judge of the elasticity or the density of the ether in that substance.

In a similar manner, if some dielectrics are absorbed more than others by the surface of a conductor, a mere knowledge of the specific inductive capacity of a dielectric will not enable one to foretell its effect upon the conductivity of a wire immersed in it.

I am aware that this hypothesis as to the nature of metallic conductivity leads to certain conclusions not experimentally established as to the nature of the field of force surrounding the current. If such oscillatory discharges as are here presumed take place between the molecules of a conductor, the entire field about the conductor would be filled with Hertzian waves of very short period. Whether the magnetic field about a current can be accounted for on the assumption of the existence of these waves, I do not know. The velocity of electro-magnetic induction could be satisfactorily explained in this way, and it is certain that very rapid ether vibrations of this kind can produce magnetic effects, but whether the magnetic polarity of the field may be accounted for by the greater intensity of the discharges in one direction than in the opposite, I do not know.

STANFORD UNIVERSITY, June 28, 1895.

A STUDY OF THE POLARIZATION OF THE LIGHT EMITTED BY INCANDESCENT SOLID AND LIQUID SURFACES. II.

By R. A. Millikan.

X.

Application of Fresnel's Formulæ for Vitreous Reflection.

THE main object of this research being to determine whether or not polarization by emission could be experimentally proven to be a phenomenon of refraction, Fresnel's laws for reflection and refraction, which have been shown by many experiments to accurately represent the facts, were now applied to the determination of the amounts of polarization which should be produced by single refraction of light passing through the boundary surface between uranium glass and air. In order to apply these laws it is necessary to assume that all of the light emitted by the uranium glass, whether coming *from the surface molecules or from the interior layers*, has undergone the process of refraction — an assumption not contained in Arago's explanation of the cause of the phenomenon.

Taking the intensity of the incident ray as unity, Fresnel's formulæ give for the intensities of the reflected and refracted rays when the incident beam is plane polarized in the plane of incidence,

$$\text{reflected ray} = r_1 = \frac{\sin^2(\alpha-\beta)}{\sin^2(\alpha+\beta)},$$

$$\text{refracted ray} = r_1' = \frac{4\cos^2\alpha\sin^2\beta}{\sin^2(\alpha+\beta)},$$

α being the angle of incidence and β the angle of refraction.

For a ray plane polarized in a plane perpendicular to the plane of incidence

$$\text{reflected ray} = r_2 = \frac{\tan^2(\alpha-\beta)}{\tan^2(\alpha+\beta)},$$

$$\text{refracted ray} = r_2' = \frac{4\cos^2\alpha\sin^2\beta}{\sin^2(\alpha+\beta)\cos^2(\alpha-\beta)}.$$

Since ordinary light may be considered as composed of two equal plane polarized beams, polarized in planes at right angles to each other, the amount of polarization in a beam of natural light which has undergone single refraction is

$$\frac{\frac{1}{2}r_2' - \frac{1}{2}r_1'}{\frac{1}{2}r_2' + \frac{1}{2}r_1'} = \frac{\dfrac{1}{\cos^2(\alpha-\beta)} - 1}{\dfrac{1}{\cos^2(\alpha+\beta)} + 1} = \frac{1-\cos^2(\alpha-\beta)}{1+\cos^2(\alpha+\beta)} = p.$$

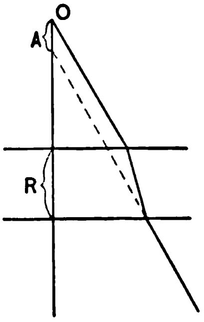

Fig. 4.

The only unknown quantity in this formula is the angle β. In order to determine p for any given angle it was only necessary to determine the index of refraction of the uranium glass.

The glass being of considerable thickness, the microscope method was the one best adapted to this determination. d being the thickness of the glass, and a the change in focus due to the introduction of the glass between the object O and the objective, the index u is given by the formula (see Kohlrausch, *Praktische Physik*, p. 151),

$$u = \frac{d}{d-a} = \frac{326\text{ mm.}}{326\text{ mm.} - 110\text{ mm.}} = 1.51 = \frac{\sin\alpha}{\sin\beta}.$$

The substitution of the various values of β, thus found, in the formula for p gave the following values: —

α	β	p	p (observed)
87° 30′	41° 25′	0.351	0.358
85°	41° 17′	0.315	0.293
80°	40° 42′	0.251	0.245
75°	39° 46′	0.206	0.191
70°	38° 29′	0.153	0.139
65°	36° 53′	0.125	0.098
50°	30° 29′	0.058	0.039

The correspondence between the results given by experiment and those given by this calculation from Fresnel's formulæ was unexpected. The experiments were completed more than a month before any calculations were made, so that I had no idea at the time of making the experiments what would be the nature of the results given by calculation.

The differences between the two sets of values are hardly greater than the possible errors of observation. The differences at 65° and 50° are quite large, but might have been due to the lack of perfect uniformity in the luminous surfaces. On the whole, the agreement between the two sets of results indicates strongly that in the case of uranium glass, at least, the phenomenon is one of simple refraction at the surface; but that the WHOLE *of the emitted light undergoes the refraction process.*

XI.

Experiments upon Platinum.

It is evident that no such comparisons as those just made for uranium glass could be made for the case of incandescent metals, unless, in the first place, the surface experimented upon could be assumed to be a perfectly definite, non-diffusing surface. The chief source of difficulty in the work upon platinum was to fulfil this condition.

It was found, after considerable work had been done upon platinum, that continual heating roughened the surface to a slight degree, and changed the amount of polarization. The results of several sets of laborious observations upon platinum were discarded altogether, because they were found to be erroneous from this cause. However, the change is so gradual that a well-polished platinum surface may be heated to incandescence for several minutes without showing any perceptible change in character. The rapidity of the change could be delicately observed by viewing the surface at a large angle of incidence by means of the polarimeter. For a period of two or three minutes no change was perceptible in the equality of the images, but for much longer periods of heating the slow blistering of the surface began to be manifest in the disturbance of the equality of the images. Hence, in order to avoid this error, the surface of the platinum was carefully polished with rouge after every set of readings for a given angle.

A second slight source of error in the observations upon platinum was the lack of exact horizontality in the surface examined. The attempt was made to avoid this error by rotating the instrument through 90° according to the suggestion of Cornu. This brought the extraordinary image either above or below the ordinary; hence, when the angle of emergence was very large, the two images corresponded to points on the surface at a considerable distance from each other, as shown in the figure. This introduced the likelihood of a much greater error than that due to a slight error in horizontality. The incandescent platinum was therefore rendered as nearly horizontal as possible by comparison with carefully leveled reference planes placed in the immediate vicinity. The adjustment could thus be easily made to within one degree.

FIG. 5.

In all of the following experiments sheets of rolled platinum 0.06 mm. in thickness were heated to a white heat by means of a Bunsen burner, care being taken to prevent light from any other sources from vitiating the results. The observations are here given in full.

80°		70°		60°	
Left.	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**
23.1	12.0	30.2	20.7	36.9	24.5
21.4	11.5	32.2	21.0	36.8	26.1
22.5	11.3	32.1	21.2	35.0	25.0
22.3	10.9	31.0	20.5	37.0	25.4
23.2	11.4	32.1	21.3	35.6	25.5
				35.5	25.4
22.5	11.42	31.52	20.94	36.05	25.2
$2\,w = 34^\circ.0$ $p = 0.829$		$2\,w = 52^\circ.4$ $p = 0.610$		$2\,w = 61^\circ.25$ $p = 0.481$	

50°		40°		30°	
Left.	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**
40.0	29.7	45.6	35.0	47.6	38.0
39.1	29.0	45.5	33.3	47.5	36.3
41.2	29.3	44.4	34.2	47.2	36.2
39.4	28.5	43.8	34.6	47.8	37.1
41.0	29.6	44.4	34.5	48.0	36.0
40.14	29.2	44.74	34.3	47.62	36.72
$2w = 69^\circ.34$		$2w = 79^\circ.0$		$2w = 84^\circ.34$	
$p = 0.349$		$p = 0.191$		$p = 0.099$	

XII.

Application of Cauchy's Formulæ for Metallic Reflection to the Case of Platinum.

Fresnel's formulæ for reflection rest upon the hypothesis that the time required in the process of reflection is infinitesimal in comparison with a wave period, and hence that the phase of vibration of the reflected ray is either the same as that of the incident ray, or else differs from it by the quantity π. It follows from this assumption that the reflected ray is plane polarized, if the incident ray is plane polarized.

When the reflection takes place at the boundary surface between air and a metal, experiment shows this assumption to be incorrect, and hence Fresnel's formulæ become inapplicable.

If the phenomenon here considered be due to reflection, the laws for reflection which apply to the boundary surface between platinum and air are, of course, the laws to apply to the determination of the amounts of polarization which ought to be caused by a single refraction at this boundary.

The application of Fresnel's laws of vitreous reflection requires, as has been seen, the determination of but one constant, the index of refraction, or the ratio of the velocities of propagation of light in the two media. Cauchy extended these laws so as to cover the case of metallic reflection by introducing another constant which he calls the coefficient of extinction. The constant corresponding to the index of refraction is, as in the case of transparent bodies, the tangent of the angle of maximum polarization. The coefficient of extinction is a constant depending upon the opacity of the body, and is found from the ratio between the amplitudes, after reflection, of two equal beams polarized respectively perpendicular and parallel to the plane of incidence, and reflected at the angle of maximum polarization. This ratio is evidently the tangent of the azimuth of re-established plane polarization, when the incident beam is polarized in a plane making an angle of 45° with the plane of incidence, plane polarization being re-established after reflection by means of a quarter-wave plate or a Babinet compensator.

This angle may be determined by experiment. Thus the two constants of metallic reflection are, (1) the angle of maximum polarization, and (2) the azimuth of re-established plane polarization at this angle. According to the theory of Cauchy, these two consonants being known, the intensity of a beam reflected at any angle may be calculated.

The complete explanation of Cauchy's theory and the deduction of Cauchy's formulæ were given by Eisenlohr in 1858. (See *Pogg. Ann.* 104, p. 368.)

The final forms of the formulæ given by Eisenlohr are

$$K^2 = \tan(f - 45^\circ),\quad K'^2 = \tan(g - 45^\circ), \tag{1}$$

in which K^2 is the intensity of the reflected beam when the incident beam is polarized in the plane of incidence, K'^2 the intensity when the incident beam is polarized in the plane perpendicular to the plane of incidence, and f and g are variables given by the equations

$$\left.\begin{aligned} \cot f &= \cos(e+u)\sin\left(2\arctan\frac{c\theta}{\cos a}\right) \\ \cot g &= \cos(e-u)\sin\left(2\arctan\frac{\cos a}{c\theta}\right) \end{aligned}\right\}, \tag{2}$$

in which u and c are variables determined by the relations

$$\left.\begin{aligned} \cot(2u+e) &= \cot e\cos\left(2\arctan\frac{\sin a}{\theta}\right) \\ c^2 &= \frac{\sin 2e}{\sin(2u+2e)} \end{aligned}\right\}, \tag{3}$$

in which a is the angle of incidence and e and θ are given by the final formulæ

$$\left.\begin{aligned} \sin 2e &= \tan^2 A \sin (4H - 2e) \\ \theta &= \sin A \sqrt{\frac{\sin 4H}{\sin (4H - 2e)}} \end{aligned}\right\}. \tag{4}$$

A is the angle of maximum polarization, called the "principal angle of incidence," and H is the azimuth of re-established plane polarization when the incident beam is polarized in the azimuth 45°. H is called the "prime azimuth." The forms here given for e and θ are due to Jochman (see *Pogg. Ann.* CXXXVI., p. 856). These formulæ, first published by Cauchy in 1839, were shown by Jamin, by an elaborate series of measurements, to very closely represent the facts of reflection from metallic surfaces. The prime angles of incidence and the prime azimuths for all the common metals and for the different Fraunhofer lines were determined by Quincke in 1874 (see *Phil. Mag.* XLVII., p. 221).

Now, in order to apply these formulæ to calculations similar to those which have already been made with Fresnel's formulæ upon uranium glass, it was necessary to assume, as before, that the whole of the light emitted had undergone refraction, and it was also necessary to know the two optical constants for platinum at the temperature of incandescence. These constants could not be determined. However, in a number of experiments made by W. R. Grove (see *Phil. Mag.* (4) 17, p. 177) upon the reflection of light from incandescent platinum, he was unable to detect any change in the reflecting properties of the platinum due to the fact of incandescence. Plane polarized light being reflected from the cold surface, the plane of polarization of the reflected beam was not affected by heating the platinum to the incandescent temperature. These experiments were not performed with delicate apparatus, yet they give reason to assume that the optical constants of platinum are not greatly altered by temperature.

Assuming, then, the values of A and H given by Quincke for the sodium line, the calculations of the amount of polarization in the emitted beam were made for all the angles of emergence for which experiments had been made. These calculations were made as follows: —

Quincke's values for the D line are

$$A=77^\circ\ 8',\ H=32^\circ\ 46'.$$

Formulæ (4) give

$$e=64^\circ\ 22',\ \log\theta=0.62276.$$

Then for $a=80^\circ$ formulæ (3), (2), and (1), give

$$K^2=0.9348,\ K'^2=0.4013.$$

Assuming now the incident beam to have had an intensity unity, the emitted beam polarized in the plane of emergence would have an intensity

$$1-K^2=0.0652$$

and the beam polarized in the plane perpendicular to the plane of emergence an intensity

$$1-K'^2=0.5987.$$

Therefore the degree of polarization $=p=\dfrac{0.5987-0.0652}{0.5987+0.0652}=0.834.$

The complete results of the calculations for the platinum are as follows: —

a	K^2	K'^2	$1-K^2$	$1-K'^2$	p
80°	9348	4013	0652	5987	0.834
70°	8757	4044	1243	5957	0.655
60°	8234	4813	1766	5187	0.492
50°	7782	5483	2218	4517	0.341
40°	7409	5981	2591	4019	0.216
30°	7115	6330	2885	3670	0.117

Considering the number of assumptions which have been made, the correspondence between these quantities and those given by experiment is altogether remarkable, and points with as much certainty as the work upon uranium glass to the conclusion that the phenomenon is simply one of refraction.

XIII.

Difference in Color of Images.

In the course of these observations upon platinum, another at first unaccountable phenomenon was noticed. At large angles of emergence the color in the two images was notably different. The image corresponding to the component polarized perpendicular to the plane of emergence was markedly redder than the other.

If we assume the phenomenon to be due to reflection and refraction, this appearance is readily explained by a reference to Quincke's values for the angles of maximum polarization for the different Fraunhofer lines. This angle for the line *C*, Quincke gives as 78° 28′, and for the line *G* his value is 73° 39′. Now if a is the amplitude of vibration in the reflected ray when the incident beam is polarized in the plane of incidence, and a' the amplitude when the plane of polarization of the incident beam is perpendicular to the plane of incidence, the angle of maximum polarization will be reached when $\frac{a^2-a'^2}{a^2+a'^2}$ is a maximum, *i.e.* when $\frac{a'}{a}$ is a minimum. The experiments of Jamin show that this angle coincides, at least very nearly, with the angle for which a' is a minimum; a conclusion which one would expect without the aid of experiment. Hence the angle 78° 28′ is that angle for which the component of the *reflected* vibration parallel to the plane of incidence is a minimum for the case of *red* light, and the component of the *emitted* vibration in the same plane is a maximum. On the other hand, the angle of maximum emission of *violet* light in this plane occurred at 73° 39′. Accordingly, it is evident that red light predominates in the beam emitted at the angle 78° 28′, and violet in the beam emitted at 73° 39′. The approximate ratio between the two colors for any angle is shown in Fig. 6. It is evident that light emitted at any angle larger than 75° will be predominantly red. At the same time, the shape of the curves accounts for the lack of any noticeable predominance of violet in the neighborhood of 73° 39′.

The figure shows the curves of intensities of the reflected components of vibration parallel to the plane of incidence as roughly plotted from the values given above. The lines mD, m_1D_1, etc., represent the intensities of the emitted red vibrations in this plane for various angles; while the lines nD, n_1D_1, etc., represent the intensities of the emitted violet vibrations for the same incidences. The lines nM, n_1M_1, etc., are the measure of predominance of red over violet, or *vice versa.* The steepness of the curves at points corresponding to angles greater than the angle of maximum polarization, and the lack of steepness at points corresponding to angles less than the angle of maximum polarization are evidently the causes of the predominance of red at large angles, and the lack of marked predominance of violet at any angles. This characteristic of the curves follows from the fact that the points of maximum polarization correspond to very large angles.

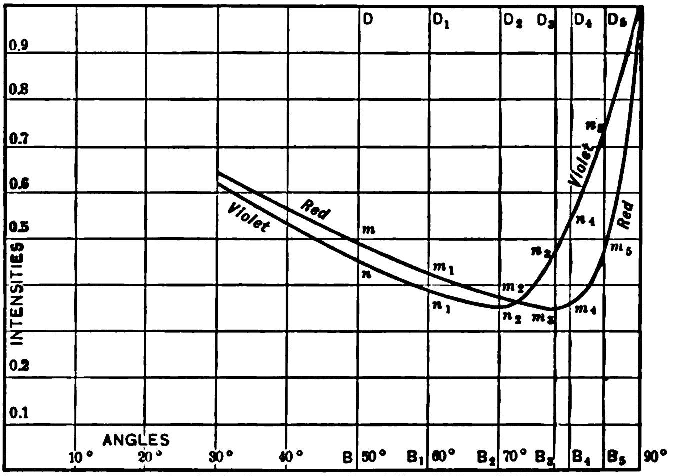

FIG. 6.

XIV.

Experiments upon Silver.

Owing to the great kindness of Mr. Herbert G. Torrey, Assayer of the U. S. Assay Office, I was next able to make a series of observations upon molten silver. These experiments were the most satisfactory of any which were made in the course of the research. All of the sources of error which had existed in preceding cases were here eliminated. The surface was perfectly defined, it was accurately horizontal, and there were no variations in intensity from point to point. The results of the experiments are given in full.

30°		35°		40°		45°	
Left.	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**
46.0	36.0	44.5	33.4	43.3	31.7	42.0	30.5
47.2	36.0	45.0	33.7	42.8	32.5	42.0	31.0
46.5	35.0	44.5	34.0	43.3	32.0	41.1	31.3
46.3	35.0	45.0	34.0	43.5	32.0	42.5	30.5
46.5	35.5						
46.5	35.5	44.75	33.8	43.72	32.05	41.9	30.8
$2w = 0^\circ.82$		$2w = 78^\circ.55$		$2w = 75^\circ.27$		$2w = 72^\circ.7$	
$p = 0.139$		$p = 0.189$		$p = 0.254$		$p = 0.297$	

50°		55°		60°		65°	
Left.	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**
40.6	28.5	38.0	27.0	34.7	24.1	32.0	21.0
40.0	29.0	38.3	27.5	35.0	24.0	32.5	21.5
40.0	29.8	37.5	27.1	34.0	24.1	32.6	21.0
40.5	29.1	37.5	26.3	35.4	23.8	32.5	20.5
40.0	28.8	38.0	26.5	35.7	24.0	32.5	21.5
				34.5	24.0		
40.2	29.04	37.8	26.8	34.9	24.0	32.4	21.3
$2w = 69^\circ.24$		$2w = 64^\circ.6$		$2w = 58^\circ.9$		$2w = 53^\circ.7$	
$p = 0.354$		$p = 0.429$		$p = 0.517$		$p = 0.592$	

70°		75°		80°			
Left.	**Right.**	**Left.**	**Right.**	**Left.**	**Right.**		
30.0	20.0	27.0	16.5	24.1	13.5		
30.0	19.5	27.0	16.5	24.1	13.5		
29.6	19.9	27.0	16.5	24.2	14.0		
30.0	20.4	26.5	16.1	23.9	13.7		
30.5	19.5	27.0	16.4	24.0	13.9		
		26.5	15.5				
30.0	19.9	26.8	16.25	24.1	13.7		
$2w = 49^\circ.9$		$2w = 43^\circ.05$		$2w = 37^\circ.8$			
$p =$ 0.644		$p =$ 0.731		$p =$ 0.789			

All of the previous observations had been subject to errors of unknown magnitude, aside from the errors of observation; and the results, while agreeing very closely with the calculated values for some angles, differed from them by considerable amounts at others. For example, the agreement for platinum at 80° was very close, while at 70° the difference was as large as .045. Similarly for uranium glass, the difference at 50° and 65° was quite large. Hence I did not consider the results given by the experiments upon uranium glass and platinum altogether trustworthy as accurate quantitative measurements. The experiments upon silver, however, were free from all possible error so far as I was able to discover, except the observational error. Mention has already been made of the fact that Violle had previously made a number of determinations of the same general nature upon silver. His results do not agree very closely with those given above, being uniformly larger. I am altogether unable to account for the uniformity in the excess of his values over those given by these experiments. His results are here inserted for the sake of comparison.

Angle.	**Violle.**	**Millikan.**
30	0.168	0.139
50	0.383	0.354
60	0.546	0.517
65	0.630	0.592
70	0.708	0.644
75	0.770	0.731
80	0.826	0.789

The application of Cauchy's formulæ to silver was made in the same way as in the case of platinum. For polished silver Quincke gives for the D line,

Prime angle of incidence, $A=72^\circ\ 10'$,
Prime azimuth, $H=41^\circ\ 40'$.
Formulæ (4) give $e=82^\circ\ 34'.3$, $\log\theta=0.4480$.

Formulæ (3), (2), and (1) then give

a	K^2	K'^2	$1-K^2$	$1-K'^2$	p
80	0.9735	0.8037	0.0265	0.1963	0.762
75	0.9606	0.7628	0.0394	0.2372	0.716
70	0.9482	0.7510	0.0518	0.2489	0.655
65	0.9361	0.7540	0.0639	0.2460	0.588
60	0.9250	0.7632	0.0750	0.2368	0.519
55	0.9136	0.7740	0.0864	0.2260	0.446
50	0.9033	0.7869	0.0967	0.2131	0.376
45	0.8937	0.7985	0.1063	0.2015	0.309
40	0.8847	0.8093	0.1153	0.1907	0.246
35	0.8767	0.8187	0.1233	0.1813	0.190
30	0.8695	0.8268	0.1305	0.1732	0.140

It will be noticed that the agreement between these quantities p and those given by my experiments is closer than for either the platinum or the uranium glass; the largest difference being at 80°, where it amounts to 0.027.

XV.

Experiments upon Gold and Iron.

Through the kindness again of Mr. Torrey and the Superintendent of the Subtreasury, I was permitted to make observations upon a pot of molten gold; but accuracy of work was impossible on account of (1) the rapidity with which I was obliged to work; (2) the lack of quiescence of the liquid surface; (3) the impossibility of excluding other light from the surface; and (4) the rapidity of oxidization of the molten gold. The results were therefore altogether untrustworthy as quantitative measurements. Hence no attempt was made to compare them with results given by Cauchy's formulæ. Molten iron was also made the subject of similar observations with equally unsatisfactory results.

XVI.

Discussion of Results.

The comparisons made between experimental determinations and calculated values are condensed in the following tables: —

Uranium glass.				Platinum.				Silver.			
Angle.	**p. obs.**	**p. calc.**	**Difference.**	**Angle.**	**p. obs.**	**p. calc.**	**Difference.**	**Angle.**	**p. obs.**	**p. calc.**	**Difference.**
87½	0.358	0.351	0.007	80	0.829	0.834	−0.005	80	0.789	0.762	+0.027
85	0.293	0.315	−0.022	70	0.610	0.655	−0.045	75	0.731	0.716	+0.015
80	0.245	0.251	−0.006	60	0.481	0.492	−0.011	70	0.644	0.655	−0.011
75	0.191	0.206	−0.015	50	0.349	0.341	+0.008	65	0.592	0.588	+0.004
70	0.139	0.153	−0.014	40	0.191	0.216	−0.025	60	0.517	0.519	−0.002
65	0.098	0.125	−0.027	30	0.099	0.117	−0.018	55	0.429	0.446	−0.017
50	0.039	0.058	−0.019					50	0.354	0.376	−0.022
								45	0.297	0.309	−0.012
								40	0.254	0.246	+0.008
								35	9.189	0.190	−0.001
								30	0.139	0.140	−0.001

In view of the general agreement between the observed and calculated values, and in view of the further fact of the coloration of the images at large angles, so beautifully accounted for by the reflection theory, it may be considered that the phenomenon of polarization of light by emission has thus been quantitatively proven to be a phenomenon of reflection and refraction.

It will be remembered that the apparently insuperable objection to the explanation which Arago offered was that that explanation attributed to all of the surface molecules the property of emitting natural light, and gave as the entire cause of the polarization, the refraction of light which works its way up from a certain depth beneath the surface.

The above calculations were all made upon the assumption that *all* of the light emitted by the glowing body had undergone a refraction. Considering the closeness of agreement be tween the calculated and observed values, it is difficult to escape the conclusion that this assumption is correct, and that *no* particles whatever of the incandescent solid send out into the air natural light, save in the case in which the angle of emergence is zero. This simply means that all of the particles of the light-emitting body, *including* the so-called surface layers, lie within the denser medium, and beneath the plane at which reflection and refraction take place. This relieves the refraction theory of the causes of the phenomenon of its greatest difficulty: viz., the difficulty of conceiving that, in the case of an exceedingly opaque body like platinum, the uppermost molecules send out but a very small proportion of the whole light emitted. If we follow the explanation of Arago and Verdet, we are obliged by the results of this research to conclude that the emitted light originates almost entirely in molecules other than those of the uppermost layer. On the contrary, it seems much more reasonable to assume that in the case of such a body as platinum the light emitted is due mainly to this topmost layer, but that the reflection process takes place entirely *above* the platinum.

Quincke has shown that when light from an external source is reflected at the surface of a metal, the reflection does not take place in the geometrical plane between the two media, but rather takes place in the metal itself, the vibration penetrating for a certain depth into the denser medium. The converse is also doubtless true that the vibration originating in the metal is not reflected instantaneously at the surface of the rarer medium, but is reflected in the layer of air of finite thickness which borders upon the metal. Thus all light originating in the platinum, whether in the surface layer or the sub-surface layers, must undergo the process of reflection and refraction before it can emerge into the air.

Lastly, the calculated values were all obtained under the assumption that the optical constants of the metals are the same for high temperatures as for low; that is, that the reflecting properties of an incandescent metallic surface are precisely the same as the reflecting properties of a cold metallic surface. The closeness of agreement between the results given by this assumption and the facts as determined by experiment seems to warrant the conclusion, that the change in the optical properties of metals due to incandescence is *exceedingly slight;* a conclusion to which the somewhat inexact experiments of Grove upon the reflecting properties of incandescent platinum would also lead.

The results of the investigation may therefore be summarized as follows: —

(1) Experiments upon polarization by emission have been extended to a wider range of substances than had previously been investigated, and these substances have been classified with reference to their power of producing the phenomenon.

(2) The polarization of the light emitted by flourescent bodies has been, I believe for the first time, observed and measured.

(3) The difference in the color of the principal components of the light emanating at large angles from white-hot metals has been observed and explained. So far as I am able to discover, this fact had not been before known.

(4) Some experimental ground has been given for the conclusion that all light originating in an incandescent body, whether in the surface molecules or in the interior molecules, must suffer a reflection and refraction before actual emergence.

(5) The reflecting properties of metals have been shown to be but little, if at all, affected by the fact of incandescence.

(6) The phenomenon of polarization of light by emission has been shown conclusively to be a phenomenon of refraction, first, by the closeness of agreement between a large number of experimental and calculated quantities, and second, by the fact of the difference in the color of the images at large angles of emergence which finds complete explanation in the refraction theory.

In conclusion, I will add that this investigation was suggested to me by Professor Rood, and I wish here to express my thanks to him, and to Professor Hallock, and also to Professor A. A. Michelson, of Chicago University, for aid furnished during its progress. I am also under obligations to Herbert G. Torrey, Assayer of the U. S. Assay Office, who most kindly placed at my disposal large masses of molten gold and silver.

PHYSICAL LABORATORY OF COLUMBIA COLLEGE.

ON TERNARY MIXTURES. III.

By Wilder D. Bancroft.

In addition to the results given in Tables XIX.–XXXI.[1], Pfeiffer made a few measurements on amylalcohol, monochlor-, dichlor-, and trichloracetic ester in the presence of alcohol and water. The solubility of amylalcohol in water is given by Roscoe and Schorlemmer as two parts in a hundred, and I have used this value. I could find no data whatsoever in regard to the chloracetic esters, so I have calculated the values on the false assumption that they are non-miscible with water. The effect of this error is seen very markedly in the case of the monochloraceticester, which is undoubtedly the most soluble of the three. I give these tables in spite of the known inaccuracy, because the absolute values of the constants are, for the time being, of little value, whereas it is essential to show that the same general law covers all substances and that the substitution of chlorine for hydrogen does not affect the action of the Mass Law. The coincidence of the three chloraceticesters having the same exponential factor is probably only superficial, as the correction for the solubilities would alter the exponential factor somewhat.

Table XXXII.

$y = 3$ c.c. Amylalcohol; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x(y = 0.02\,x)^{0.4}/z^{1.4} = C$; $\log C = 0.100$. Temp. 9.1°.

	x.		
z.	Calc.	Found.	log C.
3	3.81	3.21	—
6	10.26	10.35	0.104
9	18.53	18.34	0.095
12	28.45	27.47	0.085
15	40.85	41.25	0.104
			0.097

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[1] Tables XXIII.–XXXI. are given at the close of this article.

TABLE XXXIII.

$y = 3$ c.c. Amylalcohol ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.
Formula $x(y - 0.02x)^{0.4}/z^{1.4} = C$; $\log C = 0.112$. Temp. 19.2°.

	x.		
z.	Calc.	Found.	log C.
3	3.93	3.50	—
6	10.55	10.80	0.122
9	19.10	19.10	0.112
12	30.05	29.15	0.099
15	42.30	43.15	0.121
			0.114

TABLE XXXIV.

$y = 3$ c.c. Monochloraceticester ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.
Formula $xy^{0.43}/z^{1.43} = C$; $\log C = \bar{1}.700$.

	x.		
z.	Calc.	Found.	log C.
3	1.54	1.32	$\bar{1}.644$
6	4.05	4.01	$\bar{1}.695$
9	7.23	7.30	$\bar{1}.705$
12	10.91	10.78	$\bar{1}.695$
15	15.04	16.16	$\bar{1}.731$
18	19.50	22.16	$\bar{1}.756$
21	24.33	28.74	$\bar{1}.772$
			$\bar{1}.714$

TABLE XXXV.

$y = 3$ c.c. Dichloraceticester ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.
Formula $xy^{0.43}/z^{1.43} = C$; $\log C = \bar{1}.479$.

	x.		
z.	Calc.	Found.	log C.
3	0.90	0.90	$\bar{1}.477$
6	2.44	2.45	$\bar{1}.481$
9	4.35	4.33	$\bar{1}.477$
12	6.54	6.60	$\bar{1}.482$
15	9.04	9.20	$\bar{1}.487$
			$\bar{1}.481$

TABLE XXXVI.

$y = 3$ c.c. Trichloraceticester; $x =$ c.c. Water; $s =$ c.c. Alcohol.

Formula $xy^{0.43}/s^{1.48} = C$; $\log C = \bar{1}.336$.

	x.		
s.	Calc.	Found.	log C.
3	0.65	0.65	$\bar{1}.336$
6	1.76	1.80	$\bar{1}.347$
9	3.13	3.02	$\bar{1}.321$
12	4.72	4.50	$\bar{1}.315$
15	6.50	6.50	$\bar{1}.336$
			$\bar{1}.331$

Tables XIX.-XXXI. furnish a striking confirmation of the way in which the Mass Law applies to this class of phenomena; while some of the results are not as satisfactory, perhaps, as I should like, there are some, notably those with propylbutyrate, where the agreement between the observed and the calculated values is something marvelous, though it is unfortunate that the solubility of propylbutyrate in water has never been determined experimentally.

As it might be thought a mere assumption that the first measurements in several series were determinations of another equilibrium, namely, of a saturated solution from which water or ester precipitated water, I have made a few measurements with the few esters I had on hand. The object of these measurements was to show that the change from one equilibrium to another did come at the point shown by Pfeiffer's results, and to make sure that the variations in Pfeiffer's data were due to experimental error. On this account I have made no measurements on the end curves, where water and where ester are part solvents, and in the case of ethylisovalerate I have measured only one series. The results are given in Tables XXXVII.-XXXIX.

Table XXXVII.

x = c.c. H_2O; y = c.c. Ethylisovalerate; 5 c.c. Alcohol. Temp. 20°.

Formula $(x - 0.004\,y)^n\,(y - 0.002\,x)/z^{n+1} = C$; $n = 2.45$; $\log C = \bar{1}.149$.

Water.		Et. Val.		
Calc.	Found.	Calc.	Found.	log C.
9.98	10.00	0.15	0.15	$\bar{1}.152$
8.05	8.00	0.24	0.23	$\bar{1}.142$
6.01	6.00	0.46	0.46	$\bar{1}.147$
4.99	5.00	0.72	0.72	$\bar{1}.152$
4.00	4.00	1.23	1.23	$\bar{1}.149$
				$\bar{1}.148$

Table XXXVIII.

x = c.c. H_2O; y = c.c. Ethylbutyrate; 5 c.c. Alcohol. Temp. 20°.

Formula $(x - 0.005\,y)^{n_1}\,(y - 0.008\,x)/z^{n_1+1} = C_1$; $n_1 = 2.44$; $\log C_1 = \bar{1}.449$.

x.		y.		
Calc.	Found.	Calc.	Found.	log C_1.
9.99	10.00	0.34	0.34	$\bar{1}.450$
8.01	8.00	0.51	0.51	$\bar{1}.447$
5.97	6.00	0.95	0.96	$\bar{1}.453$
5.01	5.00	1.45	1.44	$\bar{1}.447$
3.99	4.00	2.46	2.47	$\bar{1}.451$
				$\bar{1}.449$

Formula $(x - 0.005\,y)^{n_2}\,(y - 0.008\,x)/z^{n_2+1} = C_2$; $n_2 = 1.20$; $\log C_2 = \bar{1}.623$.

				log C_2.
2.96	2.96	3.99	4.00	$\bar{1}.624$
2.46	2.48	4.94	5.00	$\bar{1}.628$
2.12	2.10	6.07	6.00	$\bar{1}.618$
				$\bar{1}.623$

TABLE XXXIX.

x = c.c. Water; y = c.c. Isoamylacetate; 5 c.c. Alcohol. Temp. 20°.

Formula $(x - 0.012y)^{n_1}(y - 0.002x)/z^{n_1+1} = C_1$; $n_1 = 3.50$; $\log C_1 = \bar{1}.414$.

x.		y.		
Calc.	Found.	Calc.	Found.	log C_1.
7.00	7.00	0.41	0.41	$\bar{1}.414$
6.00	6.00	0.70	0.70	$\bar{1}.414$
5.01	5.00	1.32	1.31	$\bar{1}.411$
				$\bar{1}.413$

Formula $(x - 0.012y)^{n_2}(y - 0.002x)/z^{n_2+1} = C_2$; $n_2 = 1.50$; $\log C_2 = \bar{1}.559$.

				log C_2.
3.62	3.61	3.00	3.00	$\bar{1}.558$
3.00	3.01	3.99	4.00	$\bar{1}.560$
2.60	2.60	5.00	5.00	$\bar{1}.559$
				$\bar{1}.559$

Although Pfeiffer does not say so, his amylacetate and ethylvalerate are unquestionably iso- and not the normal compounds. We can now take up the results given in Tables XXXVII.–XXXIX. and see how satisfactorily they fulfil their object. Ethylbutyrate and amylacetate show the change from one equilibrium to the other at the same point that Pfeiffer found. The ethylbutyrate and ethylisovalerate mixtures are perfectly regular at concentrations beyond those used by Pfeiffer, and the isoamylacetate is normal throughout both in Pfeiffer's work and in mine, so that the variations in Tables XXIX.–XXXI. are due to experimental error. The agreement in results between the two sets is shown in Table XL., where I give in the first column the value of the exponential factor $n+1$ from the formula

$$(x-s_1y)(y-s_2x)^n/z^{n+1}=C,$$

and in the second column the values for the simplified integration constant log K.

Table XL.

Ester.		$n+1$.	log K.
Ethylisovalerate	Pfeiffer	1.40	$\bar{1}.773$
Ethylisovalerate	W. D. B.	1.41	$\bar{1}.754$
Ethylbutyrate	Pfeiffer	1.41	$\bar{1}.847$
Ethylbutyrate	W. D. B.	1.41	$\bar{1}.840$
Isoamylacetate	Pfeiffer	1.294	$\bar{1}.893$
Isoamylacetate	W. D. B.	1.286	$\bar{1}.870$

As will be seen, the values of $n+1$ are identical, the values for log K, though very close, are not quite the same. This may be due to inaccuracies in the work, but I am more inclined to attribute it to differences in temperature. It is not known at what temperature Pfeiffer worked, and it would take only a slight difference to account for the variation. In Table XLI. I have tabulated the $n+1$ values from Pfeiffer's results, together with log C and log K.

Table XLI.

Ester.	$n+1$.	log C.	log K.
Methylisovalerate	1.37	$\bar{1}.807$	$\bar{1}.859$
Ethylisovalerate	1.40	$\bar{1}.682$	$\bar{1}.773$
Ethylisovalerate[1]	1.41	$\bar{1}.653$	$\bar{1}.754$
Methylbutyrate	1.52	$\bar{1}.888$	$\bar{1}.926$
Ethylbutyrate	1.41	$\bar{1}.785$	$\bar{1}.847$
Ethylbutyrate[1]	1.41	$\bar{1}.774$	$\bar{1}.840$
Propylbutyrate	1.378	$\bar{1}.651$	$\bar{1}.747$
Ethylpropionate	1.39	$\bar{1}.931$	$\bar{1}.878$
Propylpropionate	1.45	$\bar{1}.733$	$\bar{1}.816$
Ethylacetate[1]	1.555	—	—
Propylacetate	1.23	0.166	0.135
Butylacetate	1.30	$\bar{1}.912$	$\bar{1}.932$
Isoamylacetate	1.294	$\bar{1}.861$	$\bar{1}.893$
Isoamylacetate[1]	1.286	$\bar{1}.832$	$\bar{1}.870$
Propylformiate	1.38	$\bar{1}.967$	$\bar{1}.976$
Butylformiate	1.333	0.057	0.043
Isoamylformiate	1.35	$\bar{1}.808$	$\bar{1}.858$

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[1] My own measurements.

The first thing that strikes one about this table is the way in which so many of the $n+1$ values approximate to 1.40. Why this should be so is entirely unknown. In the $\log K$ values we notice that, for the same acid, increasing the carbon atoms in the alcohol radical diminishes the constant. There is only one exception to this, butylformiate, and here the possible error is very large. It looks also as if the constants might be additive, being made up of one factor for the alcohol and another for the acid radical; but the experimental data are too insufficient to justify this hypothesis. It is very much to be hoped that some one will make a careful series of experiments to settle this point.

Formula II. was deduced for the case when the reacting weights of the substances in equilibrium are not functions of the concentration. The measurements of Pfeiffer and myself show that, with the possible exception of the chloroform-water-acetone series, this condition has been satisfied in all the cases studied, though the experiments extended over a wide range of concentrations. This is in flat contradiction with the determinations of the reacting weights by the boiling-point and freezing-point methods. These methods give accurate results only for very dilute solutions, and even then only for certain solutes in certain solvents. To explain the variations, we are forced to assume "double molecules" in some cases, polymerization with increasing concentration in practically all cases, and "variations from the gas laws." I have brought together a large series of measurements in which there is no sign of any of these things. I see only two possible hypotheses to account for this discrepancy: first, to enunciate a new and most interesting law, to wit, presence of a third substance prevents "polymerization" and "variations from the gas laws"; second, the formula for the change of vapor pressure with the concentration is incorrect. The first hypothesis seems to me out of the question, and there remains only the second. It is a bold thing to question so universally accepted a formula, but I feel convinced that it is not right, and that equal reacting weights of different substances do not produce the same change of vapor pressure. I think that the mistake in the past lay in assuming that the work done in compressing a dissolved substance from the volume V_1 to the volume V_2 by means of a semipermeable piston is equal to $\int p\,dv$ between those limits, irrespective of the nature of solute and solvent. I have already collected some experimental evidence in favor of this view, and I hope before long to be able to establish my point.

The facts brought out in this paper throw light on a research by Abegg[1] carried out under the direction of Arrhenius. Abegg let alcohol diffuse into a salt solution and found, to his surprise, that the salt, instead of remaining equally divided throughout the liquid, diffused somewhat into the part not yet reached by the alcohol. He concludes that this extraordinary behavior can only be accounted for on the assumption that alcohol increases the osmotic pressure of a dissolved salt. What happens is very simple. When the alcohol has diffused only a little way, one may consider the solution as composed of two parts, one containing a large amount of alcohol, the other very little. The dissolved substance, being in this case less soluble in the first layer than in the second, diffuses into the second only to go back again as the alcohol becomes more evenly divided throughout the liquid. Except that the part containing much alcohol and little water merges insensibly into the part containing much water and little alcohol, and is not in equilibrium with it, the case does not differ from two layers formed by ether and water, where it is well known that the concentration of a third substance is not the same in the two layers. The effect of the alcohol is not, as Abegg assumes, to increase the osmotic pressure of the solute, but to diminish its solubility in that portion of the liquid. If, instead of taking salts which were only slightly soluble in alcohol, Abegg had let water diffuse into water containing in solution some substance very soluble in alcohol, slightly soluble in water, he would have observed the opposite effect, and the dissolved substance would have diffused partially into the layer rich in alcohol.

Another line of reasoning which is not quite defensible is that taken by Wildermann,[2] in his paper, "Ueber cyclische Gleichgewichte." His train of thought is something as follows: Suppose he has a system of three phases, bromine, a solution of bromine

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[1] Zeitschr. f. ph. Chem., XI. 248. 1893.

[2] Ibid., XI. 407.

in water, and the vapor of bromine and water, it being assumed that the amount of water which dissolves in the bromine can be neglected. He adds to the aqueous solution some substance which does not dissolve in bromine perceptibly, such as potassium bromide or sulphuric acid. The three phases, when in equilibrium, have still the same concentration of liquid bromine and of bromine vapor. Therefore the solubility of the bromine in the liquid cannot have changed. It does change experimentally; therefore, in order to reconcile the reasoning with the facts, he concludes that the apparent change, decrease or increase, is due to chemical action, and that the amount of bromine dissolved as such remains unchanged. This may be true in the special examples studied by Wildermann.[1] That I cannot say; but it is not true that it is a necessary theoretical conclusion, and there is no proof that it is correct in any case. If, instead of adding potassium bromide, we add to the water some liquid in which bromine is readily soluble, the amount of bromine dissolved will increase without there being any reason to assume chemical action in order to account for it. Bromine is not a good substance to consider, because there are so few liquids soluble in water in which it dissolves without decomposition, and also because we cannot ignore the solubility of the added substance in it. Let us rather treat the case when we have iodine instead of bromine. Suppose we have the system, solid iodine, a solution of iodine in water, and vapor of iodine and water; we add alcohol to the solution. The concentrations of the solid iodine and the iodine vapor will remain practically unchanged; therefore the solubility of iodine in the water and alcohol should remain unchanged according to Wildermann. As a matter of fact it does change, and I do not see how this variation can be attributed to chemical action unless all solution is defined as chemical action, which begs the question, though very possibly true. There may be a radical difference between the action of the alcohol and the action of potassium iodide; but that difference has not been shown. As far as I can see, Wildermann's conclusions require that adding alcohol to a saturated salt solution should have no effect on the concentration of the salt, because the equi-

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[1] See Jakovkin, Zeitschr. f. ph. Chem., XIII. 539. 1894.

librium between the solid salt and its own vapor would remain unchanged.

Early in this paper I proposed the word "solute" as something distinct from "solvent," and it is necessary for me to justify that distinction. The usual way of looking at binary solutions is to consider them as mixtures, and that it is purely arbitrary which of the two substances we consider as solvent and which as dissolved substance. The following citations will show what the prevailing opinion at the present moment is.

Lothar Meyer, after pointing out that in alcohol-water mixtures it depends on the nature of the semipermeable membrane which substance exerts the osmotic pressure, says:[1] "Mit der Beschaffenheit der Membran tauschen beide Stoffe die Rollen; es ist daher eine Willkür wenn wir den einen als gelöst, den anderen als das Lösungsmittel bezeichnen." Ostwald is consistent to the bitter end, saying:[2] "Lösungsmittel ist derjenige Stoff des Gemenges, welcher bei dem betrachteten Vorgange ausgeschieden wird." This view is heroically logical, for it means that when a salt crystallizes from a saturated solution, the mother liquor consists of water dissolved in the salt.

Nernst's position on the subject is doubtful. He puts solutions under the head of physical mixtures and remarks:[3] "Die verdünnten Lösungen sind Gemische welche eine Komponente in grossem Ueberschuss zu den übrigen enthalten; erstere bezeichnen wir in diesem Falle als das Lösungsmittel, letztere als gelöste Stoffe." On the other hand, he draws a distinction between freezing out the solvent and crystallizing out the solute.[4] He does not accept the view that the salt is the solvent in a saturated solution; but he does not suggest in any way that there may be different laws for the solute and the solvent. Planck is very clear and precise; he defines dilute solutions in almost the same words as Nernst, and goes on:[5] "Bei einer beliebigen Lösung kann jeder Bestandtheil derselben als Lösungsmittel oder als gelöster Stoff aufgefasst werden." This means that in a mixture of two liquids

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[1] Zeitschr. f. ph. Chem., V. 24. 1890.

[2] Ibid., XII. 394. 1893.

[3] Theoretische Chemie, p. 115.

[4] Ibid., p. 393.

[5] Grundriss der Thermochemie, p. 131.

either may be considered as the dissolved substance, and will therefore decrease the partial vapor pressure of the other, and this decrease of the vapor pressure will be greater the greater the concentration of the dissolved substance. This is not in agreement with the facts. A saturated solution of ether in water has the same partial vapor pressures as a solution of water in ether saturated at the same temperature.[1] For the moment we will consider ether as the dissolved substance. In the first solution, the volume concentration is roughly 10 per cent; in the second, about 99 per cent at 20°; and yet this enormous change of concentration has no effect on the partial vapor pressures. The figures are still more remarkable if we consider solutions of chloroform in water and water in chloroform, when one of the components is present in infinitesimal quantities. We must assume one of two things: either that our present formula for the change of the vapor pressure with the concentration is all wrong, since it does not admit of the vapor pressure of one of the components passing through a minimum; or that there is a difference between solvent and solute, and that each has its own law expressing the change of its vapor pressure with the concentration. This time I prefer the second assumption, with all that it implies. The equations of van 't Hoff and Raoult are the rough statements of the laws for the solvent. The corresponding expressions for the solute have not yet been worked out. The distinction between solvent and solute is very clear in solid solutions of metals in metals. Starting from either of two pure metals a depression of the freezing point is noted when the other is added, the two curves thus formed meeting at the melting point of the eutectic alloy. Here there can be no question that along one curve the first metal is solvent, while on the other it plays the role of solute. In the case of two partially miscible liquids there is also no difficulty in determining which is solvent and which solute. When ether and water are shaken together, the upper layer contains water as dissolved substance, the lower ether. With completely miscible liquids having a maximum (or minimum) vapor pressure at some concentration, such as propylalcohol and water (formic acid and water), it is probable

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[1] Wied. Ann., XIV. 219, 1881; Ostwald, Lehrbuch, I. 644.

that the change of solvent occurs at the concentration corresponding to the maximum (or minimum) vapor pressure. With such things as ethylalcohol and water, which are infinitely miscible and which show no maximum or minimum vapor pressure, it is impossible at present to say at what concentration alcohol ceases to be the solvent and water assumes that duty. As soon as we have worked out the relation between the concentrations in the solution and in the vapor, I feel certain that we shall find that it requires two curves to express the relation, and not one. The intersection of these curves will be the point where the solvent changes. I look upon my own results with ternary mixtures as very significant in this respect, the change from one curve to another coming at the point where the precipitate or the solvent changed. It is interesting to note that at the point, for instance, where an excess of one of the partially miscible liquids first has no effect, the solubility curve of the dissolved substance has a "break." The possibility of such a case has always been denied except by the upholders of the "hydrate theory."

The effect of temperature on the various equilibria will form the subject of a special paper, and I shall reserve for it the discussion of changes of temperature coefficient at the intersections of two curves, one or two very striking instances of which I have come upon incidentally in my work so far. I hope also to be able to present a paper on equilibrium in two liquid layers, a subject which is of especial interest because the theoretical treatment based on the experimental work in this paper gives results which are not in accordance with the assumptions on which Nernst bases his Distribution Law. Besides, there is the application of the Mass Law to the case where one or more of the components is solid, and to the instances where there is an increase instead of a decrease of solubility.

The results of this paper may be summarized briefly as follows:

1. The equilibria between two partially miscible liquids and a consolute liquid follow the Mass Law.
2. There are four sets of equilibria corresponding to four different series of solutions.

3. If the two liquids are practically non-miscible, there are only two sets of equilibria.

4. The reacting weights of the liquids studied were not functions of the concentration, — possibly with one exception.

5. There is a fundamental difference between the solute and the solvent.

6. The solubility curve of a substance in a varying mixture of two liquids at constant temperature has a break.

TABLE XXIII.

$y = 3$ c.c. Propylbutyrate; $x =$ c.c. Water; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.002\,x)^{0.378}/z^{1.378} = C$; $\log C = \bar{1}.651$.

	x.		
z.	Calc.	Found.	log C.
3	—	1.19	—
6	3.49	3.55	$\bar{1}.658$
9	6.11	6.13	$\bar{1}.652$
12	9.05	9.05	$\bar{1}.651$
15	12.31	12.31	$\bar{1}.651$
18	15.92	15.90	$\bar{1}.650$
21	19.68	19.68	$\bar{1}.651$
24	23.72	23.72	$\bar{1}.651$
27	27.92	27.84	$\bar{1}.650$
30	32.20	32.10	$\bar{1}.649$
33	36.71	36.71	$\bar{1}.651$
36	41.66	41.55	$\bar{1}.650$
39	46.64	46.49	$\bar{1}.649$
42	51.56	51.60	$\bar{1}.652$
45	56.80	56.90	$\bar{1}.652$
48	62.64	62.40	$\bar{1}.649$
51	67.84	68.00	$\bar{1}.652$
54	73.93	73.85	$\bar{1}.650$
			$\bar{1}.651$

TABLE XXIV.

$y = 3$ c.c. Ethylpropionate; $x =$ c.c. Water; $z =$ c.c. Alcohol.
Formula $x\,(y - 0.03\,x)^{0.39}/z^{1.39} = C$; $\log C = \bar{1}.931$.

	x.		
z.	Calc.	Found.	log C.
3	2.36	2.32	$\bar{1}.924$
6	6.89	6.87	$\bar{1}.930$
9	12.38	12.35	$\bar{1}.930$
12	19.10	19.17	$\bar{1}.933$
15	27.12	27.12	$\bar{1}.931$
18	36.84	36.84	$\bar{1}.931$
21	50.35	50.42	$\bar{1}.932$
24	—	∞	
			$\bar{1}.930$

TABLE XXV.

$y = 3$ c.c. Propylpropionate; $x =$ c.c. Water; $z =$ c.c. Alcohol.
Formula $x\,(y - 0.0065\,x)^{0.45}/z^{1.45} = C$; $\log C = \bar{1}.733$.

	x.		
z.	Calc.	Found.	log C.
3	—	1.58	—
6	4.45	4.70	$\bar{1}.757$
9	8.27	8.35	$\bar{1}.738$
12	12.25	12.54	$\bar{1}.743$
15	17.04	17.15	$\bar{1}.736$
18	22.27	22.27	$\bar{1}.733$
21	28.00	27.83	$\bar{1}.731$
24	34.20	33.75	$\bar{1}.727$
27	40.80	40.24	$\bar{1}$·727
30	47.95	47.15	$\bar{1}.725$
33	55.70	54.65	$\bar{1}.725$
36	63.50	63.18	$\bar{1}.731$
39	72.25	71.59	$\bar{1}.729$
42	81.15	83.05	$\bar{1}.743$
45	91.30	93.91	$\bar{1}.746$
48	102.00	107.46	$\bar{1}.756$
			$\bar{1}.737$

TABLE XXVI.

$y = 3$ c.c. Propylacetate; $x =$ c.c. Water; $z =$ c.c. Alcohol.
Formula $x\,(y - 0.03\,x)^{0.23}/z^{1.23} = C$; $\log C = 0.166$.

	x.		
z.	Calc.	Found.	log *C.*
3	4.44	4.50	0.170
6	10.57	10.48	0.163
9	17.75	17.80	0.167
12	25.95	26.00	0.167
15	35.72	35.63	0.165
18	46.50	47.50	0.178
21	59.00	58.71	0.164
24	—	∞	
			0.168

TABLE XXVII.

$y = 3$ c.c. Butylacetate; $x =$ c.c. Water; $z =$ c.c. Alcohol.
Formula $x\,(y - 0.007\,x)^{0.3}/z^{1.3} = C$; $\log C = \bar{1}.912$.

	x.		
z.	Calc.	Found.	log *C.*
3	—	2.08	—
6	6.06	6.08	$\bar{1}.914$
9	10.29	10.46	$\bar{1}.920$
12	15.04	15.37	$\bar{1}.922$
15	20.10	20.42	$\bar{1}.918$
18	25.64	25.60	$\bar{1}.911$
21	31.49	31.49	$\bar{1}.912$
24	37.60	37.48	$\bar{1}.911$
27	44.05	43.75	$\bar{1}.909$
30	50.74	50.74	$\bar{1}.912$
33	58.00	59.97	$\bar{1}.927$
			$\bar{1}.916$

TABLE XXVIII.

$y = 3$ c.c. Amylacetate ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.02\,x)^{0.294}/z^{1.294} = C$; $\log C = \bar{1}.861$.

	x.		
z.	Calc.	Found.	log C.
3	—	1.76	—
6	—	4.24	—
9	9.03	9.03	$\bar{1}.861$
12	13.11	13.24	$\bar{1}.866$
15	17.43	17.52	$\bar{1}.864$
18	22.22	22.22	$\bar{1}.861$
21	26.99	26.99	$\bar{1}.861$
24	32.24	32.14	$\bar{1}.860$
27	37.59	37.23	$\bar{1}.856$
30	42.78	42.66	$\bar{1}.859$
33	48.41	48.41	$\bar{1}.861$
			$\bar{1}.861$

TABLE XXIX.

$y = 3$ c.c. Propylformiate ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.04\,x)^{0.38}/z^{1.38} = C$; $\log C = \bar{1}.967$.

	x.		
z.	Calc.	Found.	log C.
3	2.82	2.83	$\bar{1}.969$
6	7.52	7.50	$\bar{1}.966$
9	13.65	13.50	$\bar{1}.962$
12	21.30	21.60	$\bar{1}.973$
15	30.95	30.60	$\bar{1}.962$
18	52.40	53.00	$\bar{1}.972$
21	—	∞	$\bar{1}.967$

TABLE XXX.

$y = 3$ c.c. Butylformiate ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.

Formula $x\,(y - 0.01\,x)^{\frac{1}{3}}/z^{\frac{4}{3}} = C$; $\log C = 0.057$.

	x.		
z.	Calc.	Found.	log C.
3	3.43	3.45	0.060
6	8.71	8.83	0.063
9	15.02	14.75	0.049
12	22.32	21.45	0.041
15	30.25	29.65	0.048
18	39.00	39.00	0.057
21	48.80	51.80	0.083
24	—	∞	
			0.057

TABLE XXXI.

$y = 3$ c.c. Amylformiate ; $x =$ c.c. Water ; $z =$ c.c. Alcohol.

Formula $x(y - 0.005\,x)^{0.35}/z^{1.35} = C$; $\log C = \bar{1}.808$.

	x.		
z.	Calc.	Found.	log C.
3	—	1.80	—
6	4.92	5.17	$\bar{1}.829$
9	8.54	8.77	$\bar{1}.820$
12	12.63	12.64	$\bar{1}.809$
15	17.10	17.01	$\bar{1}.806$
18	21.90	21.86	$\bar{1}.807$
21	27.06	27.06	$\bar{1}.808$
24	32.50	32.31	$\bar{1}.805$
27	38.31	38.31	$\bar{1}.808$
30	44.40	44.50	$\bar{1}.809$
33	50.71	50.71	$\bar{1}.808$
36	57.20	57.82	$\bar{1}.813$
39	62.70	65.21	($\bar{1}.830$)
42	71.35	77.05	($\bar{1}.842$)
45	78.75	85.10	($\bar{1}.842$)
48	86.55	94.20	($\bar{1}.845$)
			$\bar{1}.811$

ON THE CHANGES IN LENGTH PRODUCED IN IRON WIRES BY MAGNETIZATION.

BY LOUIS TRENCHARD MORE.

THIS investigation was undertaken at the suggestion of Professor Rowland, and has for its object the finding of a relation between the change of length produced in iron wires by magnetization, and the intensity of magnetization existing in the wire. It was hoped thus to obtain results that would be comparable, and to avoid certain errors common to all previous work.

Historical.

That magnetizing an iron rod causes it to alter in length was first discussed by Joule[1] in 1847. His attention was called to the phenomenon by a machinist of Manchester, who imagined that the volume of a mass of iron was increased by magnetizing it. Joule, to test the opinion of the machinist, immersed a mass of iron in a closed vessel full of water in which stood a fine capillary tube. When the iron was strongly magnetized, the height of the column of water in the tube remained unaltered, showing that within the limits of accuracy of his apparatus, for the intensity employed, the volume of the iron was unchanged. Bidwell[2] has also investigated this subject and found, on the contrary, that the volume was altered by magnetization. The volume diminishes at first and attains a minimum; it then increases until with sufficiently intense fields the original size is regained; after reaching this point the volume continues to increase. As a consequence of this relation, if Joule had used an intensity either greater or less, he probably would have noticed a change in the volume. Joule afterwards, by means of a system of levers, found that the length

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[1] Joule, Phil. Mag. (3), Vol. XXX., pp. 76, 225.

[2] Bidwell, Proc. Roy. Soc., Vol. LVI., p. 94.

of a rod was increased by the magnetizing force, and gave as a result of his observations the following laws: —

1. When soft iron rods are magnetized, their length is increased and the elongation is approximately proportional to the square of the magnetizing force.

2. Tension applied to the rod diminishes the elongating effect, and — "In the case of a bar one foot long and one-quarter inch in diameter, a tensile force of about 600 pounds caused all the phenomena of changes of length to disappear."

3. "That the elongation is greater, for the same intensity of magnetism, in proportion to the softness of the metal. It is greatest of all in the well annealed iron bars, and least in hardened steel. This circumstance appears to me to favor the hypothesis that the phenomena are produced by the attractions taking place between the magnetized particles of the bar, an hypothesis in perfect accordance with the law which I have pointed out," — that the elongation was proportional to the square of the intensity of magnetization.

The first two laws pointed out by Joule have been often confirmed, but the third seems to rest on a single experiment, and until very recently there have been no published records, that I have seen, bearing on the result found by Joule. Shelford Bidwell[1] while investigating the subject obtained results the converse of Joule's, — that not only hardening, but also annealing, the iron diminished the elongating effect. He mentions one specimen that when annealed contracted in length instead of elongating upon the application of the feeblest magnetizing force.

Barrett[2] in 1870 discovered that nickel when magnetized contracts instead of elongating. Three years later A. M. Mayer[3] published an account of his experiments on this subject. His results in the main verified Joule's observations, with the exception of the action of hard steel. This discrepancy was shown some years later by Bidwell to follow from their different methods of experimenting. Joule applied a current of the same intensity but once, and both on making and on breaking the circuit observed an elongation; while Mayer used specimens already perma-

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[1] Bidwell, Proc. Roy. Soc. Vol. LV., p. 228.

[2] Barrett, Nature, 1882.

[3] Mayer, Phil. Mag. Vol. XLVI., p. 179.

nently magnetized, and on observing the temporary magnetization, found a contraction on making circuit and an elongation on breaking it.

Mayer also observed hysteretic effects; that is, the elongation due to a magnetizing force was less if the force had been reached by successively increasing values, than it was if the current had been decreased from a maximum, the rod remaining slightly elongated after the magnetizing force had been removed, an effect analogous to the lagging of the induction behind the magnetizing force. Nagaoka[1] has discussed this phenomenon in the article cited, and has obtained complicated curves showing the complete cycle of the hysteretic phenomena for both iron and nickel.

The experiments mentioned were limited to comparatively weak fields; the work of finding the effects due to intense fields has been most thoroughly done by Shelford Bidwell,[2] who has found that rods do not continue to elongate indefinitely with increasing strengths of field, as the other investigators supposed, but that a maximum value is after a time reached. The rod then begins to shorten, and very intense fields produce an absolute contraction which approaches a limiting value asymptotically. He also experimented with rings of iron, and with rods of steel, nickel, manganese steel, cobalt, and bismuth.

Investigations upon this subject have also been made by Berget,[3] Nagaoka,[4] Lochner,[5] Jones,[6] and Bock.[7]

For convenience, I have collected in a summary the results obtained by the different observers.

Soft Iron. — Soft iron elongates when magnetized. The elongation attains a maximum and then diminishes with increasing strength of field until a state is reached when the rod returns to its original length. Further increase of field causes the rod to contract.

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[1] Nagaoka, Phil. Mag., Vol. XXXVII., p. 131.

[2] Bidwell, Proc. Roy. Soc., Vol. XXXVIII., p. 265; Vol. XL., pp. 109, 237; Vol. XLVII., p. 469; Vol. LV., p. 228; Trans. Roy. Soc., Vol. CLXXIX. (A), p. 205.

[3] Berget, Comp. Rend., tom. CXV., p. 722.

[4] Nagaoka, Wied. Ann., LIII., pp. 481, 487; 1894.

[5] Lochner, Phil. Mag., Vol. XXXVI., p. 504; 1893.

[6] Jones, Phil. Mag., Vol. XXXIX., p. 254; 1895.

[7] Bock, Wied. Ann.; 1895.

There is no minimum length, the rod approaching asymptotically a limiting value.

With a given strength of field, both hardening and annealing diminish the elongation and increase the contraction shown by the rod before it was subjected to these operations. (Bidwell.)

Tension also diminishes the elongation and increases the contraction of the rod.

For a sufficiently great tension no elongation occurs, the rod contracting upon the application of the smallest magnetizing forces.

For a given length, the effects both of elongation and of contraction are greater for thin than for thick rods. (Bidwell.)

S. J. Lochner[1] comes to the conclusion from his own experiments that the converse is true, — that thick bars show greater elongation than thin ones.

Very little reliance can be put in these last experiments, and the dependence of the change of length upon the ratio of the length to the diameter cannot be inferred from them. Bidwell used three rods 10 cm. long and 2.65, 3.65, and 6.25 mm. in diameter, and assumed them to be of iron of similar composition. It is well known that different specimens of iron, apparently similar in structure, give results that vary 25 per cent and more, so that the small variations in the change of length noted by him cannot safely be said to be due to the differences in their diameters, especially as he made no determination of the permeability. Lochner avoided this error by testing an iron rod, and then after having cut off a portion, testing it again. He, however, took no precaution to have the field uniform. His solenoid was nearly four times as long as the shortest rod used, and the ratio of the diameter to the length of the rod was only 1 to 32. Besides the uncertainties introduced by such a poor arrangement for a uniform field, great errors would be produced by the strong poles created at the ends of the rod.

Object of Experiment.

A careful study of the results obtained for iron by the different observers will show that although the general appearance of their

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[1] Lochner, *loc. cit.*

curves is very similar, yet their absolute values vary widely, two specimens often having maximum elongations that differ 20 or 30 per cent. There is, unfortunately, no way of comparing these results, for it has been the custom to use as co-ordinates the change of length and the intensity of the external field. For a given apparatus this intensity depends only on the current used, and not at all on the specimen to be examined. The elongation is dependent upon the intensity of magnetization in the wire, and this is the quantity that varies with the specimen employed. For that reason the relation should be found between these two quantities.

It is, of course, essential to have the rod uniformly magnetized throughout its length; that is, the field should be uniform and there should be no free poles. These conditions may be best obtained in one of two ways, either by having the metal in the shape of a ring, and observing the change in diameter of the ring when magnetized by a solenoid wound upon it, or by using long wires of the metal. In the second case only the middle part of the wire should be observed, and the solenoid used to magnetize it should be considerably longer than the portion of the wire experimented upon. In this investigation the latter method was chosen, as rings are less convenient, and also because it was desirable to observe the effects of tension in the metal.

When a rod of iron is magnetized, the change in length observed is due to several causes, — three at least, — and to obtain a correct idea of the phenomena these causes and their effects should be separated. There is first the *direct action* of the magnetism, and this may possibly be due to the orienting of the magnetized particles of the rod. Secondly, there are indirect actions of the magnetism which tend to change the length of the rod. These indirect actions are the mechanical stresses created in the rod by the magnetism. The first of these mechanical stresses is the tractive force of the magnet and is measured by $\frac{B^2}{8\pi}$. That this force exists, tending always to contract the rod, is seen from the fact that if the magnet is cut in two, the ends are held together by a force $\frac{B^2}{8\pi}$ per square centimeter, showing that this force must always be present when a rod is magnetized. The agreement between the theoretical value $\frac{B^2}{8\pi}$ and the experimental law for the lifting power has been recently shown by E. Taylor Jones.[1] This effect for high intensities of magnetization is a large one, and becomes one of the most important factors in the observed changes in length. The second of these mechanical stresses is the effect due to the change in Young's modulus when the rod is magnetized. That the elasticity is influenced by magnetization was shown theoretically by J. J. Thomson,[2] and the phenomenon was observed last year in some experiments made by the writer; but no quantitative results could be obtained beyond the fact that the elasticity for soft iron was slightly diminished. A. Bock[3] concludes from his work that the decrease in elasticity must be less than one-half per cent. If the wire is not stretched by weights, this decrease in the elasticity will affect only the contraction due to the $\frac{B^2}{8\pi}$ force. On the other hand, if the wire is loaded with weights, this effect becomes very marked, since a large quantity, the stretch of the wire by the great weight, is altered. This question will be more fully discussed later in the paper.

If these two indirect actions were allowed for, there would remain only the direct action of the magnetism upon the metal under a constant tension. This latter relation would evidently furnish comparable results, and may in the future throw some light upon the action of magnetism on matter.

Apparatus.

Since it was necessary to obtain the modulus of elasticity for the specimen experimented on, in order to make a proper correction for the electro-magnetic stress, and as I wished to observe the effects of mechanical stress, it was convenient to experiment on thin, long wires of the metal placed in a vertical position. To magnify the phenomena a system of levers was used, involving the

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[1] Jones, *loc. cit.*

[2] J. J. Thomson, Application of Dynamics to Physics and Chemistry, p. 58.

[3] Bock, *loc. cit.*

tilting of a mirror mounted on three legs very close together, — a method first invented by Professor Rowland. The general plan of using levers and a jacket cylinder was suggested to me by Dr. Ames.

The wire to be tested was suspended from a tall tripod standing on a stone slab that rested on two brick piers. A hole was cut in the slab so that the wire could be passed through it and the free end permitted to almost reach the floor of the room. A hollow brass cylinder 1.6 cm. in diameter and about 68.0 cm. long (Fig. 1) was screwed to the wire at a point *a*, a short distance above the stone slab; a loosely fitting cork plug in its open upper end served to keep the wire in the axis of this cylinder. To the cylinder was screwed the brass arm *deb*. At *e* was screwed a hard steel support for the fulcrum of the lever. The side view of the support was of this shape, └──────┘, the two projections supporting the knife edge, and the body of the lever passing between them. To keep the lever horizontal and to register changes of length, another knife edge with its blade upwards was embedded in the lever. This knife edge pressed against the piece *mn*, which was screwed to the wire at *m*. Now if the points *m* and *a* were separated or brought close together, the knife edges would no longer remain in a horizontal line, and the lever would tilt. The end *p* of the lever, and the surface *d* of the arm *bed*, were made planes to support a small brass table having on its upper face a vertical plane mirror, and for legs three short bits of needles, two of which stood on *p* and one on *d*. By this arrangement the change in the length of *ma*, already magnified by the lever, was much more apparent when the tilting of the mirror table was read by means of a telescope and scale. The most important dimensions are: —

Length of wire stretched, *ma*	69.9	cm.
Ratio of lever arms	$\frac{119}{4.65}$	
Distance between needle points . . .	2.3	mm.
Distance to telescope and scale . . .	1660.0	mm.

The multiplying power of the apparatus was, therefore, —

$$\frac{119}{4.65} \times \frac{1660}{2.3} \times 2 = 36941.$$

And as the scale was graduated to millimeters, one scale division represented an actual change of length of 2.7×10^{-6} mm.

The coil to magnetize the wire stood on the stone slab and was long enough to reach just below the arm *ce*, so that the part of the wire *ma* experimented on was in a practically uniform field.

The principal dimensions of this coil were as follows: —

Length of coil	83.7 cm.
External diameter	6.3 cm.
Internal diameter	3.6 cm.
Number of wire	18.
Number of turns	3045.
Number of layers	7.
Number of turns per cm.	36.4
Resistance of coil	10.53 ohms
Strength of field per ampère . . .	45.75 C.G.S.
Maximum field	260.00 C.G.S.

The core of this coil was made of two co-axal brass cylinders fastened together by the end plates of the coil. The space between these two cylinders was filled with water, which proved to be an excellent way of retarding the heat effects produced by the current.

Method.

I at first intended to measure the elongation and the corresponding induction simultaneously, but found this difficult, and so adopted a more convenient and apparently as accurate a method. This was to first measure the current used to produce a given intensity of magnetism and the consequent changes in length, and afterwards to get the relation between the strength of field and the intensity of magnetization in the iron, the apparatus in the meanwhile remaining untouched. As the laboratory is situated in the city, the work had to be done late at night after traffic had stopped; for, in spite of all the precautions that could be thought of, the shaking of the apparatus could not be prevented. For this reason the induction was not determined immediately after obtaining the elongation curve, but was done the next morning. The induction was measured by the method of reversals.[1] The induction coil used for this purpose consisted of 200 turns of No. 36 wire wound in one layer on a paper cylinder slightly greater in diameter than the specimen. This little cylinder was slipped over the wire and fixed half-way between *am*. The galvanometer was calibrated by means of a standard coil having a wooden core. The secondary of the standard coil also consisted of 200 turns of wire, which plan saved much computation. The intensity was then calculated by the formula $B=H+4\pi I$. Knowing the change in length and the intensity of magnetization for any current, of course the relation between these two quantities could be easily platted. The current was supplied by a battery of storage cells, and the resistance was regulated by a slide resistance of copper sulphate.

Results.

My first results were obtained from a specimen of moderately soft commercial iron wire, one millimeter in diameter. This wire was free from stress, except that due to the jacket cylinder screwed to it, which weighed 350 grams. The elongations given (Table I.) are those due to temporary magnetism, and each value is the mean of two or three readings which did not vary by more than one per cent. The current was applied suddenly, and as soon as a reading was taken the contact was broken. This operation was then repeated, the current being increased each time, and readings taken until the maximum current was reached. By this means temperature effects, which are relatively slow to act, were avoided.

Figure 3, *C* shows the relation between the elongation per unit length, $\frac{\delta l}{l} \times 10^7$, and the intensity of the field, *H*. This curve is seen to closely resemble in form those given by Shelford Bidwell. When the relation is expressed between change of length and intensity of magnetization, the curve takes the very different form given by Fig. 3, *B*. The wire slowly increases in length until an intensity of about 800 is reached. From that point, until a maximum length is attained, at an intensity of 1200, the elongation is

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[1] Ewing, Lond. Electrician, April, 1894.

more marked. After reaching this maximum it rapidly contracts, the last portion of the curve being approximately a nearly vertical straight line. The figure also shows that the point of maximum length does not correspond to the point of greatest permeability of iron, as is seen by comparing this curve with the curve for permeability plotted on the same figure.

It is now necessary to make corrections for the contraction due to the $\frac{B^2}{8\pi}$ force. This contraction is obtained from the formula

$$\frac{\delta l}{l} \times 10^7 = \frac{B^2/8\pi}{M},$$

where M is the modulus of elasticity. My apparatus was well fitted for measuring the latter quantity. A weight of about five kilograms was hung on the wire, and the elongations due to the additions of weights of 20, 50, and 100 grams were read. From these Young's modulus was calculated in the usual manner. It was found to be 2.2×10^{12} for the specimen used. The contractions due to the $\frac{B^2}{8\pi}$ force were then calculated, and are given in column 6 of Table I.

The last column of this table was found by taking the difference between the observed elongation and the $\frac{B^2}{8\pi}$ contraction. The relation between this corrected elongation, due to what has been called the direct action of the magnetism, and the intensity of magnetization, is graphically shown by Fig. 3, *A*. The effect of this correction is to make the elongation much greater for a given intensity. The maximum value of the elongation is more than twice as great as the observed maximum. And the greatest intensity employed, 1300 C.G.S. units, produces an elongation and not a contraction as observed.

No correction for the change in elasticity was made. For the present case it would be insignificant. See discussion of errors at end of this paper.

TABLE I.

H	μ	I	B	$\frac{\delta l}{l}$ (obs.)	$\frac{\delta l}{l}\left(\frac{B^2}{8\pi}\right)$	$\frac{\delta l}{l}$ (corr.)
4.6	384.8	141	1770	+0.10	−0.7	+0.80
7.3	507.0	294	3700	—	—	—
10.5	752.4	623	7900	1.16	11.3	12.46
11.8	733.0	700	8800	—	—	—
12.8	726.7	739	9300	2.71	15.65	18.36
15.5	695.0	856	10770	5.71	20.98	26.69
19.7	627.0	981	12350	14.71	27.60	42.31
24.2	541.4	1041	13100	18.78	31.05	49.83
28.8	482.7	1104	13900	22.92	34.95	57.87
37.6	389.1	1163	14630	25.55	38.53	64.13
53.0	286.3	1203	15170	24.78	41.69	66.47
60.4	253.7	1214	15320	23.23	42.47	65.70
67.7	227.7	1222	15410	21.30	42.96	64.26
80.0	193.8	1228	15500	18.74	43.46	62.20
93.3	167.2	1235	15600	15.49	44.02	59.51
103.8	150.8	1238	15650	12.81	44.30	57.11
111.6	140.7	1241	15700	11.03	44.59	55.62
121.2	130.0	1244	15750	9.20	44.88	54.08
145.4	109.6	1257	15930	5.42	45.90	51.32
159.1	100.6	1261	16010	+1.94	46.37	48.31
186.5	86.9	1274	16200	−2.94	47.47	44.53
210.3	77.8	1281	16360	6.97	48.42	41.45
246.9	67.1	1299	16570	12.97	49.67	36.70
260.6	63.9	1304	16650	16.65	50.15	33.30

The effect of hardening the wire was next considered. A piece of the same quality of iron was heated to a bright red by passing a current through it, and then suddenly cooled. After the operation the wire was much harder, and only slightly burnt on the surface. The observed changes in length, those due to $\frac{B^2}{8\pi}$ and the corrected values are given in Table II. Hardening the iron makes the elongation smaller, and for the present specimen the least intensity of magnetization caused the iron to contract (Fig. 4, *B*). The corrected relation between the change of length and the intensity is shown by *B'*. On this plate is also plotted curve *A*, the same relation, taken from Fig. 3, for the wire when not hardened; and curve *A'* shows the corrected relations for the same.

Although the observed change for the hardened wire was a contraction, the contraction due to the $\frac{B^2}{8\pi}$ force was sufficient to bring the values above the zero axis. So, again, the direct action of the magnetization is to elongate the wire, and the corrected curve is very similar to the curve for the iron in its original state. The absolute values are, however, much diminished, and the maximum occurs, for this specimen, with a less intensity. The correction for the change of elasticity can be neglected as in the first case.

Table II.

H	I	B	$\frac{\delta l}{l}$ (obs.)	$\frac{\delta l}{l}\left(\frac{B^2}{8\pi}\right)$	$\frac{\delta l}{l}$ (corr.)
5.0	8	100	−0.00	−0.00	+0.00
8.7	53	670	0.05	0.08	0.03
12.8	272	3420	0.10	2.12	2.02
18.3	709	8920	0.20	14.41	14.21
27.4	923	11620	0.50	24.44	23.94
36.6	947	11940	0.70	25.77	25.07
45.7	1012	12770	1.85	29.48	27.63
57.2	1044	13180	3.10	31.42	28.32
68.5	1060	13390	4.10	32.42	28.32
96.5	1074	13600	7.40	33.43	26.03
118.8	1064	13490	5.44	32.93	27.53
138.5	1100	13560(?)	15.00	34.24	20.24
180.1	1126	14320	24.20	37.11	12.91

To find the effect of strain the wire was loaded with a weight of 750 kg. per square centimeter, and the relation between the elongation and the intensity of magnetization obtained as in the previous cases. The wire was then loaded with a weight of 1750 kg. per square centimeter, and the same relations found. The values are given in Tables III. and IV. The effects of strains are also shown graphically by Fig. 5, for the observed and corrected values. By consulting the figure it is seen that straining the wire produces the same change that hardening it does. The values are reduced, and the maximum points occur with less intense magnetization. The curves in this figure, as well as in the two former figures, marked no load, have an inaccuracy due to the strain caused by the weight of the jacket cylinder, and should have ordinates a trifle greater.

Although the change in elasticity has hitherto produced little effect, as soon as the wire is much strained this correction becomes very important, and will modify the curves materially. This alteration in the curves it has not been possible to make, as the relation between the change in elasticity and the intensity of magnetization is unknown. However, from Bock's results some approximations may be arrived at; and these will be considered when the errors likely to occur in this investigation are discussed.

TABLE III.

H	I	B	$\frac{\delta l}{l}$ (obs.)	$\frac{\delta l}{l}\left(\frac{B^2}{8\pi}\right)$	$\frac{\delta l}{l}$ (corr.)
6.9	636	8000	+0.12	−11.58	+11.70
11.4	918	11550	0.62	24.14	24.76
18.5	1080	13600	2.63	33.46	36.09
24.2	1109	13960	3.73	35.27	39.00
30.2	1139	14340	3.87	37.19	41.06
34.7	1150	14480	3.48	37.94	41.42
43.9	1167	14700	2.42	39.09	41.51
55.8	1184	14930	+1.20	40.33	41.53
73.2	1204	15200	−0.39	41.79	41.40
81.8	1212	15300	1.16	42.35	41.19
100.6	1223	15470	4.41	43.30	38.89
122.5	1235	15640	9.10	44.24	35.14
148.1	1247	15820	14.13	45.27	31.14
157.7	1253	15910	15.80	45.80	30.00
175.1	1265	16070	18.58	46.71	28.13
192.1	1276	16230	25.05	47.65	22.60
228.6	1287	16400	29.03	48.65	19.62
251.4	1293	16500	32.13	49.26	17.13

Possible Errors.

It has been shown that the change in elasticity occurring when an iron wire is magnetized modifies the relation between the intensity of magnetization and the elongation; and it has been assumed that, except for heavily loaded wires, this effect will be very small. Bock[1] found as a result of his experiments that magnetizing soft iron made it more incompressible, and that the change in elasticity was less than one-half per cent. He could not find any relation between the intensity of magnetization and change in elasticity, so that it is impossible to give more than a probable maximum to the correction it is necessary to make in the curves given in this investigation.

TABLE IV.

H	I	B	$\frac{\delta l}{l}$ (obs.)	$\frac{\delta l}{l}\left(\frac{B^2}{8\pi}\right)$	$\frac{\delta l}{l}$ (corr.)
5.5	581	7300	−0.19	−9.64	+9.54
9.1	922	11600	0.58	24.35	23.77
13.7	1011	12720	1.26	29.27	28.01
21.5	1070	13470	2.90	32.83	29.93
27.4	1100	13860	4.06	34.76	30.70
36.6	1134	14280	5.90	36.89	30.99
45.7	1155	14560	7.36	38.36	31.00
54.9	1167	14710	9.68	39.14	29.46
73.2	1178	14880	13.84	40.05	26.21
86.9	1186	14990	16.64	40.65	24.01
96.0	1190	15050	19.74	40.97	21.23
111.1	1198	15160	23.63	41.58	17.95
128.0	1207	15290	27.87	42.29	14.42
139.4	1212	15370	32.51	42.74	10.23
150.9	1217	15440	33.97	43.12	9.15

If we take $B = 20{,}000$,

$$\frac{B^2}{8\pi} = \frac{1}{2\pi} \times 10^8 \text{ dynes per square centimeter,}$$

and

$$\frac{\delta l}{l} \times 10^7 = -\frac{\frac{1}{2\pi} \times 10^8}{M} = -73.$$

A change of one-half per cent in $\frac{\delta l}{l}$ would give a correction of $0.005 \times 73 = .4$ of a unit. This correction may therefore be neglected, as errors greater than this would occur in measuring the induction.

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[1] Bock, *loc. cit.*

It was also assumed that when the wire was not stretched, except by the jacket, the correction might be neglected.

The weight of this jacket was 350 grams, or 42000 dynes per square centimeter; then

$$\frac{\delta l}{l} \times 10^7 = \frac{42000}{M} \times 10^7 = 200.$$

A change of one-half per cent in 200 is 1.0. Consequently the curves marked no load are not significantly changed by making this correction.

But when we consider the case of the wire loaded with 750 kg. per square centimeter, we get, by a similar calculation, a correction of 15 units; and for the wire under the greatest tension, 1750 kg. per square centimeter, a correction of 40 units. Since the magnetism makes the metal more incompressible, this correction enters as a contraction, and must be added to the ordinates of the curves plotted on Fig. 5. It is impossible to say how these curves would be affected by the correction, but probably the correction increases with the intensity of magnetization.

Changes in the length of the wire due to variations in temperature are another possible source of error. These changes take place more slowly than the elongation produced by the magnetization, so that the two effects may be separated. To retard them still more, the core of the solenoid was made of two co-axal cylinders, and the space between them filled with water. With this arrangement the current could be applied, the reading taken, and the current shut off, before the gradual change of the zero point due to the heating of the wire by the current could be observed. Changes in the temperature of the room when they did occur were too slow to noticeably affect the results.

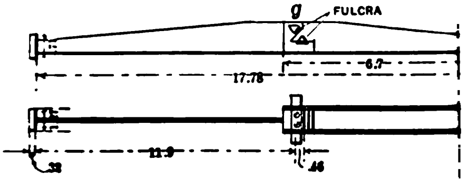
Summary.

The following is a summary of the results obtained by this investigation: —

1. A relation has been obtained between the elongation due to magnetization and the intensity of magnetization for soft iron. When the elongation has been corrected for the contraction caused

Fig. 1.

Fig. 2



DETAIL OF LEVER

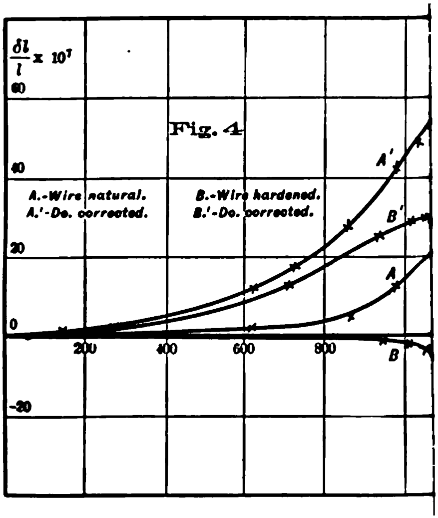


Fig. 4

MORE: C

by the $\frac{B^2}{8\pi}$ force, the relation may be expressed thus: A rod of iron elongates slowly until an intensity of about 800 is reached. After that point the rod elongates more rapidly and attains a maximum value of about 60×10^{-7} part of its length at an intensity of 1200. With greater intensities the elongation diminishes, the curve being approximately a nearly vertical straight line.

2. Hardening the wire diminishes the corrected elongation, and the wire attains its maximum length in a less intense field.

3. It has been shown that when the wire is stretched, the change in elasticity due to the magnetization produces an important effect. Neglecting this correction, the effects of stretching are similar to those caused by hardening the wire.

Before concluding I would acknowledge my indebtedness to Professor Rowland, not only for suggesting the investigation to me, but also for his assistance and kind consideration afterwards.

I also owe many thanks to Dr. Ames and to Dr. Duncan for advice and help.

NOTES.

Eli W. Blake.—Professor Blake was born in New Haven, Conn., April 20, 1836; he died at Hampton, Conn., October 1, 1895.

He was graduated at Yale in the class of 1857. After graduation he devoted a year to teaching in a private school at Unionville, Conn., and subsequently another year to study in the Sheffield Scientific School. Next he studied in Germany for three years and a half,—at Heidelberg under Bunsen and Kirchhoff, at Marburg under Kolbe, at Berlin under Dove and Magnus. He devoted his attention to both chemistry and physics; for although he became ultimately a physicist, it was his original intention to be a chemist. Upon his return, he was for a year (1866–67) professor of chemistry and physics in the University of Vermont and State Agricultural College; for the year 1868–69, acting-professor of physics in Columbia College, New York; and later, professor of physics and mechanic arts at Cornell University, then just opened. From 1870 to 1895, he was Hazard professor of physics in Brown University. Owing to the ill health of a member of his family, he resigned this chair to take effect June, 1895; but before that date he was taken slightly ill himself, and he did not recover. His constitution was weakened by the continuous and confining labors incidental to his profession, and he died after an illness of about five months. He was twice married, his second wife surviving him. By his first wife, who was a sister of Professor Ogden N. Rood, he leaves two children,—a son, Eli Whitney Blake, and a daughter, Mrs. Barclay Hazard, of California.

Professor Blake received the honorary degree of A.M. from the University of Vermont and State Agricultural School, and the degree of LL.D. from Brown University.

While he was at Brown University, that institution received from the late George F. Wilson, a bequest of above $100,000, to be devoted to a physical laboratory. Wilson Hall, immediately erected, will long stand, a monument to the generous donor; but it is also a monument to Professor Blake, to whose able, unwearied, and conscientious labors are largely due its appropriate and convenient arrangements.

Professor Blake had mental and spiritual qualities of a very high order. His sincere devotion to truth led to a conscientiousness, a high sense of honor, and great moral courage,—beautiful elements of character which he wore like parts of himself, and in no sense as garments, to be put on and off. His interest in his students was intense and genuine. He was one of the most unselfish of men. He was the warmest and truest of friends. While he devoted little time to society he was welcomed as a brilliant writer and talker, and as an affectionate and delightful companion.

By nature, Professor Blake had very strong mechanical and scientific tendencies. Indeed, they were in the blood; for he was grand-nephew of Eli Whitney, whose cotton-gin was an epoch-making machine. He was son of Eli Whitney Blake, of New Haven, himself a scientific man, manufacturer, and an inventor.

Professor Blake was an indefatigable worker in the laboratory. He was there from morning to night. He pursued experimental study in every department of physics, oftenest with apparatus of his own designing and the product of his own hands. Of his published work, the best known is the *Method of recording Articulate Vibrations by Means of Photography* (American Journal of Science, vol. 16, 1878).

JOHN HOWARD APPLETON.

The American Association for the Advancement of Science. — The forty-fourth meeting of the association was held at Springfield, Massachusetts, beginning on August 28, 1895. The hall for the general sessions, and the rooms for the various sections and affiliated societies, were conveniently located in the Christian Association Building and the Springfield High School, while a hall in the immediate neighborhood was put at the disposal of the association for the presentation of such papers as required the use of the lantern. Among the many pleasant features of the meeting were the receptions offered by the citizens of Springfield to the members of the association, and the Saturday excursion to Amherst and Northampton.

Although the attendance of physicists was not above the average, the sustained interest shown in the sessions of Section B, as well as the number and character of the papers presented, justify the remark made by several members that the meeting of this section at Springfield was one of the most satisfactory in recent years. In addition to the address of the vice-president, Professor W. Le Conte Stevens, on "Recent Progress in Optics," twenty-five papers were read as follows: —

"Expansion of Jessop's Steel, measured by Interferential Method," by E. W. Morley and William A. Rogers; "Flow of Alternating Current in an Electrical Cable," by M. I. Pupin; "The Most General Relation between Electric and Magnetic Force and their Displacements," by M. I. Pupin; "Relations of the Weather Bureau to the Science and Industry of the Country," by Willis L. Moore; "Solar Magnetic Radiation and Weather Forecasts," by Frank H. Bigelow; "Clouds and their Nomenclature," by

Cleveland Abbe; "Cloud Photography," by Alfred J. Henry; "A New Apparatus for Studying Color Phenomena," by E. R. von Nardroff; "Voice Production, with Photographs of the Vocal Cords in Action," by F. S. Muckey and William Hallock; "Note on the Limits of Range of the Human Voice," by W. Le Conte Stevens; "Voice Analysis, with Photographic Record," by F. S. Muckey and William Hallock; "Observations on the Relations of Certain Properties of Line Spectra to the Physical Conditions under which they are produced," by J. F. Mohler and W. J. Humphreys; "The Reproduction of Colors by Photography," by F. E. Ives; "Color Definitions for the Standard Dictionary," by William Hallock; "The Significance of Color Terms," by J. H. Pillsbury; "On Standard Colors," by J. H. Pillsbury; "The Analysis of Floral Colors," by J. H. Pillsbury; "On the Comparison in Brightness of Differently Colored Lights, and the 'Flicker' Photometer," by Frank P. Whitman; "Electrolytic Reproduction of Resonators," by William Hallock; "A Photographic Method of Comparing the Pitch of Tuning Forks," by William Hallock; "Illustration of Gems, Seals," etc., by William Hallock; "An Experimental Investigation of the Rotary Field," by H. S. Carhart; "Phenomena with Electric Waves analogous to those of Light with a Diffraction Grating," by C. D. Child; "The Effect of Age upon the Molecular Structure of Bronze, Glass, and Steel," by William A. Rogers; "A New Determination of the Relative Lengths of the Yard and Meter," by William A. Rogers; "An Examination of the Statement of Maxwell that all Heat is of the Same Kind," by William A. Rogers.

A noticeable feature of the meetings of Section B was the extensive use made of the lantern, not only for ordinary projection, but also for purposes of demonstration, as in the case of several of the papers dealing with color. The conditions under which papers are presented to the association render it, in fact, especially desirable that facilities for illustration and demonstration should be at hand. The plan of printing abstracts in advance, which has been adopted with such excellent results by many societies, does not yet appear feasible in the case of the American Association. Few members know even the titles of the papers presented until the day on which they are read. In order, therefore, that the points brought out may be fully appreciated, and that the discussion of a paper may be of value, the greatest possible clearness in presentation is essential. It is for this reason that the use of the lantern deserves to be encouraged; for there is nothing that contributes so much to clearness and concreteness as a well chosen illustration or experiment. In view of the rapid improvement in the provision made for scientific and technical education throughout the country, we may perhaps hope that in the near future Section B will always be able to find a place of meeting that offers *all* the facilities of a modern physical lecture-room. In the meantime the committee in whose hands is placed the arrangements for the coming meeting should realize that for the physics section the projecting lantern has become a necessity, and should make provision accordingly.

The next meeting of the association will be held in Buffalo, beginning on Monday, August 24, 1896. The officers of Section B are: *Vice-President*, Professor C. L. Mees, of Terre Haute, Ind.; *Secretary*, Professor F. P. Whitman, of Cleveland, O.

The change in the time of the first general session from Thursday to Monday is an innovation which it is hoped will lead to good results. Heretofore the Saturday and Sunday excursions have fallen at such a time as to divide the meeting practically into two; and in spite of the fact that the excursions are always enjoyable, and often possess a scientific interest, it has been the opinion of many that the interruption of the regular business meetings was undesirable. Under the new arrangement, four consecutive days will be available for the regular meetings of the sections.

The change mentioned above in the time of meeting is only one of the changes that were proposed and discussed in the council meetings. Several plans for strengthening the association were suggested and earnestly discussed; but it appeared best to postpone final action until these plans could be more thoroughly considered in committee. If we may judge by the earnestness and enthusiasm which marked the meetings of the council, an increased interest in the work of the association, and in consequence an increase in its usefulness, are to be confidently expected.

MINOR CONTRIBUTIONS.

THE LIMITS OF PITCH FOR THE HUMAN VOICE.

BY W. LE CONTE STEVENS.

IN connection with the interesting experiments on voice production and voice analysis, as communicated by Dr. Muckey and Dr. Hallock at the recent Springfield meeting of the American Association for the Advancement of Science, it may be advisable to record some observations on the limits of range actually reached.

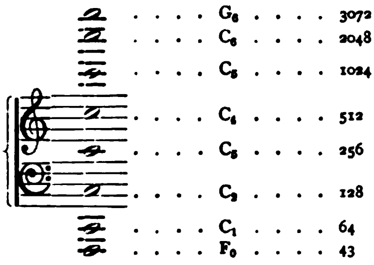
The determination of pitch in vocalization depends usually upon the musical training of the observer. With moderate practice it is quite possible to estimate the vibration frequency with such accuracy that the error is much less than a semitone. Assume that the observer has a tuning-fork of known pitch, such as C_4 (512 double vibrations per second). If the frequency of the tone to be investigated is between 256 and 1024, differing thus less than an octave from the standard, and if it makes a recognizable interval, such as a major third or minor sixth, with the standard taken as keynote, the application of the corresponding numerical ratio gives the pitch at once. If the interval be not exact, its departure from exactness has to be estimated; and here the training of the physicist has to be conjoined with that of the musician. If the observed pitch differ from the standard by an interval much wider than an octave, a tone in unison with it can be instantly sounded with the voice or by whistling. The succession of octaves above or below are then sounded until a pitch is attained that is easily comparable with the standard; or this process may be reversed, the standard being taken as starting-point, and a succession of octaves above or below it quickly furnishes the means for comparison. During my college days I acquired the habit of carrying a tuning-fork (512 vs.); and this habit has been retained to the present day, though the fork is utilized much less frequently than during the earlier period of musical activity. The estimation of pitch by its aid was so much practised as to become very easy, and the extremes of pitch noticed in concert or at the opera were often estimated. When the printed music is at hand, the correctness of such an estimate is readily verified.

The lowest vocal pitch hitherto recorded is F_0, about 43 vs., which is credited to a German basso, Fischer, who lived during the sixteenth century.

In modern opera the basso is rarely ever required to sound lower than C^1 (64 vs.). This limit may be passed by an ordinary masculine voice under abnormal conditions. With the vocal cords thickened by an attack of influenza, I have sounded as low as A_0 (53 vs.), but the sound was faint and of the poorest musical quality.

An ordinary soprano voice may reach C_5 (1024 vs.); and it may be safely stated, in round numbers, that the limits of range of the average adult human voice are from 100 for basso to 1000 for soprano. Adelina Patti is said to sing as high as G_5 (1536 vs.) without sacrifice of good quality. At Parma in 1770 Mozart tested the voice of Lucrezia Ajugari, who trilled on D_5 (1152 vs.), and sang several passages of higher pitch, one of which included C_6 (2048 vs.). An American soprano, Miss Ellen B. Yaw, has lately surpassed this limit, attaining a pitch which is stated to be E_6 (2560 vs.). This statement is made in the advertisement of a concert manager. For the exceptional adult human voice the limits may, therefore, be given as about 50 for basso and 2500 for soprano.

In early childhood all the tissues of the human body are softer and more elastic than after maturity is reached, and it is well known that the conversational pitch in childhood is higher than it is afterward in youth. But I have seen thus far no published record of the highest observed pitch of a child's voice. A few years ago my attention was casually attracted to the squeal of a child at play. The tuning-fork standard at once enabled me to estimate the pitch as G_6 (3072 vs.). This result was so remarkable that, in the absence of any immediate opportunity for verification, I rejected it as possibly the outcome of faulty observation. A few months afterward, while lingering near a group of children at play, I estimated the pitch of quite a succession of squeals, with results varying from 2500 to 3000 double vibrations per second. The observation has since been repeated many times, so that there is no reasonable doubt of the correctness of the first estimate. Under the excitement due to either terror or enthusiasm, the voice may, without conscious strain, reach a limit quite unattainable in song.



These results are conveniently expressed in musical notation. The extreme range is seen to be a trifle in excess of six octaves. For a single voice the range after maturity is rarely greater than three octaves. Ajugari sang as low as G_2 (192 vs.), reaching the phenomenal range of four and a half octaves. Two octaves is the range commonly assigned for the average adult voice.

THE NEW PHYSICS LABORATORY AT LILLE.

By E. L. Nichols.

On June 1 and 2, 1895, the University of Lille,[1] celebrated by a series of magnificent *fêtes* the opening of seven new buildings devoted to learning. The cost of these, which amounted to 3,500,000 francs, was shared equally by the state and by the city of Lille.

One of the new buildings, the exterior of which is shown in Fig. 1, is an institute of physics. It is not large, compared with many modern European laboratories, but it is well arranged; and it shows in its interior fittings a sumptuousness such as nature, until very recently at any rate, has been unaccustomed to find in the temples devoted to her service. Some of these decorative features appear in the view of a corner of the large lecture-room, Fig. 2.

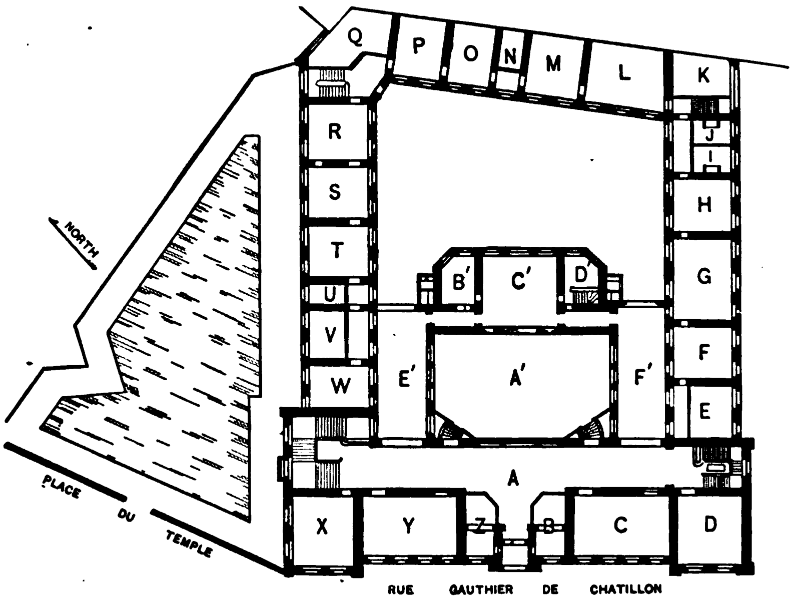


Fig. 3.

The characteristic feature of this laboratory is the subdivision of its interior into many small rooms, each of which is well lighted and easily accessible. These are arranged around a central court.

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[1] Officially known as the "Académie de Lille," an institution which, like all the French provincial universities, is affiliated with the University of France.

Fig. 2. — Large Lecture-room.

Fig. 1. — The Physical Laboratory at Lille.

Thus, on the first floor, Fig. 4, there is a suite of nineteen small laboratory rooms, devoted to elementary practice work. In these the apparatus for such work is permanently mounted, there being only one or two experiments in a room. These rooms are not thrown together, but all may be entered from a corridor which serves as means of communication.

On the lower floor, the plan of which is shown in Fig. 3, the corresponding set of rooms is used for research laboratories, offices, etc. There is no corridor, but the adjoining rooms are connected throughout by doors.

This arrangement of many small rooms, within which the multitude of special operations of which experimental physics consists may be performed, each in an apartment assigned to it and planned for it, will meet the approval of nearly all physicists.

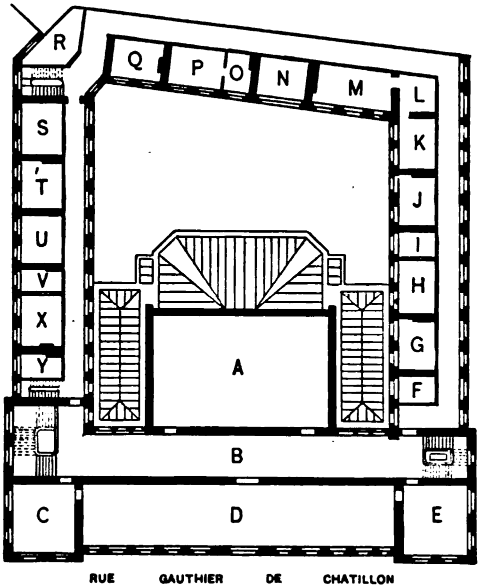

Fig. 4.

The Lille laboratory has its own installation of electric lighting. This, like that of nearly all the newer European laboratories, consists of a gas engine, two small dynamos, and a set of accumulators of considerable capacity. The voltage of these batteries is sufficient to serve for arc and glow lighting, as well as for general laboratory purposes.

The low price of gas, and the high stage of development to which both the gas engine and the storage battery have been brought in Europe, render this an economical and a very convenient arrangement.

NEW BOOKS.

Electric Waves, being Researches on the Propagation of Electric Action with Finite Velocity through Space. By Dr. Heinrich Hertz, Professor of Physics in the University of Bonn. Authorized English Translation by D. E. Jones. 8vo, pp. xv, 278. London, Macmillan & Co., 1894.

At this time of writing, there is small need to describe Hertz's experiments. The term Electric Waves has become a household word, and the demonstration of electromagnetic radiations has become a matter for the popular lecture as well as the class-room. A host of investigators has followed in the steps of Hertz, and this region of research is at present in the heyday of popularity. The ether is a favorite subject of conversation and of publication by authors whose knowledge of mathematics is of the most rudimentary character. This is one of the unfortunate results of the existence of fashions in science, and of the attempt at popularization of difficult subjects by such men as Kelvin and Lodge. Not that the reviewer wishes to discourage popularization, but that it has its disadvantages. One has only to pick up a newspaper or magazine article with the heading "Tesla" to see an example. The present work does not deal with "waggling the charge of the earth," although it contains the account of the original experiments on oscillations of the charges of conductors disturbed from equilibrium, and *measurements* of the action of these oscillations. It is a matter for congratulation that the different researches of Hertz on this subject were collected by him into a volume, and it is a matter for satisfaction to the non-German-reading scientific world (alas that there is one!) to have them translated into English. The title of the work has been changed in the translation, which is also furnished with a preface by Lord Kelvin on the history of the controversy between the adherents of Action at a Distance and the contrary, from the times of Newton and Descartes to that of Hertz. Hertz is indeed fortunate in his preface-writers. To have one's principal works prefaced by the greatest physicists of two of the greatest nations in science does not fall to the lot of many authors, and is not to be lightly valued. In the preface it is stated that Faraday himself, when last seen by Lord Kelvin, was attempting to discover whether magnetic force was propagated with a finite velocity. Nothing came of these experiments, however.

The author is also fortunate in his translator. Mr. Jones has given us an excellent rendition of the sense of the original without considering it necessary to preserve the German spirit by the use of such misshapen English as we often get from enthusiastic pupils of distinguished German professors. Whether it was this fact, or the insight displayed in wishing to present Hertz's work in an English dress, or the experimental work done by the translator under the direction of Hertz, that the Royal Society considered worthy to be honored by a medal, we can only guess.

In the introduction Hertz gives an account of the manner in which he came to make these researches. An account of his first introduction to the subject has been given in a previous number of this journal.[1] The prize question set by the Berlin academy for a relation between electromagnetic force and dielectric polarization of insulators, set him to thinking of what results could be obtained by the use of Leyden jars or the open circuits of induction coils. Consideration seemed to show that the effects desired would be too small to measure. Not discouraged, however, but continually ruminating on the properties of electrical oscillations, a chance observation of a side spark from one of a pair of coils, when a Leyden jar was discharged through the other, set him at work on methodical observations of the phenomenon which contained the germ of his whole subsequent discoveries. His subsequent course of procedure is described with charming frankness, his mistaken conclusions being related with the same readiness as his successful ones, and full acknowledgment being made of the work of other savants with whom he at times found himself in controversy. It is interesting to see how very nearly Professor Lodge came to making the same discoveries as Hertz, who declares that Lodge was on the way to the observation of waves in air, and would probably thus have discovered the finite velocity. The last part of the introduction is devoted to a comparison of the old theories with Maxwell's theory, and to answering the question, "What is Maxwell's theory?" After admitting his inability to understand just what Maxwell intended as the physical representation of his mathematical conceptions, — a state of mind that will be sympathized with by every careful student of Maxwell, — he gives the very sensible answer: "Maxwell's theory is Maxwell's System of equations. Every theory which leads to the same system of equations, and therefore comprises the same possible phenomena, I would consider as being a form or special case of Maxwell's theory." This will be seen to be in line with the views of Helmholtz on mechanics mentioned above. This is a point that cannot be too strongly impressed on amateur theorizers, that the test of a theory is that it leads to the equations which are known to express the facts. If it does not, it is good for the waste-basket. The writer, and, as he supposes, all teachers

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[1] PHYSICAL REVIEW, Vol. III. p. 73.

of physics, is in frequent receipt of visits from people with favorite elaborate theories, destined to overthrow Newton, Maxwell, or somebody else, the inventor having invariably no knowledge whatever of mathematics. If these people could be put at some mild employment that would keep them from inventing theories it would be a great gain to the world.

The whole of these fourteen papers, with the exception of the second, on the influence of ultra-violet light in reducing the potential at which discharge takes place, possess a remarkable degree of continuity. Few are more admirable than the first, in which is shown the means of disturbing the charge in a wire conductor so as to cause oscillations, and in which the function of the spark of the induction coil in giving the necessary impulse and lowering the resistance of the air gap enough for the oscillations to occur is clearly described. The existence of wave propagation in the wires is recognized, and the position of the nodes of vibration determined. The existence of resonance was first predicted from theoretical considerations, and then observed and found to increase and decrease precisely as theory demanded.

After admiring the close thinking shown in the performance of these experiments, it comes somewhat as a shock to the reader to find in the next paper quotations from a paper by von Bezold, published seventeen years before, in which many of the same phenomena were observed, the methods of exciting the vibrations being identical. Of the existence of this paper Hertz was at the time of his work of course unaware. It is curious to look over the work of Lodge done at about this time, and to see how similar were the methods used, also with a perfect comprehension of the issues involved. The one thing lacking in Lodge's work was quantitative results of the same order of precision as Hertz's. The present writer remembers that soon after the time of these researches, while he was engaged in demonstrating some of Lodge's experimental results in the laboratory in Berlin, on the occasion of the visit of a number of distinguished physicists connected with the newly established Reichsanstalt, Professor von Bezold seemed quite interested in the experiments, and quietly remarked that he had noticed something similar several years before, giving the reference to his paper. The question naturally arises, how could von Bezold's paper have attracted so little attention, while Hertz produced such a stir years after. Probably because Hertz followed up his researches with others in a logically conducted series resulting in a new discovery. In the next of the series, the effect of the oscillator at various points in space is calculated, and the effects of the magnetic force separated from the electric force by experiments devised with extreme penetration. Next the effect of the electromagnetic action upon insulators is demonstrated, and thus one of the original objects of the investigation fulfilled. Next by the interference of waves in air with waves propagated in a wire, the existence of a finite velocity is proved, and an attempt made to estimate it by the determination of the wave-length in the wire, the period of the vibration being calculated by the old theory. It is to be noticed that this is the case in the whole series of researches, the calculation of the period depends upon a theory, and hence no direct verification of the velocity demanded by Maxwell's theory would thus be possible. It is worthy of note that neither Hertz nor any of his immediate successors, though they measured wave-lengths without number, ever made a direct determination of the velocity by observing the other needed element, the time. The present writer described such a direct method to Professor Kundt five years ago, and was advised to carry it out, but the facilities not being available, it was put by till a more convenient season. Before this occasion arrived, the experiment had been carried out by Blondlot in the same manner, described in his paper on the determination of the Velocity of Propagation by a method independent of any theory. This was the first and only direct determination until the recent publication of the work of Professor Trowbridge and Mr. Duane, which again anticipated the completion of a precisely similar piece of work done under the direction of the writer. It is, however, desirable to have this velocity determined as often as possible, until it can take its place with other well-authenticated physical constants.

It is in this last research that Hertz had his only disappointment. He thought he had shown that the velocity was different in air and in wires, a mistake that was soon corrected by others. Hertz says that although he may have been lucky elsewhere, certainly here he was unlucky. This is certainly too much modesty. Never could a man with less justice have had his success attributed to luck. With Hertz everything was deliberately planned. After proving the velocity of propagation to be finite, knowing that the waves should be capable of reflection and refraction, he makes them reflect and refract. Knowing that oscillatory currents should not penetrate into the interior of conductors, he demonstrates that they do not. Having calculated what mechanical forces they should exercise, he straightway observes them. These researches are a notable example of how experimental work should be prosecuted, and convey a lesson that should be taken to heart by the student. The proper order of procedure may be stated: "Think, calculate, plan, experiment, think, — and first, last, and all the time, *think.*" The method often pursued is: "Wonder, guess, putter, guess again, theorize, and above all avoid calculation." Throughout Hertz's work we are constantly reminded of Faraday by the remarkable acuteness of interpretation of results as well as in the skilful devising of the experiments. Hertz adds to Faraday's experimental skill a mathematical ability that Faraday did not possess, although he had an intuition which nearly replaced it.

Finally, and, in the opinion of the writer, of most importance, Hertz concludes with two mathematical papers on the fundamental equations, that is, with an exposition of Maxwell's theory. In these he brings out with the greatest vividness the complete duality of all electrical and magnetic phenomena, with the exception of conduction. It is no discredit to Hertz that Heaviside had previously done the same thing with equal clear-sightedness. Heaviside suffers under the disadvantage of having written so much and so diffusely that ten students will read Hertz's papers for one that reads Heaviside's. Maxwell's great work is full of obscurities, incongruities, and contradictions. These he would doubtless have removed in rewriting the work if he had lived. None of his commentators have done it for him, with the exception of these two. Both have adopted unconsciously the same method, namely, that of considering the two vectors, electric and magnetic force, as the essential quantities that are propagated, avoiding introduction of the potentials and vector-potentials, and eliminating altogether the magnetizations. The notation of Hertz commends itself by its perfect symmetry and simplicity. A pair of equations saying that the time derivative of the *induction*, electric or magnetic, is proportional to the curl of the other *force*, another pair saying that either induction is a linear vector function of its own force, — that is all. The real electricity or magnetism is defined by the corresponding induction, the free, or apparent, by the force in the same manner. The treatment of the equations for moving bodies is the most logical that has been given, and by proceeding in a straightforward manner terms are introduced which are lacking in Maxwell's equations. The effect of static charges carried by moving conductors, demonstrated by Rowland's famous experiment, is one of these. There are other effects of a dual nature that are still left to verify, of which more may be said later.

The only fault that can be found with Hertz's notation is that it involves the use of German letters for the components of the inductions. These are inconvenient for writing by Anglo-Saxons, and the writer ventures to suggest a substitution, which he has been accustomed to make use of in his lectures, of the French round letters frequently used by architects in lettering, which are easy to write, not impossible for printers, and easy to name in reading, distinguishing "round $\mathcal{X}$" and "square X." He hopes that this mild suggestion will not be run afoul of by some member of the American Institute of Electrical Engineers, stating that M. Hospitalier has already proposed these for something entirely different.

In conclusion, let us advise the student to place this volume on his shelves with its first, experimental side next to Faraday's Experimental

Researches, and with its second, or mathematical part, next to Maxwell's Treatise, "for on these three hang all the law and the prophets" of electricity.

ARTHUR G. WEBSTER.

Mechanics, an Elementary Text-Book, Theoretical and Practical, for Colleges and Schools: Dynamics. By R. T. GLAZEBROOK, M.A., F.R.S. 8vo, pp. xii+256. Cambridge, the University Press, 1895.

The past year has been prolific of works on Physical Science. Having come to realize that existing text-books are of doubtful utility, because of their ancient character, the scientific world has aroused itself to the task of producing new ones that are at once the result and the harbinger of a more practical method. The text-books by R. T. Glazebrook are especially deserving of notice. The one mentioned above is one of a series by this writer which bear the same general character as to method, and which give promise of covering quite thoroughly and efficiently that portion of physics usually taught as a Sophomore or Junior course in college.

The conviction is at once forced upon the reader that the book in question is the outgrowth of the author's method of teaching, and he is therefore the more gratified on turning to the preface to read: "The portions of the following book designated Experiments have, for the most part, been in use for some time as a Practical Course for Medical Students at the Cavendish Laboratory." . . . "The rest of the book contains the explanation of the theory of those experiments, and an account of the deductions therefrom." In fact, it would seem that the author's method of presenting physics to a class is the best calculated to secure results, and is at the same time within the reach of any teacher, and of any institution — even one of limited resources. The author develops the theory, and immediately proceeds to give definite instructions for its verification and practical application, describing in connection therewith apparatus suitable for the purpose, of so simple a character that it can be easily set up and adjusted in any laboratory. The same apparatus, moreover, is suitable for lecture-room purposes; for in the preface we find the statement: "most of the lecture-room experiments are performed with the apparatus which is afterwards used by the class, and wherever it can be done, the theoretical consequences are deduced from the results of these experiments." This plan seems an ideal one for teaching physics, giving, as it does, to the lecture, recitation, and laboratory a unity of character that can scarcely be obtained otherwise; and it is no small advantage in a book that makes this method possible. The style of the book is best described as tangible.

A first book in Mechanics should appeal to the experience of the student, for the science itself is built upon the everyday experiences of life. In expounding Newton's Third Law, he makes clear what is meant by "Action" and "Reaction," nor does he consider it undignified to appeal to the case of horse drawing the canal boat, and even the tyro in mechanical science cannot fail to see clearly the application.

The classification of the subject is a happy one. The first chapter is devoted to measurements of length, area, and volume. Two chapters are then taken up by Kinematics — Velocity and Acceleration, respectively. Momentum is then presented in an inductive manner, while the fourth chapter deals with rate of change of momentum, — Force. The sixth, seventh, and eighth chapters are devoted to Newton's Laws of Motion, the last one including, naturally enough, the treatment of energy. In the ninth chapter curvilinear motion is presented, which subject includes quite a full treatment of Projectiles. The tenth chapter is devoted to Collisions, while the eleventh, entitled "Motion in a Circle," deals with a variety of subjects, including the Hodograph, Circular Motion, Simple Harmonic Motion, and The Pendulum.

The chapters on force and energy are especially clear and full. The treatment of Newton's Laws is no less good, as is also that on Collisions. It would seem, however, from the small amount of space devoted to the subject, that the author underrates the importance of simple harmonic motion. The same criticism might well be passed upon his treatment of the pendulum; and an even more glaring defect is the entire absence of any mention of the moment of inertia and the whole subject of moments. In fact, it would seem that after a most excellent treatment of the subjects included in the first ten chapters, the publication of the book was hurried to the extent of grouping all that was left of mechanics — not a small portion — in the last, the eleventh, chapter.

The book is remarkable for its accuracy, both of principle and detail. Seldom does it happen that a first edition does not present errors to be corrected in a second. The absence of even typographic errors makes the book conspicuous in this particular. The excellent historical treatment of the subject is also to be noted. Nor should a review of the book omit mention of the excellent collection of problems included at the close of each chapter.

Text-books on this subject are generally too simple or too elaborate for a conception of elementary mechanical principles. This book cannot fail to recommend itself, therefore, for a first course, preliminary to the study of physical science. No other book presents in the same space, with the same clearness and exactness, so large a range of mechanical principles.

HENRY E. LAWRENCE.

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THE PHYSICAL REVIEW.

ON THE PHOTOMETRY OF DIFFERENTLY COLORED LIGHTS AND THE "FLICKER" PHOTOMETER.[1]

BY FRANK P. WHITMAN.

IN November, 1893, during measurements on some colored disks, it became necessary to know the relative luminosities of the colored papers employed. An attempt was first made to estimate the luminosity directly by comparison with Maxwell disks of black and white, smaller in diameter, and mounted on the same axis. The relative proportions of black and white were changed until, on rotation, they formed a gray, which was estimated to be about equal in brightness to the colored disk under examination. This method, practiced by certain experienced observers, doubtless has afforded good results, but in my hands proved difficult and uncertain.

Trials were then made by four other observers, all somewhat skilled in physical measurement, whose general color-sense was found to be similar, but their estimates of luminosity were found to vary in such an irregular fashion as to make any comparison impossible.

Later experiments, carried out with the help of some thirty undergraduate students, led to similar results. Differences of 50 per cent between two different observers frequently arose,

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[1] Read at the Springfield meeting of the A. A. A. S., Aug. 30, 1895.

when the light to be compared differed no more than an ordinary from a Welsbach gas-burner; while the same observers, working with light of the same color, would agree at least within 2 or 3 per cent.

By practice the margins of difference may be rendered smaller, yet experts often differ in their estimates of the brightness of arc lights when compared with standards of different color; and it is questionable whether one can always be sure that by practice in such measurements he gains greatly in accuracy. His measurements agree with each other better than at first, but if his method of comparison have in it something of an arbitrary or personal quality, as it must from the very nature of the case, it remains uncertain whether he may not be fixing himself in an erroneous practice rather than approaching a correct one.

The character of these results, and the need of some more exact method of comparing color-luminosities, led to the consideration of Professor Rood's "flicker" experiments.[1]

Rood prepared about fifty gray disks differing successively, as equally as possible, in depth of tint from black to white. If a dark shade was combined with a light shade in the usual way, and rotated rather slowly, the familiar unpleasant sensation known as a flicker was produced; but if successive pairs, more and more nearly alike, were chosen, the flicker became less, until it almost or quite disappeared. Nearly the same effect was produced if, instead of a gray, some other color was substituted on one of the disks. It was always possible to combine with it a gray disk of such a shade that the flicker nearly ceased, showing that this sensation is apparently independent of the wave-lengths of the lights compared, and dependent only on their relative luminosities. Professor Rood suggests that the principle may be easily applied to ordinary photometric work, but indicates no method. The special arrangement described in his paper serves admirably to compare pigments, when in such form that they can be spread upon disks and mounted in the whirling machine.

For ordinary photometric purposes, however, there is necessary some arrangement by which luminosity can be varied continuously

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[1] American Journal of Science, Vol. XLVI., September, 1893.

instead of step by step, as with a set of gray disks, which can be mounted on a photometer bar so as to compare colored lights as well as colored pigments, and which is reasonably quick and convenient in use. No doubt there are many ways of applying Professor Rood's flicker principle; the one which I, after some trial, found most successful was as follows: —

A card was cut in the shape *AHBG*, in the figure, so as to form two semicircles of about 5 and 8 cm. radius respectively, joined along a common diameter. This could be rotated at any desired speed about the axis *K*, in earlier experiments by clockwork, but afterward, and more conveniently, by hand. A diagrammatic plan of the apparatus as used is shown in the figure. *DE* represents the photometer bar, *AB* is the revolving disk, *C* is a card, which may be white or colored with any pigment which it is desired to study, *F* is a tube through which the observer looks. It is evident that when the apparatus is in the position shown in the figure, the outer portion of the revolving disk only will be visible through the tube, but when the disk is rotated half a turn, the small semicircle will not come into view at all, and the observer will see only the card *C*. As the disk revolves, the two pieces will

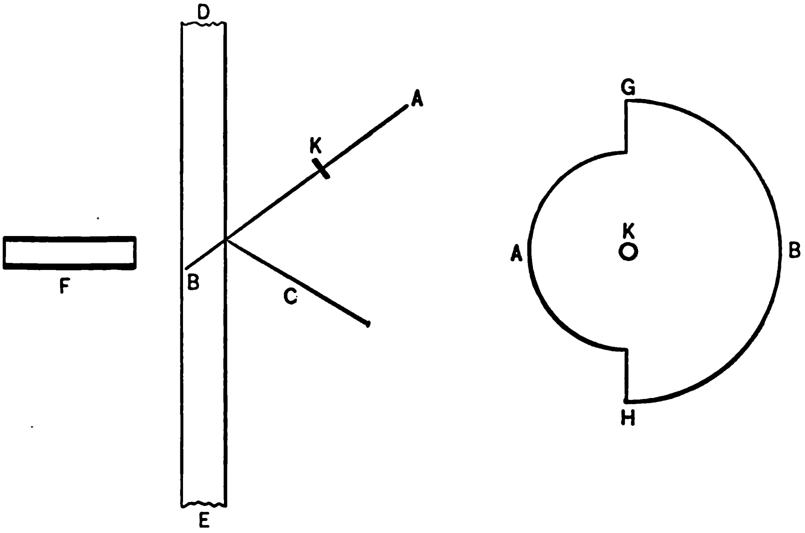

Fig. 1.

be presented to the eye in rapid succession, and, if they differ in luminosity, will produce the sensation of "flicker." If equal lights are placed at the ends of the photometer bar, the relative illumination of the card and disk can be varied by sliding the photometer along the bar. The flickering sensation can thus be entirely destroyed, whatever the colors are upon the card and disk. (Various colors were tried upon the disk, — red, white, and different grays, — but white was finally adopted as in all cases the most convenient.) When the proper position of the photometer was reached, not only did the flicker vanish, but the sense of color in the field of vision became much weaker or entirely disappeared, so that it was frequently difficult or impossible to tell what color was upon the card. A slight movement of the photometer in either direction revived the sense of color and reëstablished the flicker. The results obtained with this instrument were surprisingly good in ease, rapidity, and precision.

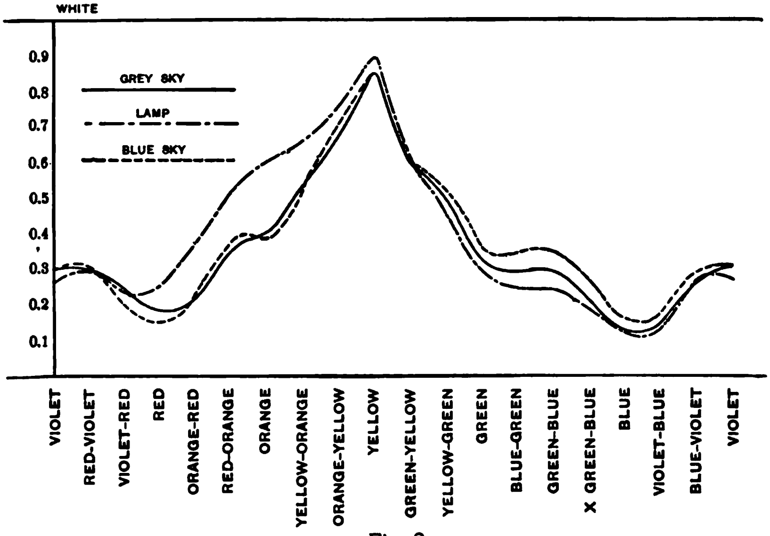

Fig. 2.

Work was interrupted at this point until May, 1895, when the measurements were taken up again, and the instrument itself somewhat carefully studied.

The colors used for experiments on pigments were chosen from the well-known series of colored papers made by the Milton Bradley Company of Springfield, Mass., and included the whole range of the spectrum. These papers were pasted upon perfectly flat cards, and placed successively in the position marked *C* in the figure. Three curves are shown to illustrate the capacity of the instrument, exhibiting the relative luminosities of these nineteen colors, when illuminated by the light of a kerosene lamp, of a dull gray sky, and of a bright blue sky.

The predominance of the lamp-curve toward the red end of the spectrum and of the clear sky at the other end is manifest, while the similarity of the curves shows that the measurements are of like character and definiteness, whatever the source of illumination. In all these cases the revolving disk was white, lighted by a lamp, while the colors on the card were exposed to the light under investigation. Since the flicker effect is independent of the wave-length, any source of light which is constant may be used to illuminate the disk without changing the results dependent on the luminosity of the colored card. The curves from sky light and cloud light, though the mean of several trials, were not entirely satisfactory on account of the comparatively inconstant brightness of these sources of light. The observations on lamplight, however, were made twice, at an interval of over two months, with practically identical results.

A greater interest, perhaps, lies in the instrument itself. An apparatus so new, and depending on a physiological principle which has been so little studied, presents many points for investigation, before its utility as a practical photometric apparatus is assured. The remainder of this paper is occupied with a study of some of these points.

1. The precision of setting, as compared with other types of photometer, was tested in over one hundred settings on nineteen different colors. The difference between two successive readings was seldom more than one per cent, though a few readings differed as much as two or three per cent. As these readings were made over the whole range of the spectrum, it seems fair to say that the instrument can be used upon lights presenting the widest differences of wave-length, with a precision approaching that of ordinary types of photometer when comparing lights of the same color.

2. Since the photometer depends, not on the actual comparison of like quantities, but on the distinctness of a peculiar physiological sensation, — the flicker, — it is worth while to see whether different observers will agree. To test this question, and incidentally to try the instrument with colored lights instead of colored papers, both disk and card were made white, and equal lamps, the colors of which could be changed at pleasure by the interposition of colored glass, were placed at the ends of the photometer bar. Two observers, whose eyes were known to be similar, compared successively the brightness of the two naked lamps, first by an ordinary photometric method, then by the flicker. A red glass was then placed in front of one lamp, a green glass in front of the other, and the same observations were made again. One of the two observers had never seen the instrument before. The results follow, each being the mean of four or five concordant observations. The actual readings are given in feet and hundredths, not reduced to comparative luminosities. One lamp stood at 3.00, the other at 9.00 on the photometer bar.

Observer F.		Observer W.	
Ordinary.	Flicker.	Ordinary.	Flicker.
Both lights naked.			
5.98	5.96	5.98	5.98
Left lamp red, right green.			
5.59	6.79	6.08	6.88

Thus, in the last case, the setting of F by direct estimation differed from that by flicker by 1.20 feet, that of W by 0.80 foot.

The setting of F by estimation differed from that of W by 0.49 foot ; while F's flicker setting differed from W's by only 0.09 foot. The last disagreement is comparable with the errors of observation.

At a later time, three other observers, making comparisons for technical purposes between coal-oil lamps and a standard candle which differed from them somewhat in color, were able with the flicker photometer to obtain accordant results among themselves much more easily and surely than by ordinary methods.

3. Two "disks" like those in the cut were mounted on the same axis in the photometer. By sliding one upon the other, the fraction of a revolution during which the card was visible could be varied between 180° and 0°. The relative length of exposure of the eye to the two lights could thus be varied within wide limits. Several comparisons were made of lights differing widely in color, and with openings from 22½° to 180°, but no differences in reading were observed that could be traced to this cause. While it is true that the sensitiveness of the retina differs for lights of different wave-lengths, and probable that differently colored lights require different periods of time to produce equal sensations in the eye, it appears from these experiments that there is time, at the comparatively slow rate of rotation of the disk, for every color to produce its full effect, so that errors which might be produced by irregularity in rate of rotation or in shape of the disk are negligible.

4. In much of the work, the photometer and the standard lamp were kept at fixed points, and the balance obtained by moving the other light, thus making all comparisons at the same actual degree of illumination. This method of using any photometer has some obvious advantages, though the sensitiveness is not quite so great as when the photometer itself is moved. To determine whether the absolute brightness has any effect on the settings, measurements were made of six colors — red, orange, yellow, green, blue, violet — under widely differing illuminations. When the light was faint the measurement became much more difficult, but the results obtained with bright and faint light did not appreciably differ, showing that the well-known greater sensitiveness of the eye to blue light is not important in measurements made under conditions proper to this photometer. When the illumination is small the flicker is very faint and may be invisible while the photometer is moved over as much as 6 or 8 cm., but by reading the points each side of this space where the flicker again becomes visible, and taking the mean of the two readings, results may be obtained almost as trustworthy as with brighter light. It should be remarked that this method in general depends for its value somewhat on the state of the eye. It appears certain that

two normal eyes, in a reasonably fresh condition, would obtain like results, but if the eye is wearied from long-continued observation or loss of sleep, the perception of the flicker becomes more difficult, and the difficulty appears to vary with different colors in a way that has not yet been studied.

5. The question still remains, whether the flicker method gives in all cases a true measure of luminosity comparable to that which would be obtained by any more direct photometric method. To test this, the luminosity measures afforded by Maxwell's disks were used.

Suppose, for example, three colors — say red, green, blue — combined on the whirling machine into a neutral gray, which is matched by the combination of a black and a white disk. The amount of white in the latter combination, corrected for the white light reflected by the black portion, is of course the measure of the luminosity of the colored disk in terms of white, which quantity, again, is dependent upon the luminosities of the three colors of which it is composed.

If now the fraction of the whole circle occupied by any color is multiplied by its luminosity as measured with the flicker photometer, the result will be the amount of white equivalent to that colored sector, and the sum of the results obtained by treating each of the colored sectors in this way should equal the amount of white in the black and white disk. Two examples are given below. The circumference of the disk was divided into one hundred equal parts, so that the numbers given are direct percentages of the whole circle.

The upper row of figures in each case is the ordinary color-disk equation. The second is the luminosity of the given colors referred to white, as measured by the flicker, the lower line gives the product in each case. The sum of these products given under white should be the same as the white in the upper row, which is the corrected reading from the black and white Maxwell disks.

	Red.	Green.	Blue.	White.	Red.	Green-Yellow.	Blue.	White.
Color-equation	40.5	49.2	10.3	22.6	18.5	34.0	47.5	30.4
Luminosity	0.238	0.295	0.106	—	0.238	0.617	0.106	—
	9.64	14.50	1.09	25.23	4.41	20.96	5.03	30.40

Fourteen such trials were made with different colors, the results differing by one to three per cent from exact equality.

Summary.

The flicker photometer used to compare lights of any color approximates in convenience and accuracy any of the ordinary photometric appliances used with lights of the same color. Different observers whose vision is normal obtain like results.

Irregularities in the division of the disk or the rate of rotation are without appreciable effect on the precision of the measurements.

Differences in the absolute brightness of the lights compared present no greater difficulties than in any photometric method.

The instrument gives a true measure of luminosity comparable with that obtained in other trustworthy ways.

Adelbert College, Nov. 1, 1895.

THE CHEMICAL POTENTIAL OF THE METALS.

BY WILDER D. BANCROFT.

IN a previous paper[1] I have communicated the numerical values of the electromotive force of certain cells, consisting of two metals and a single solution. It is now desirable to consider the relation between these single-liquid polarizable cells and the corresponding constant reversible cells of the Daniell type. According to the theory of Nernst, the potential difference between a metal and a solution of a salt of that metal is given by the expression[2]

$$\pi = \frac{RT}{ne} \log \frac{P}{p} \times 10^{-4} \text{ volts,}$$

where π is the potential difference, n the valency of the kation, p its partial osmotic pressure, e the quantity of electricity transported by a gram-equivalent, and P the solution pressure of the electrode metal. The electromotive force of a cell of the Daniell type $M_1|p_1M_1X|p_2M_2X|M_2$ will be the algebraic sum of the two potential differences between the metals and the solutions, plus the difference of potential between the solutions. I leave out of account a possible potential difference between the metals, as this term is negligible so far as our present knowledge goes. The electromotive force of this type of cell will be

$$\pi = \frac{RT}{ne}\left(\log \frac{PM_1}{PM_2} + \log \frac{p_2}{p_1}\right) \times 10^{-4} + z \text{ volts,}$$

where z represents the difference of potential between the solutions, and the valency of the metals M_1 and M_2 is the same. If the wandering velocities of the ions M_1 and M_2 are nearly equal,

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[1] Zeitschr. f. ph. Chem., 12, 289, 1893. Through a misprint on p. 290, the correction for Pb|Hg in NaI, and Bi|Hg in NaCl, reads 0.25 and 0.75 volts, instead of 0.025 and 0.075 volts respectively.

[2] Ibid., 4, 148, 1889.

and p_1 and p_2 be made so, the value of z approaches zero, while the term $\log \frac{p_2}{p_1}$ drops out entirely. The electromotive force of the cell, $M_1|pM_1X|pM_2X|M_2$, is given very nearly by the expression

$$\pi = \frac{RT}{ne} \log \frac{PM_1}{PM_2} \times 10^{-4} \text{ volts},$$

and is independent of the absolute concentration of the salts M_1X and M_2X. Let us take as a concrete case the cell $Zn|ZnSO_4|CuSO_4|Cu$, and let the concentrations of the zinc and copper sulfates always be equal. It has been found experimentally that the electromotive force of this cell is independent of the absolute concentration.[1] Suppose that instead of diluting the two solutions with pure water, we add a solution of K_2SO_4. According to Nernst's theory, this will have no influence on the electromotive force, except in so far as it affects the dissociation of the two sulfates, and thereby the concentrations of the Zn and Cu ions. If the dilution be carried far enough, we shall come at last, without change of electromotive force, to the cell with neither zinc nor copper sulfate, to the cell $Zn|0\,ZnSO_4 + x\,K_2SO_4|0\,CuSO_4 + x\,K_2SO_4|Cu$, which is the same as the cell $Zn|x\,K_2SO_4|Cu$. In other words, the one-liquid, non-reversible cells are the limiting cases of the two-liquid, reversible cells in which the concentrations and wandering velocities of the reversible ions are equal, the dissociation being assumed to be complete. This last clause is necessary; for if the percentage dissociations of the zinc sulfate and copper sulfate were different, equal concentrations of the two sulfates would not correspond to equal concentrations of zinc and copper ions, and this would affect the potential difference between the solutions. The concentration of the K_2SO_4 should have no effect, and it was shown in my previous paper[2] that this was the case. It is clear that in measurements made with two-liquid, reversible cells, there are two sources of error besides those due to the surface conditions of the electrodes. These are differences of concentration and differences of wandering velocities.

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[1] Wright, Phil. Mag. (5), 13, 265, 1882.

[2] Zeitschr. f. ph. Chem., 12, 294, 1893, Tables II., V.

The effects of these two errors are that the terms $\log \frac{p_2}{p_1}$ and s do not disappear. The determinations made with single-liquid cells are free from these sources of error; but the difficulties due to polarization are so great that the variations are apt to be much larger than in measurements made with two-liquid, reversible cells. In Table I. are some of the results obtained with the two styles of cells. In the first four columns are the measurements of Paschen,[1] myself, Overbeck and Edler,[2] Ostwald,[3] all made with single-liquid cells. In the next three are the figures of Wright and Thompson,[4] Neumann,[5] Braun,[6] with reversible cells. In the eighth are the data of Magnanini,[7] and in the ninth those of Regnauld,[8] the former being for polarizable, the latter for non-polarizable cells.

TABLE I.[9]

Electrodes.	Electrolyte.	Paschen.	W. D. B.	O. & E.	Ostwald.	W. & T.	Neumann.	Braun.	Magnanini.	$D = 100$. Regnauld.
ZnCd	Chlorides	0.296	0.333	0.368	0.360	0.330	0.329	0.334	0.32	0.235
ZnCd	Bromides	0.293	0.333	0.364	0.340	0.315	—	0.256	0.30	0.235
ZnCd	Iodides	0.298	0.331	0.365	0.304	0.322	—	0.262	0.20	0.235
ZnCd	Sulfates	0.35	0.334	0.430	0.401	0.360	0.362	0.33–37	0.36	0.307
ZnCd	Nitrates	—	0.332	0.446	0.411	0.352	0.352	0.27–37	0.38	0.235
ZnCd	Acetates	—	0.332	—	0.373	—	—	0.336	—	—
ZnPb	Chlorides	0.512	0.526	0.561	0.610	* 0.591	* 0.598	—	0.51	—
ZnPb	Bromides	0.525	0.528	0.541	0.599	0.571	—	—	0.45	—
ZnPb	Iodides	0.545	[1]0.527	0.558	0.587	0.455	—	—	0.38	—
ZnPb	Sulfates	0.525	0.527	0.502	0.592	* 0.50–55	—	—	0.51	—
ZnPb	Nitrates	—	0.526	0.589	0.598	0.585	0.589	0.44	0.51	—
ZnPb	Acetates	—	[1]0.527	—	0.638	0.607	0.601	0.54–58	—	—
CdPb	Chlorides	0.216	0.195	0.192	0.249	* 0.260	* 0.269	—	—	—
CdPb	Bromides	0.232	0.194	0.181	0.259	0.256	—	—	—	—
CdPb	Iodides	0.247	[1]0.194	0.188	0.256	0.24	—	—	—	—
CdPb	Sulfates	0.18	0.194	0.17	0.191	* 0.13–17	—	0.18–22	—	—
CdPb	Nitrates	—	0.193	0.243	0.187	0.233	0.237	0.240	—	—
CdPb	Acetates	—	[1]0.194	—	0.265	—	—	—	—	—

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[1] Wied. Ann., 43, 590, 1891.

[2] Ibid., 42, 209, 1891.

[3] Zeitschr. f. ph. Chem., 1, 583, 1887.

[4] Phil. Mag. (5), 19, 1, 1885.

[5] Zeitschr. f. ph. Chem., 14, 193, 1894.

[6] Wied. Ann., 16, 575, 1882.

[7] Rend. Acc. Linc., 6, 182, 1890.

[8] Wiedemann Electrizität (2. Aufl.), 1, 792.

[9] Values marked [1] are calculated from the other experiments and are not direct observations.

The agreement is not so striking as one might wish; but it is sufficient. The values marked with a star are not properly comparable, because the two solutions were not of the same concentration. Nernst's formula for the cells we have been discussing is

$$\pi = \frac{R\tau}{n\epsilon} \log \frac{Pm_1}{Pm_2} \times 10^{-4} \text{ volts.}$$

It is, therefore, necessary to consider the nature of $\log P$. Nernst has not made any direct statement, so far as I know, about a possible connection between $\log P$ and the negative ion of the salt solution. Ostwald[1] and his pupils look upon $\log P$ as a function of the electrode metal and the temperature only, and hold that it is independent of the nature of the negative ion. If this be so, we ought to find that all cells of the type $M_1|pM_1X|pM_2X|M_2$, should have the same value so long as M_1 and M_2 remained the same and that a change in X should have no effect, barring secondary disturbances such as differences of wandering velocities, of dissociation, etc. In the non-reversible cells $M_1|RX|M_2$, where these disturbing influences are eliminated, this should be even more noticeably true. That this is the case for certain metals, I have already shown.[2] The results of other investigators, as given in Table I., show this same thing, though not quite so clearly. The values for Zn|Cd in solutions of chlorides, bromides, and iodides are found to be identical by Paschen, by Overbeck and Edler, and by Regnauld, though the three sets differ hopelessly in absolute value. Braun makes the bromides and iodides the same, and puts the chlorides, sulfates, and nitrates in a group together.

There is not the same agreement among the reversible cells in which Pb forms one of the electrodes; but this is due in part to the insolubility of the lead salts. With the polarizable cells things are much clearer, though the discrepancies between the values found by different observers complicates matters very much. Ostwald finds practically the same value for Zn|Pb in all solutions except acetates. Paschen makes the bromides and sulfates the same, while Overbeck and Edler find the chlorides and iodides

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[1] Lehrbuch, II., 855.

[2] Zeitschr. f. ph. Chem., 12, 294, 1893, Table III.

identical. On the whole we may say that the theory of Nernst has predicted the facts with great accuracy thus far. If, however, the single-liquid cells are the limiting cases of the two-solution reversible cells, and if $\log P$ is a function of the electrodes and temperature only, the electromotive force should always be independent of the nature of the negative ion of the salt solution. That this is not so will be seen from Table II.

TABLE II.

Electrodes.	Electrolytes.	Paschen.	W. D. B.	O. & E.	Ostwald.	W. & T.
ZnHg	Chlorides	1.112	1.151	1.121	1.173	1.12–26
ZnHg	Bromides	0.983	0.991	0.996	1.036	0.972
ZnHg	Iodides	0.846	0.847	0.830	0.841	0.801
ZnHg	Sulfates	1.300	1.302	1.302	1.484	1.46–51
ZnHg	Nitrates	—	1.200	1.330	1.422	1.499
ZnHg	Acetates	—	1.228	—	1.451	—
CdHg	Chlorides	0.816	0.818	0.755	0.813	0.812
CdHg	Bromides	0.690	0.659	0.632	0.696	—
CdHg	Iodides	0.548	0.515	0.465	0.535	—
CdHg	Sulfates	0.968	0.969	0.962	1.083	—
CdHg	Nitrates	—	0.867	0.884	1.011	—
CdHg	Acetates	—	0.898	—	1.078	—

The variation in passing from a chloride to an iodide solution is about 0.3 volts, far more than can be accounted for by any experimental error. This necessitates a reconsideration of the Nernst hypothesis to see where the flaw in the reasoning occurs. The assumption made is that, if a metal be dipped into a solution of one of its salts, the metal will go into solution, and the electrode become charged negatively towards the electrolyte, if the "solution pressure" of the metal is greater than the osmotic pressure of the corresponding ion in the solution. If the latter is greater than the "solution pressure," ions will be precipitated upon the metal which would become positive to the solution. This reasoning is applicable to zinc in a solution of potassium chloride, for instance. The initial concentration of the zinc ions in the solution is zero, and the metal will therefore send off ions until the potential difference corresponding to equilibrium is reached. This will not be the case when we consider mercury in a solution of potassium chloride. There are no mercury ions in solution to precipitate on the metal, and it remains an unanswered problem how the mercury is to become charged positively in respect to the solution. Yet this takes place and the value of the potential difference, as determined by the dropping-mercury electrode method, is a perfectly well defined one. This value should be independent of the nature of the salt solution if Ostwald's assumption about log P is correct. This is not the case. In this connection I may say that the question as to the value of the dropping-mercury electrode as a means of measuring single potential differences does not affect this discussion at all. It is an experimental fact that the sum of the potential differences $M_1|RX$ and $RX|M_2$, as determined by this method is equal to the electromotive force of the cell $M_1|RX|M_2$ and it is immaterial for the present purposes whether the single determinations are wrong by a constant amount, as I am only considering variations in the values. I will now try to show what conclusions may be drawn from the measurements of Paschen[1] on the potential differences between metals and salt solutions not containing the metal of the electrode as ion. He points out himself that the potential difference is not a function of the positive ion of the salt solution. It is not a function of the concentration. Paschen inclines to the opposite view; but I think he is wrong and that his own results as tabulated in Table III. will bear me out. The first column gives the nature and concentration of the solution; the second, third, and fourth the potential differences between the metals, mercury, zinc, and cadmium, and the solution. Mercury is positive towards the solution, zinc and cadmium negative.

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[1] Wied. Ann., 43, 590, 1891.

TABLE III.

Solution.	Sol|Hg	Zn|Sol	Cd|Sol	Solution.	Sol|Hg	Zn|Sol	Cd Sol
HCl = 1 l.	0.560	0.560	0.248	H_2SO_4 = 200 l.	0.825	0.668	0.261
= 10	0.551	0.610	0.272	HBr = 0.272	0.503	0.393	0.175
= 100	0.584	0.643	0.242	= 0.983	0.490	0.423	0.202
KCl = 0.28	0.524	0.525	0.260	= 10	0.493	0.567	0.238
= 1	0.539	0.547	0.249	= 100	0.496	0.610	0.246
= 10	0.553	0.575	0.251	KBr = 0.402	0.474	0.399	0.203
= 100	0.584	0.523	0.240	= 1	0.483	0.441	0.186
NaCl = 0.239	0.562	0.521	0.262	= 10	0.493	0.422	0.167
= 1	0.556	0.512	0.266	= 100	0.505	0.496	0.183
= 10	0.557	0.541	0.268	HI = 10	0.411	0.427	0.117
= 100	0.590	0.557	0.268	= 100	0.417	0.515	0.159
$MgCl_2$ = 0.971	0.546	0.525	0.252	= 1000	0.386	0.584	0.214
= 2	0.547	0.531	0.277	KI = 0.795	0.400	0.250	0.113
= 20	0.548	0.598	0.258	= 1	0.400	0.233	0.113
= 200	0.580	0.516	0.245	= 10	0.412	0.308	0.110
$BaCl_2$ = 0.809	0.562	0.512	0.259	= 100	0.412	0.369	0.120
= 2	0.555	0.554	0.249	= 1000	0.386	0.454	0.199
= 20	0.553	0.583	0.281	K_2SO_4 = 2.152	0.700	0.618	0.287
= 200	0.586	0.566	0.240	= 20	0.720	0.573	0.274
H_2SO_4 = 2	0.835	0.653	0.319	= 200	0.730	0.592	0.252
= 20	0.817	0.668	0.284				

The values for Sol|Hg are identical for dilutions of 1 l. and 10 l. with the exception of KCl, KBr, K_2SO_4, and H_2SO_4; the variations for K_2SO_4 and H_2SO_4 are in opposite directions and certainly due to experimental error. There is no reason to assume that KCl is different in behavior, theoretically, from NaCl or $BaCl_2$, and we must conclude that this discrepancy is also accidental. In passing from dilutions of 10 l. to those of 100 l. there is a distinct increase in potential difference between mercury and chloride solutions. With the other solutions the change is either non-existent or much less marked. On the other hand, cadmium shows this behavior only with HI and KI solutions, zinc with HCl, NaCl, HBr, KBr, HI, and KI solutions. The solutions of HBr, KBr, HI, and KI are not the ones where mercury shows a marked change of value with increasing dilution, so that there is no qualitative regularity in the phenomena. As there is also no quantitative connection to be detected between the change of concentration and the change of potential difference, and as the experimental error is very large in the case of determinations with dilute solutions, I see no reason to assume that there is any change of potential difference, at any rate within wide ranges of concentration.[1] I am led to this conclusion the more strongly because, if we admit with Paschen that the potential difference increases with increasing dilution, we must admit that the electromotive force of the cell Cd|KCl|Hg is a function of the concentration, and I have already shown that this is not the case.[2]

Paschen has pointed out that these potential differences are functions of the metal forming the electrode and of the anion. This can hardly be accounted for on the Ostwald-Nernst hypothesis. If the potential difference between Hg and KCl or KBr solutions are due to the amount of mercury as ion which has gone into solution, we must say that the amount varies as we change from KCl to KBr, or, in other words, that the negative ion has an effect. This is quite apart from the difficulty of accounting for the sign of the potential difference. I do not see that the relative solubilities of mercurous chloride and bromide can be used to help out matters, because we do not have a saturated solution at all, and the difference in the electromotive forces is more likely to be connected with the difference of solubility as cause than as effect.

There are no experimental data, so far as I know, on potential differences at the contact surface of reversible electrodes except some measurements by Neumann,[3] and these do not establish the point they were intended to prove owing to an unfortunate choice of solutions. He measured the potential difference between thallium and solutions of thallium salts. Most of the salts were salts of organic acids, and Ostwald[4] had already found that when

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[1] This will not hold true till the concentration of the salt becomes zero; else we should get in all cases the same potential difference, that of the metal against pure water, which is not true. There will certainly be a minimum concentration beyond which the dissolved substance will not have the properties of matter in mass, and the potential difference will then be a function of the concentration.

[2] Zeitschr f. ph. Chem., 12, 295, 1893, Table V.

[3] Ibid., 14, 225, 1894.

[4] Ibid., 1, 605, 1887,

the negative ion was an organic radical its nature was immaterial. To settle this question one should take negative ions which show marked differences with non-reversible electrodes, such as chlorides, bromides, and iodides. As the negative ion has a very marked influence in these last-named cases, and as there is no reason to suppose that the haloid salts form a class by themselves, the simplest assumption is that the negative ion always has an effect, and that in the cases in which this does not appear, such as the organic radicals, we are measuring something else which is the same in all the cases. Le Blanc[1] found something similar in his studies on polarization, where, beyond a certain point, he obtained the value for the primary decomposition of water.

There are certain quantitative relations connected with the change of the negative ion which deserve to be brought out, and in Table IV. are given the most probable values for the potential differences of the metals Hg, Zn, and Cd in solutions of chlorides, bromides, and iodides; while in Table V. are the corresponding

TABLE IV.

Solution.	Zn|Sol	Cd|Sol	Sol|Hg
Chlorides	0.589	0.255	0.562
Bromides	0.507	0.174	0.483
Iodides	0.436	0.104	0.410

TABLE V.

Solution.	Zn|Sol|Hg	Cd|Sol|Hg
Chlorides	1.151	0.817
Bromides	0.990	0.657
Iodides	0.846	0.514
Sulfates	1.302	0.969

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[1] Zeitschr. f. ph. Chem., 8, 315, 1891.

values for the single-liquid non-reversible cells with Zn and Hg, Cd and Hg as electrodes.[1]

We notice that the numerical change in passing from a chloride to a bromide or iodide solution is the same for these three metals and that the sign is the same for zinc and cadmium as is shown in Table VI. This enables us to formulate matters a little more clearly. The potential difference between a metal and a salt solution is the sum of two terms, one due to the metal and the solvent, the other to the negative ion. For certain metals in certain solutions, the term due to the negative ion is independent, numerically, of the nature of the metal considered. For instance, the potential difference Zn|KCl, Zn|KBr, Cd|KCl, Cd|KBr, Hg|KCl, and Hg|KBr will be $A+a$, $A+b$, $B+a$, $B+b$, $C-a$, and $C-b$. The electromotive forces of the cells Zn|KCl|Cd and Zn|KBr|Cd will be $E_1=A+a-B-a$ and $E_2=A+b-B-b$, whence we see that $E_1=E_2$, which had already been found experimentally. For Zn|KCl|Hg and Zn|KBr|Hg we shall have $E_1=A+a-C+a$ and $E_2=A+b-C+b$, and E_1 will not be equal to E_2. By means of the data in my first paper on this subject,[2] we can now extend our generalization and make it more precise. With the metals, Mg, Zn, Cd, Sn, Pb, and Bi in solutions of chlorides, bromides, iodides, sulfates, nitrates, acetates, carbonates, and oxalates, the term due to the negative ion is not a function of the electrode. There is not much doubt but that the alkaline metals, the metals of the alkaline earths, and the metals of the iron group belong in this

TABLE VI.

Solution.	Zn	Cd	Hg
KCl – KBr	0.082	0.081	–0.079
KBr – KI	0.071	0.070	–0.073
KCl – KI	0.153	0.150	–0.152

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[1] There is certainly an error in the relative positions of Sn and Pb as shown by my determinations, and I do not therefore give any data for them in Table V.

[2] Zeitschr. f. ph. Chem., 12, 294, 1893, Table III.

series. Oswald's measurements show that most organic acids may be added to the above list of solutions. With mercury the numerical value of the term due to the negative ion is the same as with the previous metals, but the sign is opposite. With platinum the numerical value is no longer the same. In which of these three groups copper, silver, gold, and the other metals belong I cannot say, though silver is probably like mercury. The results in Tables IV.–VI. open up a whole series of problems to be settled by future investigators. The values for the differences of the terms for any two negative ions have to be determined with accuracy; the behavior of the metals Cu, Ag, etc., must be examined. The work of Magnanini[1] shows that other relations hold when the dissolved salt is an oxidizing or reducing agent, and that the value Zn|RX|Cd, for instance, is independent of the metals only when RX is not an oxidizing agent. It is also well known that in cases where the electrode metal cannot exist in the solution as ion, the general relations already pointed out do not hold. From the results of Negbaur[2] and of Jones[3] we must conclude that the term which I have represented by *A*, *B*, *C*, etc., varies with the nature of the solvent. The amount of this variation is entirely unknown as yet, and it is equally impossible to say beforehand how a change in the solvent will affect the term due to the negative ion.

If we consider the cell $Zn|ZnCl_2|ZnBr_2|Zn$, the two solutions being assumed to be of the same concentration and dissociation and the wandering velocity of the bromine ion being further assumed to be identical with that of the chlorine ion, we should expect an electromotive force of 0.080 volts. This has not been taken into account by Goodwin[4] in his determinations of the solubilities of silver chloride, bromide, and iodide. Goodwin determined the electromotive force of the cells

$$Ag|AgNO_3|AgCl + KCl|Ag,\ Ag|AgNO_3|AgBr + KBr|Ag,\ Ag|AgNO_3|AgI + KI|Ag.$$

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[1] Rend. Acc. Linc., 6, 182, 1890.

[2] Wied. Ann., 47, 27, 1892.

[3] Zeitschr. f. ph. Chem., 14, 346, 1894.

[4] Ibid., 13, 645, 1894. It is only fair to Mr. Goodwin and to myself to say that I have pointed out to him privately the objections I made to his results in order that he might correct them himself if he felt so inclined. He thinks, however, that it would be better for me to make my comments in print, and I have accordingly done so.

From the observed electromotive forces the solubilities were calculated by the formula $S=\sqrt{\frac{p_1 p_2}{\phi}}$, where $\log \phi = \frac{E}{C}$. In this equation s is the solubility, p_1 the concentration of the Ag ions in the nitrate solutions, p_2 the concentration of the Cl, Br, or I ions in the corresponding solutions, E is the electromotive force of the cells, and C the integration constant which is equal at 25° to 0.0256. It is more than probable that a correction should be applied for a possible difference of $\log P$ in nitrate and chloride solutions, but as this value is not accurately determined, I will first calculate the solubilities on the assumption that $\log P_{NO_3} = \log P_{Cl}$.[1] We find from Table VI. $\log P_{Cl} - \log P_{Br} = 0.080$ and $\log P_{Cl} - \log P_{I} = 0.152$ volts. These values are to be subtracted from the electromotive forces observed in the cells with AgBr and AgI, in order to get the term E called for by the formula. In Tables VII.–IX. I give the results of these calculations. In the first column are the values for p_1; in the second those for p_2; in the third the observed electromotive forces; in the fourth the solubilities as calculated by Goodwin; in the fifth the solubilities as calculated by myself under the assumption that $\log P_{NO_3} = \log P_{Cl}$; and in the sixth the values if one assumes further that $\log P_{NO_3} - \log P_{Cl} = 0.03$ volts. I also give the solubilities found by Kohlrausch and Rose,[2] and by Holleman[3] with the conductivity method.

It will be seen that the second column of solubilities agrees much better with the results obtained by other investigators than the solubilities calculated by Goodwin. The solubilities in the last column do not show so good an agreement; but I do not feel sure that this proves that the formula by which they are calculated is wrong. It seems to me quite as probable that these figures represent the actual solubilities in the cells examined by Goodwin, but not the real solubilities of AgCl, AgBr, AgI. The solubilities of AgCl and AgBr are much changed by contin-

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[1] I use the term $\log P_{Cl}$ to denote the value of $\log P$ for a given metal when in a chloride solution. $\log P_M$ denotes $\log P$ for the metal M without reference to any particular solution, and is a purely abstract conception having no numerical value as yet.

[2] Zeitschr. f. ph. Chem., 12, 324, 1893.

[3] Ibid., 12, 125, 1893.

TABLE VII.[1]

Conc. Ag ions = p_1.	Conc. Cl ions = p_2.	E.M.F.	Calc. S_1	Calc. S_2	Calc. S_3
0.0813	0.0861	0.451	1.24×10^{-5}	1.25×10^{-6}	2.25×10^{-6}
0.0813	0.0861	0.449	1.28×10^{-5}	1.30×10^{-5}	2.34×10^{-6}
0.04295	0.04455	0.418	1.25×10^{-6}	1.25×10^{-5}	2.24×10^{-6}
0.04295	0.04455	0.419	1.23×10^{-6}	1.22×10^{-6}	2.20×10^{-6}
Solubility. AgCl at 25° Average . .			1.25×10^{-5}	1.25×10^{-5}	2.26×10^{-6}
Kohlrausch & Rose			1.44×10^{-5}	at 25°	
Holleman			1.81×10^{-5}	at 25°	

TABLE VIII.

Conc. Ag ions = p_1.	Conc. Br ions = p_2.	E.M.F.	Calc. S_1	Calc. S_2	Calc. S_3
0.0813	0.0861	0.598	7.1×10^{-7}	33.8×10^{-7}	60.7×10^{-7}
0.0813	0.0861	0.603	6.4×10^{-7}	30.1×10^{-7}	55.0×10^{-7}
0.0813	0.0861	0.597	7.2×10^{-7}	34.4×10^{-7}	61.9×10^{-7}
0.04295	0.04455	0.570	6.4×10^{-7}	30.5×10^{-7}	54.9×10^{-7}
0.04295	0.04455	0.571	6.3×10^{-7}	29.9×10^{-7}	53.8×10^{-7}
0.04295	0.04455	0.570	6.4×10^{-7}	30.5×10^{-7}	54.9×10^{-7}
Solubility. AgBr at 25° Average . .			6.6×10^{-7}	31.5×10^{-7}	56.9×10^{-7}
Kohlrausch & Rose			20.9×10^{-7}	at 25°	
Holleman			30.2×10^{-7}	at 25°	

TABLE IX.

Conc. Ag ions = p_1.	Conc. I ions = p_2.	E.M.F.	Calc. S_1	Calc. S_2	Calc. S_3
0.0813	0.0861	0.815	1.02×10^{-8}	19.9×10^{-8}	35.7×10^{-8}
0.0813	0.0861	0.813	1.06×10^{-8}	20.7×10^{-8}	37.2×10^{-8}
0.0813	0.0861	0.815	1.02×10^{-8}	19.9×10^{-8}	35.7×10^{-8}
0.04295	0.04455	0.787	0.94×10^{-8}	18.0×10^{-8}	32.3×10^{-8}
0.04295	0.04455	0.786	0.96×10^{-8}	18.3×10^{-8}	32.9×10^{-8}
0.04295	0.04455	0.790	0.88×10^{-8}	17.0×10^{-8}	30.5×10^{-8}
Solubility. AgI at 25° Average . .			0.98×10^{-8}	19.0×10^{-8}	34.0×10^{-8}
Kohlrausch & Rose			60.00×10^{-8}	at 18°.0	
Holleman			395.00×10^{-8}	at 28°.4	

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[1] S_1 and S_2 in this table should be identical, as they are calculated from the same data by the same formula; the variations are due to errors in calculation.

ued shaking,[1] and I cannot find that Goodwin has taken this into account at all. I conclude, therefore, that if he had shaken his AgCl and AgBr, he would have found much smaller electromotive forces than those recorded in his paper. He has tried to prove the accuracy of his formula in two ways. Having calculated the solubilities by substituting the experimental data for the electromotive forces in the formula, he reverses the operation, and substituting the solubilities he calculates the electromotive forces. It is true that there is an intervening step, but the principle is the same, also the result. If he had taken the cells

$$\mathrm{Ag|AgNO_3|AgCl + KCl|Ag} \text{ and } \mathrm{Ag|AgNO_3|AgBr + KBr|Ag}$$

and substituted directly in these the fallacy of such a test would have been patent. Instead of this he has combined the two cells

$$\mathrm{Ag|AgCl+KCl|AgNO_3|Ag|AgNO_3|AgBr+KBr|Ag}$$
$$= \mathrm{Ag|AgCl+KCl|AgBr+KBr|Ag},$$

calculated the electromotive force of the resultant cell, and compared this with the experimental value and with the difference of the mean of the two component cells. Any other formula, which had given fairly constant values for the solubilities, would have stood the test equally satisfactorily. If, instead of taking Goodwin's formula and his value for AgBr, 6.6×10^{-7} reacting weights per liter, one takes, for instance, my first modification of his formula and the corresponding value for AgBr, 31.5×10^{-7} units, one will reproduce his table exactly. One cannot agree with him when he says in regard to this table:[1] "Die Uebereinstimmung der beobachteten mit der berechneten Werten ist eine sehr gute, wie sie ja nicht anders sein konnte, wenn die frühere Formel (25), nach der die Löslichkeiten berechnet wurden, überhaupt richtig war. Sie bestätigt also diese Formel." The other proof is not satisfactory in the light of my experiments. Goodwin determined the solubility of thallium bromide by the electrical and by the analytical methods, the difference between the two being about 10 per cent of the total solubility. This result cannot be compared with the experiments on the solubilities of the silver haloids, because the conditions were not the same.

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[1] Proc. of Am. Acad., 30, 325, 1894.

[2] Zeitschr. f. ph. Chem., 13, 651, 1894.

In the thallium determinations the cell used was of the form $Tl|TlBr+KNO_3|TlBr+KBr|Tl$. There were bromine ions in contact with both electrodes, while with the silver salts the bromine ions came in contact with one electrode.

One other point remains to be considered, whether the potential difference at the surface of a reversible electrode is a function of the concentration at all. The only direct measurements are those of Neumann,[1] which confirm the Nernst theory in every detail. In addition, there are many determinations on two-liquid cells, made chiefly by Ostwald's pupils, and in all these cases there is a most satisfactory agreement between the theory and the facts. On the other hand, there are a few observations by other people which are not so easily reconciled with the theory. In Table X. I give some measurements of Paschen's[2] on cells having zinc and mercury electrodes, and solutions of $ZnSO_4$ and $MgSO_4$ of varying concentrations as electrolyte. The first column gives the nature of the cell; the second, the specific gravity of the electrolyte; the third, the concentration in grams per hundred grams of the solution; the fourth, the electromotive force observed. The values for the concentrations are only approximate because they were not determined by Paschen directly, and I have taken them from Landolt and Börnstein's tables.

TABLE X.

Electrodens.	Electrolyte.	Density.	Per cent in grams.	E.M.F.
ZnHg	$MgSO_4$	1.042	4.0	1.194
ZnHg	$MgSO_4$	1.040	4.0	1.236
ZnHg	$MgSO_4$	1.040	4.0	1.186
ZnHg	$ZnSO_4$	1.433	32.9	1.249
ZnHg	$ZnSO_4$	1.409	31.5	1.252
ZnHg	$ZnSO_4$	1.403	31.1	1.309
ZnHg	$ZnSO_4$	1.402	31.1	1.327
ZnHg	$ZnSO_4$	1.400	31.0	1.236
ZnHg	$ZnSO_4$	1.315	25.5	1.310
ZnHg	$ZnSO_4$	1.305	25.0	1.238

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[1] Zeitschr. f. ph. Chem., 14, 225, 1894.

[2] Wied. Ann., 43, 570, 1891.

These figures lose a good deal of their value owing to the considerable variation in the determinations for the same solutions, and because the range of concentrations is too limited; but two things are very noticeable in spite of this. In the cells $Zn|ZnSO_4|Hg$, the electromotive force does not decrease with increasing concentration of zinc sulfate, as it should according to the theory. The cells $Zn|MgSO_4|Hg$, have the same value as the cells $Zn|ZnSO_4|Hg$, or a smaller one, while the theory demands a larger one. The same thing is seen, though in a less satisfactory manner, in the experiments of Damien.[1] He used zinc and copper as electrodes, and his results are given in Table XI. The first column shows the electrolyte; the second, the specific gravity of the solution; the third, the percentage composition; the fourth, the electromotive force when ordinary zinc was used; the fifth, the corresponding values when the electrode was amalgamated.

TABLE XI.

ZnCu Electrodes.

Electrolyte.	Density at 15°.	Per cent in grams.	E.M.F.	Amalg. Zn E.M.F.
K_2SO_4	1.036	4.5	1.035	1.067
Na_2SO_4	1.038	*10.0	1.012	1.037
$(H_4N)_2SO_4$ . .	1.075	13.1	1.012	1.019
$MgSO_4$	1.035	*5.8	1.047	1.059
$Al_2(SO_4)_3$ . . .	1.135	5.8	1.050	1.062
$ZnSO_4$	1.064	*9.2	1.004	1.047
KCl	1.077	12.0	0.788	0.802
$NaCl$	1.061	8.5	0.805	0.810
NH_4Cl	1.039	13.0	0.845	0.850
$BaCl_2$	1.110	12.0	0.782	0.820
$CaCl_2$	1.212	23.0	0.743	0.751
$ZnCl_2$	1.384	37.5	0.746	0.752.

Values with a * refer to hydrated salt.

As will be noticed, there are marked variations even in cases where no one claims that there should be any, such as between

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[1] Ann. chim. phys. (6), 6, 289, 1885. The reference to Vol. V. in Wied. Elektrizität I, 734, also in Beibl. 10, 185, is a misprint.

ammonium sulfate and potassium sulfate solutions, between calcium chloride and ammonium chloride. This weakens the conclusions which one would like to draw from these experiments; but, making allowance for a large experimental error, it is still very curious that $Zn|ZnSO_4|Hg$ should give so nearly the same value as the cells with indifferent sulfates, and that zinc chloride should be indistinguishable electrically from calcium chloride. The experiments of Hockin and Taylor[1] may be interpreted either way. They found that the combination of zinc and another metal in sulfuric acid gave a higher electromotive force than the same two metals in a saturated solution of zinc sulfate. This is not so convincing as if they had used potassium sulfate instead of sulfuric acid, because in all except dilute solutions free acids do give a higher value than the corresponding salts. The reason for this variation is unknown. When it comes to the absolute values in the zinc sulfate solution, matters are no better. In some of the metals, notably cadmium and mercury, the zinc sulfate appears to give the same value as any other sulfate; with others there is a qualitative agreement with Nernst's theory. The same remarks hold true of the work of Lindeck.[2] I have not access to the original paper of Wolff, and the review of it[3] is two meager to be of much assistance. He investigated, among other things, the effect of changing the concentration of the zinc sulfate in a one-liquid cell. His results are given in Table XII. The first column

TABLE XII.

	Density.	E.M.F.
$Zn\vert ZnSO_4\vert Cu$	1.438-1.001	0.965-1.066
$Zn\vert ZnSO_4\vert CuO$	1.427-1.003	1.008-1.015
$Zn\vert ZnSO_4\vert Fe$	1.427-1.003	0.378-0.385
$Zn\vert ZnSO_4\vert Pb$	1.427-1.003	0.456-0.587
$Zn\vert ZnCl_2\vert Cu$	1.637-1.003	0.734-0.930
$Zn\vert ZnCl_2\vert Fe$	1.917-1.003	0.385-0.390
$Zn\vert Zn(NO_3)_2\vert Cu$	1.496-1.004	0.669-0.698

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[1] J. Tel. Eng., 8, 282, 1879.

[2] Wied. Ann., 35, 311, 1888.

[3] Beibl., 12, 700, 1888.

shows the electrodes and the electrolyte; the second, the concentrations of the latter in specific gravities; the third, the corresponding electromotive forces.

In all cases there is a qualitative agreement with the theory; that is, the electromotive force increases with decreasing concentration of zinc sulfate. The quantitative agreement is not so satisfactory. In the second, third, sixth and last cells given in the table the variations are much too small; while, in the other cases, they are too large. The ratio of the strongest solutions to the weakest in the experiments of Wolff lies between 100 and 1000 to 1, which corresponds to a change of electromotive force of 0.05–9 volts owing to the bivalence of zinc. Some experiments which I made with the cell $Cd|CdCl_2|Hg$, the strength of the solution being unknown, gave me 0.815, 0.821, 0.814, average 0.817 volts, the same value which I had already found for the KCl solution.

The simplest way to decide what effect the concentration of the reversible ion, if I may use such a phrase, has on the electromotive force would be to make a series of measurements on reversible electrodes by the dropping-mercury method. I have not been in a position to do this, and I have had to find an easier, though less satisfactory manner of settling the question. Suppose we have electrodes of zinc and copper in a mixture of zinc and copper sulfates, one solution. Increasing the concentration of the zinc sulfate or decreasing the concentration of the copper sulfate must diminish the electromotive force of the cell, and *vice versa* if the reverse operations be performed. Through the courtesy of Professors Trowbridge and Peirce of the Physical Laboratory, I have been able to make the few experiments necessary. As it was only required to find out whether there was any change at all, there was no need of determining the absolute value of the electromotive force. This made the experimental part very easy. I connected the cell with a large external resistance and a galvanometer. I changed the ratio of the two components in the solution and noted the position of the galvanometer needle. I made measurements with the electrodes in pure zinc sulfate solutions, in pure copper sulfate solutions, and in mixtures of these in varying proportions. Under all these different conditions I obtained the same electromotive force, showing that it is a function neither of the relative nor of the absolute concentrations.[1] Although one obtains the same value from the different solutions, they do not behave exactly alike. With solutions of pure copper sulfate or with mixtures containing copper sulfate in any quantity, the maximum value is obtained at once and is very constant. With solutions of pure zinc sulfate or mixtures containing only traces of copper sulfate, the maximum value can be obtained only by vigorous stirring and is very inconstant. There is, of course, nothing surprising about this, as it is what one would have predicted. It is a very curious fact that the Nernst formula, though deduced from apparently erroneous assumptions, should yet give the effect of changes of concentration in a two-liquid cell with such surprising accuracy.

It will be noticed that the electromotive forces of the non-reversible cells have nothing to do with the heats of reaction. This has always been known; but it acquires a new significance, since it has been shown that the non-reversible cells are to be considered, as far as the electromotive forces are concerned, as limiting cases of the reversible two-liquid cells. In the cell $Zn|H_2SO_4|Ag$ there is not much doubt what reaction takes place; but it has nothing to do with determining the electromotive force. An interesting example of this, which also brings up another point, is the cell $Cu|CuSO_4|Pt$. Here the reaction consists in the replacement of copper by copper. What happens experimentally, on closing the circuit, is that copper is dissolved from the copper electrode and precipitated on the platinum until the latter becomes, electrically considered, an electrode of pure copper, when further action becomes impossible.[2] Overbeck[3] made some experiments a few years ago to determine what thickness of copper made a platinum electrode behave like a piece of pure copper. His

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[1] This applies only to electrodes reversible in respect to the kation. I hope to treat the case of electrodes reversible in respect to the anion in another paper.

Since this paper was written I have seen the article of J. Meyer, Wied. Ann., 53, 898, 1894, which confirms my views, though with certain exceptions.

[2] When I performed this experiment I was not aware that a similar one had been described by Gladstone and Tribe, Proc. Roy. Soc., 1876.

[3] Wied. Ann., 31, 337, 1887.

method was to deposit copper on platinum electrolytically, and was open to the objection that it was almost impossible to be certain that the copper was deposited uniformly over the surface of the platinum. By using the cell $Cu|CuSO_4|Pt$, it would seem that this difficulty might be avoided, as the plating is stopped automatically as soon as the minimum thickness is reached. Suppose we balance this cell to some extent by an electromotive force less than its own. There will still be a tendency for copper to be deposited on the platinum; but it cannot be deposited to the thickness corresponding to pure copper, as it must then dissolve up again under the influence of the external electromotive force. It can precipitate only till equilibrium is reached, and we shall have the condition referred to by Gibbs,[1] of a substance present in too small quantities to have the properties of "matter in mass." By making the external electromotive force differ infinitely little from the electromotive force of the cell, it would be possible, theoretically at any rate, to obtain an infinitely thin film of copper. It is to the separation of the ion on the electrode in such small quantities as not to have the properties of matter in mass that is due the gradual change of the polarization instead of having a sudden jump from the initial to the final value.

The main results of this research may be summed up as follows:

1. The potential difference between a metal and an electrolyte is not a function of the concentration of the salt solution nor of the nature of the positive ion except in certain special cases.

2. It is a function of the electrode, of the negative ion, and of the solvent.

3. In aqueous solutions, the potential difference is the sum of the term due to the electrode and the term due to the negative ion in the normal cases.

4. For most metals in most electrolytes the term due to the negative ion has the same numerical value and the same sign.

5. For mercury it has the same numerical value, but the opposite sign; for platinum, neither the same numerical value nor the same sign.

CAMBRIDGE, December, 1895.

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[1] Thermodynamische Studien, p. 393.

ON THE FREEZING-POINTS OF DILUTE AQUEOUS SOLUTIONS.

BY E. H. LOOMIS.

TWO years ago I submitted a series of freezing-points of dilute aqueous solutions.[1] After a year of unavoidable interruption the work was resumed, and the new results form the material of the present paper.

The method has remained entirely unchanged and is fully described in the former papers.

The only change in the apparatus was the enlargement of the "freezing-tube," so that it now receives 200 cc. of the solution instead of 70 cc. as before. It was thought that this change would eliminate a possible source of error which might have come from the "sensitiveness" of the smaller quantity of the solution to external temperatures, No reduction, however, of the experimental error has resulted from this change.

The thermometer was the same instrument used in the former observations. The work was done in a basement room of the John C. Green School of Science Building. Here it was possible to avoid serious temperature changes during the entire day. The temperature was kept as near 0° C. as possible, and maintained fairly constant by means of the strong draught of a ventilation shaft opening into the room. By regulating the admission of cold air at the window, the temperature changes were kept within the limits of 1–2 degrees. It is much to be regretted that this work could not be done at the constant temperature of 0° C. A degree of accuracy could thus be reached, I think, which is otherwise unattainable.

The thermometer was kept throughout the entire period of the observations within about 1° C. of the freezing-point.

Attention may be called to four points in regard to the method.

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[1] Physical Review, Vol. I., 1893, pp. 199 and 274.

1. The freezing-point is determined with so slight traces of ice present that no correction for change of concentration in the solution is necessary. (The overcooling is but 0°.15 C.) I am not aware that the value of this correction so generally applied in other methods has been experimentally determined, and since it not infrequently amounts to 10 per cent of the entire observed depression it may perhaps be dangerous to apply it without some experimental justification.

2. The method eliminates all possibility that the observer's bias may affect the results.

3. The reading of the thermometer is made with the mercury column absolutely stationary during 1–2 minutes.

4. The solution to be examined, as well as the water in which the zero point of the thermometer is determined, is surrounded by a medium which is but 0°.3 C. below its own freezing-point, and is further carefully insulated from this by two glass walls and the air layer between them. Thus the solution and its "ice" are able to come to their equilibrium temperature in as nearly an adiabatic condition as possible.

It may be said that as soon as this last feature of the method suggested itself I employed, as was natural, a bath whose temperature was *exactly* that of the freezing-point to be determined, but it was soon found that the observed freezing-points were too high (Nernst's convergence temperature), and the temperature difference of 0°.3 C. was finally chosen, since it was found that this reduced the "convergence temperature" to the actual freezing-point sought. The method by which this was ascertained was by observing at what temperature of the bath the freezing-points of water, obtained with only slight traces of ice in the water, agreed with those obtained with large quantities of ice present.[1]

The vast theoretical importance of these freezing-points has occasioned much very careful work in this field during the past few years, and many questions have arisen in regard to the various methods thus developed. Some of the more important of these questions will be considered in a subsequent paper.[2]

The present series of observations comprises the following compounds, all of which are electrolytes: —

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[1] Physical Review, Vol. I., p. 213.

[2] p. 293.

Table I.

1 Compound.	2 m	3 Grams per liter solution at 18° C.	4 Specific gravity, $\frac{18^\circ}{4^\circ}$	5 Electrical conductivity,[1] $k \cdot 10^8$, 18° C.	6 Specific gravity solution, $m = 0.20$, $\frac{18^\circ}{4^\circ}$.	7 Firm name.	8 Standard solution prepared.
KCl	1	74.59	1.0450	919	1.0082	Eimer & Amend.	By direct weight.
NH_4Cl	1	53.49	1.0152	909	1.0018	Eimer & Amend.	By direct weight.
$BaCl_2$	½	103.95	1.0889	655	1.0352	Merck & Co.	Gerlach's Tables.[2]
MgCl	½	47.63	1.0381	$m = 0.20$[4] 290	1.0148	Eimer & Amend.	Kohlrausch's Tables.[3]
HCl	1	35.45	1.0166	2794	1.0024	Eimer & Amend.	Kohlrausch's Tables.[5]
K_2SO_2	½	87.17	1.0662	$m = 0.20$ 304	1.0262	Eimer & Amend.	Direct weight.
Na_2SO_4	½	71.09	1.0606	474	1.0239	Eimer & Amend.	Direct weight.
K_2CO_3	½	69.14	1.0578	660	1.0231	Trommsdorff.	Direct weight.
Na_2CO_3	½	53.06	1.0518	Standard	1.0206	Prepared in Lab.	Direct weight.
KNO_3	1	101.18	1.0603	752	1.0114	Trommsdorff.	Direct weight.
$NaNO_3$	1	85.10	1.0546	615	1.0102	Trommsdorff.	Direct weight.
NH_4NO_3	1	80.09	1.0309	831	1.0053	Trommsdorff.	Direct weight.
H_3PO_4	⅓	32.67	1.0166	209	1.0096	Trommsdorff.	Hullet's Titration.

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[1] In "mercury units."

[2] Hoffmann's Tabellen, Berlin, 1877, p. 121.

[3] Wiede. Ann., Bd. VI., 1879, p. 38.

[4] Solution $m = \frac{1}{2}$ accidentally thrown away before k was determined.

[5] Leitfaden d. Physik, 1892, p. 403.

In the foregoing table, and elsewhere throughout the present paper, m denotes the *gram-molecular* concentration of the solution; that is, $m=1$, for example, indicates that a liter of the *solution* contains as many grams of the compound as there are units in its molecular weight. Columns 4 and 5 give respectively the specific gravity $\left(\frac{18^\circ}{4^\circ}\right)$, and electrical conductivity of the standard solutions whose respective concentrations are found in column (2). In addition, for the sake of ready reference, the table gives the specific gravity of the solutions for the molecular concentration, $m=0.20$, and further the name of the makers from whom the compound was obtained. In the last column is given the manner in which the solution was prepared.

Solutions.

The solutions which were prepared by direct weighing were made from carefully recrystallized salts. The drying was accomplished as thoroughly as the nature of the salt would permit in accordance with the prescribed methods.

The solution, H_3PO_4, $m=\frac{1}{3}$, was prepared for me by Mr. Hullet of the Princeton Chemical Laboratory, and I wish here to thank him for the careful manner in which the titration and subsequent analysis were performed by him.

In every case the specific gravity and electrical conductivity of the standard solutions were determined in order to control their accuracy. I cannot agree with Mr. Jones,[1] who appears to be of the opinion that the specific gravity and conductivity of a supposedly standard solution can furnish no conclusion in regard to its accuracy.

In fact, there seems to be no reason to believe that a normal solution made from carefully prepared salts, in accordance with accepted tables of specific gravity, and found to have the exact specific gravity and electric conductivity corresponding to such a solution should not be "pure," at least within the limits of accuracy yet reached in the present methods of making freezing-point observations. I think it cannot be too strongly urged that in all

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[1] Weide. Ann., Bd. 53, 1894, p. 394.

such work both these constants be determined, not more for the sake of the easy control which they furnish, than for the convenient comparison with others' results, which these data in regard to a solution permit.

By comparing the results in Table I. with those of Kohlrausch[1] it is found that sufficient agreement exists except in the case of HCl. This solution was titrated by Mr. Hullet from acid found to be free from the impurities likely to be present in it. The standard solution against which it was balanced, was a normal Na_2CO_3. The Na_2CO_3 was made from Trommsdorff's c. p. $NaHCO_3$ by glowing to constant weight. The specific gravity of this solution is given in the foregoing table.

The electrical conductivity was measured according to the familiar method of Kohlrausch. The "Resistance Capacity" of the electrolytic cell employed was found in the usual manner by assuming Kohlrausch's values for the conductivity of NaCl and Na_2CO_3.

Determination of Specific Gravity.

The specific gravity was determined by using a modified form of Sprengel picnometer, whose volume at 18° C. was 51.3232 c.c. At (*a*) the glass tube is constricted to a bore of 1 mm., and at this point a fine mark is etched around the tube. At (*b*) the tube is reduced to a point, whose opening is less than 1 mm., so that the greater capillary attraction at this point over that at (*a*) may hold the liquid always at (*b*), and thus permit changes of volume in the liquid contents to be observed at (*a*). The body of the picnometer is further provided with a small glass ball. This provides for the easy displacement of air bubbles, which sometimes form on the inside walls. It is found, however, that these bubbles do not form, if one takes the precaution to keep the picnometer when not in use always supplied with water, so that its walls may not become dry. This seems to indicate that the source of these troublesome air bubbles is not

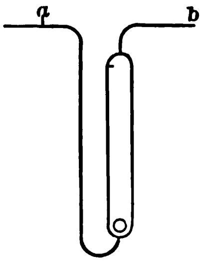

Fig. 1.

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[1] Leitfaden d. Physik, Leipzig, 1892, p. 404.

the air dissolved in the solutions, but the air "condensed" on the dry walls of the glass itself.

The picnometer is filled and placed in a water bath whose temperature is kept at 18° C. ± 0°.05. The solutions were usually about 20° C. when introduced into the picnometer, and thus when placed in the colder bath the liquid in the arm (*a*) would shrink back toward the body of the picnometer, rapidly at first, and slowly at last, as its temperature became more nearly equal to that of the bath. Liquid is added at the point (*b*) as may be needed from time to time, by touching it with a glass rod or stopper moistened with the solution. When the liquid column remains stationary at (*a*), 1–2 minutes, it is known that the solution in the picnometer has the same temperature as the bath, 18° C.

Experiment showed that whether the solution was initially at temperatures below or above 18° C., the same result was obtained, so far at least as would affect the fifth place of decimals.

It is to be noted that three entire series of freezing-point observations, KHO, NaHO, and HNO_3, had to be rejected, since their specific gravity and electrical conductivity were found to be at such variance with the Kohlrausch values as to indicate some marked impurity. At the earliest opportunity I hope to determine the specific gravity and electrical conductivity of normal solutions of these compounds, together with HCl, using the utmost care in preparation of the material, and shall then measure their respective freezing-points.

The distilled water used throughout the present work had an electrical conductivity 8.10^{-10}.

Results.

The following tables present the experimental results. — In column (2) is given the molecular concentration (*m*) of the solution, in (3) the observed depression of the freezing-point (Δ), and in (4) is found the molecular depression $\left(\frac{\Delta}{m}\right)$. This is the value of the molecular depression as reckoned by Arrhenius. Raoult and others reckon with gram-molecules *per* 1000 *grams of water*, instead of 1 *liter of solution*. In order to compute this

[illegible]	[illegible]	[illegible]	4 [illegible]	5 Theoretical value of [illegible]	6 Theoretical value of [illegible]	7 Difference. [illegible]	8 Difference. [illegible]
[illegible]	0.01	0.0360	3.60	3.65	0.0365	+0.0005	+1.3
	0.02	0.0709	3.55	3.62	0.0724	+0.0015	+2.1
	0.03	0.1055	3.52	—	—	—	—
	0.035	0.1235	3.53	—	—	—	—
	0.05	0.1749	3.50	3.56	0.1780	+0.0031	+1.7
	0.10	0.3445	3.445	3.498	0.3498	+0.0053	+1.5
	0.20	0.6808	3.404	3.441	0.6882	+0.0074	+1.1
	0.40	1.3411	3.353	—	—	—	—
NH_4Cl	0.01	0.0356	3.56	3.67	0.0367	+0.0011	+3.2
	0.02	0.0711	3.56	(3.64)	(0.0728)	+0.0017	+2.3
	0.035	0.1224	3.50	—	—	—	—
	0.05	0.1740	3.48	3.58	0.1790	+0.0050	+2.8
	0.10	0.3434	3.434	3.515	0.3515	+0.0081	+2.4
	0.20	0.6792	3.396	(3.470)	(0.6940)	+0.0148	+2.2
	0.40	1.3573	3.393	—	—	—	—
HCl	0.01	0.0361	3.61	3.71	0.0371	+0.0010	+2.8
	0.02	0.0719	3.60	3.69	0.0738	+0.0019	+2.6
	0.05	0.1797	3.59	3.66	0.1830	+0.0033	+1.9
	0.10	0.3546	3.546	3.616	0.3616	+0.0070	+2.0
	0.20	0.7130	3.565	3.563	0.7126	−0.0004	±0.
	0.30	1.0837	3.612	—	—	—	—

$BaCl_2$	0.01	0.0499	4.99	(5.20)	(0.0520)	+0.0021	+4.4
	0.02	0.0990	4.95	(4.92)	(0.0984)	−0.0006	−0.6
	0.05	0.2385	4.77	4.74	0.2370	−0.0015	−0.6
	0.10	0.4690	4.690	(4.58)	(0.458)	−0.0110	−2.3
	0.20	0.9310	4.655	(4.36)	(0.872)	−0.0590	−6.3
$MgCl_2$	0.01	0.0514	5.14	No ata accessible.			
	0.02	0.1014	5.07				
	0.05	0.2489	4.98				
	0.10	0.4948	4.948				
	0.15	0.7444	4.965				
	0.20	1.0039	5.019				
	0.25	1.2699	5.079				
	0.30	1.5557	5.186				
K_2SO_4	0.01	0.0492	4.92	4.95	0.0495	+0.0003	+0.6
	0.02	0.0952	4.76	(4.76)	(0.0952)	±0.	±0.0
	0.05	0.2271	4.54	4.52	0.2260	+0.0011	+0.5
	0.10	0.4317	4.317	4.328	0.4328	+0.0011	0.2
	0.20	0.8134	4.067	(4.13)	(0.8260)	0.0130	1.6
	0.30	1.1672	3.891	—	—	—	—
Na_2SO_4	0.01	0.0509	5.09	(4.96)	(0.0496)	−0.0013	−2.5
	0.02	0.0974	4.87	(4.74)	(0.0948)	−0.0026	−2.5
	0.05	0.2297	4.59	4.49	0.2247	−0.0050	−2.2
	0.10	0.4340	4.340	(4.26)	(0.4260)	−0.0080	−1.8
	0.20	0.8141	4.071	(3.97)	(0.7940)	−0.02	−2.5
	0.30	1.1604	3.875	—	—	—	—

TABLE II. (*continued*).

1 Compound.	2 Gram molecule per liter solution. m.	3 Depression of freezing-point, Δ.	4 Molecular depression of freezing-point, $\frac{\Delta}{m}$.	5 Theoretical value of $\frac{\Delta}{m}$.	6 Theoretical value of Δ.	7 Difference. Δ_{th}-Δ_{exp}.	8 Difference. Δ_{th}-Δ_{exp} in per cents of Δ_{exp}.	
		o			o	o	$\mu_{\infty}=140$.	$\mu_{\infty}=122$.
K_2CO_3	0.01	0.0507	5.07	(4.66)	(0.0466)	−0.0041	− 8.0	−0.0
	0.02	0.0986	4.93	(4.49)	(0.0898)	−0.0088	− 9.0	−1.2
	0.05	0.2356	4.71	4.27	0.2135	−0.0221	− 9.0	−2.0
	0.10	0.4540	4.540	(4.09)	(0.4090)	−0.0450	−10.0	−2.2
	0.20	0.8770	4.385	(3.91)	(0.782)	−0.0950	−11.0	−3.8
							$\mu_{\infty}=122$.	$\mu_{\infty}=104$.
Na_2CO_3	0.01	0.0507	5.07	(4.54)	(0.0454)	−0.0053	−10.0	−3.0
	0.02	0.0986	4.93	(4.32)	(0.0864)	−0.0122	−12.0	−5.0
	0.05	0.2321	4.64	4.03	0.2015	−0.0306	−13.0	−6.0
	0.10	0.4416	4.416	(3.78)	(0.3780)	−0.0640	−15.0	−7.0
	0.20	0.8339	4.170	(3.55)	(0.710)	−0.1240	−15.0	−8.0
KNO_3	0.01	0.0346	3.46	3.62	0.0362	+0.0017	+ 4.9	
	0.02	0.0703	3.52	(3.58)*	(0.0716)	+0.0013	+ 1.8	
	0.025	0.0865	3.46	—	—	—	—	
	0.05	0.1705	3.41	3.50	0.1750	+0.0045	+ 2.6	
	0.10	0.3314	3.314	3.409	0.3409	+0.0095	+ 2.8	
	0.20	0.6388	3.194	(3.31)	(0.662)	+0.023	+ 3.6	

$NaNO_3$	0.01	0.0355	3.55	3.65	0.0365	+0.0010	+ 2.8
	0.02	0.0690	3.45	(3.62)	(0.0724)	+0.0034	+ 5.0
	0.025	0.0866	3.46	—	—	—	—
	0.05	0.1722	3.44	3.55	0.1775	+.00053	+ 3.1
	0.10	0.3428	3.428	3.472	0.3472	+0.0044	+ 1.3
	0.20	0.6689	3.345	(3.409)	(0.6818)	+0.0129	+ 1.9
[1] NH_4NO_3	0.01	0.0358	3.58				
	0.02	0.0707	3.54				
	0.025	0.0873	3.49				
	0.05	0.1737	3.47				
	0.10	0.3424	3.424				
	0.20	0.6641	3.321				
H_3PO_4	0.01	0.0282	2.82				
	0.02	0.0536	2.68				
	0.05	0.1245	2.49				
	0.10	0.2358	2.358				
	0.20	0.4498	2.249				

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[1] It should be noted that in case of the NH_4NO_3 solutions more concentrated than $m = 0.05$ the rise of the thermometer after the freezing begins is *extremely* slow. The same is the case with NH_4Cl though in a less marked degree. The usual sudden "jump" of the mercury when freezing begins after an overcooling of a liquid is *entirely* wanting. It may be noted also that the "ice" presents a milky appearance in sharp contrast to its crystalline appearance in other cases. The same was observed in the solutions $MgCl_2$, $m = 0.15, 0.20, 0.25, 0.30$. The observed depressions are clearly affected by this slowness of these solutions to come to the equilibrium temperature, and are thus too great. In the case of NH_4NO_3 $m = 0.20$ the matter was tested experimentally and it appeared that the maximum temperature was not reached in the usual interval of two minutes, but required at least five minutes, and gave at the end of that time a reading fully 0°.005 C. higher than at the end of two minutes. No such difference was observed in case of $MgCl_2$, showing that here the maximum was reached in the customary two minutes. No corrections are applied, as the matter is not yet well enough understood.

value of the molecular depression, one needs in addition the specific gravity of the solution. This is found in Table I., column (6), from which the value of $\frac{\Delta}{m}$ in accordance with Raoult's definition is easily reckoned. The difference, however, is so slight, even in the most concentrated solution used, that there seems to be no advantage in publishing both values as was done in the former papers. Thus this difference amounts to only 1 % in the case of NH_4NO_3, $m=0.20$ where it is the greatest, while in Na_2CO_3 it vanishes altogether.

The value of the depression in column (3) is the mean of 5–9 *entirely independent* determinations, which show on the average a variation of 0°.001 C. The *largest* average variation shown in any complete series was 0°.0013 C. in the case of $BaCl_2$ (43 separate observations). The smallest average variation was 0°.0006 C. in the case of Na_2CO_3 (36 distinct observations). This is almost exactly the variation observed in the former work, and shows that the enlargement of the freezing-tube has not affected the sources of error.

Graphic Representation of Results.

The values of $\frac{\Delta}{m}$ as a function of m are presented graphically in Plate I., Fig. 1. Ordinates represent values of $\frac{\Delta}{m}$, abscissas those of (m). To avoid confusion, the nitrates are represented by themselves in Fig. 2. The scale is the same as that before employed. Together with the new series are represented the values of NaCl and H_2SO_4 from the observations of 1893. To the NaCl results another has been added at $m=0.40$, and thus the course of the curve beyond $m=0.20$ is determined. The present method of representing *molecular depressions* rather than actual depressions commends itself, since it alone is able to show at a glance the general nature of the results and throw much light on the accuracy of the method. Neither of these appear when the depressions themselves are graphically represented, since on the one hand the *departures* from Blagden's law of strict proportionality between depression and concentration are so very slight compared with the total *depressions* that they do not appear in the graphic representation of depressions. Thus even where these departures are the most marked, as, for example, in case of Na_2CO_3, the "curve" of total *depressions* differs so little from a straight line that it may be distinguished from a straight line only with the closest scrutiny. On the other hand, probable errors of many thousandths of a degree are scarcely noticeable in the curve of *depressions.*

The curves for the most part are determined by five observations, whose points are connected with straight lines. In the greater number of cases the experimental errors appear to be so comparatively small, that it would perhaps have been justifiable to assume a *perfect* regularity of results, and connect the points accordingly with the most probable *curve*, as was done in the former papers.

In case of $MgCl_2$, these five observations, at $m = 0.01$, $m = 0.02$, 0.05, 0.10, and 0.20, were so surprising that three additional ones were made, at $m = 0.15$, $m = 0.25$, and $m = 0.30$. So too with KCl and NH_4Cl an additional observation was made at $m = 0.40$, to determine whether the converging curves actually crossed somewhere near $m = 0.20$. It should be added that these two observations, together with that on NaCl at the same point, were made immediately after a special determination of the zero-point of the thermometer. Thus an error in the zero-point could not affect the *relative* depressions of the three salts. The same precaution was observed for the two observations on Na_2SO_4 and K_2SO_4 at $m = 0.30$, so that there is no possible doubt that the members of these pairs of curves intersect in the region of $m = 0.20$.

Discussion of Results.

Apart from any theory it appears here as in the case of the electrolytes formerly studied: —

(1) That the molecular depression increases continuously with increase of dilution. The only exceptions are $MgCl_2$ and HCl in the region of greater concentration, each of which thus presents a *minimum* value of the molecular depression at $m = 0.10$. In $MgCl_2$ this minimum is pronounced. In case of HCl it is perhaps less striking, but no less well established. It was to remove pos-

sible doubt about this minimum in HCl that the value at $m=0.30$ was determined. The position of this new point makes the existence of the minimum certain at about $m=0.10$.

I find that this same minimum in case of $MgCl_2$ appears in the results of Arrhenius,[1] although he must have looked upon it as due to exceptionally large errors, since he makes no reference to it in his discussion of results. I find also that in the case of HCl, Jones's[2] observations suggest unmistakably the presence of such a minimum, although his failure to call attention to it, particularly since he calls special attention to the *regularity* of the results,[3] would indicate that he believed it due to an error of some 0°.002 C.

(2) The curves are all more or less concave on their upper side.

(3) It now appears that the electrolytes thus far studied are sharply divided into two marked groups, the *first* made up of compounds containing univalent acid and basic radicals, NaCl, KCl, HCl, NH_4Cl, KNO_3, $NaNO_3$, NH_4NO_3; the *second* made up of those containing bivalent radicals, $MgCl_2$, $BaCl_2$, $MgSO_4$, H_2SO_4, Na_2SO_4, K_2SO_4, Na_2CO_3, K_2CO_3. These groups are distinct in two particulars, (1) in the *amount* of the molecular depression of the freezing-point, and (2) in the *rate* at which this increases with the increase of dilution. Thus in Plate I., Figs. 1 and 2, the two groups lie wide apart, and while the first (HCl, etc.), show slight curvature, those of the second show rapid change in curvature in the region of great dilution.

(4) It appears from the regular course of the results, especially when exhibited in the various curves, that there is nowhere in the region studied any sudden change in the nature of the solution, so far, at least, as its freezing-point is concerned. The irregularities which appear (KCl, KNO_3) indicate that the experimental error at these points is very large, at least 0°.0006 C., and though this is much larger than seems to be admissible from the other results, still I think the course of the curves in the other regions indicates that the irregularities in extreme dilution are due to errors.

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[1] Zeit. Phys. Chem., Bd. II., p. 496. [2] *Ibid.*, Bd. XII., p. 623. [3] *Ibid.*, p. 628.

(5) In view of the wide difference in the freezing-points of the more concentrated solutions belonging to the same group, it is a remarkable fact that the curves representing their molecular depressions converge rapidly as the dilution increases, and in such a manner as to suggest that *in extreme dilution they have perhaps sensibly the same freezing-points.* This convergence is the more striking when it is observed how widely the two extremes in the second group, $MgCl_2$ and Na_2SO_4, differ in their freezing-points at the concentration $m=0.30$. (See Plate I.) Here the freezing-points of the two solutions differ by 0°.395 C., while at $m=0.01$ they differ by only 0°.0004. So also in the first group, the two extremes, HCl and KCl, differ at $m=0.30$ by 0°.07 C., while at $m=0.01$ the difference is inappreciable.

The exceptions to be noted are NH_4Cl and KNO_3 in the first group, and $BaCl_2$, H_2SO_4, and $MgSO_4$ in the second group. (For $MgSO_4$ see former paper.) The last two are vital exceptions. The others show such confusion in the curves in the region of great dilution as to indicate, as stated above, experimental errors.

It is to be observed that H_3PO_4 stands by itself, and in spite of the fact that it contains a trivalent radical, it depresses the freezing-point less than the group containing the univalent radical. I hope to be able to study other analogous compounds to compare their freezing-points with those of H_3PO_4.[1]

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[1] In regard to the present values for phosphoric acid, it needs only to be remarked that the former series were known to have no significance, except so far as the regularity of the observed depressions might throw light upon the accuracy of the method.

It was distinctly stated that the "phosphoric acid" showed abnormal values, both in its specific gravity and electrical conductivity,* amounting in the latter to 7%. The particular specimen was the only phosphoric acid at hand, and since it had been known to be pure some years before, I used it for my work. Upon testing it, the fact of its great impurity was found, as stated in the note to which reference has been made. The present acid is from Trommsdorff. The normal solution was titrated by Mr. Hullet, and was then analyzed by him and found to contain 70.92 g. P_2O_5 per liter. This corresponds to a *gram-molecular* strength of 0.3329 instead of $\frac{1}{3}$, as required by the titration. The difference is altogether negligible. Its specific gravity is now in exact accord with that found by Kohlrausch, though the electrical conductivity is 209, instead of 200, as given by him.

* See Note, Physical Review, Vol. I., p. 282.

Relation of Results to Dissociation Theory.

The relation of the present results to the "Dissociation Theory" may be seen by comparing the observed depressions Δ in column (3) with those in column (6), which express the values of the depression computed on the basis of this theory.[1]

The theoretical values of the molecular depression are also found in column (5).

The theory assumes that the degree of dissociation in any given solution is represented by the ratio $\frac{\mu_x}{\mu_\infty}$, in which μ_x is the molecular conductivity of the solution for the given concentration x, expressed in gram-equivalent molecules per liter, and μ_∞ is the limiting value of this conductivity as x approaches zero as its limit, or, as more generally expressed, the value of the molecular conductivity in infinite dilution. For μ_x the values as found by Kohlrausch are chosen, and for μ_∞, I have taken the most probable values as assigned by him.[2] Van't Hoff's constant is taken as he gives it, 1.89.

In the cases of NH_4NO_3 and $MgCl_2$, data for computing the theoretical values of Δ and $\frac{\Delta}{m}$ are not at hand. In case of H_3PO_4 no theoretical values are given, since at present there seems to be insufficient knowledge in regard to the *manner* of its dissociation.

It must be remembered that the concentration of the solution is represented by Kohlrausch by μ, which expresses the concentration in gram-*equivalent* molecules, while in the present paper m represents concentration in *gram-molecules*. Thus the solution, $BaCl_2$, $m = 1$, is represented by Kohlrausch as $BaCl_2$, $\mu = 2$, and the solution which would be represented by Kohlrausch as H_3PO_4, $\mu = 1$, would be represented here by H_3PO_4, $m = \frac{1}{3}$.

The values in columns (5) and (6) which are inclosed in parentheses are found by graphic interpolations, and are subject to considerable error in the region of greatest concentration.

In addition, column (7) contains the difference between the

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[1] See notes in former paper Physical Review, Vol. I., p. 286, (1), (2), and (3).

[2] Wiede. Ann., No. 26, pp. 198 and 204.

observed and computed values of the depression Δ, and for the sake of readier comparison column (8) expresses this difference in *per cents* of the observed values.

Remarks on the Bearing of the Results on the Dissociation Theory.

It cannot be denied that in the cases of KCl and K_2SO_4 the agreement is practically complete. And in the cases of NH_4Cl, HCl, $BaCl_2$, Na_2SO_4, KNO_3, $NaNO_3$, the agreement is still surprising, and could hardly be set aside as "accidental." The differences, however, in these latter cases at least cannot be explained on the ground of some constant experimental error, since this would require that all the observed values should be uniformly either "too high" or "too low." While in general the present results are found to be lower than the theoretical values, it must be observed that in the cases of $BaCl_2$ and Na_2SO_4 they are *higher.*

It is further a matter of surprise that the two cases which show marked differences between observed and theoretical values are K_2CO_3 and Na_2CO_3, exactly the two where the uncertainty in regard to the value of μ_∞ makes any computation of the theoretical values little better than a guess. No doubt the most probable value of μ_∞, taking into account the general course of all the other curves in Kohlrausch's graphic representation of his results,[1] is that selected by him, 140 in case of K_2CO_3, and 122 in case of Na_2CO_3. If one, however, chooses the highest *observed* value of μ for the limiting value μ_∞, *i.e.* 122 for K_2CO_3, and 104 for Na_2CO_3 (plainly an arbitrary choice so far as present knowledge goes), then the theoretical values of the depressions become almost identical with those observed for the dilute solutions of K_2CO_3, and even in the case of Na_2CO_3 the agreement is perhaps all that the advocates of the theory require. (See Tables, column (8), for the two sets of percentage difference for K_2CO_3 and Na_2CO_3.)

As has been before remarked, the course of the curves for the molecular depression of $BaCl_2$, NH_4Cl, and KNO_3 indicates that in the region of greatest dilution the values are apparently affected

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[1] Wiede. Ann., 26, No. 10, Figs. 1 and 2

by exceptionally large experimental errors, and it now appears that these apparent errors occur at the points where the difference between observed and theoretical values are found to be the greatest.

In regard to the differences, in general it may be said that they amount to 2.5%, which represents, in the case of extreme dilution, a difference, say, of 0°.0015 C. As the concentration increases, the percentage difference generally increases, reaching 6 % in the case of $BaCl_2$ for $m=0.20$. In general, in the greater concentrations the percentage difference may be put down roughly as 3 %, where it represents an actual difference extending into the *hundredths* of a degree. These differences, both in the dilute and in the concentrated solutions, are many times greater than any experimental error which the method and its results would seem to make admissible.

Further, it must be said that the dissociation theory requires uniformly that the potassium salts should depress the freezing-point more than the corresponding sodium salts. This follows directly from the fact that the degree of dissociation is uniformly greater in the case of the potassium salts. The present results, however, show the reverse, except in the case of the carbonates.

In case of the nitrates, the confusion of the curves in extreme dilution makes any comparison of the depressions difficult.

The KCl depressions are less than the NaCl, but it is to be remembered that the NaCl series was the one series made at a room-temperature of 18° C., and I now know that trustworthy results are to be had only at temperatures not far from 0° C. I think it necessary to repeat the NaCl observations before any final comparison between the KCl and NaCl depressions should be made, though in regard to the observations at $m=0.40$ there is no doubt; the NaCl depresses the freezing-point much more than the KCl.

Accuracy of the Method.

It will be remembered that in the former paper, the experimental data were presented from which the reader was able himself to estimate the method's accuracy. No attempt was made to fix its numerical value. The same course will be followed here, and the greater amount of experimental material now at hand throws much light upon this important matter.

Now, as then, these two questions are fundamental: —

(1) How far can one rely upon the constancy of these fine mercury thermometers?

(2) What sort of agreement exists between the individual observations of a series whose *mean* value is taken as the required freezing-point?

The answer to the *second* question given in the former paper is entirely unaffected by the new material. Now, as then, a series of five entirely distinct observations show on the average a variation of 0°.001 C.

This variation may be attributed to three causes: first, assuming the temperature of the solution in each of the different observations to be the *same*, then the variation could be referred to the inconstancy of the thermometer itself; second, assuming that the thermometer actually records the temperature of its "bulb," then the variation could be referred to the failure of the method to bring the solution to its "freezing-point" in each of the separate determinations; third, the variations in the temperature of the mercury projecting into the air is able to account for the variation. *The variation cannot be referred to reading errors.* Reading errors play absolutely no part in the experimental errors of the present method. There is no doubt that a $\frac{1}{100}$° thermometer may be *read* accurately to the 0°.00005 C. The question is, would these *readings* indicate anything in regard to the *temperature* of the solution.

Since the reading error in comparison with the errors referred to above is insignificant, I have directed my attention entirely to the elimination of the latter rather than to the entirely superficial refinement of reducing reading errors either by using larger powers in the reading microscope or finer graduation of the thermometer.

In regard to the *first* question stated above, the same method of answer will be observed as in the former paper.

For this purpose the following table is given of all the observed zero-points of the thermometer during the three months of the observations.

TABLE III.

1 Date, 1895.	2 Barometer.	3 Room-temperature.	4 Observed zero-point.	5 Zero-point corrected to 0° C. and 760 mm.
		°	°	°
Jan. 2	762.0	+ 5.0 C.	0.0416	0.0397
7	759.7	10.0	0.0435	0.0404
14	756.7	0.0	0.0407	0.0412
21	756.0	2.0	0.0416	0.0416
25	765.3	2.0	0.0413	0.0397
28	764.3	0.0	0.0404	0.0397
29	754.1	2.0	0.0393	0.0397
30	757.4	0.0–4.0	0.0391	0.0389
Feb. 4	754.4	3.0	0.0402	0.0402
5	760.1	3.0	0.0402	0.0392
11	760.6	4.0	0.0407	0.0394
13	746.9	2.0	0.0402	0.0418
18	754.6	5.0	0.0420	0.0414
20	754.1	6.0	0.0422	0.0414
25	759.8	4.0	0.0420	0.0408
27	761.6	5.0	0.0426	0.0407
Mar. 4	754.5	8.0	0.0439	0.0423
5	764.0	9.0	0.0457	0.0422
6	769.4	7.5	0.0455	0.0416
13	761.1	10.0	0.0460	0.0427
14	758.4	10.0	0.0450	0.0421
18	754.0	7.0	0.0432	0.0420
19	757.6	6.5	0.0420	0.0404
20	759.2	5.0	0.0416	0.0402
25	757.7	7.5	0.0437	0.0417

The table needs no explanation further than to say that the correction for pressure was determined in the Reichsanstalt, Berlin, and given in the certificate accompanying the thermometer as 0°.001 C. for a change of 6 mm. in barometric pressure. The correction for room-temperature is the usual one, in which it is assumed that the entire mercury column in the air is at room-temperature. The apparent coefficient of expansion for mercury in glass is taken as 0.000156.

The results are graphically represented in Plate II., Fig. 6, where the dotted zigzag line shows the observed zero-point and the full zigzag line represents the corrected zero. The scale is 5 mm. to the $\frac{1}{1000}$° C. It thus has the same sensibility as the curves of molecular depression possess in the region of extreme dilution. Since the length of a $\frac{1}{100}$° division in the thermometer is 0.4 mm., the actual observed variations in the thermometer are magnified 125-fold in the "curve."

It is to be observed: —

(1) The zero of the instrument has risen during the period of its rest at ordinary temperatures (March, 1893–January, 1895) from 0°.029 to 0°.040, or roughly at the rate of 0.0005 C. per month. This would produce a rise of 0°.0015 C. during the period of the observations. In Fig. 6 the straight line represents such a uniform rise of 0°.0015 C. during the three months. The actual observed rise is 0°.0020 C., an agreement which most likely is altogether accidental, since, of course, the assumption of a uniform rise of the zero-point of a thermometer is not warranted, even though the instrument, as in this case, has been long "seasoned."

(2) It is no less remarkable that the zigzag course of the zero-point seems to be governed by two *laws;* first, when the thermometer rested for more than a single night the zero remained either constant, as during the period Jan. 25–28 and Feb. 5–11, or else rapidly rose, as during the periods Feb. 11–13, Feb. 27–Mar. 4, etc. The only exception is the period Jan. 21–25. Second, when the thermometer was used two days in succession the zero-point is found on the second day to be sharply depressed, thus Jan. 29–30, Feb. 4–5, etc. The only exception here is Mar. 4–5. Could it be that the long-continued jarring of the thermometer during a day's observations should *depress* its zero! and that it recovered itself during the longer intervals of rest! The results seem to indicate these conclusions. These two singular regularities which appear to characterize the zigzag course of the observed zero-point were not known to me until the results were plotted in Fig. 6, long after the work was done, and I have thus had no opportunity to test the foregoing conclusions.

This series of freezing-points shows us that the *observed* zero-point of the thermometer was by no means constant.

This must be carefully considered.

On the one hand we may assume that the lack of constancy is only *apparent*, and to be explained on the ground of experimental errors. Accordingly the zero for Jan. 21 would be assumed to be 0°.001 C. too high, and on Jan. 25 as much too low. Similarly at Jan. 30 and Feb. 4, and at Feb. 11 and 13, in which latter case opposite errors, amounting to 0°.0015 C., would be assumed. (See Fig. 6.) These errors would then appear as errors in the depressions which were measured from the faulty zero-points, and since they would have to be assumed to be very great, we should find great irregularities in the curves of molecular depressions. For the most part such irregularities are entirely wanting. A closer analysis of the results in this respect is not without value. To this end let us examine the individual depressions measured on the days when these assumed erroneous zero-points were taken.

Jan. 21. — Zero-point apparently too high.

The depressions measured on that day were

$BaCl_2$, $m = 0.01, 0.02, 0.05, 0.10, 0.20$.

Our assumption that the zero-point was too high would make the observed depressions too great in the dilute solutions. The curve seems to indicate that they are too small.

Jan. 25. — Zero-point apparently too low.

NH_4Cl, $m = 0.01$, was repeated and a result was obtained which was 0°.0005 C. *higher* than the mean value of the table. Thus here the assumption that the zero-point was too low on this day does not accord with the observed depression.

Jan. 30. — Zero-point apparently two low.

The solutions observed were

KNO_3, $m = 0.01, 0.02, 0.05, 0.10$, and 0.20.

In this case the assumption that the zero-point was erroneous agrees with the apparent error in the curve.

Feb. 4. — Zero-point apparently too high.

The entire series, Na_2CO_3, was observed.

The curve is entirely regular. This, however, would not decide whether the zero-point was too high or too low, since a perfectly regular curve would result even with a faulty zero-point, providing all the freezing-points of the solutions were themselves *without* error, or affected only by constant errors.

Feb. 11.—Zero-point apparently too low.

$MgCl_2$, $m = 0.15$ and 0.25, observed.

The curve at these points is slightly depressed and a possible error may be assumed which would be in accord with the assumption that the observed zero-point was too *low*.

Feb. 13.—Zero-point apparently too high.

$MgCl_2$, $m = 0.30$, was observed. The curve at this point is not "sensitive" enough to allow any judgment of possible error.

Feb. 27.—Zero-point apparently too low.

KCl, $m = 0.035$ and NH_4Cl, $m = 0.035$, observed.

The irregularity in the KCl curve would suggest, however, an opposite error in the zero-point.

Mar. 4.—Zero-point apparently too high.

K_2CO_3 complete series.

Here, as in the case of Na_2CO_3, the curve presents no irregularities. (See remark under Feb. 4.)

Mar. 6.—Zero-point apparently too low.

The rejected series, KHO and NaHO, $m = 0.01$ and 0.02, were made. The curves were without irregularities, and were rejected, as has been stated already, because their specific gravity and electrical conductivity were found to be abnormal.

Mar. 13.—Zero-point apparently too high.

$NaNO_3$ and NH_4NO_3, $m = 0.01$, 0.02, and 0.03, were observed.

The curves suggest no errors in this region.

Mar. 20.—Zero-point apparently too low.

KNO_3, $m = 0.025$, $NaNO_3$, $m = 0.20$, and NH_4NO_3, $m = 0.20$, were observed.

The observed points in the three curves are perfectly regular and point to no error.

Mar. 25.—Zero-point apparently too high.

H_3PO_4 entire series observed.

The curve is perfectly regular and suggests no error. (See remark under Feb. 4.)

It thus appears that the assumption that the zero-points were erroneously observed on the days when the marked zigzags occur in the "curve" of zero-points is insufficient to explain the observed changes in the zero-point of the thermometer, since, if this were the case, the corresponding errors would, in general, appear in the measured depressions. We are thus obliged to admit that and Wildermann,[1] are almost identical with mine in the region of middle concentration. This agreement becomes more striking from a glance at the following table, which I here reproduce from the former paper.[2] It contains the freezing-points of a $\frac{1}{10}$ normal sugar solution as found by the various observers named, together with the year of publication and the estimated error of the observers.

To this table I now add my own value and the values of the more recent observers.

Observer.	Year of Publication.	Freezing-point.	Estimated error.
Raoult I.	1886	0°.24	0°.01-2
Arrhenius I.	1888	0°.210	0°.0-05
Traube	1891	0°.235	0°.005
Eykmann	1891	0°.216	—
Arrhenius II.	1891	0°.204	—
Tammann	1891	0°.206	—
Pickering	1891	0°.202	0°.0005
Raoult II.	1892	0°.205	0°.002
Loomis	1893	0°.190	—
Jones	1893	[3] 0°.197	0°.0001-2
Nernst and Abegg	1894	[4] 0°.187	—
Wildermann	1894	[5] 0°.190	0°.0001-2

3. It has been suggested by Mr. Wildermann in regard to the three organic compounds examined by me *that the observed increase in the molecular depression with the increase of concentration may be due to some experimental error which he thinks may have rendered the observed zero point too low.* The results hardly admit of this assumption, since the assumption would be justified only by a succession of constant *differences* between the freezing-points of the successive solutions, $m = 0.01$, $m = 0.02$, $m = 0.03$, etc., to $m = 0.20$. These *differences*, however, show an unmistakable increase, which in the case of sugar is from **0°.0184** to **0.0206**. That is, the addition of each $\frac{1}{100}$ gram-molecule to the solution lowers the freezing-point by an ever-increasing amount. We conclude then that the observed increase of molecular depression cannot be due to any error

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[1] Zeit. Phys. Chem., 1894, 3, p. 337.

[2] Phys. Review, Vol. I., 1893, p. 200.

[3] Graphic interpolation. Mean of two series which differ in this region about 0°.002.

[4] Extrapolation. Mean of three series which differ so widely in their essential nature that the extrapolation is very uncertain.

[5] Very slight extrapolation.

in the determination of the zero point of the thermometer. The same remarks apply to the results for alcohol and urea.

Further, such an error would necessarily be a *constant* error, as these three compounds were studied in precisely the same manner as all the other compounds, now numbering some twenty. That these other results seem to be free from such a constant error makes the given assumption at least improbable. That the supposed error could have been an *accidental* error peculiar to two or three determinations of the zero point from which the depressions were obtained, is impossible, since these particular depressions for sugar and alcohol were measured from no less than *fourteen* separately determined zero points, each of which was the mean of 7–9 entirely independent observations.

It seems well to compare my results in this particular with those of other observers. Among the previous observers, Arrhenius and Tammann each had observed this increase of molecular depression with increasing concentration. Of the more recent observers all except Mr. Jones find the same increase which I have observed. Thus the results of Nernst and Abegg[1] for sugar, although their three separate series of observations differ very widely among themselves, — one series showing an *increase* of molecular depression with the increase of concentration, a second, a decrease, and the third presenting such irregularity that no conclusion may be drawn from it in this regard, — still the *mean* values of the three series show a pronounced *increase*. Jones' results show the same increase from the point $m = 0.10$; Raoult's results from the point $m = 0.16$, while those of Wildermann show this increase throughout the *entire* region. See Fig. 4, Plate II., where Wildermann's results for sugar are represented by the dotted lines. Curve I. was made with an "ice cap" about the bulb of his thermometer, II. without this "ice cap," while III. was made under still "more favorable conditions."[2] Mr. Wildermann regards II. as correct to within 0°.0001–2 C. The three facts, then, which appear in this remarkable series must be looked upon as final.

1. There is a marked *increase* in the molecular depression from the value 1.76 in the most dilute solutions, to 1.89 in the most concentrated.

2. The molecular depression reaches the value 1.89 *only* in the most concentrated solutions, where Mr. Wildermann tells us, later, the value can have no significance.

3. The series shows no tendency to become constant at this highest observed value, since a glance at the curve in Fig. 4 makes it plain that the results merely cross the horizontal line of constant molecular depression, 1.89.

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[1] Zeit. Phys. Chem. 189, p. 681.

[2] Phil. Mag. 1895, No. 242, p. 126.

Having reached this value 1.89, Mr. Wildermann stopped his investigation.

Mr. Wildermann *says* of this interesting series, "der *constante* Werth (1.89) kommt sehr gut zum Vorschein."

As Mr. Wildermann explains a similar increase of the molecular depression in series I. as due to the "ice cap" about the thermometer bulb, it would be desirable to know on what grounds he sets it aside in Series II., where no "ice cap" was at hand.

Although this Series II. is regarded by Mr. Wildermann as correct to within 0°.0001–2, still it does not seem to have been so conclusive to Mr. Wildermann as his discussion of it would seem to indicate, since he repeated the work "under more favorable conditions."[1] As a result we have Series III. This new series differs irregularly from Series II. by about 0°.001, — or about five-fold the possible error of the former series. If this Series III. is now to be taken as having reached the utmost limits of experimental accuracy, we must, I suppose, conclude that Mr. Wildermann underestimated the experimental error of his former work.

The unprecedented accuracy of this final series makes it worthy of attention (see Fig. 4, Curve III.).

1. It shows a variation from 1.84 to 1.89.
2. The value 1.89 is reached very abruptly by one only of the five observations. This value is preceded by two observations whose values are 1.84, and followed by two whose mean value is also about 1.84.

Still Mr. Wildermann *says* of this series of observations: "Thus I have shown that the constant (1.87–9) holds good in dilute solutions."[1]

This divergence between Mr. Wildermann's results and his interpretation of them should be kept constantly in mind in studying his work.

Thus in the case of alcohol (see Fig. 5, Plate II.) his results obtained "without ice caps" (Curve II.) show a steady *increase* of molecular depression from 1.81 to 1.85. The only exception is at $m = 0.006527$. Now Mr. Wildermann says[2] of these results: "*We obtain the constant value 1.84 in all concentrations.*"

The third series, "repeated under more favorable conditions," shows even more strikingly the same unmistakable increase of the molecular depression with the concentration. I do not think it profitable to extend this examination to the remaining case of urea where the same facts appear.

It may be well here to call attention to the remarkable agreement between Mr. Wildermann's results, obtained with "ice caps," and my own results for sugar and alcohol. This agreement in the case of alcohol (see Fig. 5, Plate II., Curve I.) is so close that the two series must be looked upon as identical except in the small region of greatest dilution. He explains

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[1] Phil. Mag. No. 242, 1895, p. 126.

[2] Zeit. Phys. Chem. No. 3, 1894, p. 342.

this agreement by saying that there was undoubtedly a similar "ice cap" about the bulb of my thermometer. If Mr. Wildermann will take the trouble to refer to my former publication, he will find that the formation of these ice layers was carefully discussed there, and will learn that one reason for confining the "overcooling" to the narrow limits, 0°.15 to 0°.25, was to make the building of these troublesome ice layers impossible. In fact, no *trace* of ice ever forms on either the bulb of the thermometer or wall of the freezing vessel.

This remarkable agreement is the more difficult to explain since Mr. Wildermann regards my results as "merely qualitative," and further says the concentrations of the various solutions were incorrectly determined.

4. *May not some such constant error as that discussed in* (3) *account for the fact that in the three non-electrolytes examined by me the "curves" of molecular depression, which differ so little from straight lines in the great part of their course, should all alike show a downward curvature in the region of extreme dilution?*

The results, I think, do not permit a final answer to this question. To render the "curve" a straight line throughout its entire course would require the admission of experimental errors by no means large, and it is perhaps well to regard this matter as still in doubt.

That such an error is not altogether improbable appears from the fact that in the case of those *electrolytes* which seem to be affected with errors in the region of extreme dilution a similar downward tendency of the curves appears ($BaCl_2$, HCl, NH_4Cl).

The fact that Wildermann's results show this same peculiarity should not be regarded in the light of a confirmation of my results.

5. A most important question still remains: *What are the respective advantages to be had by using a thermometer graduated in* $\frac{1}{1000}$° *and one graduated in* $\frac{1}{100}$°?

I am able to discuss this question only on the basis of my own work with a $\frac{1}{100}$° thermometer and the published results of other workers who have employed the $\frac{1}{1000}$° instruments.

First, it must be emphasized that the $\frac{1}{100}$° thermometers are easily read to the ten-thousandth of a degree with a possible reading error of half that amount. The sufficient proof of this is the fact that I have frequently interrupted a series of observations to allow some student who might happen to be present to make the reading for me. In *no case* have such readings differed from my own by more than $\frac{1}{10000}$°. This is not at all surprising since it is to be remembered that the micrometer scale in the microscope enables the observer to read the thousandths directly, and the *ten-thousandths* are as accurately estimated as the tenths of millimeters on an ordinary millimeter scale.

How, then, is the fact to be explained that a series of five independent determinations of a given freezing-point vary on the average about 0°.001? First, it must be due to the *inconstancy* of the thermometer itself, or second, to the failure of the method to bring the solution to its actual freezing-point by amounts within these limits. The first cause of variation has been discussed already.[1] While it undoubtedly plays some small part in this respect, still, I think it may be easily shown that the second cause is the all-important one, and represents the *fundamental difficulty* in all freezing-point determinations.

Thus, to cite the results of Mr. Jones,[2] it appears that the great accuracy with which he could *read* his $\frac{1}{1000}$° thermometer, together with a few preliminary observations lead him to fix his *experimental* error at 0°.0001–2. Certainly the *reading* error is even less than that. The fact, however, appears throughout Mr. Jones' *results* that his method failed to bring the solutions to their freezing-points with this estimated accuracy, since in *every* instance where Mr. Jones furnishes us with two series of observations, the corresponding observations on the same solution frequently differ by $\frac{1}{1000}$° and not rarely by two or three times this large amount. These surprising differences appear quite generally throughout his two K_2SO_4 series and $BaCl_2$ series. See Plate II., Fig. 1.

It would seem that a method which thus fails in the fundamental matter of bringing a solution to its freezing-point to within 0°.001–3 has little to gain by the use of a thermometer which may be read to 0.0001° C. That Mr. Jones seems to have become himself aware of this failure of his method to bring the solution to its freezing-point with any great degree of accuracy appears certain, since he explicitly refers to the *regularity* in the decrease of molecular depression shown by his HCl results.[3] See Plate II., Fig. 1, for the graphic reproduction of his results. That such a "curve" is regarded by Mr. Jones as *regular* indicates his belief that the method easily permits experimental errors amounting to several thousandths of a degree.

But we are not left to infer this knowledge on the part of Mr. Jones, since he says[4] of his results for Na_2CO_3: "Their *apparent irregularity* is due without doubt to a slight experimental error." See the graphic representation of his Na_2CO_3 results in Fig. 1, Plate II. It here appears that the "*apparent* irregularity" amounts to only a little less than a *hundredth* of a degree. That Mr. Jones should refer to this as a slight error shows how clearly he understood the complete failure of his method in the particular under discussion.

What is true of his Na_2CO_3 series appears also in all his later results,

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[1] p. 287–91.

[2] Zeit. Phys. Chem., 1893–1894.

[3] *Ibid.*, 1893, xii., p. 628.

[4] *Ibid.*, p. 638.

noticeably in H_2SO_4, sugar, $BaCl_2$, K_2CO_3, etc. The curves for the two latter are given in Fig. 1 and Fig. 2, Plate II.

It is hard to see what particular advantage resulted from the use of a $\frac{1}{1000}^\circ$ thermometer, or on what grounds Mr. Jones justifies his attempts to measure the molecular depressions of solutions in the extreme dilution, $\frac{1}{100}$ to $\frac{1}{1000}$ normal, where an experimental error of 0°.0001–2 is absolutely *fatal*.

The only other observer who has made use of a $\frac{1}{1000}^\circ$ thermometer, so far as is known to me, is Mr. Wildermann in the application of a method devised by Mr. Lewis. That this method likewise fails in this fundamental matter of bringing the solutions to their actual freezing-points appears from a similar examination of the two series of results which he has furnished for both sugar and alcohol.

Series II. in each case is affected according to Mr. Wildermann with a possible error 1–3 ten-thousandths of a degree, and Series III. is regarded by him as made under "more favorable circumstances."

Among the differences which these two series for sugar present may be mentioned the following:

At $m = 0.01$, 0°.0008
$m = 0.02$ 0°.0004
$m = 0.03$ 0°.0006

while in the case of the alcohol series we meet the following:

At $m = 0.01$, 0°.0004
$m = 0.02$ 0°.0008
$m = 0.05$ 0°.0010
$m = 0.09$ 0°.0027[1]

Unfortunately he does not publish a "repeated" series for urea, though we are left to infer that he made such a series, since he writes: "This year I repeated the investigations of cane sugar, alcohol, *etc*."[2]

However, we are able to conclude from the data already at hand that his estimated experimental error, 0°.0001–2, is in fact about fivefold too small to explain his results.

I know of no way to explain these great differences except by supposing that the method failed to bring the various solutions to their real freezing-points by 1–2 thousandths of a degree. The great irregularity of his results would be explained by Mr. Wildermann, I suppose, in the same way. And yet Mr. Wildermann *reads* his thermometer to the ten-thousandth of a

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[1] In order to obtain the actual difference of the two observed freezing-points one has to multiply the difference as given in the curves by the corresponding abscissa, or value of m.

[2] Phil. Mag., 1895, 242, p. 126.

degree, and to avoid *reading errors* makes from 5 to 10 observations of his thermometer. This is the more surprising when it is remembered that it is now quite generally understood that the mercury in one of these fine thermometers, when once it comes to rest in the capillary, remains *fixed* so long as the bulb experiences only slight changes of temperature (such as thousandths of a degree) and the thermometer is not vigorously *jarred*. Still Mr. Wildermann assumes that having brought his thermometer to a constant *reading* he has likewise brought his solution to a constant *temperature*.

How, then, does Mr. Wildermann account for the fact that his $\frac{1}{100}^\circ$ thermometer placed side by side with his $\frac{1}{1000}^\circ$ instrument shows variations of some thousandths (1–3)? He tells us that these are reading errors! Is it not perhaps possible that these variations may not be wholly due to carelessness in reading the instrument, but may arise from actual changes of the mercury! The $\frac{1}{100}^\circ$ thermometer with its small bulb is perhaps able to thus indicate the temperature-changes in his solutions which would be wholly lost to his $\frac{1}{1000}^\circ$ instrument with about *300 grams* of mercury in its bulb.

I think a careful analysis of the results obtained with a $\frac{1}{1000}^\circ$ thermometer obliges one to conclude that its use as yet has added nothing to the accuracy of the various methods, and indicates that further accuracy is to be sought in the direction of greater control of the temperature of the solution itself.

In conclusion it may be well to point out a few matters which long practice seems to make worthy of attention.

1. It cannot be emphasized too strongly that the reading of the thermometer, whatever the method, should *never* be made until all manipulation of the solution is done with.

2. The experimental error of a given method may be safely estimated by making a series of entirely independent determinations of the freezing-point of *water*. These should be made on a day when the barometer is fairly constant, and special attention should be given to the matter mentioned in (1).

3. It seems to be important to preserve a record of all the observed zero points of the thermometer, together with the dates of observations. Thus the very great variation of $0^\circ.008$[1] in the apparent zero of Wildermann's $\frac{1}{1000}^\circ$ thermometer, during the short period of his observations would perhaps lead to some valuable conclusions if systematically studied.

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[1] The maximum is found on p. 339 (Zeit. Phys. Chem. 1894, III.), where the third observed zero point is 0.4873, which becomes, when reduced to 760 mm, 0.4884. The minimum is found on p. 362, when the observed zero is 0.4781, or reduced to 760 mm., 0.4804.

It remains to be added that there seems to be little profit in correcting the misstatements of Mr. Wildermann in regard to the work of the present writer.

PRINCETON, N. J., Aug. 15, 1895.

A COMPARISON OF TWO CONCAVE ROWLAND GRATINGS.

BY ALICE H. BRUÈRE.

To any one who has worked with the spectra produced by diffraction gratings, the irregularities which occur in them are only too well known. Even when the grating has been constructed with the utmost care in every detail of the work, as is the case with Professor Rowland's concave gratings, variations of intensity in the spectra of different orders, or in the different parts of a single spectrum, are peculiarities which it seems impossible to avoid, and the appearance of ghosts, or the lack of symmetry with respect to the focal distance of the various spectra, are matters of frequent observation.

Professor Rowland[1] notes and discusses many of these peculiarities in a paper published in 1893.

Kayser and Runge,[2] in their article upon the spectra of the elements, mention a sudden diminution of intensity for the shorter wave-lengths obtained from what, in other respects, was an exceedingly fine grating. This seemed extraordinary because the phenomenon was repeated at the same wave-length in the spectra of all orders, and could therefore not be attributed to the shape of the groove.

The asymmetry of gratings is discussed at length in an article upon his observations by Dr. Rydberg,[3] of the University of Lund, Sweden, in 1893.

F. Paschen,[4] in the same year, published some results of bolometric determinations of the spectra of glowing solids. Previous to the investigation, he believed that the conditions of his experiment were exceptional, because in obtaining the spectra by means of a concave grating he would avoid the difficulties which arise through the use of a rock-salt prism and lenses. The energy curves which he obtained were, however, irregular and discontinuous to such an extent, that it was evident the spectrum he was

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[1] H. A. Rowland, Gratings in Theory and Practice, Astronomy and Astrophysics, 12, 1893. Phil. Mag. S. 5, 35.

[2] Kayser and Runge, Ueber die Spectren der Elemente; Abh. der Berl. Ak. der Wiss. 1888. Theil I.

[3] Dr. J. R. Rydberg, On a certain Asymmetry in Professor Rowland's Concave Gratings. Phil. Mag. S. 5, 35. Astron. and Astroph., May, 1893.

[4] F. Paschen, Bolom. Untersuchungen im Gitterspectrum. Wied. Ann. 48 [1893].

using was not fit for the purpose. Further investigation showed that all spectra thus obtained gave different curves for the same substance under exactly similar conditions of arrangement and temperature, and that all were equally irregular.

These and similar observations suggested a comparative study of two concave Rowland gratings belonging to the Physical Department of Cornell University, with a view to obtaining additional data upon the irregularities of gratings by a method not previously tried.

One grating is marked " 14438 lines to the inch " ; on the second, there is no statement with respect to the ruling, but all observations indicate that it is ruled with the same or nearly the same number of lines to the inch as the one marked. The length of radius marked upon each is six feet. Although not of the best Professor Rowland has ruled, the gratings are considered good.

The first experiment was a photometric comparison of the spectra obtained from the two gratings. For this purpose, the grating whose spectra appeared more nearly uniform was chosen as a standard. This one, for convenience, will be designated as grating " A," and the other as grating " B." The two gratings were mounted, one above the other, on a vertical support. The arrangement of the apparatus was similar to that of Professor Rowland in his spectroscopic work. By means of three screws back of each grating, they were adjusted until perpendicular, and then inclined toward each other enough to bring the two spectra on the screen sufficiently close for accurate observations.

The intensity of the spectrum obtained from a grating varies with the amount of light admitted to it. A comparison of the intensities of the spectra obtained from two gratings, receiving light from the same source, may therefore be made by comparing the widths of the slits through which light is admitted to them. All other conditions being the same, the ratio of these widths, when the spectra are of equal intensities, will be the inverse ratio of the intensities of the two spectra obtained with equal illumination on the gratings.

This was the method employed. The two gratings were illuminated by light from independent slits. A double slit was used, each part of which was operated by a micrometer screw. It was carefully mounted, with a screen horizontally before it. The latter was adjusted until the beams emerging from the two parts were completely separated. This occurred when the light on the gratings was divided by a sharp black line, the shadow of the screen, midway between them. When the two slits were adjusted so that the spectra obtained were of equal intensities, the measurement was taken in terms of the widths of the slits. For this reason these were carefully calibrated to thousandths millimeters.

The spectra were received upon a screen of oiled paper bent into an arc of the circle. The diameter of this circle was equal to the radius of the grating. Before the screen could be slid an opaque screen, in which a rectangular aperture about one centimeter in width had been cut. In this way the entire spectrum, except the part in which observations were to be made, could be cut off. During the observations upon one spectrum, the position of the translucent screen was fixed. For the best conditions, its position should have been at the focal distance of the spectra. It was impossible to place it so, however, for these distances differed for the two gratings by about six inches, and an intermediate position had therefore to be chosen. This introduced an error into the measurements, but as the entire distance was great as compared with the discrepancy, the error is small.

The light used was that from a zircon disk heated to incandescence by the oxyhydrogen flame. The time for one set of observations could not exceed one hour, for the sensitiveness of the eye diminished greatly if it was extended beyond this. For this length of time, the light from the zircon disk was found to be most brilliant and constant.

The screen was calibrated to wave-lengths by means of bright-line spectra. These were obtained by using an arc-lamp whose carbons were cored and filled with substances having distinct lines in well-known positions.

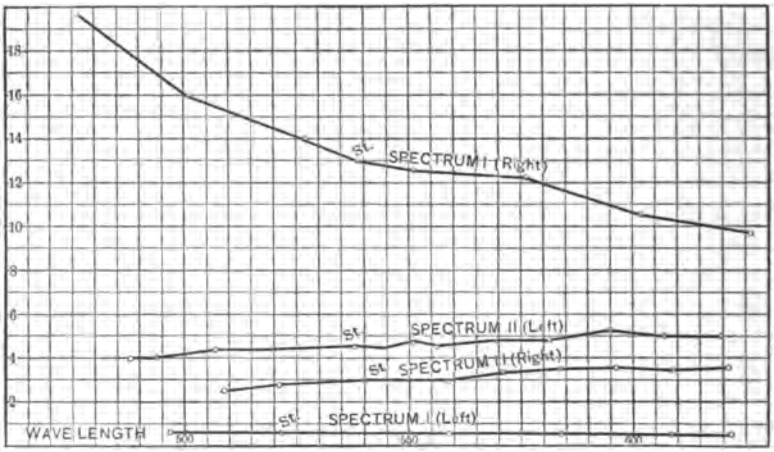
In the measurements, the slit which illuminated grating *A* was set at a fixed width. Comparisons were then made for a number of positions throughout the spectra of the first and second orders on both sides. The slit which illuminated grating *B* was adjusted until the spaces in the spectra were of equal intensities, and the width of the slit was then read in divisions of its micrometer screw-head. This could be reduced to thousandths millimeters from a calibration curve drawn for this purpose.

The intensity of a spectrum is dependent on three factors: the intensity of the light on the slit, the width of the slit, and the intensity due to the grating itself for unit width of slit and unit intensity on the slit. The product of the quantities expressing the values of these factors for grating *A* then expresses the true intensity for a given space in the spectrum obtained from this grating. Using corresponding quantities, the true intensity for the corresponding space in the spectrum from grating *B* may be expressed as a product. In the observations these intensities were made equal; we therefore have an equation between them.

Before and after each observation in a given part of the spectrum an observation was taken in that part of the spectrum to which the eye had been found to be most sensitive. This served as a check upon the ratio of the intensities of the light which fell upon the slits, since for any one position this was the only factor which could vary. A second equation was obtained from the intensities at this position of reference. From the two equations, a value for the intensity factor due to grating *B* at a given position was obtained, involving only the ratios of the widths of the slits, and the ratio of the intensity factors due to the gratings at the position of reference. The former were directly obtained by the experiment; the latter, being always in the same part of the spectrum, was a constant.

Since only a ratio of the intensity due to grating *B* to that due to grating *A*, which was assumed as unity, was desired, this constant could be given any convenient value. With the product of the ratios of the widths of the slits by this value for ordinates, and wave-lengths for abscissæ, curves were drawn.

From the values for the ratios of the widths of the slits indicating the relation of the intensities of the two spectra, an average ratio for each of the four pairs of spectra was obtained. On the left, that of spectrum I. to the standard was 0.5 : 5; that of spectrum II., 4.5 : 5. On the right, that of spectrum I. to the standard was 13 : 5; that of spectrum II., 3 : 5. If now the constant mentioned above be given the values, 0.5, 4.5, 13 and 3 in the respective spectra, and the product of the ratios of the widths of the slits by this quantity be platted as ordinates, and wave-lengths as abscissæ, curves are obtained showing the relation of the four spectra to each other. Each curve also indicates the variation throughout a single spectrum.



The adjoining curves have been obtained in this manner. The first spectrum to the left was an exceedingly weak one. The spectrum of the same order to the right, which was obtained by reversing the grating, has the greatest intensity of those measured. From this it would appear that the shape of the groove is such that most of the light for this angle of incidence is thrown in one direction. In both spectra there is a marked diminution of intensity in passing from the shorter to the longer wavelengths. In the spectra of the second order, the intensities are more nearly equal. The variation of intensity is, however, in the opposite direction from that in the first spectra. In both cases the general character of the curves for the two spectra of the same order is the same.

The grating from which these curves were obtained has a change in its ruling which is discernible with the eye. It was thought that there might be a connection between this defect and the peculiar character of the spectra of the first order. A second experiment was therefore performed in which the spectra from the two gratings were compared by photography. The bright-line spectrum of the carbons of an arc-light was photographed when obtained by each entire grating, also when obtained by using parts of each grating.

The only peculiarity found in the spectra obtained from the standard grating was a slight shifting of the spectrum in several cases. From the grating with the irregular ruling, the spectrum of the first order to the left was double, the two spectra being separated 0.01 inch. That of the second order was distinct and single. Both spectra to the right were double. The lines of the two spectra in the spectrum of the first order were so close as to appear like a broadening of the lines of one spectrum; in the second spectrum the two were distinct. In the case of each double spectrum, one of the spectra corresponded to the single spectrum obtained by using the irregular part of the grating alone.

From this fact, and the appearance of the grating, the double spectrum was thought to be due to a change in the number of lines ruled to the inch. The position of the spectrum indicated an increase of dispersion; the number of lines is therefore greater than the marked number, 14438. It was calculated to be 14446.

The results found in these experiments bear in the same directions with those mentioned in articles referred to at the beginning of this paper. There is nothing from which a definite conclusion may be drawn, and they therefore only serve as further evidence of a few facts with regard to gratings in general, and as a statement of some of the peculiarities of the gratings compared.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY.

A NEW APPARATUS FOR THE STUDY OF COLOR PHENOMENA.

BY ERNEST R. VON NARDROFF.

THIS apparatus is virtually an attachment that converts an ordinary projection lantern into a triple lantern in which the three beams are independent as to intensity and direction.

The beam from the lantern is first rendered "parallel," either by pushing forward the illuminant, or, better, by removing the forward lens of the condenser. In the latter case, if a physical lantern be employed having a triple condenser, no adjustment of illuminant is necessary, but with a double condenser such as is found in ordinary picture lanterns, besides the removal of the forward lens, the illuminant must be drawn back a short distance. Next, the regular focusing lens of the lantern is to be removed, and in the path of the parallel beam is to be placed the apparatus, preferably as near to the condenser as possible.

The apparatus (Figs. *A* and *B*) consists of a mahogany base supporting two uprights, to which are attached lenses, slide-holders, and diaphragms. The lenses, *a*, are auxiliary condensers, which produce images of the illuminant in the plane of the adjustable diaphragms at *d*. It is the property of such an image that each part of it receives light equally from all parts of the lens producing it, and hence the circles of light on the screen, which are images of the apertures, *p*, formed by the focusing lenses, *f*, will be uniformly dulled by partially closing the diaphragms, *d*. The focusing lenses, *f*, are mounted in sliders. By shifting these, the circles on the screen are shifted. The experimenter may thus obtain any desirable amount of overlap or separation. The range of this shifting was doubled by having the centers of the apertures, *p*, somewhat nearer together than the optic centers of the condensing lenses, *a*. These lenses, therefore, were chosen of a diameter considerably greater than the diameter of the apertures, *p*. The accurate focusing of the apertures, *p*, is accomplished by sliding in or out the broad telescopic tube, *t*, in which they are mounted. Slide-holders are placed at *k* for the reception of colored glasses, collodion or gelatin films, or glass cells containing colored liquids. Of the many colored liquids at one's disposal, I have found solutions of the sulphate, the nitrate, the ammonio sulphate of copper, and the permanganate of potash particularly useful.

The description of a few experiments will make clear the general method of working.

Inserting in the slide-holders red, green, and blue media, and adjusting the front sliders for a perfect overlap on the screen, there is obtained a evenly illuminated disk, probably tinted with some hue. Any attempt

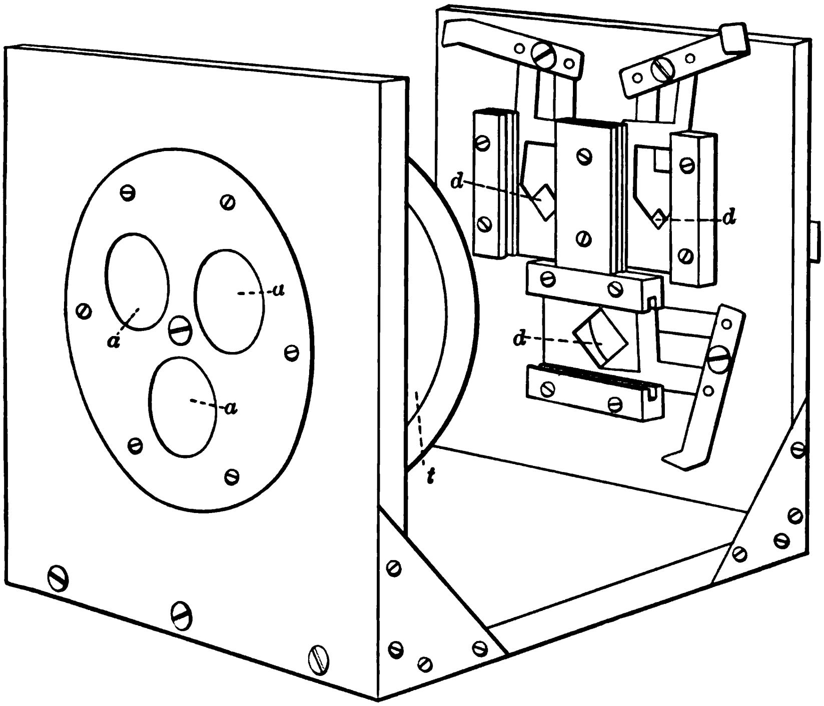


Fig. A. — Rear View.

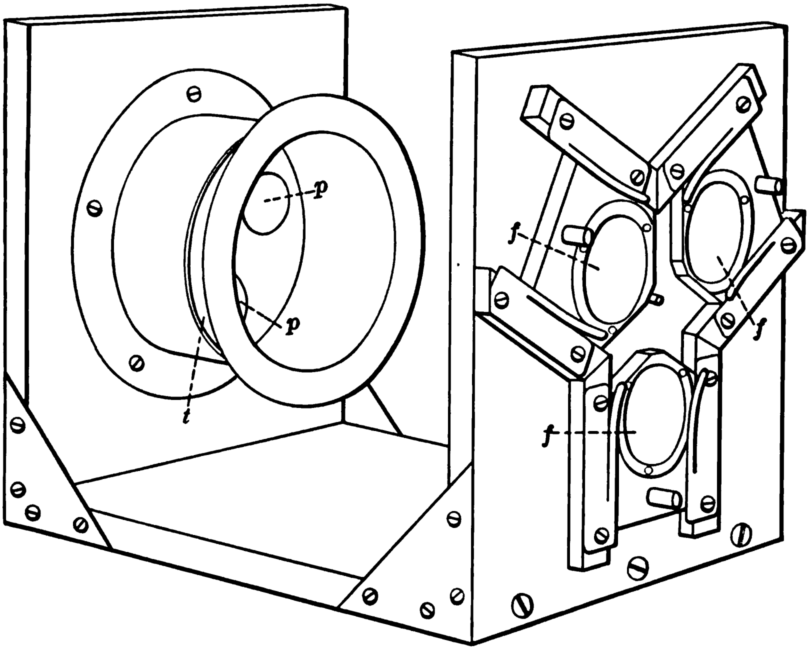


Fig. B. — Front View

E. R. VON NARDROFF: COLOR PHENOMENA

to remove this residual hue by a more careful selection of color media is discouraging, because the result is so strongly affected by the illuminant, the color of which is uncertain when either the lime-light or the electric arc is employed. However, the whole difficulty is avoided by means of the adjustable diaphragms. By manipulating these, the residual hue may easily be abolished, and an absolutely pure white always obtained. This white is also very intense, because its intensity is equal to the sum of the intensities of its components, instead of to their average, as with rotating colored paper disks.

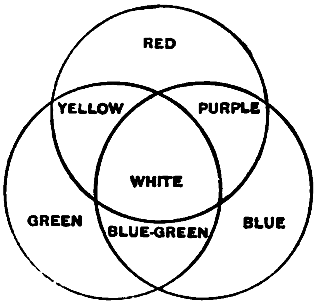


Fig. 1.

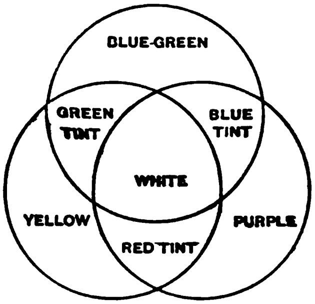


Fig. 2.

If, now, the disks forming the compound white be separated in triangular fashion, the resulting figure (Fig. 1) will display the result of mixing the primaries in pairs. This mixing may be further developed by cutting off, say, the red and the blue by closing their diaphragms, leaving only the green. Then, by turning on the red gradually, and when full, by turning off the green, the overlap will pass through all gradations of hue from green, through yellow, to red. The same kind of thing can, of course, be done with the other pairs of primaries.

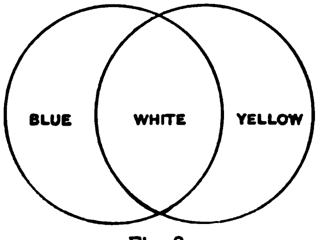


Fig. 3.

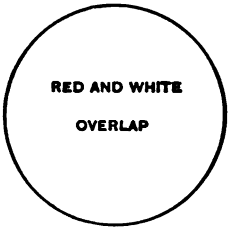


Fig. 4.

When, instead of with red, green, and blue, we start with purple, yellow, and blue-green, we may still by proper use of the diaphragms obtain all possible hues as well as white (Fig. 2). Because the purple is a sensation that cannot be induced by light of a single wave-length, but requires a comnat the sensation itself is complex, and does not represent the primary color ... obtained by compounding these false ... than with red, green, and blue.

... hues may be illustrated by using carefully ... Fig. 3, or else by simply referring to the ... here it is evident that each initial hue is ... compound hue.

... no explanation. A simple reference to

... yellow-ochre, and olive-green, require a ... screen, *alone*, dull red still appears red, — not a suggestion of brown, — just as dull white alone never appears gray. Sombre effects require the assistance of contrast with some standard intensity. With color disks this is present in the general illumination of the room, but with screen apparatus it must be especially supplied. The front sliders being arranged for perfect overlap, two of the slide-holders are left clear for white light, and the third is provided with some color, as red for example. A glass disk, Fig. 5, having attached to it a brass ring, *r*, and ... telescope tube, and in contact with the ... to come in front of the aperture corre- ... diaphragm corresponding to the disk, *d*, ... a white circle having a black center. If

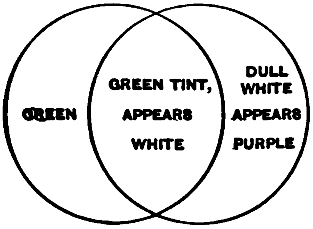


Fig. 7.

... a little, a small quantity of red light ... standing in contrast to the surrounding ... brown (Fig. 6). The effect may be varied by turning on a little white by opening the third diaphragm; and then by using a variety of hues instead of the red, a set of tinted grays may be obtained.

Contrast effects are strikingly presented when some saturated color, as green for example, is projected and then a white disk previously arranged to partially overlap is turned on. The overlap, which is really a tint, appears nearly white, while the remaining white appears strongly colored of the complementary hue. (See Fig. 7.) If the order of projection be reversed, — the white first and then the color, — the sudden change in the appearance of the white is very impressive.

This apparatus, essentially as described, has been in use in my classes for several years, but the details have recently been much improved by Mr. F. W. Huntington, of Montclair, N. J.

ON A NEW FORM OF WATER BATTERY.

BY LOUIS W. AUSTIN AND CHARLES B. THWING.

THE ordinary old form of water battery, consisting of zinc-copper couples dipping in short test tubes set in paraffine, while perfectly satisfactory in its working, is extremely inconvenient to fill as soon as a large number of cells are used, since each cell must be filled separately and with great care lest the insulating medium should be wetted. Some years ago Professor Rowland[1] proposed a battery, very convenient for many purposes, which consisted of a series of zinc-copper pairs cemented to the lower side of a glass plate, each pair being so near to the next that when the tips of the metal strips have been dipped in water a drop is held between each strip and the adjacent one of the opposite metal in the next pair by capillary action. This drop will evaporate in about half an hour, when of course the battery must be dipped again. If for any reason it is desired to keep up the potential undisturbed for a longer time than this, some other battery must be used.

The battery about to be described is one designed by the authors for use in some electrometer work on which they were engaged. It has proved so satisfactory and convenient in its working that we have decided to describe it for the benefit of other physicists. It is constructed as follows: The required number of zincs and coppers are cut and bent by means of a form made by driving small nails into a block of wood in the shape shown in Fig. 1. The zinc strips differ from the copper ones only in having the short bent portion at the top (*t*, Fig 1) omitted. Cuts 4 mm.

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[1] Phil. Mag., March, 1887, p. 303.

deep and 28 mm. apart are then sawed in strips of dry pine wood 34 cm. long, 21 mm. wide, and about 7 mm. thick. The zinc and copper pairs are then soldered together and slipped into the cuts, after which ten strips are mounted together, with the addition of a blank strip to hold the last line of metal pairs in place in the grooved end pieces, and fastened firmly with nails. To secure perfect insulation, the wooden portions are next dipped for a few moments in a pan containing shellac varnish. The battery is completed by springing a 1-drachm homeopathic vial over each pair, the metal strips being so placed that they hold the bottles in position without any other support. The battery is filled by setting it over a pan (30 cm. by 30 cm. and 9 cm. deep) filled with water. The general appearance of one of the frames is shown in Fig. 2. In our battery ten such frames of 100 cells each are placed four deep in a portable rack of wood. A battery of this sort, while it can be filled almost as easily as Rowland's, can be used without refilling for several weeks.

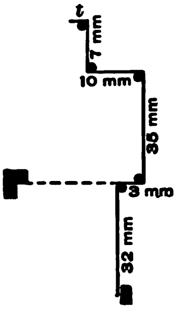

Fig. 1.

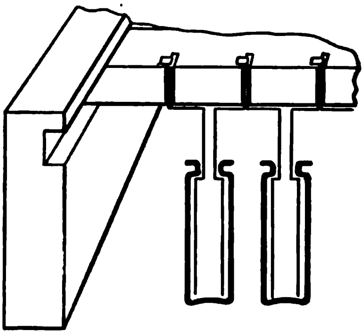

Fig. 2.

The Physical Laboratory of the University of Wisconsin,
August, 1895.

EW BOOKS.

ples of Physics. By ALFRED DANIELL.
i enlarged. 8vo, pp. xxiii+782. Macmillan

hysics is adapted to the wants of students who
ensive knowledge of general physics rather than
accurate details of any branch of it. Numerous
ted branches have issued from the press of Great
arter of a century, and these, to some extent, have
text-book. But the study of general physics, in
l branches, has obvious advantages, and the text-
in general education. Nevertheless the literature
no less remarkable for its poverty of English text-
ealth of special treatises. The works of Arnott and
especially of Olmsted and Silliman in America, which
ysics in the middle decades of this century, had no
ors down to the beginning of the last decade. English
place of English authorship. Ganot and Deschanel, in
glish dresses given them respectively by Atkinson and
st universal sway until 1884, when Daniell's Physics first

r Stewart, I think, who first broke away from the traditional
ting physics in disconnected fragments, and courageously
science of matter and energy. But Balfour Stewart's work
lume adapted to younger students. Daniell, viewing physics
of the same great truth, but from a standpoint fourteen years
that of Stewart, redrew the science in bolder outlines, on a
more elaborate and adapted to maturer readers. A third edi-
standard text-book, carefully revised and considerably enlarged,
re us. A glance along its pages reveals the fact that the spirit
d of the book have not been changed. But the work of revision
en everywhere. Sometimes it is detected in the change of a
metimes in the remodelling of a sentence; and sometimes in the
f a paragraph. In some cases it is found in the extension of a
on to a more general conclusion; in others, in the incorporation

of subject matter which is entirely new. The motive of it all is easily discovered. Greater accuracy and precision have been secured, important gaps have been filled, and the later results of research have been embodied. The limits of this review forbid more than a brief record, with scant illustrations of a few selected features of this revision.

A very welcome modification of the notation has been made. To each physical quantity a symbol is assigned which, as far as possible, it retains throughout the book. Quantities in general are represented by capital letters, while quantities per unit area are designated by the corresponding small letters. Mr. Heaviside's suggestion that blackfaced type be used for directed quantities has been adopted, and other devices in type furnish other distinctive characters. A two-page "index of symbols," in which every character in this system is explained, is thoughtfully supplied. Why may not this effort be extended to the literature of physics in general? The adoption of a uniform and carefully adjusted system of notation is next in importance to the adoption of a uniform system of units.

We notice next the incorporation of recently suggested terms, such for example as inductance, conductance, and impedance; permittance and permittivity for electrostatic and specific electrostatic capacity. Magnetomotive force, magnetic flux, and reluctance appear with their units, and their relation, analogous to Ohm's law, is pointed out. The work of the international congress, Chicago, is referred to in the appendix as recommendations only, but the henry is placed among the practical units without reserve. Among the properties of matter we find shearability as the reciprocal of rigidity, cubical compressibility as the reciprocal of elasticity of volume, and in another connection we find dilatancy to designate the change in volume which accompanies change in shape of granular masses.

Another motive appears throughout the work which, I think, cannot be too highly commended. I refer to the author's anxiety to impart clear-cut conceptions of physical quantities and to protect the student from the pernicious influence of ambiguous terms. Think of the difficulties fostered by the long-time vague use of the word *force*. The author tries to avoid them by rejecting absolutely the notion of force as a physical entity, and using the word as a convenient term to designate a measurable quantity — the mutual action of bodies. Think of the inaccuracies involved in the ordinary use of the word *weight*. The author would forestall them by defining weight as a measurable action, assigning to it a symbol G, representing its value in a formula $G = ma$, and recording its value in dynes. Think of the confusion incidental to the use of one term in many senses — a most common and distracting feature of physical nomenclature. The author would preclude it, if possible, by setting the several uses of each ambiguous term precisely before the student. "We shall, except where the context makes it plain, avoid the use of the unqualified word *stress*, and endeavor to make it clear whether in any particular instance we refer (1) to a condition of stress, (2) to a stress of so many dynes, or (3) to a stress of so many dynes per square centimeter" (p. 24). The several meanings of an overloaded term are sometimes compiled, with a reference number given to each. In the list for pressure no less than five are formulated (p. 25).

There is a gratifying extension of the text to cover the later researches. This feature of the revision is especially marked in the chapter on electricity. Thus we find new paragraphs on the ether as the universal medium involved in the phenomena of electricity, magnetism, electro-magnetism, light, radiant heat and actinic radiations. New pages are devoted to electric waves, Maxwell's theory, and the inferential properties of the ether, oscillating currents, dynamo machines, and the transmission of energy to a distance. This last-named subject is too briefly treated, and Tesla's motives and successes receive scant recognition.

To those who have yet to make acquaintance with this treatise a brief *résumé* of its contents may be useful. An introduction supplies the axiomatic truths and fundamental laws on which physical investigation is based. The work then opens with a discussion of measurement as the foundation of all accurate knowledge of phenomena. One short chapter is devoted to the fundamental units of time, space, and mass; another to the derived ideas of motion, velocity, acceleration, momentum, and force as measurable quantities; a third describes in general terms some practical methods adopted in the measurement of those quantities; while a fourth discusses work and energy, giving definitions of their units and the law of conservation.

A second group of four chapters follows, based on the doctrine of energy, and devoted to the principles of kinematics, kinetics, potential, and gravitation. Harmonic motion and the propagation of waves, potential and the conception of space as a field of force, are here discussed with sufficient fullness and great care. The older problems also, — acceleration and rotation, impact and friction, moments and mechanical powers, gravitation and the pendulum, — are examined in the light of the all-pervading principle of energy.

These two groups of chapters, I. to VIII. inclusive, may be regarded as a preparatory course. While they keep the problems of the material world constantly in view, they withhold the student from an immediate attempt to grapple them. Filled with fundamental principles, definitions, and physical conceptions, they are the armory and drill-ground where the student may get an adequate equipment and training. In Chapter IX., for the first time, the study of physics as a science of phenomena comes to the front.

A third group of four chapters here begins, which is devoted to the study of matter. They comprise, in general, a discussion of its properties, states, and constitution; and then, in particular, the special features of solids, liquids, and gases. These chapters fairly bristle with modern views. Ether takes its place among the states of matter. Molecular structure, viscosity, the critical state, and the kinetic theory are prominent. The conception of matter as substantially one thing, and of its different forms and states as incidental variations determined by the energy which each body is, for the time being, the reservoir, cannot escape the thoughtful reader.

Following these is a fourth group of four chapters, discussing the phenomena of energy under the titles of heat, sound, ether waves, and electricity and magnetism. The discussion of heat is brief. One is somewhat surprised to find so much of so large a subject in so small a space. But as heat is a form of energy, the principles relating to heat may, to a great extent, be extracted from the general principle. This is the secret of the author's successful brevity. The propositions relating to heat are set in the doctrine of energy, like crystals of metal in their native vein-stone. The student will sometimes find his strength and skill severely taxed to think them out. The chapter is not an easy one. The next, on sound, is fairly well written, discloses the essential features of the subject, and is quite full on pitch and temperament. It permits close thinking, but does not seem to compel it. Not so with the chapter on ether waves. One must in the outset learn to think of ether as he thinks of air, — a medium whose reality is to be admitted as an inference from the phenomena to which it gives rise. The reader must firmly grasp the difficult conception of ether motions and ether stresses, and as he has already learned to look upon bodies of matter as reservoirs of energy, so must he now behold ether as the vehicle for its transfer.

Beginning with the nature of radiations, the path leads on through color, Prevost's law, Stoke's law to spectrum analyses. Starting again with molecular vibrations, we follow the propagation of waves through ether, taking, on our way, the phenomena of plane polarization, reflection, refraction, interference, double refraction, to elliptical and rotary polarization, where we halt to discuss optical instruments and visual perceptions. Finally, in the last and longest chapter, the principles of electricity and magnetism are discussed with considerable detail, the omnipresent ether being invoked to unitize the whole. The time will come, no doubt, when this can be done with more complete success than seems to be possible at the present time.

The specialist need not consult Daniell's Physics for technical details. The mathematician need not go to it expecting to find a mathematical gymnasium. The historian will miss the descriptions of classical experiments and the narrations of personal achievements. But the student of science will find it to be a cabinet of well-selected facts, mathematical reasonings, and experimental results, skillfully arranged to exhibit the system of principles that underlie physical phenomena.

LeRoy C. Cooley.

Solution and Electrolysis. By William Cecil Dampier Whetham, M.A. pp. viii + 296. 19 illustrations. Cambridge, The University Press; New York, Macmillan & Co.

During the last few years the scientific advances made in physical chemistry have been marvelously rapid, and especially has this been the case in those lines which relate to solutions and electrolysis. Questions present themselves to the investigator from all sides of the subject, and their solutions are often within the reach of limited apparatus and limited time on the part of the investigator. As a result, the periodical literature is rich in memoirs on the subject. It is therefore not surprising that there are many general scientific readers who are incapable of following some of the later memoirs. To such persons the present volume will be welcome. It will also be of great value to the specialist in this line, because of its suggestiveness, and especially because of the tables at the end.

The book, as its title indicates, has two distinct parts. The first part covers six chapters. In them the kinetic theory of solutions is presented in very much the same manner as in Muir's translation of *Ostwald's Solutions.* The numerical results of experiment are omitted except occasionally, where their presence makes the presentation of the subject clearer. The five remaining chapters are devoted to electrolysis. In the first of these the early work of Davy, Faraday, and Grotthus is described, and the theory of primary and secondary batteries is presented. In connection with the latter, a paragraph on polarization appears, which makes no reference to the work done during the last fifteen years. Chapter VIII. is devoted to the ions — their nature, their migration, and their velocities of migration. Chapter IX. is concerned with the conductivity of electrolytes. At this place the dissociation theory of Arrhenius is introduced. Throughout the second paragraph of the chapter *potential differences* are wrongly called *electromotive forces.* Bouty's method of determining the resistances of electrolytes is described and illustrated. The prominence given to it constitutes a recommendation. Yet Bouty was led into false conclusions from its employment; and, as Kohlrausch stated (*Annalen der Physik und Chemie,* Band XXVI., p. 219), it is surprising that his results were as good as they were, considering the liability to temperature errors. The *convenient* [illegible] of electrolytic resistance vessel represented in Fig. 18 will hardly be considered so by American workers. The following chapter is devoted to the consideration of the connections existing between electrical conductivity, chemical activity, and osmotic pressure. The last chapter is devoted to the theories of electrolysis.

A reprint from the report to the British Association for the Advancement of Science, of a table of electro-chemical properties of aqueous solutions, compiled by the Rev. T. C. Fitzpatrick, occupies the last sixty-nine pages of the book. This will prove of great value to investigators. All ordinary electrolytes are considered in it, and a mere inspection serves to determine data concerning equivalent composition, specific gravity, electrical conductivity, migration ratios, and fluidity constants. The specific molecular electrical conductivities are given in terms of the true ohm as well as the mercury unit.

SAMUEL SHELDON.

[illegible] *Electric Currents and Alternate-Current Motors.* By [illegible] P. THOMPSON. 8vo, pp. vi, 261. New York, Spon & Chamber- [illegible]

[illegible] author assumes that the reader is familiar with the general principles [illegible] currents, and begins the book with a chapter on polyphase [illegible] In this treatment engineering requirements, details, and data [illegible] omitted, and the student's attention is directed to the physical [illegible] and characteristics of this class of machinery. Brief references [illegible] are made to the productions of various manufacturing

[illegible] chapter deals with the combination of polyphase currents, and [illegible] in the latter part of the chapter is applied to com- [illegible] magnetic fields. The first part of this chapter is useful [illegible] point. I regard the latter part as unfortunate, since at this [illegible] no longer necessary to use the rotating field hypothesis when [illegible] the induction motor. The author's evident purpose is to pre- [illegible] to accept, in lieu of the polyphase alternating field, a simple [illegible] one or more pairs of poles.

[illegible] evidence of the practical identity of polyphase alternating [illegible] rotating fields, the reader witnesses in Chapter III. [illegible] both forms of field. Much attention is paid to their [illegible] none to their differences, — differences of importance in [illegible] design and construction.

[illegible] devoted to the early development of the polyphase motor is [illegible] the early experiments that led men to investigate the properties of polyphase alternating fields similar to those of simple rotating fields. This chapter, however, unfortunately leaves the reader with the impression that symmetrical polyphase alternating fields and simple rotating fields are practically identical, and that the modern induction motor results from a recognition of these facts.

Chapter V. is probably a good description of European induction motor practice. Excepting a reference to Tesla's early experiments, nothing is said about American practice. Yet this country has produced at least three of the best forms, based rather on improvements that result from a transformer or rational study of the induction motor, than on the teachings of the rotating field hypothesis.

Chapters VI. and VII. are largely of historical value, as they present the hypothetical considerations which led to the ultimate development of the modern induction motor, and are not the working theories of the engineers who are producing the practice of the present day. The theories of this chapter would never lead to the production of an efficient monocyclic motor, nor show the important part that is played by the mechanical motion of the secondary conductors in the production of the back electromotive force.

The reference to monophase motors is quite complete and well done. The last chapters, after a brief and sufficient discussion of polyphase transformers, illustrate the application of the rotating field hypothesis for purposes of practical design, and close with some examples of European polyphase practice, including details of modern Oerlikon polyphase motors.

A highly valuable feature of this work is the complete bibliography given in Appendix I.

This book has in it much of value, as the high standing of the author warrants; nevertheless, we do not see why so much of importance belonging to American practice is absent. Doubtless distance, and the rapid rate at which the practice is developing, may in part account for this.

HARRIS J. RYAN.

Industrial Photometry with Special Application of Electric Lighting. Translated from the French of Palaz, by GEORGE W. PATTERSON, Jr., and MERIB ROWLEY PATTERSON. $4.00. pp. 322 + vii. New York, Van Nostrand, 1894.

This is a translation of the well-known work of Palaz, a notice of which has already appeared in the pages of the *Review*.[1]

It is, in the main, an excellent translation. The original has been closely

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[1] Physical Review, Vol. I. p. 238.

followed article by article, and a work, which in the French was remarkable [illegible] precision and clearness of statement, has been placed at the disposal of English readers in such a form that these valuable characteristics are not lost. Occasionally, however, the author lapses from complete lucidity, and the translators go with him. On pages 8 and 9, for example, we find a table in which the approximate limits of the ultra-violet, and visible regions, and certain regions in the infra-red of the spectrum are gathered under the heading "Character of the vibratory movement."

More frequently the translators record their disagreement with the author by means of brief notes in an appendix. This, on the whole, is a plan to be commended, since the form and arrangement of the original is nowise disturbed. Where, however, it is a question of an obvious correction, as in the case in which the absorption by a mirror is given at 1.8 per cent instead of 18 per cent, a better place to note the error would have been in the text or in a footnote upon the same page.

It should be noted that Professor Ayrton's paper on the arc light, to which reference is made in section D of the appendix, is unfortunately not to be found in the *Proceedings of the Chicago Congress*, nor elsewhere. The manuscript was accidentally destroyed before it reached the hands of the editing committee.[1]

The most important portion of the appendix is the set of regulations for using the Hefner lamp. These have been translated from *Schilling's* [illegible]. A few addenda from the personal experiences of the translators have been made in the body of the text, as, for example, where the method of testing glow-lamps pursued in the University of Michigan is described. These additions are not such, however, as to modify the character of the work.

Owing to the conservative treatment, the strong points of the original treatise, namely, the description of photometers and of photometric standards, with the data concerning the latter, remain the most important points of the translated work. Those portions of the subject which were weak or [illegible] in the original, as, for example, questions of spectrum photometry and study of differences of quality of light, have not been reinforced. [illegible] however, the normal function of the translator to remodel the [illegible] comes under his hands, and doubtless it is to be preferred that [illegible] should be closely followed even to the point of perpetuating [illegible] elements. New matter, excepting such as may be casually [illegible] in the form of an appendix, had better form the material for a [illegible]

E. L. NICHOLS.

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[1] [illegible] of the most important points will be found in a paper by Mrs. Ayrton. [illegible] 34, p. 335.

Die Oberflächen- oder Schillerfarben. Von B. WALTER. 8vo, pp. vi + 122. Braunschweig, Vieweg & Sohn, 1895.

This monograph upon the nature of surface color is intended primarily for zoölogists, mineralogists, and chemists, one of the purposes of the author being to point out that many of the colors which are usually ascribed to structure of the surface layer, and which are classified either as colors of thin plates, of grating-diffraction, or of prismatic dispersion, are really true surface colors.

To this end, the laws of the formation of surface color by reflection are taken up in a clear and simple manner, and it is shown that bodies, otherwise colorless, possess a *surface color* due to the fact that the intensity of each reflected wave length depends upon the refractive index of the reflecting body for that particular ray. Since the index varies with the wave length, the composition of the reflected differs from that of the incident light. This is a perfectly obvious matter, but rarely considered in the discussion of color formation. Dr. Walter computes the differences in intensity between red and violet of the reflected light, and shows that in the case of bodies producing high dispersion it is considerable. By normal reflection from carbon disulphide, for example, the violet ray gains 16 per cent over the red of the spectrum.

At the interface between certain substances which differ greatly in dispersive power, as, for example, between crown glass and oil of cassia, this color, due to reflection, becomes very marked. The violet may become three times as intense as the red in the reflected ray.

The succeeding portions of the monograph deal with the surface colors of metals and of the real "Schillerstoffe." These last are substances which absorb a single region of the visible spectrum strongly, other parts scarcely at all. Fuchsin is one of the best known of this class. The colors of these also are shown by the author to be colors of reflection; and, finally, in his concluding chapter, he shows that many of the colors of animals and minerals, which are ordinarily ascribed to interference, are really surface coloring, and ascribable to reflection. The work is a valuable contribution to the science of color.

E. L. NICHOLS.

The Herschels and Modern Astronomy. By AGNES M. CLERKE. $1.25. 12mo, pp. vi + 224. London, The Century Science Series, Cassell & Co.; New York, Macmillan & Co.

Miss Agnes Clerke, whose work upon the history of astronomy has rendered her an authority, is admirably equipped for writing the biography of the Herschels. A more attractive theme to the lover of biography than the relations of this remarkable family to the development of modern astronomy, it would be difficult to find. The story of the rise of the elder Herschel from the position of an oboe player in a Hanoverian military band to that of court astronomer to King George, is one to excite the warmest sympathy and interest on the part of the reader. The sketch of Caroline Herschel is scarcely less interesting than that of her brother. The position which she has held in the minds of many is simply that of an [illegible] assistant in the computing room of the astronomer; Miss Clerke's portrait reveals to us a woman of great versatility and of great strength of character, a woman to whom the reader feels strongly drawn.

The interest of the book centers in the history of William and Caroline. When we come to Sir John Herschel there is a distinct falling off. The elder Herschel won scientific fame as other poor men sometimes win fortune. John Herschel inherited his position in the scientific world as men inherit money, and with it definite work in astronomy which he deemed it his duty to undertake and carry to completion. The magnificent manner in which he fulfilled the scientific obligations which he inherited from his father is well described in the pages of this brief memoir, but it is impossible to imbue such a career, however brilliant, with the romantic interest which one feels for the heroic upward struggle of the founder of the house.

E. L. NICHOLS.

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THE PHYSICAL REVIEW.

ON THE VISCOSITY OF CERTAIN SALT SOLUTIONS.

BY B. E. MOORE.

THE subject of Viscosity was first taken up by Poiseuille,[1] who used a method depending upon the transpiration of the liquid through capillary tubes. Coulomb, in studying the same subject, observed the damping of a magnetic needle or bar when vibrating in the liquid investigated. This method was also extensively used by O. E. Meyer,[2] Grotian,[3] and others. Still a third method has been developed by Helmholtz, who placed the solution to be studied in a hollow sphere, and observed the behavior of the sphere when oscillated.

These methods have led to very different results. König[4] modified the method of Coulomb and used in the place of the swinging rod, a sphere, the equation of motion of which Kirchhoff had solved, and for which the theory can be completely developed. For calculation König made use of the expression by Kirchhoff as extended and completed by Boltzman, and reached the conclusion that the values obtained for viscosity by Coulomb's method were in complete agreement with the results obtained by allowing the liquid to flow through a capillary tube. Though the agreement

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[1] Memoirs des Savants Étrangers, T. IX. Pogg. Ann., Vol. LVIII., p. 434.

[2] Pogg. Ann., Vol. CXIII., pp. 55, 193, 383.

[3] Pogg. Ann., Vol. CLVII., p. 130.

[4] Wied. Ann., Vol. XXXII., p. 193.

of results by the different methods is of great interest and importance, yet observers have generally preferred the original method due to Poiseuille, and that because of its simplicity. The method requires also a considerably smaller amount of the solution, and admits of a much easier and more accurate temperature regulation.

Among the earlier investigations on the subject of viscosity may be mentioned those of Graham,[1] whose results suggest the presence of hydrates in solution. He states further that "slow transpiration and low volatility go together." Later investigations by Rellstab[2] dealt with several organic liquids, while numerous experiments were made by Hübner[3] on the salts of the chloride family. Sprung[4] investigated a great many cases of varying concentration and temperature, the latter ranging from 0° to 60° C.

Hagenbach[5] developed the mathematical formula for transpiration. His expression for viscosity (η) reduces, when correction for the velocity of flow is omitted, to the form known as Poiseuille's formula: $\eta = \frac{\pi}{8}\frac{r^4 hst}{lv}$. Herein r denotes the radius of the capillary; h, the height of pressure column; s, specific gravity, and therefore the product of h and s the pressure; v represents the volume that transpires in time, t; and l is used to designate the length of the capillary tube.

Pribam and Handl[6] have made extensive observations on the viscosity of organic solution and stochiometrical relations of the same. The careful work of Gartenmeister[7] in this field should not be omitted. Grotian[8] was the first to make extended comparisons of viscosity and conductivity of salt solutions. Slotte's[9] investigations cover a number of chromates and he shows that the temperature variation in viscosity, η, can be expressed by a formula, $\eta = c(1+bt)^n$, where c, b, and n are constants of the liquid.

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[1] Royal Society Proceedings, XI., p. 381. 1860.

[2] Inaugural Dissertation, Bonn, 1868.

[3] Pogg. Ann. Vol. CL., p. 248.

[4] Pogg. Ann., Vol. CLIX., p. 1.

[5] Pogg. Ann., Vol. CIX., p. 385.

[6] Wien Ber., Vols. 78, 80.

[7] Zeitschrift die Ph. Chem., Vol. VI., p. 524.

[8] Pogg. Ann., Vol. CLVII, p. 130; Vol. CLX., p. 238. Wied. Ann., Vol. VIII., p. 530.

[9] Wied. Ann., Vol. XIV., p. 13.

Since the announcement of the dissociation theory by Arrhenius, the subject of viscosity of solutions has had a much deeper interest, and experiments have been carried on, both trying to establish some stochiometrical relation, and to establish a relation between viscosity and conductivity. With this idea in view, Arrhenius has made many investigations. In his first experiments[1] he shows that the viscosity is a function of x and y, or $H(x, y)$, where x and y express either percentage of substance in solution, or gram-equivalent per liter. We may say $\eta = H(x, y) = A^x B^y$, where A and B are constants of the solution. For a single salt in solution this reduces to $\eta = A^x$. Wagner[2] and Reyher[3] validified this law for a great many solutions. In Gartenmeister's[4] experiments the Arrhenius exponential formula is not so well satisfied. Reyher found a characteristic relation between the friction or viscosity of free acids and those of the sodium salts, according as a strong or weak acid was present. This variation he made to depend upon the unequal dissociation of the strong and weak acids. The dissociation theory has given great confidence to the belief in a relation of viscosity to conductivity. However, G. Wiedemann,[5] previous to this theory, noticed that the friction which the ions undergo varies in the same way as inner friction; *i.e.* viscosity. The mobility of the ions must then be a function of their fluidity. Arrhenius showed that conductivity did not depend upon fluidity alone. This investigator made a strong point when he showed that the introduction of a non-conducting substance into an electrolyte affected both its conductivity and its viscosity in the same way.[6] Other experimenters, by a direct comparison of conductivities and viscosities, have come to the conclusion that while the conductivities of a series of salts increased, the viscosities in general decreased. However, the increasing and decreasing series stand in no definite ratio to each other.

The following experiments have followed much in the same line.

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[1] Zeitschrift die Ph. Chem., Vol. I., p. 285.
[2] Zeitschrift die Ph. Chem., Vol. V., p. 31.
[3] Zeitschrift die Ph. Chem., Vol. II., p. 744.
[4] Zeitschrift die Ph. Chem., Vol. VI., p. 524.
[5] Pogg. Ann., Vol. XCIX., p. 177.
[6] Zeitschrift die Ph. Chem., Vol. IX., p. 487.

The viscosities of a series of salts have been determined, and, in so far as was possible, the conductivities of the same compared with their viscosities.

The method employed was the one due to Poiseuille, the apparatus being similar to that used by Arrhenius. A glass vessel *A* (Fig. 1), of about 24 c.cm. capacity, is connected with two tubes, *a* and *b*, above and below respectively. Each tube has a diameter of about 4 mm. A stopcock closes *a* about 4 cm. from *A*. *b* was joined to a capillary tube *d*, some 40 cm. long. The lower end of the capillary dips into the solution to be studied, contained in a glass vessel, *B*, of about 200 c.cm. capacity. *B* is kept water-tight by means of a rubber cork *e*, and is encased in a brass support *h*. Exactly 50 c.cm. of the solution was always brought into the vessel *B*, and the extremity *c* of the capillary brought into the plane of the upper edge of the brass casing *h*. This was done to secure a constant average height of pressure in all cases. But this was later proven to be an unnecessary precaution, as a change in the length of the capillary, amounting to 18 cm., only made a difference of 2.5 seconds in the transpiration of water at 18° C. The liquid is brought into the vessel *A* to some point *a'* by exhausting the air through a rubber tube *f*. The time of flow was taken between two marks on tubes *a* and *b*. As the mean height of the pressure column is constant, it is evident that the pressure of the different liquids subjected to transpiration varies directly as their specific gravities. So that to obtain the transpiration at constant pressure, it was only necessary to multiply the observed time of flow by the specific gravity of the solution. The time of flow of water at 18° C. was taken as standard. The ratio of the corrected time of flow of a solution to that of water gives the relative viscosity in terms of water as unity. Should the absolute viscosity be desired, it is only necessary to multiply this result by the absolute value of water. Relative values only have been calculated, as the object was to make a comparison of solutions. The temperature was regulated by a water-bath, and two ther-

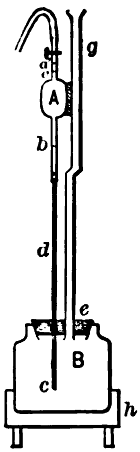

Fig. 1.

mometers enabled one to note the temperature to tenths of a degree. Hagenbach's correction for velocity of transpiration was sufficiently small to neglect in all cases.

The specific gravities of the solutions were determined by means of a calibrated Mohr's balance, which enabled one to take readings to the fourth decimal place. It was part of the original intention to make the solutions from weighed portions of the salts and of fixed molecular (*e.g.* double normal, normal, half normal, etc.) contents, but the discovery of a mistake in the weight of a crucible made it necessary to interpret in many cases the per cent of salt in solution from tables of percentages and specific gravities. Solutions of K_2CO_3, KOH, NaOH, and K_2SO_4 were made from Kohlrausch's tables.[1] Solutions of Na_2CO_3, $KHCO_3$, $NaHCO_3$, $KHSO_4$ Na_2HPO_4, NaH_2PO_4, $K_2C_2O_4$ and $NaHC_4H_4O_6$ were made from carefully weighed quantities of the salts. Solutions of K_3PO_4, K_2HPO_4, KH_2PO_4 were kindly loaned by Herr Forch. All other solutions were made from Landolt and Bernstein's Tabellen (*2te Auflage*). The specific gravities of solutions of Na_2CO_3 check well with Kohlrausch's tables, but not so well with those of Landolt and Bernstein. The specific gravities of Na_2HPO_4 differ also slightly from the latter tables and in solutions of $K_2C_2O_4$ the difference is quite large. However, specific gravities of $K_2C_2O_4$ interpolated from Landolt and Bernstein's Tabellen give a viscosity curve of doubtful character.

The time of flow was noted over considerable range of temperature from which the time transpiration at 18° was graphically interpolated. By repeated observation the error in time is reduced to about 0.3 seconds. In the following table of observations and results, *m* denotes the gram-molecular contents; *s*, the specific gravity; *T*, the time; and η, the calculated viscosities. In the rows containing neither *T* nor *s*, the values of *m* and η have been graphically interpolated.

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[1] Kohlrausch: Leitfaden der practical Physik, 7te Auflage.

Table I.

Na_2CO_3

m	s	T	η
0.00	0.9987	197.0	1.000
0.25	1.0250	220.6	1.120
0.5	1.0517	251.0	1.274
1.0	1.0980	328.5	1.667
2.0	1.1880	616.2	3.128

$NaHCO_3$

m	s	T	η
0.00	0.9987	194.5	1.000
0.25	1.0139	205.5	1.057
0.5	1.0286	218.0	1.121
1.0	1.0575	245.0	1.260

K_2CO_3

m	s	T	η
0.00	0.9987	197.0	1.000
0.25	—	—	1.059
0.273	1.0340	210.0	1.066
0.4788	1.0577	223.0	1.132
0.5	—	—	1.138
0.9456	1.1100	258.0	1.310
1.0	—	—	1.341
1.974	1.2183	381.0	1.934
2.0	—	—	1.950

$KHCO_3$

m	s	T	η
0.00	0.9987	194.5	1.000
0.25	1.0146	200.5	1.031
0.495	1.0298	206.5	1.062
0.5	—	—	1.065
1.0	1.0581	218.0	1.121
1.98	1.1149	250.0	1.285
2.0	—	—	1.290

Table II.

$NaHSO_4$

m	s	T	η
0.00	0.9987	194.5	1.0000
0.25	1.0186	206.0	1.059
0.5	1.0386	214.0	1.100
1.0	1.0753	245.0	1.260
2.0	1.1475	315.5	1.622
4.0	1.2810	559.0	2.874

K_2SO_4

m	s	T	η
0.00	0.9987	194.5	1.000
0.1195	1.0165	198.1	1.019
0.125	—	—	—
0.243	1.0328	204.5	1.051
0.25	—	—	1.052
0.49	1.0650	214.0	1.100
0.50	—	—	1.106

$KHSO_4$

m	s	T	η
0.00	0.9987	194.5	1.0000
0.5	1.0439	209.5	1.075
1.0	1.0866	223.5	1.149
2.0	1.1712	263.0	1.352

$NaOH$

m	s	T	η
0.00	0.9987	194.5	1.0000
0.25	1.0099	206.0	1.059
0.5	1.0212	215.5	1.108
1.0	1.0425	240.0	1.234
2.0	1.0843	299.0	1.537
4.0	1.1551	552.0	2.837
8.0	1.2786	1470.0	7.557

KOH

m	s	T	η
0.00	0.9987	194.5	1.0000
0.25	—	—	1.025
0.456	1.0212	203.0	1.044
0.5	—	—	1.051
0.92	1.0433	213.5	1.098
1.00	—	—	1.110
1.82	1.0864	235.5	1.211
2.0	—	—	1.237
4.0	1.1793	307.0	1.578
6.8	1.2900	452.0	2.324

TABLE III.

Na_2HPO_4

m	s	T	η
0.00	0.9987	194.5	1.000
0.125	1.0190	211.3	1.086
0.25	1.0366	231.4	1.189
0.5	1.0741	277.5	1.427

NaH_2PO_4

m	s	T	η
0.00	0.9987	194.5	1.000
0.25	1.0184	209.3	1.076
0.5005	1.0391	230.0	1.182
1.001	1.0776	274.0	1.409
2.002	1.1677	450.0	2.313

KH_2PO_4

m	s	T	η
0.00	0.9987	194.5	1.000
0.25	1.0220	205.5	1.057
0.5	1.0442	223.0	1.146
1.0	1.0885	254.0	1.306

H_3PO_4

m	s	T	η
0.00	0.9987	194.5	1.000
0.25	1.0120	207.0	1.064
0.5	1.0251	222.3	1.143
1.0	1.0508	255.0	1.311
2.0	1.1022	338.3	1.739

Na_3PO_4

m	s	T	η
0.00	0.9987	194.5	1.000
0.125	—	—	1.098
0.14	1.0222	214.9	1.105
0.25	—	—	1.220
0.276	1.0440	242.3	1.246
0.50	—	—	1.504
0.54	1.0860	307.2	1.579

K_3PO_4

m	s	T	η
0.00	0.9987	194.5	1.000
0.125	1.0227	208.5	1.070
0.25	1.0471	219.0	1.126
0.5	1.0933	252.5	1.298
1.0	1.1805	342.2	1.759

K_2HPO_4

m	s	T	η
0.00	0.9987	194.5	1.000
0.125	1.0167	202.0	1.039
0.25	1.0343	213.0	1.095
0.5	1.0700	234.0	1.206
1.0	1.1383	300.0	1.542
2.0	1.2633	449.0	2.309

Table IV.

$Na_2C_4H_4O_6$				$NaKC_4H_4O_6$			
m	*s*	*T*	*η*	*m*	*s*	*T*	*η*
0.00	0.9987	194.5	1.000	0.00	0.9987	194.5	1.000
0.141	1.0185	209.0	1.075	0.20	1.0273	212.5	1.092
0.25	—	—	1.148	0.25	—	—	1.112
0.281	1.0368	226.0	1.162	0.40	1.0547	231.0	1.188
0.5	—	—	1.335	0.50	—	—	1.252
0.562	1.0730	269.0	1.383	0.789	1.1087	287.0	1.476
1.0	—	—	1.823	1.0	—	—	1.679
1.121	1.1427	395.0	2.031	1.656	1.2112	484.0	2.488
$H_2C_4H_4O_6$				$K_2C_4H_4O_6$			
0.00	0.9987	194.5	1.000	0.00	0.9987	194.5	1.000
0.233	1.013	207.5	1.067	0.1815	1.0267	205.5	1.057
0.25	—	—	—	0.25	—	—	1.080
0.467	1.0269	221.5	1.139	0.363	1.0525	220.0	1.131
0.5	—	—	1.160	0.5	—	—	1.195
0.833	1.0542	256.0	1.316	0.7345	1.1036	255.0	1.342
1.0	—	—	1.412	1.0	—	—	1.489
1.478	—	330.0	1.696	1.48	1.2072	363.0	1.866
1.666	1.1092	365.0	1.853	1.5	—	—	(1.883)
$C_4H_6O_4$				$K_2C_2O_4$			
0.00	0.9987	194.5	1.000	0.00	0.9987	194.5	1.000
0.242	1.0076	204.2	1.050	0.25	1.0283	204.0	1.049
0.25	—	—	1.052	0.5	1.0571	214.5	1.103
0.483	1.0166	215.0	1.105	1.0	1.1121	239.5	1.232
0.5	—	—	(1.110)	1.5	1.1663	270.2	1.389
$H_2C_2O_4$				$NaHC_4H_4O_6$			
0.00	0.9987	194.5	1.000	0.00	0.9987	194.5	1.000
0.25	—	—	1.045	0.147	1.0121	205.5	1.056
0.326	1.0146	206.0	1.059	0.25	—	—	1.094
0.5	—	—	1.072	0.294	1.0256	217.0	1.116
0.665	1.0300	217.5	1.118	0.441	1.0386	228.5	1.175
0.848	1.0370	224.5	1.154	0.5	—	—	(1.198)
1.0	—	—	(1.199)				

Curves.

The curves (Figs. 2, 3, 4, and 5) correspond to Tables I., II., III., and IV. of data respectively. The curve for H_2SO_4 (Fig. 3) is drawn from data by Grotian and is given in order to show the effect of displacing an atom of hydrogen in sulphuric acid. Curves for K_2SO_4 and KH_2PO_4 are not shown, as they nearly coincide with 2 KOH and H_3PO_4 respectively.

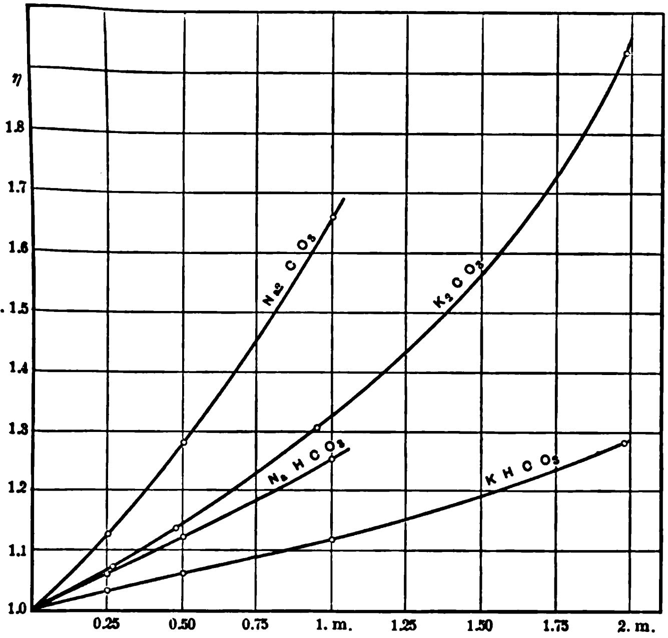

Fig. 2.

Discussion of Results.

The viscosity of sodium salts is invariably greater than that of the potassium salts, and both are greater than that of the corresponding acids. The effect of the hypothetical displacement of the first atom of hydrogen by a given base is generally not so marked as the second displacement by the same base. $NaHC_4H_4O_6$ is an exception. The effect of the second atom of Na and K in the phosphoric acid group (see Fig. 4) is very marked. Whether the position of the hydrogen atom in the perhaps, easier to raise than to answer

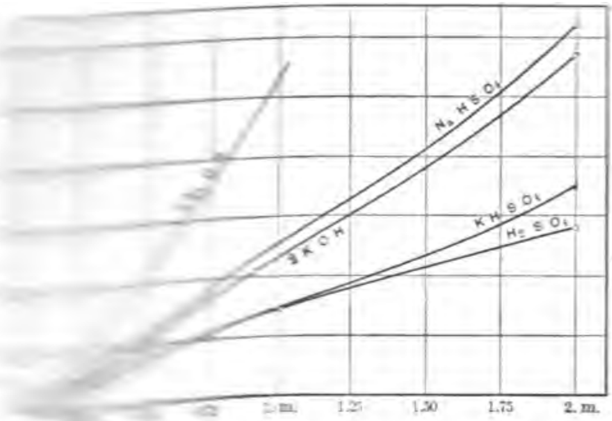

Fig. 3.

with the entrance of the second atom from marked acid to basic character,

which also suggests that the first change in H_3PO_4 $(= H - PO_2 - OH - OH)$ took place in the hydroxide radical, the second in the acid radical, and the third again in the hydroxide radical. The curve for KH_2PO_4 lies too near H_3PO_4 to be credited extensively. More confidence is to be placed in the results for H_3PO_4 than KH_2PO_4, as Slotte's observations for H_3PO_4 fall practically upon the curve here given for that acid. Again the neutral phosphate Na_3PO_4 breaks up very easily in the presence of H_2O into Na_2HPO_4 and NaOH, which would make curve Na_3PO_4 with some hesitation. So would be rather difficult to draw conclusions concerning changes in the radicals from the viscosities. So much difficulty does not present itself with the organic compounds. The addition of $(CH_2)_2$ to $C_2H_2O_4$ (=COOH−COOH) (see Fig. 5, curves), giving COOH−CH_2−CH_2−COOH, increases the vis-

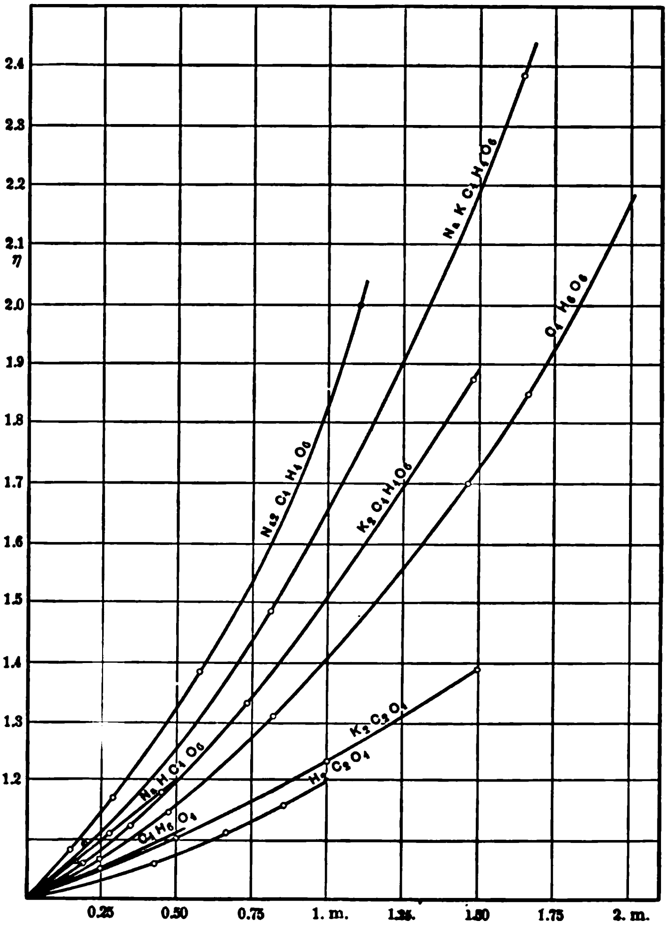

Fig. 5.

cosity over three times as much as the substitution of potassium for hydrogen in $(COOH)_2$. The farther substitution of two hydroxyl radicals for two atoms of H in $(CH_2)_2$ gives also a marked increase, and also greater than the effect of potassium substituted in $H_2C_2O_4$. Again, a comparison of curves for $H_2C_2O_4$ and $K_2C_2O_4$ with the curves for $C_4H_6O_4$ and $K_2C_4H_4O_6$ shows a marked difference in the effects of potassium on the two salts. In the first pair of solutions potassium entered the carboxyl, giving COOK–COOK, while in the second group the element potassium has worked upon the hydroxide, yielding COOH–CHOK–CHOK–COOH.

Arrhenius Exponential Formula.

When Arrhenius announced the exponential formula, $\eta = A^x$, he only tested it to 1.5 gram-molecule solutions. Wagner, who validified the law for so many solutions, did not go above the normal solution. So that it was thought well to see if such a formula would hold for more concentrated solutions. To test the validity of the law for very dilute solutions, where the law is most serviceable, it would be necessary to limit oneself to very narrow range of and small changes in temperature. It would be imperative to use a bulb *A* (Fig. 1) of smaller volume and a capillary *d* (Fig. 1) of very small bore. The latter invariably clogs and prevents accurate results. Even such precautions would, at the best, only give very small differences, and failure to observe these precautions could not account for the variations from the logarithmic law observed in these experiments. The logarithmic curve, which would represent the viscosities of the more dilute solutions of NaOH, *e.g.* would, if extended to 4 and 8 molecule solutions, give values 36 per cent and 75 per cent too small respectively. No other solutions show so great a divergence. Yet in the double normal solutions the agreement is rarely better than 3 per cent to 5 per cent.

Conductivities and Viscosities.

The values for *A* in the following table have been taken direct from the tables of observations on η, except in the phosphoric acid group, where *A* is reckoned from the equation $\eta = A^x$ and $x = m = \frac{1}{3}$. The conductivities K are those of the normal solutions except when otherwise noted. Only those salts are given for which the conductivities could be learned. They are divided in four groups corresponding to Tables I., II., III., and IV. of Viscosities respectively.

TABLE V.

Substances.	A	$10^9 \cdot K$	
$\frac{1}{2}$ Na_2CO_3	1.274	42.7	
$\frac{1}{2}$ $NaHCO_3$	1.121	37.9	
$\frac{1}{2}$ K_2CO_3	1.138	66.2	
$\frac{1}{2}$ $KHCO_3$	1.065	61.3	
NaOH	1.234	149.0	
KOH	1.11	171.8	
$\frac{1}{2}$ Na_2SO_4	—	47.5	
$\frac{1}{2}$ $NaHSO_4$	1.10	—	
$\frac{1}{2}$ K_2SO_4	1.106	67.2	
$\frac{1}{2}$ $KHSO_4$	1.075	173.6	
$\frac{1}{3}$ Na_3PO_4	1.305	97.5	$\frac{1}{32}$ normal solution.
$\frac{1}{3}$ Na_2HPO_4	1.260	79.6	
$\frac{1}{3}$ NaH_2PO_4	1.105	69.8	
$\frac{1}{3}$ H_3PO_4	1.08	20.0	
$\frac{1}{2}$ $C_4H_6O_6$	1.160	46.04	$\frac{1}{16}$ normal.
$\frac{1}{2}$ $C_4H_6O_4$	1.110	16.03	
$\frac{1}{2}$ $C_2H_2O_4$	1.070	26.7	
$\frac{1}{2}$ $K_2C_2O_4$	1.100	68.8	

That, while the viscosities in general decrease, the conductivities of a series of salts increase, as noted in the early part of this article, cannot be concluded at all from these salts. This action is noticeable, however, in passing from the sodium salt to the potassium in the first and second group, but when one passes either from sodium carbonate or from potassium carbonate to the acid salts, viscosities and conductivities increase and decrease together. The sulphates behave in the same manner. In the third or phosphate group, in passing from Na_3PO_4 to H_3PO_4, both viscosities and conductivities decrease. In the fourth or organic group, there is an irregularity in the conductivity column. This list, though small, is enough to show that there is little hope for a successful comparison of viscosity and conductivity, without an extended series of observations, [illegible] ute solutions in which the increase in the [illegible] will be largely due to the ions, as it is [illegible] alone with which we have to deal in

Conclusions.

[illegible] ns decreases quite rapidly with rise in [illegible] ter of this decrease is very different [illegible] and for different salt solutions.[1]

[illegible] ons, though doubtless existing, are [illegible] convincing.

[illegible] ntial formula or law, though affording [illegible] mparison of viscosities of dilute, even [illegible] hold good for the more concentrated

[illegible] ations must be made upon the relation [illegible], perhaps even some new method of [illegible] the two subjects are placed in their

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[1] [illegible] Soc., 55, p. 148, have pointed out that tempera- [illegible] method for comparison of viscosity. These experi- [illegible] hen the article by Thorpe and Rodgers appeared, [illegible] enough to make such a comparison.

NOTES ON THE THEORY OF OSCILLATING CURRENTS.

By Charles Proteus Steinmetz.

§ 1. *Introduction.*

THE object of the following article is to present a short outline sketch of a modification of the method of complex imaginary quantities, applied to oscillating currents. Such oscillating currents have frequently been considered as ordinary alternating currents of very high frequency, and treated as such, while the essential differences between alternating and oscillating currents have been overlooked. An electric current varying periodically between constant maximum and minimum values, that is, in equal time intervals repeating the same values, is called an alternating current if the arithmetic mean value equals zero; and is called a pulsating current if the arithmetic mean value differs from zero. Alternating currents have found very extensive application for light and power. Pulsating currents are the currents given by open coil arc-light machines, or by the superposition of alternating and continuous currents, etc.

Assuming the wave as a sine curve, or replacing it by the equivalent sine wave, the alternating current is characterized by the period or the time of one complete cyclic change, and the amplitude or the maximum value of the current. Period and amplitude are constant in the alternating current.

A very important class are the currents of constant period, but geometrically varying amplitude, that is, currents in which the amplitude of each following wave bears to that of the preceding wave a constant ratio. Such currents consist of a series of waves of constant length, decreasing in amplitude, that is in strength, in constant proportion. They are called oscillating currents in analogy with mechanical oscillations, for instance of the pendulum, in which the amplitude of the vibration decreases in constant proportion.

Since the amplitude of the oscillating current varies, constantly decreasing, the oscillating current differs from the alternating current in so far that it starts at a definite time, and gradually dies out, reaching zero value theoretically at infinite time, practically in a very short time, short even in comparison with the time of one alternating half-wave. Characteristic constants of the oscillating current are the period T or frequency $N=\frac{1}{T}$, the first amplitude and the ratio of any two successive amplitudes, the latter being called the decrement of the wave. The oscillating current will thus be represented by the product of a periodic function, and a function decreasing in geometric proportion with the time. The latter is the exponential function A^{l-rt}.

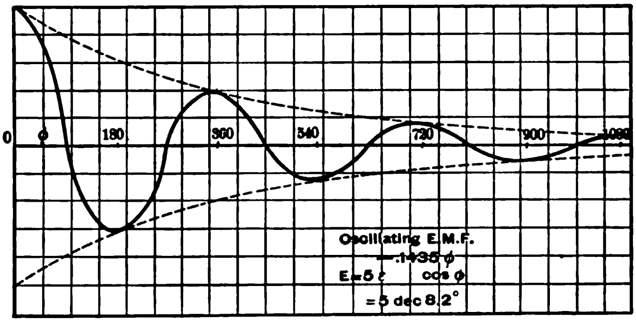

Fig. 1.

Thus, the general expression of the oscillating current is

$$C=A^{l-rt}\cos(2\pi Nt-\hat{\omega}),$$

since $$A^{l-rt}=A^{l}A^{-rt}=c\epsilon^{-kt}.$$

Where ϵ = basis of natural logarithms, the current may be expressed

$$C=c\epsilon^{-kt}\cos(2\pi Nt-\hat{\omega})=c\epsilon^{-a\phi}\cos(\phi-\hat{\omega}),$$

where $\phi=2\pi Nt$; that is, the period is represented by a complete revolution.

In the same way, an oscillating electromotive force will be represented by

$$E = e\epsilon^{-a\phi} \cos(\phi - \hat{\omega}).$$

Such an oscillating electromotive force for the values

$$e = 5, \quad \alpha = .1435 \text{ or } \epsilon^{-2\pi a} = .4, \quad \hat{\omega} = 0,$$

is represented in rectangular co-ordinates in Fig. 1, and in polar co-ordinates in Fig. 2. As seen from Fig. 1, the oscillating wave in rectangular co-ordinates osculates the two exponential curves

$$y = \pm e\epsilon^{-a\phi}.$$

In polar co-ordinates, the oscillating wave is represented in Fig. 2 by a spiral curve passing the zero point twice per period, and osculating the exponential spiral

$$y = \pm e\epsilon^{-a\phi}.$$

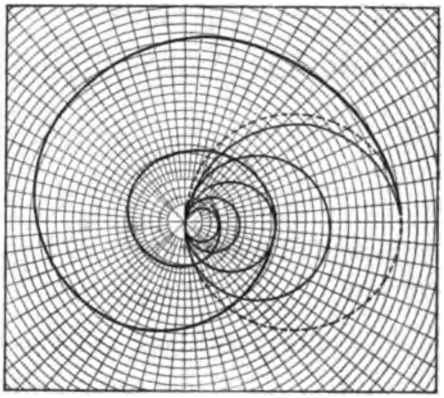

Fig. 2.

The latter is called the envelope of the oscillating wave, and is shown separately, with the same constants as Figs. 1 and 2, in Fig. 3. Its characteristic feature is: The angle, which any concentric circle makes with the curve $y = e\epsilon^{-a\phi}$, is

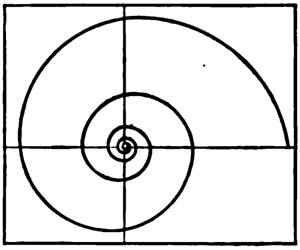

Fig. 3.

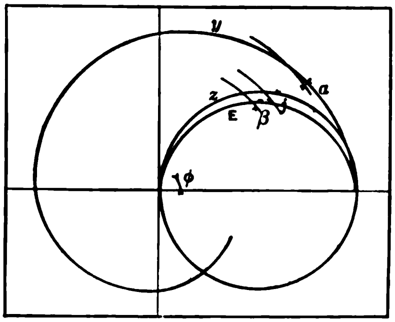

Fig. 4.

$$\tan \alpha = \frac{dy}{y\,d\phi} = -a,$$

which is, therefore, constant, or in other words: "The envelope of the oscillating current is the loxodromic spiral, which is characterized by a constant angle of intersection with all concentric circles, or all radii vectores." The oscillating current wave is the product of the sine wave and the loxodromic spiral.

In Fig. 4 let $y=e\epsilon^{-a\phi}$ represent the loxodromic spiral;

let $z=e\cos(\phi-a)$ represent the sine wave;

and let $E=e\epsilon^{-a\phi}\cos(\phi-\omega)$ represent the oscillating wave.

We have then

$$\tan\beta=\frac{dE}{Ed\phi}$$

$$=\frac{-\sin(\phi-\hat{\omega})-a\cos(\phi-\hat{\omega})}{\cos(\phi-\hat{\omega})}$$

$$=-\{\tan(\phi-\hat{\omega})+a\};$$

that is, while the slope of the sine wave, $z=e\cos(\phi-\hat{\omega})$, is represented by

$$\tan\gamma=-\tan(\phi-\hat{\omega}),$$

the slope of the loxodromic spiral $y=e\epsilon^{-a\phi}$ is

$$\tan\alpha=-a=\text{constant}.$$

That of the oscillating wave $E=e\epsilon^{-a\phi}\cos(\phi-\hat{\omega})$ is

$$\tan\beta=-\{\tan(\phi-\hat{\omega})+a\}$$

Hence, it is increased over that of the alternating sine wave by the constant a. The ratio of the amplitudes of two consequent periods is

$$A=\frac{E_{2\pi}}{E_0}=\epsilon^{-2\pi a}.$$

A is called the numerical decrement of the oscillating wave, a the exponential decrement of the oscillating wave, α the angular decrement of the oscillating wave. The oscillating wave can be represented by the equation

$$E=e\epsilon^{-\phi\tan\alpha}\cos(\phi-\hat{\omega}).$$

In the instance represented by Figs. 1 and 2, we have, $A=.4$, $a=.1435$, $\alpha=8.2°$.

§ 2. *Impedance and Admittance.*

In complex imaginary quantities, the alternating wave

$$z=e\cos(\phi-\hat{\omega})$$

is represented by the symbol

$$F=e(\cos\hat{\omega}+j\sin\hat{\omega})=e_1+je_2.$$

By an extension of the meaning of this symbolic expression, the oscillating wave $E=e\epsilon^{-a\phi}\cos(\phi-\hat{\omega})$ can be expressed by the symbol

$$E=e(\cos\hat{\omega}+j\sin\hat{\omega})\operatorname{dec}\alpha=(e_1+je_2)\operatorname{dec}\alpha,$$

where $a=\tan\alpha$ is the exponential decrement, α the angular decrement, $\epsilon^{-2\pi a}$ the numerical decrement.

Inductance.

Let $r=$ resistance, $L=$ inductance, and $s=2\pi NL=$ reactance.

In a circuit excited by the oscillating current,

$$C=c\epsilon^{-a\phi}\cos(\phi-\omega)=c(\cos\hat{\omega}+j\sin\hat{\omega})\operatorname{dec}\alpha=(c_1+jc_2)\operatorname{dec}\alpha,$$

where $$c_1=c\cos\hat{\omega},\quad c_2=c\sin\hat{\omega},\quad a=\tan\alpha.$$

We have then,

The electromotive force consumed by the resistance r of the circuit

$$E_r=rC\operatorname{dec}\alpha.$$

The electromotive force consumed by the inductance L of the circuit,

$$E_s=L\frac{dC}{dt}=2\pi NL\frac{dC}{d\phi}=s\frac{dC}{d\phi}.$$

Hence $$E_s=-sc\epsilon^{-a\phi}\{\sin(\phi-\hat{\omega})+a\cos(\phi-\hat{\omega})\}$$

$$=-\frac{sc\epsilon^{-a\phi}}{\cos\alpha}\sin(\phi-\hat{\omega}+\alpha).$$

Thus, in symbolic expression,

$$E_s=-\frac{sc}{\cos\alpha}\{-\sin(\hat{\omega}-\alpha)+j\cos(\hat{\omega}-\alpha)\}\operatorname{dec}\alpha$$

$$=-sc(a+j)(\cos\hat{\omega}+j\sin\hat{\omega})\operatorname{dec}\alpha;$$

that is, $$E_s=-sC(a+j)\operatorname{dec}\alpha.$$

Hence the apparent reactance of the oscillating current circuit is, in symbolic expression,

$$S = s(a+j) \text{ dec } \alpha.$$

Hence it contains an energy component as, and the impedance is

$$U = (r-S) \text{ dec } \alpha = \{r - s(a+j)\} \text{dec } \alpha = (r - as - js) \text{ dec } \alpha.$$

Capacity.

Let r=resistance, K=capacity, and $k = \frac{1}{2\pi K}$ = capacity reactance. In a circuit excited by the oscillating current C, the electromotive force consumed by the capacity K is

$$E_k = \frac{1}{K}\int C dt = \frac{1}{2\pi NK}\int C d\phi = k\int C d\phi;$$

or, by substitution,

$$\begin{aligned} E_k &= k\int c\epsilon^{-a\phi} \cos(\phi - \hat{\omega}) d\phi \\ &= \frac{k}{1+a^2} c\epsilon^{-a\phi}\{\sin(\phi-\hat{\omega}) - \alpha\cos(\phi-\hat{\omega})\} \\ &= \frac{kc\epsilon^{-a\phi}}{(1+a^2)\cos\alpha}\sin(\phi-\hat{\omega}-\alpha); \end{aligned}$$

hence, in symbolic expression,

$$\begin{aligned} E_k &= \frac{kc}{(1+a^2)\cos\alpha}\left\{-\sin(\hat{\omega}+\alpha) + j\cos(\hat{\omega}+\alpha)\right\} \text{dec } \alpha \\ &= \frac{kc}{1+a^2}(-a+j)(\cos\hat{\omega} + j\sin\hat{\omega}) \text{ dec } \alpha; \end{aligned}$$

hence,

$$E_k = \frac{k}{1+a^2}(-a+j) C \text{ dec } \alpha,$$

that is, the apparent capacity reactance of the oscillating circuit is, in symbolic expression,

$$K = \frac{k}{1+a^2}(-a+j) \text{ dec } \alpha.$$

We have then:

In an oscillating current circuit of resistance r, inductive reactance s, and capacity reactance k, with an exponential decrement a, the apparent impedance, in symbolic expression, is:

$$U=\left\{r-s(a+j)+\frac{k}{1+a^2}(-a+j)\right\}\text{dec}\,\alpha,$$

$$=\left\{r-a\left(s+\frac{k}{1+a^2}\right)-j\left(s-\frac{k}{1+a^2}\right)\right\}\text{dec}\,\alpha,$$

$$=r_a-js_a;$$

and, absolute,

$$u_a=\sqrt{r_a^2+s_a^2}$$

$$=\sqrt{\left[r-a\left(s+\frac{k}{1+a^2}\right)\right]^2+\left[s-\frac{k}{1+a^2}\right]^2}.$$

Admittance.

Let $C=c\epsilon^{-a\phi}\cos(\phi-\hat{\omega})=$ current.

Then, from the preceding discussion, the electromotive force consumed by resistance r, inductive reactance s, and capacity reactance k, is

$$E=c\epsilon^{-a\phi}\left\{\cos(\phi-\hat{\omega})\left[r-as-\frac{a}{1+a^2}k\right]-\sin(\phi-\hat{\omega})\left[s-\frac{k}{1+a^2}\right]\right\}$$

$$=cu_a\epsilon^{-a\phi}\cos(\phi-\hat{\omega}+\delta),$$

where $\tan\delta=\dfrac{s-\dfrac{k}{1+a^2}}{r-as-\dfrac{a}{1+a^2}k},$

$$u_a=\sqrt{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2};$$

substituting $\hat{\omega}+\delta$ for $\hat{\omega}$, and $e=cu_a$, we have

$$E=e\epsilon^{-a\phi}\cos(\phi-\hat{\omega}),$$

$$C=\frac{e}{u_a}\epsilon^{-a\phi}\cos(\phi-\hat{\omega}-\delta)$$

$$=e\epsilon^{-a\phi}\left\{\frac{\cos\delta}{u_a}\cos(\phi-\hat{\omega})+\frac{\sin\delta}{u_a}\sin(\phi-\hat{\omega})\right\};$$

hence in complex quantities,

$$E=e(\cos\hat{\omega}+j\sin\hat{\omega})\operatorname{dec}\alpha,$$

$$C=E\left\{\frac{\cos\delta}{u_a}+j\frac{\sin\delta}{u_a}\right\}\operatorname{dec}\alpha;$$

or, substituting,

$$C=E\left\{\frac{r-as-\frac{a}{1+a^2}k}{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2}\right.$$

$$\left.+j\frac{s-\frac{k}{1+a^2}}{\left(s-\frac{k}{1+a_2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2}\right\}\operatorname{dec}\alpha.$$

Thus in complex quantities, for oscillating currents, we have: conductance,

$$\rho=\frac{r-as-\frac{a}{1+a^2}k}{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2};$$

susceptance,

$$\sigma=\frac{s-\frac{k}{1+a^2}}{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2};$$

admittance, in absolute values,

$$v=\sqrt{\rho^2+\sigma^2}=\frac{1}{\sqrt{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2}};$$

in symbolic expression,

$$\Upsilon=\rho+j\sigma=\frac{\left(r-as-\frac{a}{1+a^2}k\right)+j\left(s-\frac{k}{1+a^2}\right)}{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2}.$$

Since the impedance is

$$U=\left(r-as-\frac{a}{1+a^2}=k\right)-j\left(s-\frac{k}{1+a^2}\right)=r_a-js_a,$$

we have $$\Upsilon=\frac{1}{U};\quad v=\frac{1}{u_a};\quad \rho=\frac{r_a}{u_a^2};\quad \sigma=\frac{s_a}{u_a^2};$$

that is, the same relations as in the complex quantities in alternating current circuits, except that in the present case all the constants r_a, s_a, u_a, ρ, σ, v, depend upon the decrement a.

§ 3. *Circuits of Zero Impedance.*

In an oscillating current circuit of decrement a, of resistance r, inductive resistance s, and capacity reactance k, the impedance was represented in symbolic expression by

$$U=r_a-js_a=\left(r-as-\frac{a}{1+a^2}k\right)-j\left(s-\frac{k}{1+a^2}\right),$$

or numerically by

$$u=\sqrt{r_a^2+s_a^2}=\sqrt{\left(r-as-\frac{a}{1+a^2}k\right)^2+\left(s-\frac{k}{1+a^2}\right)^2}.$$

Thus the inductive reactance s, as well as the capacity reactance k, do not represent wattless electromotive forces as in an alternating current circuit, but introduce energy components of negative sign

$$-as-\frac{a}{1+a^2}k;$$

that means,

"In an oscillating current circuit, the counter electromotive force of self-induction is not in quadrature behind the current, but lags less than 90° or a quarter period, and the charging current of a condenser is less than 90°, or a quarter period ahead of the impressed electromotive force."

In consequence of the existence of negative energy components of reactance in an oscillating current circuit, a phenomenon can exist which has no analogy in an alternating current circuit, that is, under certain conditions, the total impedance of the oscillating current circuit can equal zero:

$$U=0.$$

In this case we have

$$r-as-\frac{a}{1+a^2}k=0;\quad s-\frac{k}{1+a^2}=0,$$

hence in complex quantities,

$$E=e(\cos\hat{\omega}+j\sin\hat{\omega})\operatorname{dec}\alpha,$$

$$C=E\left\{\frac{\cos\delta}{u_a}+j\frac{\sin\delta}{u_a}\right\}\operatorname{dec}\alpha\,;$$

or, substituting,

$$C=E\left\{\frac{r-as-\frac{a}{1+a^2}k}{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2}\right.$$

$$\left.+j\frac{s-\frac{k}{1+a^2}}{\left(s-\frac{k}{1+a_2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2}\right\}\operatorname{dec}\alpha.$$

Thus in complex quantities, for oscillating currents, we have: conductance,

$$\rho=\frac{r-as-\frac{a}{1+a^2}k}{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2}\,;$$

susceptance,

$$\sigma=\frac{s-\frac{k}{1+a^2}}{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2}\,;$$

admittance, in absolute values,

$$v=\sqrt{\rho^2+\sigma^2}=\frac{1}{\sqrt{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2}}\,;$$

in symbolic expression,

$$\Upsilon=\rho+j\sigma=\frac{\left(r-as-\frac{a}{1+a^2}k\right)+j\left(s-\frac{k}{1+a^2}\right)}{\left(s-\frac{k}{1+a^2}\right)^2+\left(r-as-\frac{a}{1+a^2}k\right)^2}.$$

Since the impedance is

$$U=\left(r-as-\frac{a}{1+a^2}=k\right)-j\left(s-\frac{k}{1+a^2}\right)=r_a-js_a,$$

we have $\Upsilon=\frac{1}{U}\,;\ v=\frac{1}{u_a}\,;\ \rho=\frac{r_a}{u_a^2}\,;\ \sigma=\frac{s_a}{u_a^2}\,;$

that is, the same relations as in the complex quantities in alternating current circuits, except that in the present case all the constants r_a, s_a, u_a, ρ, σ, v, depend upon the decrement a.

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In an oscillating current circuit of decrement a, of resistance r, inductive resistance s, and capacity reactance k, the impedance was represented in symbolic expression by

$$U = r_a - js_a = \left(r - as - \frac{a}{1+a^2}k\right) - j\left(s - \frac{k}{1+a^2}\right),$$

or numerically by

$$u = \sqrt{r_a^2 + s_a^2} = \sqrt{\left(r - as - \frac{a}{1+a^2}k\right)^2 + \left(s - \frac{k}{1+a^2}\right)^2}.$$

Thus the inductive reactance s, as well as the capacity reactance k, do not represent wattless electromotive forces as in an alternating current circuit, but introduce energy components of negative sign

$$-as - \frac{a}{1+a^2}k;$$

that means,

"In an oscillating current circuit, the counter electromotive force of self-induction is not in quadrature behind the current, but lags less than 90° or a quarter period, and the charging current of a condenser is less than 90°, or a quarter period ahead of the impressed electromotive force."

In consequence of the existence of negative energy components of reactance in an oscillating current circuit, a phenomenon can exist which has no analogy in an alternating current circuit, that is, under certain conditions, the total impedance of the oscillating current circuit can equal zero:

$$U = 0.$$

In this case we have

$$r - as - \frac{a}{1+a^2}k = 0; \quad s - \frac{k}{1+a^2} = 0.$$

substituting in this equation

$$s = 2\pi NL\,;\ k = \frac{1}{2\pi NK}\,;$$

and expanding, we have

$$a = \frac{1}{\sqrt{\frac{4L}{r^2K} - 1}}\,;$$

$$2\pi N = \frac{r}{2L}\sqrt{\frac{4L}{r^2K} - 1} = \frac{r}{2aL}$$

That is,

"If in an oscillating current circuit, the decrement $a = \frac{1}{\sqrt{\frac{4L}{r^2K} - 1}}$, and the frequency $N = \frac{r}{4\pi aL}$, the total impedance of the circuit is zero; that is, the oscillating current, when started once, will continue without external energy being impressed upon the circuit."

The physical meaning of this is: "If upon an electric circuit a certain amount of energy is impressed and then the circuit left to itself, the current in the circuit will become oscillating, and the oscillations assume the frequency $N = \frac{r}{4\pi aL}$, and the decrement $a = \frac{1}{\sqrt{\frac{4L}{r^2K} - 1}}$."

That is, the oscillating currents are the phenomena by which an electric circuit of disturbed equilibrium returns to equilibrium.

This feature shows the origin of the oscillating currents, and the means to produce such currents by disturbing the equilibrium of the electric circuit, for instance by the discharge of a condenser, by make and break of the circuit, by sudden electrostatic charge, as lightning, etc. Obviously, the most important oscillating currents are those flowing in a circuit of zero impedance, representing oscillating discharges of the circuit. Lightning strokes usually belong to this class.

§ 4. *Oscillating Discharges.*

The condition of an oscillating discharge is $U = 0$; that is:

$$a = \frac{1}{\sqrt{\frac{4L}{r^2K} - 1}}, \qquad 2\pi N = \frac{r}{2aL} = \frac{r}{2L}\sqrt{\frac{4L}{r^2K} - 1}.$$

If $r=0$, that is, in a circuit without resistance, we have $a=0$, $N=\frac{1}{2\pi\sqrt{LK}}$; that is, the currents are alternating with no decrement, and the frequency is that of resonance.

If $\frac{4L}{r^2K}-1<0$, that is, $r>2\sqrt{\frac{L}{K}}$, a and N become imaginary; that is, the discharge ceases to be oscillatory. An electrical discharge assumes an oscillating nature only, if $r<2\sqrt{\frac{L}{K}}$. In the case $r=2\sqrt{\frac{L}{K}}$ we have $a=\infty$, $N=0$; that is, the current dies out without oscillation.

From the foregoing we have seen that oscillating discharges, — as for instance the phenomena taking place if a condenser charged to a given potential is discharged through a given circuit, or if lightning strikes the line circuit, — is defined by the equation: $U=0 \operatorname{dec} a$.

Since $\quad C=(c_1+jc_2)\operatorname{dec}\alpha, \qquad E_r=Cr\operatorname{dec}\alpha,$

$$E_s=-sC(a+j)\operatorname{dec}\alpha, \quad E_k=\frac{k}{1+a^2}C(-a+j)\operatorname{dec}\alpha,$$

we have

$$r-as-\frac{a}{1+a^2}k=0,$$

$$-s+\frac{k}{1+a^2}=0;$$

hence, by substitution,

$$E_k=sC(-a+j)\operatorname{dec}\alpha.$$

The two constants, c_1 and c_2, of the discharge, are determined by the initial conditions, that is, the electromotive force and the current at the time $t=0$.

Let a condenser of capacity K be discharged through a circuit of resistance r and inductance L. Let e = electromotive force at the condenser in the moment of closing the circuit, that is, at the time $t=0$ or $\phi=0$. At this moment the current is zero, that is,

$$C=jc_2, \quad c_1=0.$$

Since $\quad E_k=sC(-a+j)\operatorname{dec}\alpha=e$ at $\phi=0$,

we have $\quad sc_2\sqrt{1+a^2}=e$ or $c_2=\frac{e}{s\sqrt{1+a^2}}$

Substituting this, we have,

$$C = j\frac{e}{s\sqrt{1+a^2}}\operatorname{dec}\alpha, \qquad E_r = je\frac{r}{s\sqrt{1+a^2}}\operatorname{dec}\alpha,$$

$$E_s = \frac{e}{\sqrt{1+a^2}}(1-ja)\operatorname{dec}\alpha, \quad E_k = -\frac{e}{\sqrt{1+a^2}}(1+ja)\operatorname{dec}\alpha,$$

the equations of the oscillating discharge of a condenser of initial voltage e.

Since $s = 2\pi NL,$

$$a = \frac{1}{\sqrt{\frac{4L}{r^2K}-1}},$$

$$2\pi N = \frac{r}{2aL},$$

we have $s = \frac{r}{2a} = \frac{r}{2}\sqrt{\frac{4L}{r^2K}-1}\,;$

hence, by substitution,

$$C = je\sqrt{\frac{K}{L}}\operatorname{dec}\alpha, \quad E^r = jer\sqrt{\frac{K}{L}}\operatorname{dec}\alpha,$$

$$E_s = \frac{er}{2}\sqrt{\frac{K}{L}}\left(\sqrt{\frac{4L}{r^2K}-1}-j\right)\operatorname{dec}\alpha,$$

$$E_k = -\frac{er}{2}\sqrt{\frac{K}{L}}\left(\sqrt{\frac{4L}{r^2K}-1}+j\right)\operatorname{dec}\alpha,$$

$$a = \frac{1}{\sqrt{\frac{4L}{r^2K}-1}}, \quad N = \frac{r\sqrt{\frac{4L}{r^2K}-1}}{4\pi L},$$

the final equations of the oscillating discharge, in symbolic expression.

§ 5. *Numerical Examples.*

To get an estimate of the numerical values of the constants of oscillating discharges, some cases may be investigated.

A. VERY HIGH FREQUENCY.

A short, straight conductor may be terminated by two balls. The balls represent the capacity, while the conductor represents the resistance and inductance. Without entering into the exact calculation, let the resistance of the conductor

$r = .0001$ ohms; the inductance of the conductor $L = .00025$ millihenry; the capacity of the two balls $K = 10^{-6}$ microfarads. We have then

$$a = 10^{-7};\ \text{angle}\ \alpha = 5.7 \times 10^{-6};\ N = 32 \times 10^{4};$$

that is, 320,000,000 cycles per second.

The amplitude is reduced to $\frac{1}{100}$ after the time t_0, or angle ϕ_0, where

$$\epsilon^{-a\phi_0} = .01;\ \phi_0 = 2\pi N t_0;$$

hence,

$$\phi_0 = 4.6 \times 10^{7};\ t_0 = .023;$$

that is, after .023 second the oscillation has practically died out; that is, decreased to $\frac{1}{100}$ of its amplitude, after making 7,400,000 complete oscillations.

The equations of the oscillating discharge are in this case, at $e = 10{,}000$ volts initial charge,

$$C = 20j\ \text{dec}\,\alpha;\ E_r = .002j\ \text{dec}\,\alpha.$$

$$E_s = (10{,}000 - .001j)\ \text{dec}\,\alpha;\ E_k = -(10{,}000 + .001j)\ \text{dec}\,\alpha.$$

As seen, for a moment 20 amperes flow at a potential of 10,000 volts, representing an instantaneous flow of about 100 K.W.

To make the discharge non-oscillatory, the resistance would have to be $r > 2\sqrt{\frac{L}{K}} > 1000$ ohms; that is, more than 10,000,000 times as much as assumed. That is, a wet string, or similar conductor, will not allow electrical oscillation.

B. UNDERGROUND CIRCUIT OF FOUR MILES IN LENGTH, OF TWO LEAD-COVERED CABLES CONSISTING OF WIRE NO. 00, B. & S.

$$r = 3.3\ \text{ohms};\ L = 7.5\ \text{microhenrys};\ K = 1.2\ \text{microfarads};$$

hence,

$$a = .021;\ N = 1670;\ t_0\phi = .021;$$

that is, in .021 seconds, or after 35 cycles, the oscillation has died out to $\frac{1}{100}$ of its initial value. At $e = 2000$ volts initial charge, the equations of phenomenon will be

$$C = 25.3j\ \text{dec}\,\alpha;\ E_r = 83.5j\ \text{dec}\,\alpha;$$

$$E_s = (2000 - 42j)\ \text{dec}\,\alpha\ \ E_k = -(2000 + 42j)\ \text{dec}\,\alpha.$$

The phenomenon will become non-oscillatory; that is,

$$N = 0;\ a = \infty;\ \text{for}\ r = 158\ \text{ohms}.$$

that is, in such cables electric oscillations can take place at comparatively moderate frequency, and of considerable duration.

C. TRANSATLANTIC CABLE.

Assuming approximately, $r = 40{,}000$ ohms, $L = 30$ h., $K = 1300$ microfarads; we then have $r < 300$, the condition under which electrical oscillations can take place.

If the resistance were $\frac{1}{100}$ the value it is in reality, that is, if we had $r = 200$ ohms, we could have $a = 0.88$, $N = 0.6$, and in this case, at $e = 100$ volts initial charge, the equations of the phenomenon would be, $C = 0.658 j \operatorname{dec} \alpha$, $E_r = 131.6 j \operatorname{dec} \alpha$, $E_s = (75 - 66 j) \operatorname{dec} \alpha$, $E_k = -(75 + 66 j) \operatorname{dec} \alpha$; that is, in a transatlantic cable electrical oscillations cannot take place, due to its high resistance. If, however, the resistance were low enough to permit electrical oscillations, that is, less than $\frac{1}{133}$ of what it is in reality, the oscillations would take place extremely slowly, each complete oscillation occupying more than one second.

In reality, due to the capacity not being centralized in a condenser, but distributed over the whole circuit, the phenomenon is more complex, and has to be investigated on the lines of circuits containing distributed capacity.

We see, however, from these instances the enormous range of frequencies, at which electrical oscillations take place, from frequencies of hundred millions of cycles per second to a frequency of more than a second per cycle.

§ 6. *Oscillating Current Transformer.*

As an instance of the application of the symbolic method of analyzing the phenomena caused by oscillating currents, the transformation of such currents may be investigated. If an oscillating current is produced in a circuit including the primary of a transformer, oscillating currents will also flow in the secondary of this transformer. In a transformer let the ratio of secondary to primary turns be p. Let the secondary be closed by a circuit of total resistance, $r_1 = r_1' + r_1''$, where $r_1' =$ external, $r_1'' =$ internal, resistance. The total inductance $L_1 = L_1' + L_1''$, where $L_1' =$ external, $L_1'' =$ internal inductance, total capacity, K_1. Then the total admittance of the secondary circuit is

$$\Upsilon_1 = (\rho_1 + j\sigma_1) \operatorname{dec} \alpha = \frac{1}{\left(r_1 - a s_1 - \frac{a}{1+a^2} k_1\right) - j\left(s_1 - \frac{k}{1+a^2}\right)},$$

where $s_1 = 2\pi N L_1 =$ inductive reactance; $k_1 = \frac{1}{2\pi N K} =$ capacity reactance. Let $r_0 =$ effective hysteretic resistance, $L_0 =$ inductance; hence, $s_0 = 2\pi N L_0 =$ reactance; hence,

$$\Upsilon_0 = \rho_0 + j\sigma_0 = \frac{1}{(r_0 - a s_0) - j s_0} = \text{admittance}$$

of the primary exciting circuit of the transformer; that is, the admittance of the primary circuit at open secondary circuit.

As discussed elsewhere, a transformer can be considered as consisting of the secondary circuit supplied by the impressed electromotive force over leads, whose impedance is equal to the sum of primary and secondary transformer impedance, and which are shunted by the exciting circuit, outside of the secondary, but inside of the primary impedance.

Let $r=$ resistance; $L=$ inductance; $K=$ capacity; hence,

$$s = 2\pi NL = \text{inductive reactance,}$$

$k=\dfrac{1}{2\pi NK}=$ capacity reactance of the total primary circuit, including the primary coil of the transformer. If $E_1{}'=E_1{}' \operatorname{dec} \alpha$ denotes the electromotive force induced in the secondary of the transformer by the mutual magnetic flux; that is, by the oscillating magnetism interlinked with the primary and secondary coil we have $C_1=E_1\Upsilon_1 \operatorname{dec}\alpha=$ secondary current.

Hence, $C_1{}'=p,\ C_1 \operatorname{dec}\alpha=p,\ E'\Upsilon_1 \operatorname{dec}\alpha=$ primary load current, or component of primary current corresponding to secondary current. Also, $C_0=\dfrac{p'}{p}E_1{}'\Upsilon_0 \operatorname{dec}\alpha=$primary exciting current; hence, the total primary current is

$$C=C_1{}'+C_0=\frac{E_1{}'}{p}\{\Upsilon_0+p^2\Upsilon_1\} \operatorname{dec}\alpha.$$

$E'=\dfrac{E_1{}'}{p}\operatorname{dec}\alpha=$induced primary electromotive force. Hence the total primary electromotive force is

$$E=(E'+CU)\operatorname{dec}\alpha=\frac{E_1{}'}{p}\{1+U\Upsilon_0+p^2U\Upsilon_1\}\operatorname{dec}\alpha.$$

In an oscillating discharge the total primary electromotive force $E=0$; that is,

$$1+U\Upsilon_0+p^2U\Upsilon_1=0;$$

or, the substitution

$$1+\frac{\left(r-as-\dfrac{a}{1+a^2}k\right)-j\left(s-\dfrac{k}{1+a^2}\right)}{(r_0-as_0)-js_0}$$

$$+p^2\frac{\left(r-as-\dfrac{a}{1+a^2}k\right)-j\left(s-\dfrac{k}{1+a^2}\right)}{\left(r_1-as_1-\dfrac{a}{1+a^2}k_1\right)-j\left(s_1-\dfrac{k_1}{1+a^2}\right)}=0.$$

Substituting in this equation, $s=2\pi NK$, $k=\frac{1}{2\pi NK}$, etc., we get a complex imaginary equation with the two constants a and N. Separating this equation in the real and the imaginary parts, we derive two equations, from which the two constants a and N of the discharge are calculated.

If the exciting current of the transformer is negligible; that is, if $\Upsilon_0=0$, the equation becomes essentially simplified:

$$1+p^2\frac{\left(r-as-\frac{a}{1+a^2}k\right)-j\left(s-\frac{k}{1+a^2}\right)}{\left(r_1-as_1-\frac{a}{1+a^2}k_1\right)-j\left(s_1-\frac{k_1}{1+a^2}\right)}=0;$$

that is,

$$\left(r_1-as_1-\frac{a}{1+a^2}k_1\right)+p^2\left(r-as-\frac{a}{1+a^2}k\right)=0;$$

$$\left(s_1-\frac{k_1}{1+a^2}\right)+p^2\left(s-\frac{k}{1+a^2}\right)=0;$$

or, combined:

$$(r_1-2as_1)+p^2(r-2as)=0,$$

$$r_1+p^2r=2a(s_1+p^2s),$$

$$k_1+p^2k=(1+a^2)(s_1+p^2s).$$

Substituting for s_1, s, k_1, k, we have

$$a=\frac{1}{\sqrt{\frac{4(L_1+p^2L)}{(r_1+p^2r)^2(K_1+p^2K)}-1}},$$

$$2\pi N=\frac{r_1+p^2r}{2a(L_1+p^2L)}=\frac{r_1+p^2r}{2(L_1+p^2L)}\sqrt{\frac{4(L_1+p^2L)}{(r_1+p^2r)^2(K_1+p^2K)}-1},$$

$$E=\frac{E_1'}{p}\{1+p^2U\Upsilon_1\}\operatorname{dec}\alpha,$$

$$C=pE_1'\Upsilon_1\operatorname{dec}\alpha,$$

$$C_1=E_1'\Upsilon_1\operatorname{dec}\alpha,$$

the equations of the oscillating current transformer, with E_1' as parameter.

December, 1895.

AN EXPERIMENTAL STUDY OF INDUCTION PHENOMENA IN ALTERNATING CURRENT CIRCUITS.

By F. E. Millis.

I. *Circuits containing Resistance and Self-induction.*

A DISCUSSION of the current curve produced upon closing a circuit containing an harmonic electromotive force, resistance, and self-induction leads to the well-known equation:

$$i=\frac{E}{\sqrt{R^2+L^2\omega^2}}\sin\left(\omega t-\tan^{-1}\frac{L\omega}{R}\right)+ce^{-\frac{Rt}{L}}, \tag{1}$$

in which

i is the value of the current at any instant,
E is the maximum value of the electromotive force,
R is the Ohmic resistance of the circuit,
L is the self-induction of the circuit,
ω is the angular velocity,
t is the time measured from the instant of closing the circuit,
c is a constant of integration,
e is the Napierian base.

Writers have generally neglected the exponential term in this equation, since as t increases, the effect of that term upon the current rapidly diminishes, and usually becomes inappreciable after the small part of one second. Neglecting this term is equivalent to assuming that the current at once reaches its permanent condition. It is with the curves as modified by this term that the present work deals. If an open circuit be suddenly closed, i and t both being zero at the instant of closing, c in the above equation is determined by Bedell and Crehore to be

$$c=-\frac{E}{\sqrt{R^2+L^2\omega^2}}\sin\left(\omega t_1-\tan^{-1}\frac{L\omega}{R}\right), \tag{2}$$

t_1 being time at which the circuit is closed. For $\dfrac{E}{\sqrt{R^2+L^2\omega^2}}$ they write I, which represents the maximum periodic value of i;

for $\sin\left(\omega t-\tan^{-1}\dfrac{L\omega}{R}\right)$ they write[1] $\sin\psi$;

and for $\sin\left(\omega t_1-\tan^{-1}\dfrac{L\omega}{R}\right)$ they write $\sin\psi_1$.

At the instant of closing the circuit $\psi=\psi_1$, whence, by substitution,

$$i=I\sin\psi-I\sin\psi_1=0; \tag{3}$$

that is, the initial value of the exponential term is equal and opposite to the value which the current ultimately has when in the same phase as that in which the circuit was closed. The greatest value of this induced or exponential current will occur when $\sin\psi=1$, or when the phase angle at closing the circuit is 90°.

The exponential term would alone give a current curve of the form shown in Fig. 1, the values being measured from the horizontal axis downward to the curve. This curve compounded with the uniform harmonic current curve represented by the first term of the second member of equation (1), gives a resultant current curve of the general form of c in Fig. 2.

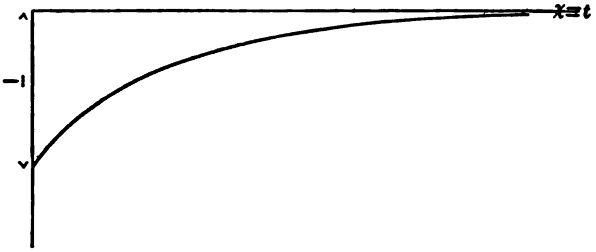

Fig. 1.

As this short-lived induced current is always to a greater or less extent present whenever the electromotive force in a circuit is suddenly changed or the load varied, it seemed a matter of importance as well as of interest to verify experimentally the above conclusions. This induced current becomes an important factor in

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[1] Alternating Currents, Bedell and Crehore, p. 55 (1st ed.).

alternate current working on circuits of large self-induction where the load is subject to great and sudden variation.

The study of small vibrating needles described in the Physical Review, Vol. III., p. 49, indicated that they may be relied upon to record the current from the instant of closing the circuit.

The experiments here described were made with the needle making 3580 double vibrations per second, mounted as shown in Figs. 1 and 2 of the above article. The coil surrounding the needle had 480 turns, carrying 2.35 amperes; and the magnetic field was produced by an electromagnet with two coils, each having 970 turns and carrying about 10 amperes. The alternating current experimented upon was produced by a small 50-volt 10-ampere Westinghouse alternator having a smooth armature. Curve II, Fig. 12, in Physical Review, Vol. III., p. 56, is taken from this alternator when there is no self-induction in the circuit. The resistance of the armature of the alternator was about 0.17 ohms. The entire resistance in the circuit for the curves which follow was 5.1 ohms and the self-induction was 0.0322 henrys.

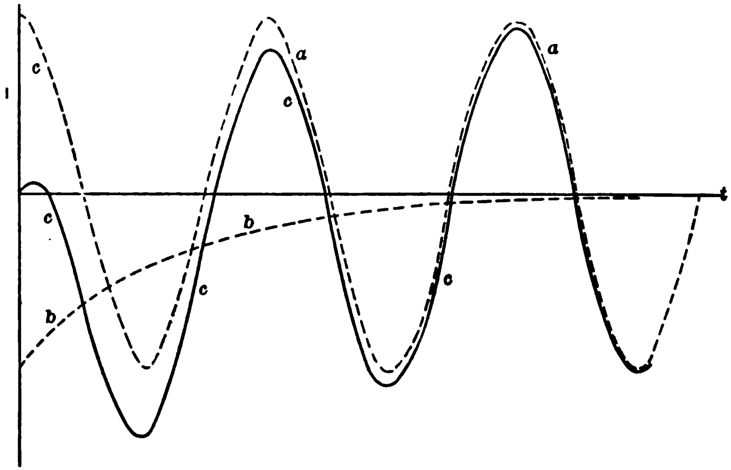

Fig. 2.

We have seen that if the current phase is zero when the circuit is closed there will be no induced current, and that the maximum induction is obtained if the circuit is closed when the phase angle is 90°. It was consequently desirable to close the circuit in the latter phase. To accomplish this, a plank $2\frac{1}{2}$ inches thick was fitted to the top of the alternator, as indicated in Fig. 3. Through this plank holes are bored to admit the electromagnet *SN*, the ends of the magnet being flush with the front surface of the plank. To the center of the magnet-armature *A* is rigidly fastened the brass upright *BC*, pivoted at *B*. The board *D*

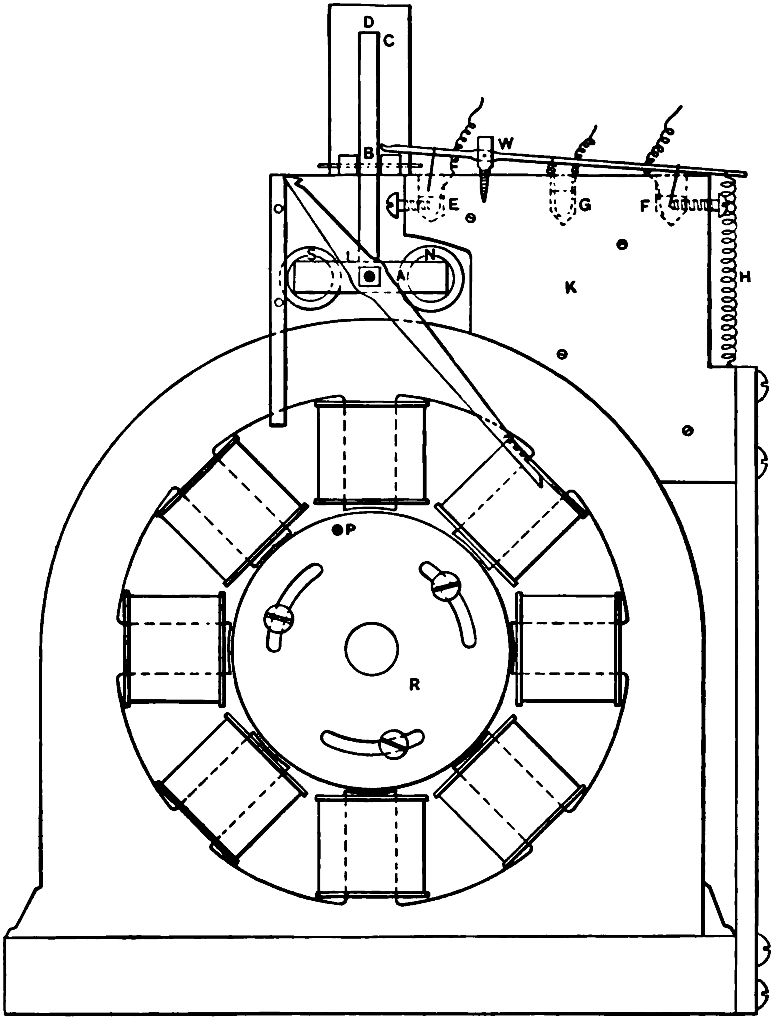

Fig. 3.

is fastened to the back of the plank and a coiled wire spring attached to *D* and *C* (not shown) draws *C* back so that the armature is held away from *SN* when the magnet is not excited. The trip-lever *L* is pivoted to the center of the armature *A*. A board *K* is fastened to the front side of the plank, and in this the mercury cups *E*, *G*, and *F*, and the support for the stout wire *W* are placed that they may be in the same plane as the top of the lever *L*. *R* is a hard-wood board secured by three set screws to the end of the armature of the generator. *P* is an iron pin projecting about $\frac{3}{8}$ of an inch from the front surface of this board.

Now suppose the lever *L* to hang vertically, its top hooked over the end of *W*, lifting the contact wire out of the mercury cup *F* and making contact in the cup *E*. One pole of the alternator is connected directly to the galvanometer; the other pole is connected to the mercury cup *G*, and the circuit is completed through the cup *E*, the self-induction coil, and the galvanometer. The spring attached to *C* holds *A* away from the electromagnet so far that the end of the lever *L* is not struck by the pin *P* revolving with the armature of the machine. But as the photographic plate in falling passes the horizontal slit in its slide it closes a battery circuit (from 10 storage cells) through the electromagnet pulling *A* in so that *P* strikes *L*, and the dynamo circuit is suddenly broken at *E*, the spring *H* exerting a considerable pull.

To *close* the circuit which we are studying we have only to connect *F* instead of *E* into the circuit. As the armature of the alternator advances, an appreciable distance between the tripping of *L* and the actual break or make of the circuit at *E* and *F* respectively, the phase in which the break or make actually took place was determined by developing a few trial plates. *E* and *F* each had a thumb screw projecting into its side by which the surface of the mercury could be accurately adjusted through a small range in height. These with the set screws in *R* brought the phase of break and make under easy control.

To get a curve showing the dying away of a current when the electromotive force is suddenly reduced to zero, under the conditions discussed below, it is necessary to cut out the electromotive force and at the same time leave the remaining portion of the circuit closed through the same resistance and self-induction as before. That is, the circuit must be closed through the self-induction and the galvanometer so as to include a new resistance equal to that cut out with the electromotive force, and this must be done at the *same instant* that the electromotive force is cut out.

To accomplish this, *E* is connected to one pole of the alternator (or to whatever source of current one wishes to study), *G* is connected to one circuit terminal, and the other circuit terminal is connected both to the dynamo and to *F*. The connection with *F* is through a resistance equal to that cut out with the electromotive force and of the same character.

The point now requiring care is to make the adjustments such that one wire shall leave the mercury at *E* at the *same instant* that the other touches the mercury at *F*. Adjustments must be made so that only a very small spark, and preferably none at all, shall be made at *E*, and yet connections at *F* must not be made soon enough to cause a short circuit. This is not difficult to accomplish, provided the mercury cups are large enough so that the wires shall not materially change the shape or the height of the surface of the mercury upon entering or leaving it. Figures 4, 5, and 6 show these different connections. A few make and break curves from continuous currents were taken as a simple means of getting a satisfactory relation between the resistance and the self-induction in the circuit, and of making the necessary adjustments.

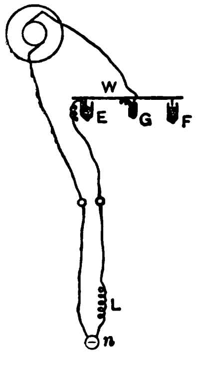

Fig. 4.
Break.

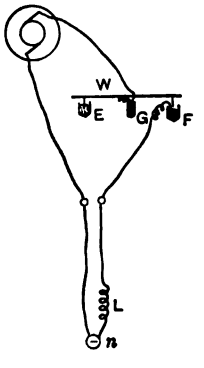

Fig. 5.
Make.

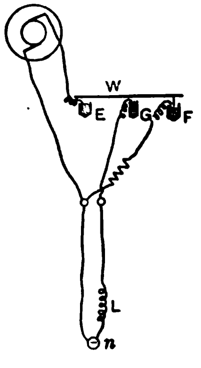

Fig. 6.
Cut Out.

Let a continuous current flow in a circuit until it has reached its steady state. If the electromotive force be then suddenly cut out and the circuit at the same time closed in such a manner that the self-induction and the resistance remain the same, the general equation

$$e=Ri+L\frac{di}{dt} \tag{4}$$

becomes

$$0=Ri+L\frac{di}{dt}, \tag{5}$$

which integrates into

$$i=ce^{-\frac{Rt}{L}}. \tag{6}$$

Substituting for c its value determined by the condition that at the instant of cutting out the electromotive force i equals its steady value I, we get

$$i=Ie^{-\frac{Rt}{L}}.[1] \tag{7}$$

From the same fundamental equation we get

$$i=I(1-e^{-\frac{Rt}{L}})$$

or

$$I-i=Ie^{-\frac{Rt}{L}}, \tag{8}$$

as the equation according to which the current attains its steady value upon closing the circuit. Hence the curve along which the current picks up to its final value upon closing the circuit is of the same form as that along which the current dies down upon removing the electromotive force, except it is turned upside down and displaced vertically the height of its maximum ordinate. Figures 7 and 8 show one of each of these curves. When superposed, these curves coincide perfectly, except a slight difference at the very beginning due to a lack of perfect adjustment of the mercury in the cups E and F.

If the alternating electromotive force be removed when the phase angle is 90°, that is, when i has its maximum value I, we have

$$i=Ie^{-\frac{Rt}{L}}, \tag{9}$$

the same as when removing a constant electromotive force. Such a curve is shown in Fig. 8 of the article above referred to. By

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[1] Alternating Currents, Bedell and Crehore, p. 45.

substituting for c in (1) its value given in (2), that term alone gives a curve of the form

$$i=-Ie^{-\frac{Rt}{L}},\quad (\psi=90^\circ), \tag{10}$$

which is identical with the curve given by equation (8) except it is below the axis of reference. This curve cannot be obtained by itself on the photographic plate, as can all the others, because as soon as the circuit is closed the *alternating* current interferes with it, and the curve actually obtained is the combination of this logarithmic curve and the alternating current curve.

The combination of an alternating curve with another curve of any form whatever is in effect the same as making the alternating curve symmetrical about the second curve as an axis. Hence the curve obtained upon closing an alternating current circuit having self-induction and resistance is symmetrical about the logarithmic component of the curve. But this logarithmic component is the same as the curve of dying out, inverted and properly displaced. Hence if we obtain this curve of dying out on one plate, and on another plate obtain the combination curve produced by closing the circuit, and then invert the first and superpose them so that the same ordinate shall pass through the point of breaking the one and the closing of the other, the combination curve should be symmetrical about the logarithmic curve as its axis. Figures 9 and 10 show the two curves obtained separately, and Fig. 11 shows them superposed as above indicated. The straight line in Fig. 9 was made by dropping the plate when the needle was not deflected, and is merely to indicate the axis of the curve. The plate was dropped a second time to obtain the curve. In superposing the curves it was made to coincide with the straight line part of Fig. 10, which being the trace of the spot of light before the circuit was closed, is in the line of the axis of the curve after the distorting effect of the exponential term has become negligible. Careful measurements with the dividers do not show any lack of symmetry.

In a further communication the writer expects to discuss experiments made upon circuits containing capacity.

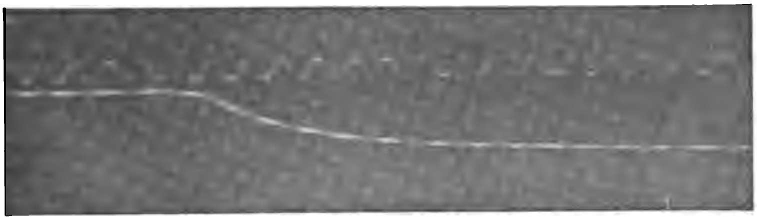

Fig. 7.

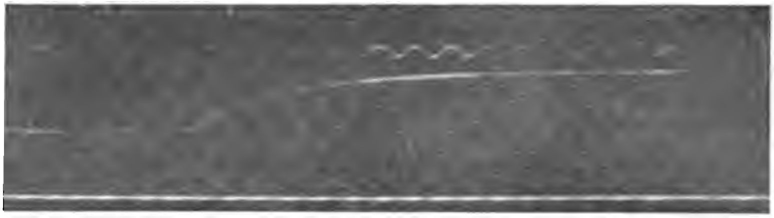

Fig. 8.

Fig. 9.

Fig. 10.

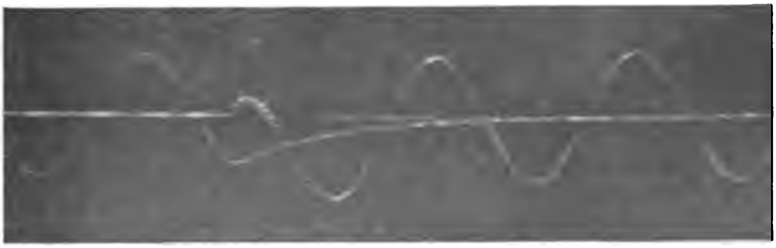

Fig. 11.

F. E. MILLIS: ALTERNATING CURRENT PHENOMENA.

DEMAGNETIZATION FACTORS FOR CYLINDRICAL RODS.

By C. Riborg Mann.

THE effect of the form of a substance on the intensity of magnetization which it assumes when brought into a magnetic field has been a much-discussed question. F. Neumann[1] attacked the problem from the analytical side, and showed that the intensity of magnetization can be calculated when the magnetization is uniform. He further demonstrated that the magnetization induced in any substance, when brought into a uniform field, will itself be uniform only when the substance is bounded by a surface of the second degree.[2] As the ellipsoid is the only surface of second degree whose dimensions are finite, it is the only form which is of practical interest to us here.

For the special case of a prolate spheroid brought into a uniform magnetic field whose lines of force run parallel to the axis of revolution of the spheroid, Neumann gives the following formula for calculating the intensity of magnetization :[3]

$$C = \kappa Z \frac{1}{1 + N\kappa};$$

Or in the modern notation,

$$\mathfrak{I} = \kappa \mathfrak{H} \frac{1}{1 + N\kappa}, \tag{1}$$

in which $\mathfrak{I}$ = intensity of magnetization,

$\mathfrak{H}$ = strength of field,

κ = susceptibility,

N = a constant depending on the ratio of the axes of the ellipsoid.

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[1] Neumann, Crelle's Journal, Vol. XXXVII., p. 44.

[2] Maxwell, Electricity and Magnetism, § 437.

[3] Maxwell, Electricity and Magnetism, § 438.

For our special case, the one of greatest practical use, this factor N is given by the following formula:

$$N = +4\pi\left(\frac{1}{\epsilon^2}-1\right)\left(\frac{1}{2\epsilon}\log\frac{1+\epsilon}{1-\epsilon}-1\right), \tag{2}$$

in which $\epsilon=\sqrt{1-\frac{b^2}{a^2}}$, when b stands for the smaller, a for the greater semi-axis of the ellipsoid.

We note that N depends only on a and b, *i.e.* on the form of the ellipsoid in question.

If we clear the equation (1) of fractions, we get

$$\mathfrak{J}=\kappa\,(\mathfrak{H}-N\mathfrak{J}). \tag{3}$$

When κ is very small, as in all substances except nickel, cobalt, and iron, the coefficient of N, *i.e.* $\kappa\mathfrak{J}$ is very small in comparison to $\kappa\mathfrak{H}$, and is, therefore, generally neglected, thus making the determination of κ practically independent of the form of the material investigated, *i.e.* independent of N. Hence in what follows, as we are to discuss N, we will speak only of the paramagnetic substances where κ is large.

When in formula (2) $a=\infty$, or $e=1$, *i.e.* when the ellipsoid considered is endless, $N=0$, and formula (3) becomes $\mathfrak{J}=\kappa\mathfrak{H}$, the fundamental equation for the intensity of magnetization. As a grows smaller, b remaining constant, N increases. Hence this N in formula (3) characterizes the effect of the free ends of the ellipsoid on its own magnetization, and is called, since the action of the free ends in paramagnetic substances is to diminish the effective magnetic field, the demagnetization factor.

If now N is known, $\mathfrak{J}$ and $\mathfrak{H}$ being measurable, formula (3) may be used to calculate κ, the magnetic susceptibility of any substance. Hence we may determine κ either on rings, where $N=0$, as Rowland did, or on ellipsoids, where N can be calculated from formula (2). Both of these methods are open to the practical objection that it is difficult to obtain either a suitable ring or an ellipsoid made of the material whose susceptibility we wish to know. Could we but make our observations on cylinders, which are easily procured, the task of determining κ would in most cases be much facilitated. The following investigation was therefore undertaken to determine whether N is independent of $\mathfrak{H}$ and $\mathfrak{J}$ for cylinders as for ellipsoids, and whether or not its value is the same for a cylinder as for the corresponding ellipsoid, *i.e.* one whose greater axis is equal to the length, and whose smaller axis is equal to the diameter of the cylinder. The magnetization in the case of a cylinder is not uniform, as it is in ellipsoids; therefore, by the intensity of magnetization of a cylinder is understood a mean value obtained by dividing the total magnetic moment by the volume. Hence the magnetometric method was preferred for this work.

It was formerly assumed that a cylinder could be used for its corresponding ellipsoid of revolution in observations on magnetization by induction.[1] Du Bois,[2] on the other hand, has shown from observations of Ewing[3] and Tanakadaté,[4] that this is not the case. From these observations he deduces a table giving N for various values of the ratio $\frac{\text{length}}{\text{diameter}}$ of the cylinder, this ratio being denoted m. These values for N may be used to reduce observations made on cylinders to those made on corresponding ellipsoids or on rings.

The observations on which this table is based, though the best that then existed, are not entirely satisfactory for computing these factors, and this for several reasons.[5] *First*, those of Ewing were made with too short a magnetizing coil, so that his magnetizing fields were not uniform throughout the whole space occupied by his core. *Secondly*, the two sets do not join, as Ewing's shortest cylinder had $m = 50$, while for Tanakadaté's longest cylinder m was only 39, thus necessitating an extrapolation over the interval $39 - 50$. *Thirdly*, the two sets of measurements were made in different ways, Ewing having used the ballistic, Tanakadaté the magnetometric method. In my opinion the results from these

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[1] W. Weber, Electrodynamische Maasbestimmungen, III., p. 573, 1867; Kirchhoff, Ges. Abh., p. 221; Oberbeck, Poggendorff's Annalen, CXXXV., p. 84, 1868.

[2] Magnetische Kreise, Berlin, 1895.

[3] Philosophical Transactions, 176, II., p. 535, 1885.

[4] Philosophical Magazine, 5 Series, Vol. XXVI., p. 450, 1888.

[5] *loc. cit.* p. 535.

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dei Lincei, 3, p. 190, 1894.

01, II., p. 771, 1870; Warburg and Hönig,

ished as a dissertation in Berlin, 1895, which may balanced by another smaller coil through which the magnetizing current flowed in the opposite direction to that which it took in the main coil. This small coil was so placed that it just balanced the effect of the magnetizing coil on the magnetometer when the needle was at the zero point. Slight corrections had to be applied in many cases to the readings of the magnetometer when the needle was deflected, because this compensation was not perfect except at the zero point. Having adjusted this smaller coil so that the reading of the magnetometer remained the same when the current through both coils was flowing in either direction or not flowing at all, the iron to be investigated was brought into the center of the magnetizing coil and subjected to a small field. The readings of both ammeter and magnetometer were taken and the polarity of the field was reversed, its strength remaining as nearly constant as possible, and then a second reading was taken. The means of these two opposite readings were used to calculate, by the usual formula,[1] the corresponding values of $\mathfrak{B}$ and $\mathfrak{J}$. The field was then strengthened and the same operation repeated, — in short, the method of ascending reversals was used. From these cylinders made of iron wire, the magnetization curves in Fig. 1 for values of *m* between 300 and 50 were made.

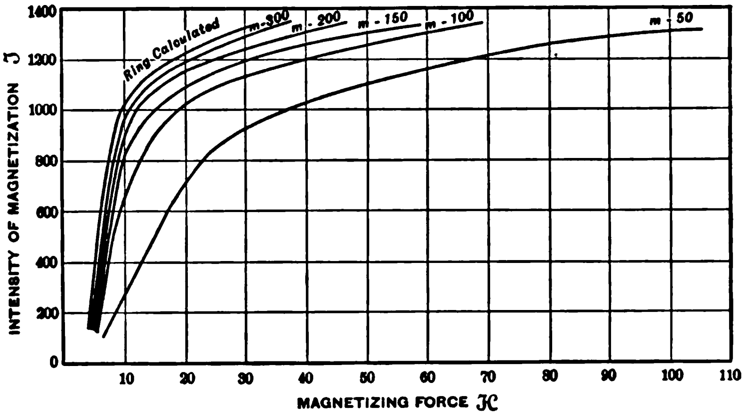

Fig. 1.

Magnetization Curves for Cylinders for Values of *m* between 300 and 50.

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[1] Wiedemann, Electricität, 3, § 428.

two different methods of measuring induction cannot be used together with certainty in a case like this.

Ascoli,[1] however, has recently published a table of these factors obtained from observations on cylindrical bundles of iron wire, which agreed very closely with that of Du Bois. Nevertheless it seemed doubtful to me if these numbers of Ascoli's could be used with certainty for the demagnetization factors of solid cylinders, because bundles of wire, as has been noted already by several physicists,[2] do not react towards magnetization as do solid cylinders of the same material, length, and cross-section, which we may term corresponding cylinders.

In order now to solve the problem satisfactorily, I proceeded as follows: I made a long series of magnetization curves, using cylinders of the same material but of different form, using also bundles of wire, being exceedingly careful that the results should be strictly comparable with each other, and from these deduced the conclusions given below. To give a detailed list of the observations were to take far too much space. The method used was briefly this:[3]

A long thin soft-iron wire was taken, for which $m = 300$ (length 25.08 cm., diameter 0.0836 cm.). After determining the curve of magnetization, giving the valuation between $\mathfrak{J}$ and $\mathfrak{B}$, equal lengths were cut from each end, so that the wire assumed the form $m = 200$. The magnetization curve was again determined and the wire again shortened to $m = 150$, etc., until m became equal to 50. These observations were made after the usual magnetometric method, using a coil 38.5 cm. long of 1.5 cm. inner diameter, thus assuring me of a uniform field throughout the entire space occupied by the iron. The current was measured by a carefully calibrated ammeter and the strength of field calculated in the usual way by multiplying the number of amperes by the constant of the coil obtained by the well-known formula.

The effect of the magnetizing coil on the magnetometer was

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[1] Rendiconti della royale Academia dei Lincei, 3, p. 190, 1894.

[2] v. Waltenhofen, Wiener Berichte, 61, II., p. 771, 1870; Warburg and Hönig, Wiedemann's Annalen, p. 828, 1883.

[3] The details of this work were published as a dissertation in Berlin, 1895, which may be obtained from the author.

balanced by another smaller [illegible] current flowed in the opposite [illegible] the main coil. This small [illegible] the effect of the magnetizing [illegible] needle was at the zero point. [illegible] in many cases to the readings [illegible] needle was deflected, because [illegible] except at the zero point. Having [illegible] that the reading of the magnetometer [illegible] the current through both coils was flowing [illegible]

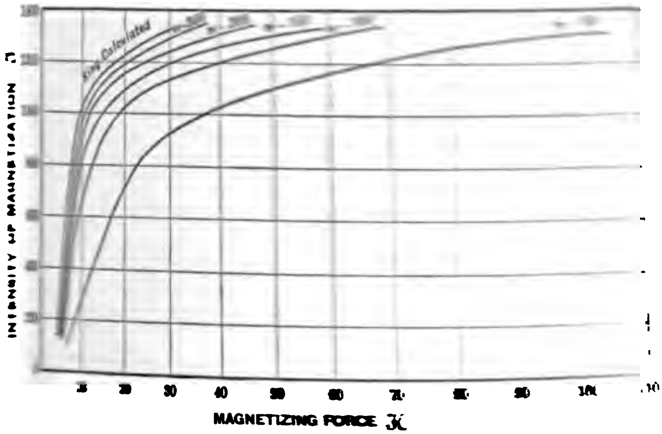

Fig. 1.

Magnetization Curves for Cylinders for Values of m between 300 and 50

not flowing at all, the iron to be investigated was brought into the center of the magnetizing coil and subjected to a small field. The readings of both ammeter and magnetometer were taken and the polarity of the field was reversed, its strength remaining as nearly constant as possible, and then a second reading was taken. The means of these two opposite readings were used to calculate, by the usual formulae,[1] the corresponding values of ℌ and ℑ. The field was then strengthened and the same operation repeated, [illegible] the method of ascending reversals was used. From these [illegible] made on iron wire, the magnetization curves in Fig. 1 [illegible] m between 300 and 50 were made.

[1] Wiedemann, Electricität, 3, § 428.

For shorter cylinders a different method was used. A short, thick rod for which *m* was only 5 (length, 11.850 cm.; diameter, 2.370 cm.), was gradually turned down, the length remaining constant, till *m* reached the value 50; *i.e.* till its form was the same as that of the shortest of the former set. Thus the two sets joined together, and in each the same iron was used throughout. This second set ($m=5$ to $m=50$) was made twice, using different qualities of iron and a different length.[1]

The first set was executed three times and the mean taken. Each curve of the other set was run at least three times and the mean taken. The curves given in Fig. 2 are these mean curves. To get the demagnetization factors N from the curves, we proceed as follows: Let $\mathfrak{H}_1$ and $\mathfrak{H}_2$ be values of $\mathfrak{H}$ which belong to the same $\mathfrak{I}$ on any two curves, and N_1 and N_2 the corresponding values of N. Then from (3)

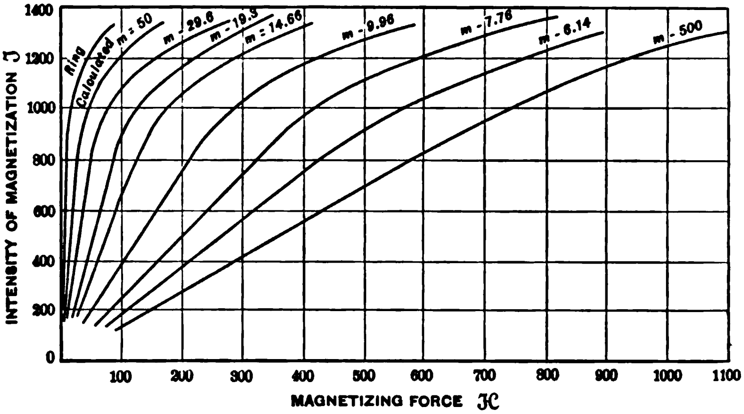

Fig. 2.

Magnetization Curves for the First Cylinder.

$$\mathfrak{I}=\kappa(\mathfrak{H}_1-N_1\mathfrak{I})=\kappa(\mathfrak{H}_2-N_2\mathfrak{I}),$$

or

$$N_2=N_1+\frac{\mathfrak{H}_2-\mathfrak{H}_1}{\mathfrak{I}}; \tag{4}$$

i.e. we must measure the difference in $\mathfrak{H}$ of the two curves under consideration along the same $\mathfrak{I}$-line, and divide this difference

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[1] For the second cylinder the length was 9.620 cm.

by the $\mathfrak{J}$ which belongs to that line, and add the quotient thus obtained to the demagnetization factor corresponding to the first curve.

This method presupposes the knowledge of N_1. There are several methods by which this factor can be determined. In my table below I assumed the curve for which $m = 300$ as the curve 1. The value of the corresponding N, which I will designate N_{800}, I unfortunately did not have time to determine by an independent method before the work was of necessity broken off. I assumed $N_{300} = 0.00075$, the value belonging to the corresponding ellipsoid, and for the following reason: Du Bois has shown theoretically that, for cylinders whose length is very much greater than their diameters, the quantity Nm^2 should be constant. From Ewing's observations he deduces the value of this constant as 45. If I assume this theoretical law of du Bois, I have the condition necessary to determine N_{800} from my observations as du Bois did.[1] The work is as follows, using the data from my observations:

m	N	x	Nm^2
300	x		
200	$0.00079 + x$	0.00041	48.0 (200 and 150)
150	$0.00172 + x$	0.00041	48.0 (200 and 100)
100	$0.00438 + x$	0.00041	47.9 (150 and 100)
Mean	. . . .	0.00041	48.0

It is quite evident that my observations do not satisfy the theoretical conclusions of du Bois. A similar calculation for ellipsoids gives:

m	N	x	Nm^2
300	x		
200	$0.00085 + x$	0.00044	51.6 (200 and 150)
150	$0.00185 + x$	0.00042	50.8 (200 and 100)
100	$0.00465 + x$	0.00040	50.0 (150 and 100)
Mean	. . . .	0.00042	50.8

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[1] Wiedemann's Annalen, XLVI., 1892.

These two tables are seen to be very similar. Therefore it is very probable that these long cylinders act very similar to their corresponding ellipsoids, as has always been assumed;[1] and hence I felt warranted in assuming the value I did for N_{800}.[2]

Having this for a starting point, the values of N for the other curves are easily calculated by formula 4.

The measurements on bundles of wire were conducted simultaneously with those on the second short cylinder. The wire used was 0.0801 cm. in thickness, and cut into lengths of 9.8 cm. These lengths were bound into cylindrical bundles, and the magnetization curves (given in Fig. 3) determined as for solid cylinders.

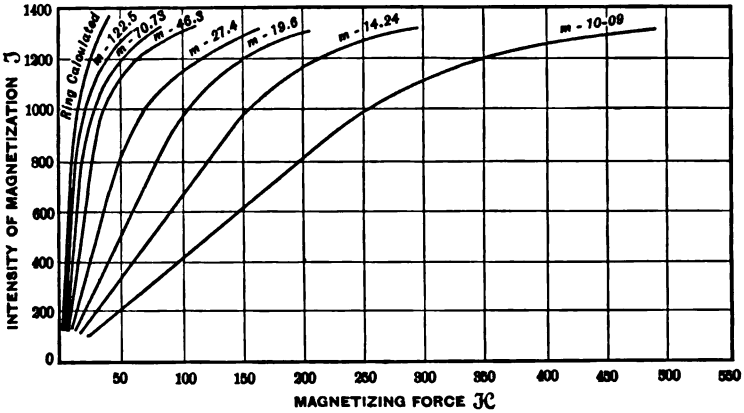

Fig. 3.

Magnetization Curves for Wire Bundles.

The size of the bundles varied from a single wire, for which $m = 122.5$, to 171 wires, for which $m = 9.37$. The value of N_1 for the wire bundles was of course that for a cylinder of the form of a single wire; *i.e.* the value corresponding to $m = 122.5$. This factor was taken from the table of N for solid cylinders. In interpolating and comparing the observations, the factor N alone was not used, but rather the expression Nm^2, as this latter serves much better for this purpose. Figure 4 contains the curves

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[1] Maxwell, Electricity and Magnetism, § 438.

[2] It is probable that it should be a trifle smaller, say 0.00070; but this difference of 0.00005 is not appreciable for the shorter cylinders.

$Nm^2 = f(m)$ for solid cylinders, ovoids, and wire bundles. The points represent the various observations.

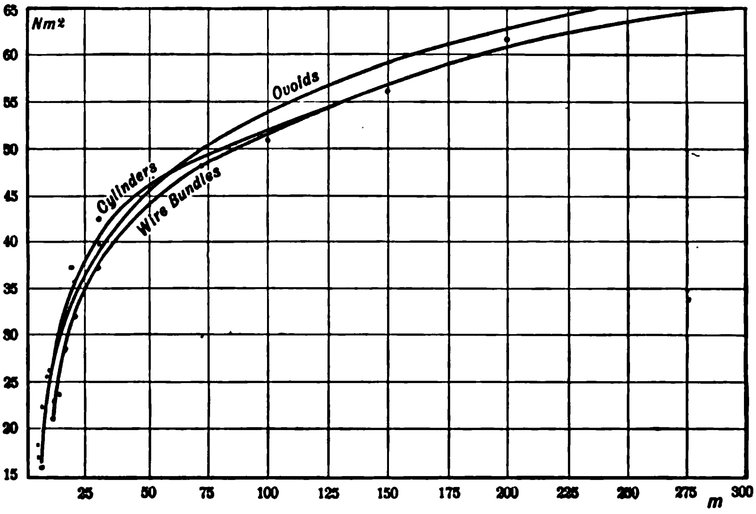

Fig. 4.

Nm^2 as a function of m.

The following table gives corresponding values of m, N, and Nm^2 for the three cases:

	Cylinders.		Ovoids.		Wire Bundles.	
m	N	Nm^2	N	Nm^2	N	Nm^2
5	0.68000	17.0	0.7015	17.5	—	—
10	0.25500	25.5	0.2549	25.5	0.22750	22.8
15	0.14000	31.5	0.1350	30.4	0.12580	28.3
20	0.08975	35.9	0.0848	34.0	0.08225	52.5
25	0.06278	39.3	0.0579	36.2	0.05680	35.5
30	0.04604	41.4	0.0432	38.8	0.04213	37.9
40	0.02744	43.9	0.0266	42.5	0.02596	41.5
50	0.01825	45.6	0.0181	45.3	0.01760	44.0
60	0.01311	47.2	0.0132	47.5	0.01277	46.0
70	0.00988	48.4	0.0101	49.5	0.00951	47.8
80	0.00776	49.7	0.0080	51.2	0.00768	49.1
90	0.00628	50.8	0.0065	52.5	0.00623	50.5
100	0.00518	51.8	0.0054	54.0	0.00515	51.5
150	0.00251	56.5	0.0026	58.3	—	—
200	0.00152	60.8	0.0016	64.0	—	—
300	0.00075	67.5	0.00075	67.5	—	—

The column N for ovoids was calculated from formula (2). They are good for all values of $\mathfrak{J}$.

When I calculated the value of N for cylinders and wires from the observations by formula (4) under the supposition $N_{800} = 0.00075$, I found that N remains practically constant only for $\mathfrak{J} < 800$. Hence the numbers given in the table are obtained by calculating from the observations the value of N for every round hundred of $\mathfrak{J}$ from 300 to 800, and taking the mean. They are, therefore, called mean demagnetization factors, and are good only until $\mathfrak{J}$ reaches the value 800 c.g.s.

It will be seen from the curves that for $\mathfrak{J} > 800$ the magnetization curves fall off rapidly from the curve 1 for which $m = 300$, causing a correspondingly rapid increase in the values of N. This same effect has been noted by Lehmann[1] in experiments on radially cut rings. The wire bundles lie intermediate between cylinders and ellipsoids in this respect, the demagnetization factors remaining constant longer than those of their corresponding cylinders.

The following table for $\mathfrak{J}$, with the corresponding value of N, will illustrate the point in hand:

$\mathfrak{J}$	N		$\mathfrak{J}$	N	
	$m = 46.30$ wires.	$m = 29.60$ cylinders.		$m = 46.30$ wires.	$m = 29.60$ cylinders.
300	0.02167	0.04718	900	0.01950	0.05166
400	0.01907	0.04822	1000	0.02085	0.05877
500	0.02024	0.04873	1100	0.02480	0.07964
600	0.01984	0.04870	1200	0.03287	0.09768
700	0.01976	0.04892	1300	0.05181	0.12777
800	0.01962	0.04735			

The results may be summed up as follows.

The mean magnetization of a cylinder does not differ greatly in amount from the magnetization of the corresponding ellipsoid for values of $\mathfrak{J} < 800$ c.g.s. For $\mathfrak{J} > 800$ an ellipsoid assumes a much stronger magnetization for the same magnetizing force than its corresponding cylinder.

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[1] Wiedemann's Annalen, XLVIII., p. 406, 1893.

Wire bundles assume, when $\mathfrak{J} < 800$, a much stronger magnetization for the same magnetizing force than either their corresponding ellipsoids or cylinders. The ellipsoid has, however, greater susceptibility for higher values of $\mathfrak{J}$.

Cylinders whose length is from 20 to 30 times their diameter differ most from the corresponding ellipsoids in their reaction towards induced magnetization.[1]

These values of N for cylinders, when used in formula (3), will give the correct value of κ, provided only that $\mathfrak{J} < 800$ c.g.s.

This result is practically of value, as it enables us to determine κ from observations made by the ordinary magnetometric method on cylinders.

The above investigation was carried on in the physical laboratory of the Berlin University, under the direction of the late Professor Kundt and Professor Warburg, whose kindness and assistance I wish here gratefully to acknowledge.

University of Chicago, January, 1896.

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[1] Cf. Tanakadaté, Philosophical Magazine, 5 Series, Vol. XXVI., p. 453, 1888.

A PHOTOGRAPHIC STUDY OF ARC SPECTRA. I.

BY CAROLINE WILLARD BALDWIN.

INTRODUCTION.

IN the course of his investigation of the Infra-Red Spectra of the Alkalies, Professor Snow[1] has shown the remarkable effect produced upon the arc spectrum when the alkalies were present in the carbons. He found that the curve obtained from his bolometric measurements was materially changed by the metals. While in the ordinary arc he had several very strong maxima in the ultra-violet and in the visible spectrum, he discovered that upon introducing the metals, these intense regions disappeared and strong maxima were now observed only in the infra-red.

The maxima in the violet and ultra-violet are the well-known characteristic, bright groups of the arc spectrum. These are produced by a peculiar crowding together of fine lines in the regions $\lambda = 3450$ to $\lambda = 3590$, $\lambda = 3700$ to $\lambda = 3885$, and $\lambda = 4030$ to $\lambda = 4211$. The disappearance of these and other similar groups would amount to a practical obliteration of the arc spectrum and substitution in its stead of the line spectrum of the particular metal used.

The phenomena seemed worthy of further study, and as the bright groups lie in the regions to which the photographic plate is most sensitive, it was thought worth while to try the application of photography to determine whether the disappearance noted was complete, or whether the bright regions were only so much reduced in intensity as to escape detection by bolometric observation.

As a matter of fact, the work was extended beyond its original limit, and in the end it assumed the form of a photographic study of the spectrum obtained from different regions of the arc under

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[1] B. W. Snow, PHYSICAL REVIEW, Vol. I., p. 28.

different conditions, and of the effect of the metallic spectra upon the original carbon arc spectrum.

APPARATUS.

The spectrum to be photographed was produced by means of a Rowland concave grating, which was arranged in the usual way upon a Brashear mounting. The latter consisted of a strong iron frame, which carried two tracks, *SG* and *SC*, Fig. 1, at right angles to one another. At their point of intersection *S*, the slit was placed. The carriage *G*, which contained the grating, moved on one track, and the carriage *C*, for the camera box, on the other. These two carriages were connected by an iron rod to which they were clamped in such a position as to keep the rod in the common normal to the grating and photographic plate. A screw on the camera box permitted the finer adjustments of position to be made.

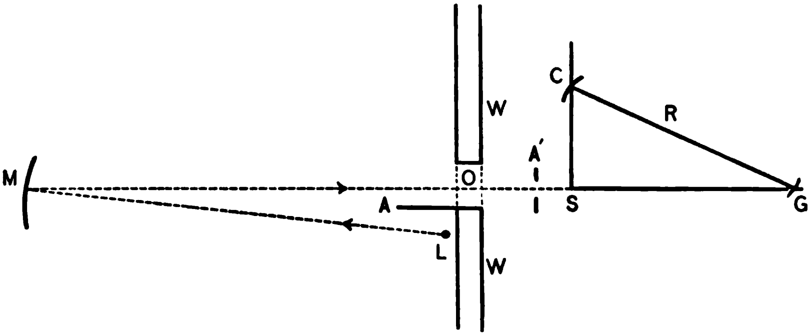

Fig. 1.

The width of the slit was adjusted by means of a micrometer screw, 0.1 mm. being the width ordinarily used. The length of the slit was gauged by means of a diaphragm having a wedge-shaped opening. A frame which held the slit could be turned by means of a screw and spring so as to place the slit accurately parallel to the lines of the grating.

The grating was of six-foot radius, and 14,000 lines to the inch.

Celluloid films were used, and, as these could be readily bent to any curvature, the film holder was curved to conform to the focus of the concave grating. A fence work of horizontal and vertical bars placed back of the film kept it from curving longitudinally, and yet permitted the spectrum to be seen from the back, so that a cleared film could be used for focussing.

The light used was obtained from a Thomson and Houston arc lamp, which was hung so that the arc could be kept nearly in the horizontal plane in which lay the center of the grating and the central points of the slit and camera box. The carbons were 1. cm. in diameter, unplated, and were made with a soft core .3 cm. in diameter. To produce the arc spectra of the metals, the cores were removed and the space was filled with the metallic salt well pounded in.

In order to prevent fogging of the photographic plates, the lamp *L*, Fig. 1, was placed in the outer of two dark rooms, and the light was reflected into the inner room, which contained the grating, by means of a large concave mirror (*M*). This mirror was mounted so as to be adjustable about both a horizontal and a vertical axis. Its radius of curvature was twelve feet. The arc light was placed nearly at the center of curvature of the mirror, which was so adjusted that a real, slightly enlarged image was formed on the slit (*S*). This arrangement was also of advantage, inasmuch as it did away with the use of a converging lens. The arrangement of the apparatus is given in Fig. 1, to which reference has already been made.

The opening between the two rooms was closed on the outer side by a slide provided with a circular opening, and on the inner side by a solid slide, by means of which the light could be entirely shut out.

A screen near the lamp cut off the direct rays of the opening between the rooms; and another screen was placed a short distance in front of the slit, to intercept the scattered light.

Outline of the Work.

The image of the arc, as examined by the eye, shows sheaths of different colors. The arc is slightly cone-shaped, the apex resting on the negative carbon. The central portion (1), which is of a violet tint, connects the two bright points of the carbons. Outside of this is a sheath of dull blue (2), which is most brilliant at the negative carbon, where it extends across in such a way as to hide the violet portion. The outer sheath (3) is yellow, shading into orange at the cooler outer edge; this last part includes the greater portion of the flame of the arc, and extends well up around the positive carbon. The different divisions are shown in Fig. 2.

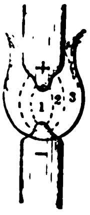

Fig. 2.

The investigation may be considered as divided into four parts:

I. Photographs were taken with the slit extending vertically through the arc in six different positions: first, through the center of the violet portion; second, at the line of separation between the violet and blue; third, in the blue; fourth, between the blue and the yellow; fifth, in the yellow; and sixth, at the extreme outer edge of the yellow (see Fig. 3).

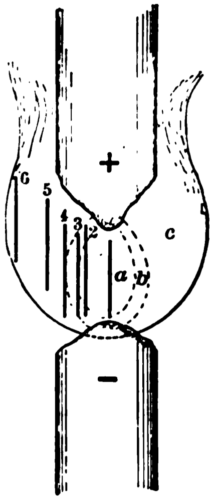

Fig. 3.

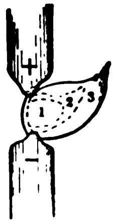

Fig. 4.

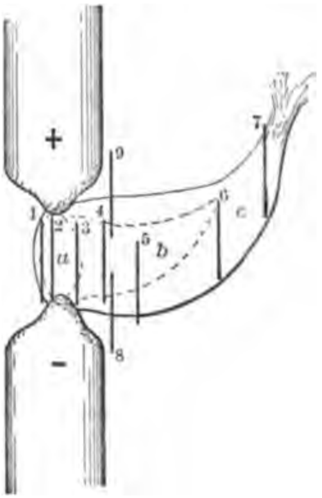

Fig. 5.

II. Photographs were also taken with the slit extending horizontally through the image of the arc. Three positions were chosen for these: first, near the tip of the negative carbon; second, half-way between the carbons; and third, near the positive carbon.

III. The flame was blown out from between the carbons by means of a horseshoe magnet. Under these circumstances the violet part does not change much in its position, but is slightly extended on the side away from the magnet; while the blue and yellow are blown out nearly three centimeters beyond the edge of the carbons. The appearance of the arc was as shown in Fig. 4. Photographs were taken with the slit extending vertically through this image in nine different places (Fig. 5): first, at the inner edge of the arc; second, in the center between the tips of the carbons; third, in the outer part of the violet; fourth, at the edge of the carbons; fifth, outside of the carbons through the blue and yellow; sixth, in the yellow; seventh, at the extreme end of the flame; eighth and ninth, at the edge of the carbons, giving the extent of the flame in the first place at the side toward the negative carbon, and in the second place at the positive carbon.

One hundred and thirty photographs were taken by these methods, from which the study of the ordinary arc spectrum has been made.

IV. Metals were introduced into the arc, and similar sets of photographs were taken.

The metallic salts used were lithium carbonate, sodium nitrate and chloride, potassium chloride, calcium chloride, strontium oxide, barium chloride, copper sulphate, silver nitrate, zinc chloride, and cadmium chloride. Sodium and zinc were studied by all three methods, the others only by the first two. This series included one hundred and fifty photographs.

All of these photographs were taken in the primary spectrum, as there was less confusion due to overlapping of spectra. The ultra-violet of the second spectrum, which extended to the green of the first, could be easily cut off by means of a glass plate placed in front of the slit. This gave a pure spectrum in the region to which the plates were sensitive.

In order to have the negatives evenly exposed, and the intensity as nearly as possible the same for different parts of the spectrum, four positions were chosen for photographing. *First*, the extreme ultra-violet, including the first bright group ($\lambda = 2263$ to $\lambda = 3600$); *second*, the region of the three principal bright groups ($\lambda=3450$ to $\lambda=4211$); *third*, from the brightest of the groups to the *D* lines, or from $\lambda=3800$ to $\lambda=5900$; and *fourth*, with a very long exposure, the region between $\lambda=4500$ and $\lambda=6400$. The exposures varied in length from thirty seconds in the violet to five or ten minutes in the extreme ultra-violet, and fifteen to twenty minutes in the red of the spectrum.

On account of the motion of the arc it was necessary to have a movable screen, by means of which the light could be cut off whenever the arc moved so as to throw the wrong part of the image upon the slit. This movement of the arc caused so much trouble that it was difficult to obtain good photographs of the different sheaths in the regions of the spectrum which required long exposure. Hence the study of the spectra of different parts of the arc has been confined to the region between $\lambda=3010$ and $\lambda=5500$; and toward the ends of this region photographs were taken only in the violet, blue, and yellow sheaths of the image. A slightly longer exposure was given in the outer part of the arc than was needed in the violet and blue portions.

The length of the arc used was about 1.4 cm.

I.

RESULTS OBTAINED WITH THE ORDINARY ARC.

The distinctive features of the arc spectrum are the bright groups[1] from $\lambda=3520$ to $\lambda=3590$, $\lambda=3800$ to $\lambda=3885$ mentioned by Kayser and Runge, Drude and Nunst, Nichols and Franklin, etc.; one from $\lambda=4400$ to $\lambda=4604$; the carbon bands[2] given by Kayser and Runge and others, $\lambda=4680$ to $\lambda=4737$, $\lambda=4746$ to $\lambda=5165$, and $\lambda=5530$ to $\lambda=5635$; together with a host of periodically placed fine lines. The bright groups appear to be due to a crowding together of these numerous fine lines. The strong lines of the various metals, which are present

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[1] Snow, PHYSICAL REVIEW, Vol. I., p. 28; Kayser and Runge, Wied. Ann., XXXVIII., p. 81, 1889; Drude and Nunst, Wied. Ann., XLV., p. 460, 1892; Nichols and Franklin, Am. J. (3), p. 106, 1889.

[2] Kayser and Runge, Ueber die Spectren der Elemente, Zweiter Abschnitt.

as impurities in the carbons, are superposed upon this under spectrum. The arc spectrum thus seems to consist of two spectra.

The general arrangement of the periodic lines is worthy of note. They are finer and nearer together toward the violet end of the spectrum; the bright groups are also nearer together in the regions of greater refrangibility. In each group, however, the lines are finer and nearer together toward the red of the spectrum, the maximum being toward the longer wave lengths, on which side the termination of the group is sudden. Each of the groups shows secondary maxima, and between each of these the same general law is followed, as in the case of the group as a whole. We shall speak of these groups hereafter under the general name of the band spectrum.

Many of the metallic lines are stronger near the negative carbon and are weak or invisible at the positive carbon,[1] while the lines of the band spectrum are strongest at the positive carbon.

As we pass from the center of the arc to the edge, the band spectrum grows fainter and finally disappears. This is also true of many of the metallic lines, while other metallic lines seem to be equally bright in all parts of the arc, and a considerable number are relatively stronger in the outer sheath. This effect is enough to change the entire aspect of the spectrum in many places. The lines which show the last effect do not belong exclusively to any one metal, neither do all the lines of a metal seem to act thus. In the case of the calcium lines, all the triplets of the 2d series given by Kayser and Runge[2] are strongest in the center, while the pairs

$$\left.\begin{matrix}3968.63\\3933.83\end{matrix}\right\}\text{ and }\left.\begin{matrix}3737.08\\3706.18\end{matrix}\right\}$$

and certain other lines as $\lambda=4226.91$ are much stronger in the yellow part of the arc flame. A few of the triplets of the first series are stronger toward the edge. Such are

$$\left.\begin{matrix}4318.80\\4302.68\\4299.14\end{matrix}\right\}\text{ and }\left.\begin{matrix}3644.45\\3630.82\\3624.15\end{matrix}\right\}$$

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[1] Lockyer, Proc. Roy. Soc., XXVIII., 1879.

[2] Kayser and Runge, Ueber die Spectren der Elemente.

In the carbon band, ending at $\lambda=4735$, the maxima remain the same as we pass from center to edge of the flame, but the law seems to be changed. In the outer sheath the maximum intensity is toward the violet and the strongest maximum is $\lambda=4645$. The shading of the band is thus completely reversed. Another band with maxima toward the violet is seen in the outer sheath from $\lambda=4840$; the maxima being $\lambda=4840$, $\lambda=4865$ and $\lambda=4892$. The strongest part of the group at 3590 becomes the weakest in the outer part of the arc, and many groups have the faintest lines at the center, the strongest at the edge.

When the photographs are taken giving the spectrum of the flame as blown out from between the carbons by the action of a magnet, the slit extends across the different sheaths of the arc, and those lines which are stronger in the outer parts of the arc reach through the spectrum with their brightness undiminished or increased at the edges, while the bands and many of the metallic lines appear only in the central part.

When the slit is arranged to pass through the image of the arc horizontally, this effect is more marked, owing to the greater steadiness of the flame. In watching the developing of the negatives, it was observed that many of the lines, as 4226, 3583, 3571, were first visible at the edge and then gradually extended toward the center, while the fine lines of the band spectra and most of the other lines appeared first at the center and then extended part way to the edge. The photographs taken by the three methods thus show complete agreement in their results.

Since the spectrum of the arc has already been mapped with more powerful apparatus than that used in these experiments, only such points will be given as may serve to indicate the differences between the spectra of the different sheaths.

(A) *Region lying between* 2263 *and* 3100.

135 lines were mapped between 2263 and 3016, all of which belonged to the central violet sheath [(1) Fig. 2].

The first lines which could be detected in the blue and yellow sheaths lay between 3018 and 3099; eleven lines among the nineteen mapped were visible in the blue and four in the yellow.

(B) *Region lying between* 3100 *and* 3440.

72 lines were mapped, all of which were confined to the central blue sheath.

(C) *Region lying between* 3440 *and* 3928.

135 lines were mapped, of which

125 were present in the violet,
96 were present in the blue,
58 were present in the yellow.

Of those which were invisible or very faint in the central violet sheath, although strong in the outer sheaths, the following are readily placed in Rowland's Standard List:[1]

3812.12	C.	3832.45	Mg.
3812.20		3834.36	Fe.
3812.34		3838.43	Mg.
3815.98	Fe.	3841.19	FeMn.
3820.59	FeC.	3856.52	Fe.
3827.03	Fe.	3860.05	FeC.

(D) *Region lying between* 3930 *and* 4550.

Throughout this region photographs were taken in the five positions indicated in Fig. 3, as *a*, 2, 3, 5, and 6.

213 lines were mapped, of which

211 lines were visible in central violet sheath (*a*),
200 lines were visible in outer violet sheath (2),
179 lines were visible in blue sheath (3),
175 lines were visible in inner yellow sheath (5),
57 lines were visible in outer yellow sheath (6).

The two lines absent from the central violet appear to be

3960.05 Fe } Rowland's scale.
4076.96 Fe }

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[1] Rowland, Astrophysical Journal, I., p. 29, 1895.

(E) *Region lying between* 4550 *and* 4960.

Photographs were taken in three regions (1, 2, and 3, Fig. 2). 129 lines were mapped, of which

129 lines were visible in the violet sheath,
103 lines were visible in the blue sheath,
95 lines were visible in the yellow sheath.

(F) *Region lying between* 4960 *and* 6042.

115 lines were mapped, of which

115 lines were visible in the violet sheath,
42 lines were visible in the blue sheath.

If we sum up these data, we find

Total lines mapped	799,[1]
Visible in central violet	787,
Visible in blue	431,
Visible in yellow	232.

Attempts to classify these lines according to their sources led to no satisfactory results. A study of the photographs, however, showed that the lines of the arc spectrum may be grouped as follows:

I. *a*. Lines which grow gradually weaker as we move from the center to the edge, and are usually invisible in the outer sheath.

I. *b*. Lines which preserve about the same intensity in the center and blue of the arc, but are suddenly much weaker or invisible in the yellow.

Forty lines of this class were counted. They were distributed throughout the spectrum from 3024 to 5616.

The lines of the band spectra grow fainter through the blue, but disappear quite suddenly there, not being seen in the yellow.

I. *c*. Faint lines which are only found in the first two positions (*a* and 2, Fig. 3). Invisible in the blue. One hundred and sixteen of these were counted.

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[1] **Exclusive of the fine lines of the band spectrum which were not counted.**

II.*a*. Lines which appear equally strong in all parts of the arc. Seventy such lines were counted.

II.*b*. Lines which become stronger as we go out from the center. Seventy-nine of these lines were mapped.

II.*c*. Lines which are not visible or exceedingly faint at the center of the arc. There are eighteen of these, of which exact positions for twelve have been given in a previous paragraph.

II.*d*. Lines which have their maxima in other sheaths, 2 or 3, rather than in the center or at the edge of the arc. There are sixteen such lines upon the photographs.[1]

II.*e*. Lines which have more than one maximum. Six such lines were noted.

The lines of division I. are as a rule *stronger at the positive carbon*, while the lines of II. are usually *stronger at the negative carbon*. II.*b*. and II.*c*. are especially strengthened at the negative carbon, II.*a*. to a less extent.

The calcium lines 4581.66 and 4586.12 appear as single lines at the negative carbon, but at the positive they seem to be double.

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[1] There is reason to think that at least ten of these are titanium lines, but the evidence is not conclusive.

(*To be concluded.*)

MINOR CONTRIBUTIONS.

THE SURFACE TENSION OF LIQUIDS.

By Arthur L. Foley.

In the *Philosophical Magazine* of November, 1893, Mr. T. Proctor Hall describes some "New Methods of Measuring the Surface Tension of Liquids." Two years ago, at the suggestion of Professor Michelson of the Chicago University, I undertook to repeat and to extend the investigation. In the present article, I shall confine myself to a brief statement of the results obtained by using Mr. Hall's method *c*, the maximum-weight method.[1]

Let *a* (Fig. 1) be an end face of a rectangular parallelopiped suspended from one arm of a balance, with its lower face horizontal, and therefore parallel to the liquid surface *Ox*. Call w' the weight of the frame (block) in this position. Lower the frame until it touches the liquid, and bring it again to the first position, as in *b*. The weight of the frame is now increased by the weight of the liquid raised above the level surface. As the frame is raised, the weight increases for a time, then suddenly decreases, passing through a distinct maximum. Call w'' the total maximum weight. The net maximum weight is

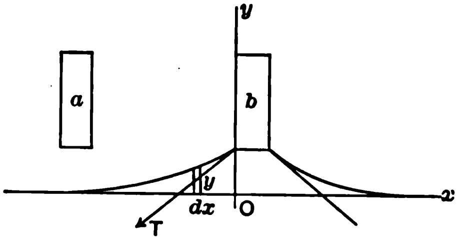

Fig. 1.

$$w = w'' - w' = 2T \sin \alpha + \rho t y, \qquad (1)$$

where T = the surface tension in grams per centimeter;

α = the angle between the X-axis and the tangent to the liquid surface at the edge of the frame;

t = the thickness of the frame;

ρ = the density of the liquid;

y = the height of the frame above the liquid surface;

l = the length of the frame, one centimeter.

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[1] Philosophical Magazine, November, 1893, p. 402.

Also,
$$T \sin \alpha = \rho \int_{-\infty}^{0} y dx, \qquad (2)$$

$$\frac{dx}{d\alpha} = \frac{T \cos \alpha}{\rho y}.$$

Placing $c^2 = \frac{T}{\rho}$, and temembering that $\frac{dy}{dx} = \tan \alpha$,

$$\frac{dy}{d\alpha} = \frac{c^2 \sin \alpha}{y};$$

$$y^2 = -2c^2 \cos \alpha + k.$$

When $y = 0$, $\alpha = 0$, and $k = 2c^2$.

$$\therefore\ y = 2c\sqrt{\frac{1 - \cos \alpha}{2}} = 2c \sin \frac{\alpha}{2}; \qquad (3)$$

$$\cos \frac{\alpha}{2} = \sqrt{\frac{4c^2 - y^2}{4c^2}}; \qquad (4)$$

$$\cos \alpha = \frac{2c^2 - y^2}{2c^2}. \qquad (5)$$

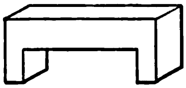

Fig. 2.

Let us now suppose that the frame has vertical legs (as in Fig. 2) extending downward into the liquid. Let l be the length between the legs.

Equation (1) becomes

$$w = 2T(l - t) \sin \alpha + \rho tly, \qquad (6)$$
$$= 2\rho c^2 (l - t) \sin \alpha + 2 lt\rho c \sin \frac{\alpha}{2}.$$

When w is a maximum, $\frac{dw}{d\alpha} = 0$. Let t be very small compared with l, then

$$2c \cos \alpha + t \cos \frac{\alpha}{2} = 0.$$

Eliminating α by (4) and (5), and inserting the value of c,

$$y = \sqrt{\frac{2T}{\rho} - \frac{t^2}{8}} - t\sqrt{\frac{T}{2\rho} + \frac{t^2}{64}}.$$

When t is small, a near approximation is

$$y = \sqrt{\frac{2T}{\rho}}. \qquad (7)$$

Supplying this value of y in (6), and solving for T,

$$T = \frac{w}{2(l - t)} + \frac{\rho l^2 t^2}{4(l - t)^2} - \frac{lt}{4(l - t)^2}\sqrt{\rho^2 l^2 t^2 + 4w(l - t)\rho}. \qquad (8)$$

Table II. gives the value of T calculated by the above formula for mica frames varying in thickness from 0.0013 cm. to 0.02067 cm.

Mr. Hall, in his investigation, used glass frames (made of cylindrical glass rods) of the shape indicated in Fig. 3. He deduced for them equations corresponding to (6), (7), and (8). He admits, however, that these equations are so complicated as to be almost unmanageable, and that the correction is obtained more easily by determining the constants of a frame by using frames of different length and of the same diameter, and again, of the same length but of different diameters. It is very difficult indeed to make such frames, and to use them after they are made.

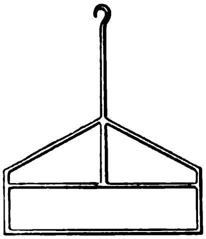

Fig. 3.

The chief objections to glass frames may be summed up as follows: —

> The value of y, and hence the correction that must be applied to the maximum weight in order to obtain the true film weight which measures the tension, depends in a very complicated way upon the diameters of the rods of the frame.
>
> This correction forms a considerable part of the total maximum weight (see Table I.). Frames cannot be made sufficiently rigid and less than 0.03 cm. in diameter. Hence the correction is at least 10 per cent of the whole.
>
> The frames are difficult to make and they require delicate handling at every stage.
>
> With cylindrical end rods the actual length of the film surface is uncertain.

It occurred to me that these troublesome corrections and inaccuracies might be partially avoided by using a different kind of frame. After experimenting with frames of various materials, among which I may mention thin sheet glass, platinum, aluminum, and mica, I found that the latter offered decided advantages over glass. The general shape of the mica frame is given in Fig. 4. The frame is supported by a forked glass stem, and the method of using is exactly as with a glass frame.

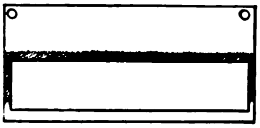

Fig. 4.

My first frames were made by cutting the mica sheet as it lay under a steel rule upon a piece of plate glass. I afterwards had made two heavy steel plates of the exact shape of the frame desired. The inner surface of each plate was ground plane with emery dust upon plate glass. A sheet of mica was clamped between them and cut to their dimensions. The advantages of frames made in this way are:

> The steel plates are accurately ground; the frames are correspondingly regular.
>
> The mica does not split along the cut edge.
>
> The edge is of the same thickness as the plate itself; there is no bur. Very thin frames are easily made, but it is difficult to work with them when they are much less than 0.002 cm. thick.

A difficulty experienced with the mica frame, as also with those of platinum and aluminum, is that the fluid does not readily and equally wet all portions of the surface. It has a tendency to collect in drops, rendering the after-weighing uncertain. This difficulty was entirely overcome by roughing the surface (darkened in Fig. 4) of the plate near the edge by rubbing very lightly with the finest French emery paper. Both weights could then be taken again and again with a variation of only a few hundredths of a milligram.

The advantages claimed for the mica frame are as follows:

1. They are easily made, and do not require careful handling.
2. They are of even thickness, with straight edges and square corners. Hence the film length is not so uncertain as with glass frames.
3. They can be made less than one-tenth of the thickness of a glass frame, reducing the correction correspondingly. Table I. gives the relative corrections for glass and mica frames, obtained by determining the maximum weight for a soap solution, and then weighing the film itself. The film weight divided by twice the length of the frame gives the surface-tension. But with many liquids it is impossible to obtain the film weight, as the film breaks immediately after it is formed. The maximum weight can be determined in almost every case, and the film weight by correction. It is evident that a slight error in the value of this correction will be lessened by reducing the total correction, as is done by using the mica frame.

TABLE I.

Kind of frame.	l	t	w	Film weight.	Per cent difference.
Glass . . .	6.346	0.0405	0.39226	0.34100	15
Glass . . .	7.584	0.0510	0.48283	0.40302	19
Glass . . .	10.163	0.0620	0.65420	0.53700	21
Glass . . .	7.475	0.0920	0.52480	0.39660	32
Mica . . .	6.012	0.0030	0.31202	0.30697	1.6
Mica . . .	5.301	0.0051	0.27776	0.27092	2.5
Mica . . .	5.140	0.0079	0.27222	0.26260	3.7

A fresh solution was used in the last three measurements.

4. The correction varies directly as the thickness of the frame; Fig. 5. Observations with two frames of varying thickness are sufficient to determine the actual film weight and hence the tension.

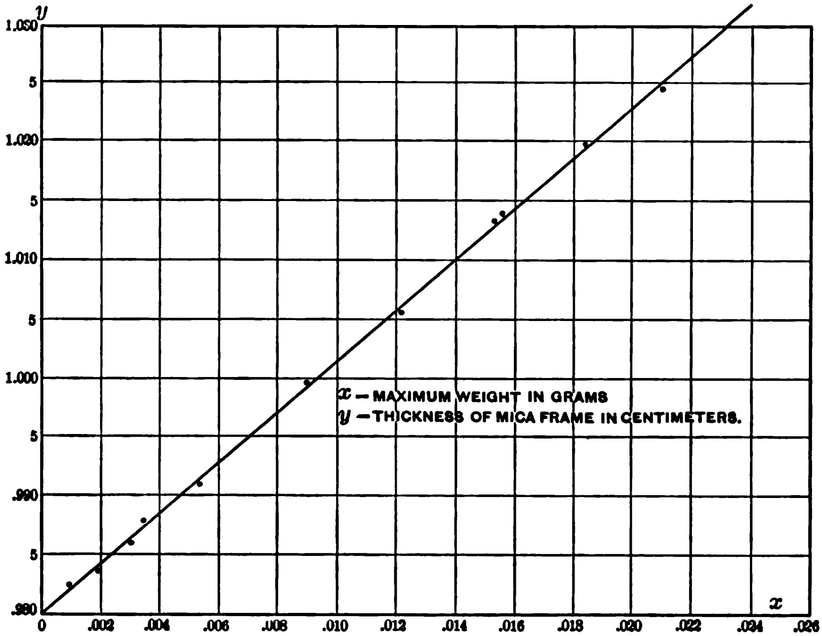

Fig. 5.

5. In the case of thin frames the tension can be determined at once from the maximum weight uncorrected, with results that vary less than do those obtained by the method of capillary tubes. For example, compare Table II. with Table III., the latter giving selected results obtained by Quincke by the capillary tube method.[1]

6. As y and t are small, a small error in the assumed value of ρ will not appreciably affect the calculated value of T, Eq. (6).

y being small, the film is much narrower than with a glass frame. Therefore there is less temperature change due to evaporation from the film surface, and less absorption of gases and impurities from the air.

7. The equations for w and y are not so complex that they cannot be used. In Table II. are given the values of T deduced by formula (8). It will be noted that the last frame is about sixteen times as thick as the first, yet the greatest difference in these values is but a little more than one part in two hundred. Of the results for the first four frames, the greatest dif-

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[1] Wiedemann's Annalen, No. 5, 1894, p. 14.

ference is one part in seven hundred. The thicker frames cannot be expected to give such consistent results, as the water tends to creep in between the thin layers of which the mica sheet is made up.

TABLE II.

t	w	T by formula. $T=\frac{w}{2l}$	T by equation (8).	Temperature of water.
0.00130 cm.	0.9826 g.	0.07396	0.07365	20°.7 C.
0.00190	0.9842	0.07408	0.07374	20°.7
0.00352	0.98791	0.07437	0.07372	20°.7
0.00516	0.99094	0.07458	0.07365	20°.7
0.00928	0.99991	0.07527	0.07352	20°.8
0.01206	1.00592	0.07572	0.07355	20°.8
0.01536	1.01358	0.07630	0.07345	20°.9
0.01828	1.01973	0.07676	0.07339	21°.0
0.02067	1.02468	0.07713	0.07332	21°.0

TABLE III.

(Temperature 18°.)

Kind of glass.	Diameter of tube.	Age of tube.	T
Common Jena glass	0.5832	0 hr.	0.07528
Common Jena glass	0.5851	24 hrs.	0.07336
English flint glass	0.5390	2 mos.	0.07490
English flint glass	0.5740	0 hr.	0.07411
Fusible (soft) Jena glass	0.6440	0 hr.	0.07258
Fusible (soft) Jena glass	0.9106	12 hrs.	0.07480

In this experiment I used distilled water from the Chemical Laboratory. Subsequent tests showed that this water contained considerable organic matter.

I have almost completed an investigation of the temperature coefficient of the surface tension of water by the maximum weight and mica frame method. I hope to give the results of this work in a subsequent paper.

PHYSICAL LABORATORY OF THE INDIANA UNIVERSITY.

THE RESISTANCE OF TIN-FOIL AS CHANGED BY ELECTRIC WAVES.

By C. D. Child.

THE results of recent investigations of the effect of electric waves on the resistance of tin-foil by Haga[1] and Mizuno[2] differ from the conclusions of Aschkinass,[3] who first observed this phenomenon. He found that the resistance of a grating made of tin-foil decreased when subjected to electric waves, and was again brought back to its original resistance when jarred or heated. He attributed this to a change in the tin-foil itself. The others ascribe the variation of resistance to a change of contact between consecutive strips. In this they confirm my own experience as given at the Springfield meeting of the A. A. A. S., 1895, and briefly reviewed in the *Electrical World* for Sept. 14, 1895, p. 284. At that time I expressed the hope that the method might be made quantitative. I have failed thus far in carrying out my desires in this respect, but think that it may not be amiss to give the results of my work.

The waves with which I worked were generated from an exciter of the type used by Righi, and were about 5 cm. in length. The exciter was placed at the focus of a parabolic mirror for receiving the waves. The resistance was made by fastening a piece of tin-foil on a block of wood and slitting it in such a way that the current must follow a zigzag path back and forth across it. When the tin-foil was cut so that there was considerable distance between consecutive strips, there was no effect whatever; when it was cut with a sharp knife, so that the consecutive strips were almost in contact, the effect was large.

Several resistances were tried, made in these two ways, but no change of resistance was observed which could not be ascribed to a change of contact between consecutive strips.

To make doubly sure, I folded a narrow strip of tin-foil back and forth on itself with very thin pieces of tissue paper laid between the folds of tin-foil, so that there could be no actual contact between consecutive strips. In this way I folded the tin-foil until it made a pile 2.5 cm. high, but was unable to detect any change of resistance.

Having satisfied myself that the effect was entirely due to change of contact between adjacent strips, I next endeavored to secure more regular effect in order to make quantitative measurements by this means. There is no doubt but that such a change of resistance affords the most sensitive method of detecting electric waves. The use of iron filings by Lodge and

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[1] Wiedemann's Annalen, Vol. LVI., p. 571. [2] Philosophical Magazine, Vol. 40, p. 497.

[3] Wiedemann's Annalen, Vol. LIV., p. 103.

others have shown this conclusively, but the action of the filings has been found to be quite irregular. I found that the regularity of the action of the tin-foil depended largely on the material with which it was fastened to the block of wood. For this purpose I tried several substances, such as shellac, paraffin, mucilage, and beeswax. In order to get good results, it seemed to be necessary that the substance should hold the tin-foil rather firmly, and yet not rigidly. Of those used, beeswax gave the best results. Better results were obtained by having the strips of tin-foil perpendicular to the direction of the electric oscillations.

The pieces of tin-foil used were 2.5 cm. square. I first made them of this size because I thought that there might be a resonance effect. However, difference in size did not seem to affect the results, and I continued to make them of this size for convenience. It was not possible to tell certainly whether one size was better than another, because no two pieces ever worked alike even when they were of the same size, — except that most of them were equally bad. Many of them would be constantly varying in resistance even when there was no mechanical jar nor electrical disturbance that could be detected; and even the best seemed to deteriorate with age.

For qualitative work, such as lecture experiments, the method can be made to give excellent results. Some of the pieces of tin-foil worked with considerable regularity, where the intensity of the oscillations was large, but when the intensity was small, the action was very irregular. I was attempting to work with an effect analogous to that got by a diffraction grating in light. It was not at all difficult to detect such an effect, but one could not be certain of the point at which a maximum was obtained, because of the irregularity in the working of the tin-foil. Unfortunately I could not be sure that the trouble was not largely with the exciter. The exciter was worked by an induction coil with an ordinary magnetic make and break. However, the very great difference between different pieces of tin-foil showed that the trouble was not all with the exciter. Moreover, one could scarcely expect the action to be regular. The resistance was connected so as to be one arm of a Wheatstone's bridge, and by keeping the connections closed at the same time that the tin-foil was being acted upon by the electric waves, one could easily watch the effect. In general, the effect was greater the longer the time during which the waves acted upon it, but there was by no means a constant change. A large change would often take place very suddenly, as indicated by the throw of the galvanometer needle. This was no doubt caused by some more violent oscillation of the exciter, and if it were possible to have exactly the same action of the exciter at all times, the change in the tin-foil would have been regular. One spark larger than usual would often produce a greater effect than would be produced at another time by long-continued action of the exciter, and a method of detecting electric waves can hardly be relied upon, when some slight irregularity in the exciter is liable to produce such large effects.

However, to show of what the method is capable, two series of readings are given below, taken when endeavoring to measure wave-lengths by means of a diffraction grating. By watching the galvanometer indicating the resistance of the tin-foil, it was usually possible to bring it back to its original resistance. I would measure its resistance, allow it to be acted upon for six seconds, and again measure its resistance. While the oscillations were occurring, the connections to the tin-foil were broken as near to it as possible; for I found that otherwise waves were liable to be caught up by the wires running to the bridge and its connections, and brought to the tin-foil, thus making its action still more irregular. In one case the initial resistance was 7.3 ohms. The changes in five consecutive readings, when the circumstances were apparently the same, were approximately 0.98, 0.71, 0.73, 1.18, 0.62 ohms. At another time, when the intensity of the waves was not so great, the resistance decreased as follows, 0.28, 0.38, 0.66, 0.79, 0.38. These are measurements which I took on the effect through a grating, which we may call a diffraction grating. They are rather better than the average.

My conclusion is that the method is an excellent one for qualitative but not for quantitative work.

NEW BOOKS.

Hydrodynamics. By Horace Lamb, F.R.S. Cambridge, University Press, 1895.

It is not difficult to understand the attraction which the study of fluid motion appears always to have had for mathematicians. Whether we look at the practical or theoretical importance of its problems, the mathematical difficulties involved in many of them, the beautiful simplicity of the solution of certain most complex motions, — as, for instance, the motion of ellipsoidal masses of fluid under their own attraction, or of two-dimensional jets with free surfaces, — and, at the same time, the large field for investigation still open, the reason for this interest is not far to seek.

The first connected treatise on the subject of any worth, in English, was Lamb's *Treatise on the Motion of Fluids*, published in 1879. This was followed, in 1888, by Basset's well-known and valuable *Treatise on Hydrodynamics*, and now we have what is practically a revised and greatly enlarged edition of Lamb's original treatise, but so altered that the author has thought it well to make a change in its title. The 258 pages of the original have expanded to 604. The chief additions are in the treatment of the Motion of Solids through Liquids (from 36 pages to 105 pages), Wave Motion (42 pages to 230 pages), Viscosity (16 pages to 84 pages), and a new chapter on the Motion of Rotating Masses of Liquid. It will thus be seen that the bulk of the new matter is on Wave Motion. So great, indeed, is this increase that this portion may be regarded as a monograph on the subject. It is, perhaps, to be regretted that the extension should be so one-sided, as the author has thereby been compelled, in order to bring the book within reasonable compass, to omit much important matter in other branches. The due selection of matter from such a wealthy storehouse of results, is not easy, and each writer will have his own preferences. In any text-book, general principles must, in any case, take a prominent place. In this respect, the treatise is a model of clearness, and cannot be too highly praised. But a mathematical text-book ought not to be a mere repertory of known facts, but an armory of weapons for further investigations. Two canons should then govern the selection of matter: is the result important in itself? does it exemplify a method? Many a problem, of small interest in itself, becomes of importance as an example of a particular method.

One could wish that, in this last respect, the treatment had been fuller. Clebsch's representation of the velocity by three functions, ϕ, m, ψ, where

$$udx + vdy + wdz = d\phi + md\psi,$$

is wanting. The general method of curvilinear co-ordinates, and the method of images, are only slightly touched on. The only example of Lagrange's method of dealing with fluid motion is the artificial wave form of Gerstner, whilst in Dirichlet and Dedekind's treatment of the motion of an ellipsoidal mass of fluid, a most striking illustration might have been given. In Chapter IV., it would have been preferable to *deduce* solutions instead of taking functions satisfying $\nabla^2\psi = 0$, and seeing what boundary conditions they satisfy. For instance, in the case of the elliptic cylinder, the opportunity is lost of introducing the method of elliptic curvilinear co-ordinates, and deducing from the general solution of $\nabla^2\psi = 0$, in these co-ordinates, the proper form for translation, rotation, or any surface motion whatever. We could have dispensed with much of the new matter on waves if thereby we could have had Kirchoff's treatment of the motion of a solid of revolution, a much fuller treatment of the motion of two bodies, of vortex motion, and especially of the motion of ellipsoidal masses of fluid. The author has apparently made it a rule to omit any investigation in which elliptic functions enter. This is unfortunate, as many solutions are most elegantly expressed in these functions — witness the motion of two parallel cylinders; it is also unnecessary, as a knowledge of the elements, at least, of these functions is possessed nowadays by all mathematicians.

One most valuable feature of the book is the number of diagrams of stream lines introduced. Nothing gives a clearer idea of what is taking place than this translation of formulæ into visible form. Compare, for instance, the stream lines for the cylinder given on pages 86 and 87 with those for the sphere on pages 137 and 265; or examine the lines of motion of a symmetrical body in a plane, in which for the first time the correct form is given. The diagram illustrating the effect of viscosity on wave motion of a finite depth, again, is most instructive. Most of these are due to the author himself. In fact, the reader already acquainted with the subject is not only pleased with the way in which old friends are introduced, but with frequently occurring bits of new work which the author modestly allows him to pick out for himself.

The two or three deviations from ordinary usage introduced by the author are scarcely to be commended. It is always a great advantage, not only in working out results, but also in interpreting them, to choose functions which have a definite physical meaning, a magnitude which is mentally seeable, and which has a direct reference to the subject we are dealing with.

Professor Lamb confesses that it is with some hesitation that he has used throughout the reversed sign for the velocity potential. His reason is that thereby it represents, when multiplied by the density, the impulsive pressure which will generate the motion from rest, and also that it is then analogous to the magnetic potential. But by the old usage it represents the flow of liquid along a line between two points, *or* the momentum per sectional area in a small uniform tube between the points. It follows at once that to generate this an impulse must be applied equal to the momentum. We can therefore much more clearly form a visual picture of the distribution of its value, and interpret results more easily with this conception, than with the new one. That it may have an analogy with the magnetic potential is no help whatever in hydrodynamical work. By all means seek for analogies; but for actual use in investigations let us employ the simplest ideas natural to the subject in hand. These remarks are illustrated again by the new definition given to a source or sink. Surely the natural measure of a source is the number of cubic centimeters or the number of grams issuing from it per second. But this would spoil the analogy with electrostatics. Therefore it is proposed that the unit source shall be one which delivers 12.566··· cubic centimeters per second. It is a curious inversion of the 4π-mania from which some eminent electricians suffer. These, instead of taking the idea natural to their subject, and defining the unit of electricity so that two units at a distance of one centimeter repel with a force of one dyne, desire to alter it so they shall repel with a force of $1/16\pi^2$ dynes, and this to make the electrostatic unit analogous to a source. For the same purpose of analogy with a foreign subject also, the letters F.G.H. are used to denote the component of the vector potential, in place of L.M.N. introduced by Helmholtz, and used by all writers in hydrodynamics since. As in the former case, mutual courtesy should induce the 4π-electricians to use L.M.N. instead of F.G.H.

On the contrary, the author conforms to common usage in one respect in which a change might be desirable. Stokes' stream function is defined as the total flux through a circle divided by 2π, so that the velocities are given by

$$u = -\frac{1}{r}\frac{d\psi}{dr}, \quad v = \frac{1}{r}\frac{d\psi}{dy}.$$

There is much to be said in favor of defining it as the flux itself. ψ then has a definite meaning. It is clear at once that, since the energy due to a thin vortex (ωdS) is that due to the initiating impulse on the diaphragm filling its aperture:

The energy

= impulse × change of flux,

= momentum in closed uniform tube bent round the vortex × flux,

= circulation × flux = $\omega dS \times \psi$.

Wherever ψ enters, it tells its own tale. The only argument for the usual definition is that the expressions for the velocities are simplified. This is so, but only with the effect of complicating other expressions by bringing in 2π where it has no meaning; *e.g.* the energy is now $2\pi\omega\psi dS$.

After all, perhaps, these points are merely matters of taste. There is no doubt that in the book before us Professor Lamb has produced a most valuable addition to mathematical literature which should find a place in every mathematical library.

W. M. Hicks.

Elements of the Mathematical Theory of Electricity and Magnetism. By J. J. Thomson, F.R.S. 8vo. pp. 510. Cambridge, The University Press, 1895.

The program, admirably carried out in this elementary treatise, is stated in the introduction. "For in the simple cases," says the distinguished author, "the absence of analytical difficulties allows attention to be more easily concentrated on the physical aspects of the question, and thus gives the student a more vivid idea and a more manageable grasp of the subject than he would be likely to attain if he merely regarded electrical phenomena through a cloud of analytical symbols."

The mathematical apparatus employed is of the simplest kind, and it is employed, not for the purpose of enabling the student to obtain results quickly by making short cuts in his physical reasoning, but only as a record of the results obtained by a purely physical method of analyzing physical phenomena. His attention is riveted upon the physical law describing what is going on in the elements of space and time, and not upon the differential equation, which is only a symbolic statement of this law, and hence "eine Nebensache," as the German saying goes.

The passage from the infinitesimal elements of the phenomena to the phenomena themselves, such as we perceive them, is not treated as a mere mathematical process of integration. The student is trained to build up synthetically the finite from the infinitely small by examining carefully what is going on in every one of the elements which he is summing up. For instance, the theorems concerning transformations of surface integrals into line integrals, or of volume integrals into surface integrals, are valuable labor-saving machines in the hands of an advanced mathematical physicist. To a young student of mathematical physics they are perplexing puzzles, unless he has been taught first how, for instance, to build up the magnetomotive force around a finite closed curve from the currents which pass through the various elementary areas of a surface bounded by that curve, etc. It is this synthetic building-up which Professor Thomson substitutes in place of abstract mathematical theorems. Such a treatment keeps the student continually in touch with the phenomena; it makes him a mathematician by teaching him how to apply physics to mathematics.

The classification of the phenomena is the usual one; it is in accordance with the historical order of development. The statical phenomena are discussed first, the current comes next, and the phenomena of electromagnetic induction in conductors and dielectrics follow last. More than half of the book is devoted to statics. This will probably displease the engineering student; but it should be remembered that our knowledge of the two most important physical constants of the electromagnetic field, that is, of specific inductive capacity and magnetic permeability, is derived from these statical phenomena. Besides, tubes of induction, especially those of electric induction, have a much deeper meaning in Professor Thomson's view of electromagnetic phenomena, and play a much more significant part than is usually attributed to them. Our ideas concerning these tubes can be derived most easily from a study of statical phenomena. Those who have followed carefully Professor Thomson's investigations within the last few years will be delighted with his electrostatics and magnetostatics as given in this elementary treatise.

The phenomena of electrolysis, and Faraday's laws relating to these phenomena, form the foundation on which Professor Thomson builds what one may call the mechanical model of the electric current. Those who are acquainted with his theory of moving electrostatic tubes, which, as a rule, have their ends attached to the atomic charges, would naturally expect him to emphasize the intimate relation between the electric current and the chemical effects accompanying it. A very forcible and exceedingly clear statement of this relation will be found in the chapter on electric currents.

The discussion of the magnetic field which accompanies an electric current is very brief, but, nevertheless, it is clear and complete. The same may be said of the discussion of magneto-electric induction in conductors. The application of the fundamental laws of induced electromotive and of the magnetomotive force to the theory of alternating currents will probably be considered as too brief to satisfy the needs of electrical engineering students. It may be answered, however, that this is not a book on electrical engineering, and that a student who has mastered this book will find no difficulty whatever in rushing through any one of the many voluminous treatises on alternating current generators, transformers, and motors. The distribution of alternating electric and magnetic forces in the interior of conducting masses is beautifully worked out, and will be much appreciated. This is probably the first time that this extremely interesting subject has been discussed in an elementary treatise.

The chapter on electrical units is not shrouded in that sepulchral gloom which generally accompanies every discussion of units. This is due to the fact that the interesting theory of the various methods of absolute measurement has been assigned to this chapter.

The chapter containing Maxwell's electromagnetic theory in general, and the electromagnetic theory of light in particular, is so interesting that the young student will undoubtedly regret that Professor Thomson has not made this chapter longer. But he can console himself with the idea that if this book has not given him the whole story of the modern achievements of the electromagnetic theory, it has certainly prepared him to hear and appreciate this story.

An elementary book like this, by so eminent an authority as Professor Thomson, contributes almost as much to the progress of science as an important discovery. Teachers and students of electricity should not be without it.

M. I. Pupin.

Crystallography, a Treatise on the Morphology of Crystals. By N. Story-Maskelyne, M.A., F.R.S. 12mo, pp. 521 + xii. Oxford, Clarendon Press, 1895.

As indicated by the sub-title, the author's aim is a complete discussion of the external form of crystals; and it may be said at the outset that nothing in English equals this book as regards detailed treatment of geometrical crystallography.

In the first chapter is given a very brief sketch of the general properties of crystals. This serves as an introduction to the more special study of their forms.

Chapters II., III., IV., and V. deal with crystal planes and axes, and with the mutual relations of the same. The treatment, as required by the nature of the case, is almost purely mathematical. It is in most respects clear and thorough, and will be found very useful to those who wish to supplement an elementary knowledge of the subject. The foundation here laid is, naturally, specially adapted to use in the later portions of the book; yet the discussion of Miller's symbols and of the possible kinds of crystal symmetry will be appreciated by any who wish to consider these subjects apart from the rest of the book.

The following chapter is divided into two sections,—one devoted to mero-symmetry (a term coined to designate all kinds of symmetry except six, viz., the highest symmetry possible in each of the six systems) and the other to twin crystals. It seems unfortunate that two subjects which are so pre-eminently matters of crystal structure should be treated from the standpoint of their external form, but this is in accord with the plan of the book, and the author is consistent in carrying it out.

In Chapter VII., which occupies 200 pages, the six crystal systems are described in detail. All the possible crystal forms are classified and named. At the end of the description of the forms in each system, several articles are devoted to the subject of twin crystals. Though no mention is made of ogdohedrism (the author would call it ogdo-symmetry), nevertheless this peculiar type of symmetry is duly noticed under the heading "Tetarto-systematic Haplohedral Forms" in the hexagonal system.

Chapter VIII., on the measurement and calculation of the angles of crystals, contains a very good description of some kinds of goniometers and their use, as well as methods of calculation which may be of service to such as desire help in this line.

The final chapter presents an extremely satisfactory *résumé* of the various methods of representing crystals, though parts of it may be found rather too condensed to be appreciated by the beginner.

The book as a whole may be characterized as independent and thorough. Its independence lends freshness and interest, to be sure, though in several respects it may also be found by some to detract from its value as a book of reference. For instance, no allusion is made to the symbols used by Naumann, Weiss, Lévy, or Dana in designating the position of planes on a crystal, although all these are simpler than Miller's. This is no oversight. The author simply (and rightly) considers Miller's method the best, and uses it. Yet three of the above-mentioned systems of symbols are still in use by crystallographers, and the fourth is found of service to beginners.

The terms *hemihedral* and *hemihedrism* are not discussed. They are replaced by words designating the symmetry. The new nomenclature can hardly be said to be an improvement on the old, so far as the significance of its derivation is concerned, as there is no more reason for calling the symmetry of calcite a *partial* symmetry, than there would be for designating the symmetry of axinite in the same way. Each substance crystallizes with the *full* symmetry belonging to itself, without reference to the greater or less symmetry which may be manifested by other substances.

The author's use of the words *merohedral* (p. 159) and *clinopinakoid* (p. 358) in a sense entirely new is certainly not defensible, and the omission of all reference to alternative names for the six systems may also be criticized, especially in the case of the sixth, which is much more generally called triclinic than anorthic. Yet only the latter name appears in the book. Reference may also be made to the employment of the Greek letters ξ, η, and ζ instead of the more usual α, β, and γ, in designating the angles between the axes. On the whole, the book may be said to lose more than it gains by its independence in the matter of terminology. Yet the words ***haplohedral*** and ***diplohedral,*** denoting the absence or presence of parallel planes in a crystal form, would seem to have good reason for existence.

In the matter of clearness the book is frequently at fault through a combination of long sentences with cumbersome technical words. More rarely a misprint or a word wrongly used is responsible for the difficulty. An example may be quoted from p. 156. "When we turn to the natural polyhedra presented in crystals in order to determine to what extent these actually accord in their geometrical characters with the crystalloid systems hitherto considered, we cannot fail to recognize that whereas the crystallographer, guided heretofore solely by observation and experience, referred every crystal to one or other of six crystallographic systems, those systems furnish precisely the several types of symmetry which coincide in their distinctive features with the six crystalloid types of symmetry resulting from the above principle;" viz., that there are only four possible varieties of isogonal zones in a ***crystalloid system.*** If the above sentence was not intended to call attention to the coincidence between the independent results of the crystallographer and of the mathematician in establishing six crystal systems, the reviewer has not yet fathomed it.

A. C. GILL.

Electricity and Magnetism, a Mathematical Treatise for Advanced Undergraduate Students. By FRANCIS E. NIPHER. 8vo, pp. 426. St. Louis, Boland Book Co., 1895.

This book occupies a field in electrical science that is of fundamental importance, but which has not been covered satisfactorily by existing literature. The older treatises, of which that of Mascart and Joubert may be taken as an example, were based upon objects and methods that antedated the remarkable development of electrical applications during recent years. It might be said that the science of electricity, considered from the purely mathematical or physical standpoint, is entirely independent of practical applications; nevertheless the fact remains that this progress, commercial though it may be, has produced the greatest stimulating effect that any science ever received. Even in such apparently abstract subjects as those of rational units and definite terminology, their appreciation and general adoption are due far more to this influence than to all others combined. Furthermore, many of the most earnest and most successful students of electrical science are those who are preparing themselves for a career in its engineering branches; therefore it is reasonable to expect that the instruction not only in technical schools, but also in courses of pure science, shall be in harmony with and lead up to the practical applications. Even those students who intend to devote themselves to the theoretical side of electricity are much benefited by and are usually anxious to acquire at least a general knowledge of the dynamo, motor, and transformer. There are many works on special subjects which are essentially mathematical in character, but so far as the reviewer is aware, this book is the first general treatment of the mathematical principles of electricity and magnetism which leads directly up to electrical engineering, but only goes into it to the extent of giving a few practical examples. Professor Nipher therefore deserves credit as a pioneer in a most important direction. His work is also to be commended for features which show ability and experience in the art of teaching. For example, the subjects of potential and energy are introduced and explained in connection with gravitation. This not only gives a definite and well-grounded conception, but also broadens the view of the electrical student, who is apt to think that potential is confined to his particular science. The frequent use of concrete numerical examples is still another great aid to the student as well as to the instructor. The scope of this book shows good judgment; that is to say, the point at which it begins and the previous knowledge assumed, as well as the limits reached, are well suited to the majority of students who are likely to use it.

Nevertheless, there are several features which are open to question or criticism. The most prominent of these is the excessive amount of matter. While four hundred pages is not an unusually large number for a text-book, nevertheless the subject is somewhat difficult and is given in condensed form, so that it would not be practicable to cover more than a few pages in one lesson. Moreover, it would have been perfectly possible to considerably reduce the length without sacrificing anything essential. For example, in the chapter on electrostatics some of the cases of potential, distribution of charge, etc., under various conditions, might have been omitted.

The old-fashioned conceptions and methods relating to magnetism, such as susceptibility, magnetic moment, etc., might have been abridged without material loss. In fact, the modern way of treating the magnetic circuit in terms of flux, M.M.F., and reluctance is not incorporated in the book as freely and completely as present custom warrants. In this connection, the idea of surface charge or distribution of magnetism used by Professor Nipher is unnatural and perpetuates the geometrical methods of treating this subject, including poles, straight lines of force, and other conditions which rarely if ever exist and differ so radically from the more modern views of the "closed loops" of Faraday.

The author's definition of current in terms of its magnetic effect is very abrupt and hardly satisfactory to the majority of minds, and the same is true of the manner in which the subject of alternating currents is introduced.

The book would have been improved by giving references to authorities and sources of information, not only to assist and encourage those who wish to pursue their studies further, but also in simple justice to writers from whom much material was derived. The fact that it is an elementary and not an advanced treatise is not a valid answer to this criticism.

In spite of these objections this book is a fairly successful attempt in a new and yet very important direction, and should be welcomed by those interested in education in electrical science, particularly when it forms part of an engineering course.

F. B. CROCKER.

Notes on the Nebular Theory. By WILLIAM FORD STANLEY. 8vo. pp. 260. London, Kegan Paul, Trench, Trübner & Co., 1895.

This book of 260 pages contains the speculations upon the Nebular Theory of a gentleman not a professional astronomer, who has evidently devoted much thought to the subject. Nevertheless, it is difficult to regard the work as a positive contribution to our knowledge of cosmogony. The author states in the preface that he has been led "to the conclusion that a modified form of the Nebular Theory of Laplace might be established on some new ideas which I had formed, and by certain calculations that I felt sure the actual conditions warranted."

The treatment of the subject is not mathematical, and, except for some fifteen pages of historical notes upon the theories of Wright, Kant, Laplace, and later philosophers of cosmogony, the book is merely a statement — and not always a clear one — of the numerous ideas that have occurred to its author. It cannot be said that these ideas are based upon our present knowledge of astronomy, mathematics, and physics, to the degree that would be expected in a book upon such a subject as this. The strong confirmation of the general theory of Laplace that has been furnished by recent spectroscopic researches seems to have been overlooked. A chapter is given to a "discussion of the mechanical principles upon which our solar-planetary system may have been formed," but many of the views advanced cannot be harmonized with the laws of mechanics. Although the margins of the reviewer's copy of the book are quite fully occupied with exceptions taken to the author's statements, yet it seems hardly worth while to cite them in detail here.

The author's style is not lucid; in fact, his language is so greatly clogged with words that it is often very difficult to grasp the idea presented, even after repeated readings of the passage. We give an example, without selecting an especially conspicuous one. "In this case, with proportional time-condensation, under the increasing amount of tangential impulse due to centralized condensation into gravitation, which produces the law of orbit, the distances of the planets from the sun and their separate masses would be symmetrically proportional, in accordance with the pull of gravitation and the tangential momentum of the amount of the condensed matter" (p. 66). On p. 105, the term *iridescence* is used where irradiation is obviously the phenomenon referred to.

Under the chapter devoted to "Comets considered as Ordinary Gravitative Matter in Rotation constructively as a Part of the Planetary System," we read: "These ideas will be now reproduced, with some extenuations that appear to me necessary in reconsidering the subject." Among the ideas requiring "extenuation," we cite this: "If the comet depart through some disturbance from its law of original construction, its matter may present afterward only what we may term a specialized confusion, too complicated to discuss by the most advanced science" (p. 127).

Something more than the last third of the book is occupied with geological theories, upon which the reviewer can express no opinion, although decided exceptions must be taken to the astronomical speculations upon which the succession of geological periods is based, in the chapter entitled "Periodic Conditions of Earth-formation produced by effects incidental to the Nebular Clouding at Inferior Planetary Formation, and at Critical Temperatures of Matter surrounding the Sun."

The typographical appearance of the book is excellent.

EDWIN B. FROST.

Mechanics and Hydrostatics. By R. T. GLAZEBROOK, F.R.S. 8vo. pp. 244, 176, and 208. Cambridge, The University Press, 1895.

This volume consists of three parts,—Dynamics, Statics, and Hydrostatics, each with its own paging. The parts may also be obtained separately. A notice of the series and a review of Dynamics has been given in the PHYSICAL REVIEW, Vol. III., No. 3.

Analytical Chemistry. By N. MENSCHUTKIN. Translated by JAMES LOCKE. 8vo, pp. xii, 511. London, Macmillan & Co., 1895. *Received.*

Elementary Mensuration. By F. H. STEVENS. pp. 243. Macmillan & Co., 1895. (*Received.*)

Elements of Physics: a College Text-Book. By EDWARD L. NICHOLS and WILLIAM S. FRANKLIN. In three volumes. Vol. I., Mechanics and Heat. pp. 228. Macmillan & Co., 1895.

Vol. II. (Electricity) and Vol. III. (Sound and Light) are in preparation.

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THE PHYSICAL REVIEW.

SOLIDS AND VAPORS.

By Wilder D. Bancroft.[1]

WHEN a substance, having no appreciable vapor-pressure of its own, is dissolved in a liquid, the vapor-pressure of the solution is less than that of the pure solvent. From this it follows that if two beakers, one containing a salt solution and the other pure water, be placed under a bell-jar, the water will all distill over into the beaker containing the solution,[2] provided that we leave out of account any effect due to gravity. A further conclusion is that all substances are deliquescent in presence of the saturated vapor of a liquid in which they are soluble. As a striking example of this I have taken the blue double salt, $CuCl_2\ 2\ KCl\ 2\ H_2O$. This salt was placed in a test-tube above absolute alcohol, so that any liquid that condensed upon it might flow back into the bottom of the test-tube again. The result was that the cupric chloride was dissolved out, leaving the white potassium chloride behind.

As the vapor-pressures of pure water and of a saturated salt solution are functions of the temperature only, it follows that, if the other conditions are kept constant, water must condense on the salt solution at an uniform rate so long as any of the solid salt is

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[1] In my paper on the Chemical Potential of the Metals, Physical Review, Vol. III., p. 253, 1896, I overlooked very carelessly the definite assumption of Nernst, Zeitschr. f. phys. Chem., 4, p. 149, 1889, in regard to the anion.

[2] Cf. Beyerinck, Zeitschr. f. phys. Chem., 9, p. 264, 1892.

present. I tried the experiment at first very roughly by putting a little ammonium chloride in a small porcelain crucible, which was then placed in a desiccator containing water instead of sulfuric acid. The whole was left at room temperature; the crucible was weighed from time to time, and the gain in weight noted. While there could be no doubt but that the ammonium chloride would absorb water, I was not at all sure that the amount absorbed in a given time would be enough to make the experiment of any value. In this I was agreeably surprised, as I found that under these circumstances the salt gained water at the rate of about twelve milligrams per hour. The rate of absorption is dependent on the difference of pressure between the solvent and the solution, on the areas of the evaporating and condensing surfaces, and on the rate of diffusion of water-vapor under the conditions of the experiment. Whether there is also an effect due to the specific nature of the dissolved substance apart from the vapor-pressure of its saturated solution is not known. Such an effect would be entirely contrary to our present ways of looking at things; but that does not prove its non-existence. With so many factors to be taken into account, it is very difficult to make absolute measurements. On the other hand, it is a comparatively simple matter to make relative determinations which are entirely satisfactory for a great many purposes. The uncertainty as to the amount of surface of the solid salt can be obviated by having a saturated solution in a cylindrical vessel so that the condensation takes place on a liquid surface only. By setting up the apparatus always in the same way, it would not be necessary, so far as purposes of direct comparison go, to know the areas of the evaporating and condensing surfaces nor the term due to the rate of diffusion. Mr. Parker has kindly made one set of determinations for me at constant temperature to show that under uniform conditions one actually gets a constant reaction-velocity. The salt taken was ammonium chloride, and the temperature was 35°. The results are given in Table I. The last determination was made when the solution was no longer saturated, all the salt having been dissolved. As was to be expected, the rate of condensation has decreased, owing to the increased vapor-pressure of the solution.

TABLE I.

No. of hours.	Gain per hour.	No. of hours.	Gain per hour.
24	0.039 g.	49	0.044 g.
25	0.040	23	0.041
71	0.036	25	0.042
48	0.042	24	0.042
71	0.042	25	0.031

The results agree as well as one could wish under the circumstances. It would doubtless be possible to get more accurate results by stirring the solution so that there should be no differences of concentration in the liquid. This method gives an easy and fairly accurate measurement of vapor-pressures of salt solutions, and I hope before long to communicate some interesting applications of it.

We are now able to state the conditions under which deliquescence will take place. An anhydrous salt is permanent if the concentration of the water-vapor is equal to or less than the vapor-pressure of its saturated solution. It is deliquescent if the pressure exceeds that value. With hydrated salts the case is a little different, because they can also lose water. It is well known that below a certain pressure of water-vapor they effloresce. If the concentration of water in the vapor space becomes greater than that corresponding to the saturated solution, they will deliquesce. Do these two concentrations coincide, or is there an interval over which the salt is permanent and in indifferent equilibrium with the vapor? In other words, does a hydrated salt have the same vapor-pressure as the solution with which it is in equilibrium? I have been unable to find any definite statement on the subject in the text-books of Ostwald or of Nernst; but the impression which I get from their writings is that they would probably apply the law of the Substitution of Phases to this case, and would say that the two phases, hydrated crystals and saturated solution, being in equilibrium with each other, must have the same vapor-pressure.[1] I am the more inclined to believe that this is a fair statement of

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[1] Cf. Zeitschr. f. phys. Chem., 1, p. 205, 1887.

their views, because there is no question but that Planck holds this view. He says:[1] "All coexisting solid and liquid phases send out the same vapor." This is the more remarkable because there is abundant evidence that this is not true. Van 't Hoff[2] has shown that slightly effloresced sodium sulfate has a less vapor-pressure than the saturated solution; Roozeboom[3] has stated that the solution and the hydrate cannot have the same vapor-pressure except at the inversion temperature; and Lescœur, while disputing the accuracy of Roozeboom's generalization, brings forward a long series of observations to show that it is true in a great many cases. In Table II. I tabulate some of Lescœur's measurements on the vapor-pressures of hydrated salts and their saturated solutions.[4] It will be noticed that the differences between the two are often enormous. The pressures are given in millimeters of mercury; the temperature is 20°.

TABLE II.

	Pressure in mm. Hg.			**Pressure in mm. Hg.**	
	Solution.	**Salt.**		**Solution.**	**Salt.**
$CaCl_2 6 H_2O$	5.4	2.3	$Na_2CO_3 12 H_2O$ . .	16.0	10.1
$SrCl_2 6 H_2O$	11.4	5.6	$Na_2SO_4 10 H_2O$ . .	15.7	13.9
$MnCl_2 4 H_2O$ . . .	8.0	3.8	$Na_2SO_4 7 H_2O$ . .	15.0	10.5
$NiCl_2 6 H_2O$	8.0	4.6	$MgSO_4 7 H_2O$ . .	14.5	7.3
$CoCl_2 6 H_2O$ . . .	9.0	4.0	$CuSO_4 5 H_2O$ . . .	58.0	30.0
$NaBr 4 H_2O$	9.6	7.6	$MgCl_2 6 H_2O$ . . .	5.7	1.8
$SrBr_2 6 H_2O$	9.1	1.7	$NaI 4 H_2O$	5.4	1.5

It is generally assumed that two phases in equilibrium must give off the same vapor, or that it would be possible to make a perpetual motion machine, but this conclusion is not necessary. Suppose we have a system composed of hydrated salt, solution, and vapor. If the solution has a greater vapor-pressure than the

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[1] Grundriss d. Thermochemie, p. 125.

[2] Zeitschr. f. phys. Chem., 1, p. 185, 1887.

[3] C. r. 110, p. 134, 1890.

[4] Ann. chim. phys. (6), 19, p. 533, 21, p. 511, 1890; (7), 2, p. 78, 1894.

hydrated salt, there will be a tendency for water to precipitate on the crystals; but the effect of this will be to cause some of the salt to go into solution, and at the same time water will evaporate to restore the vapor-pressure of the saturated solution, precipitating the same quantity of salt which has just dissolved. No change has taken place in the system, and there is no surplus energy with which to run a machine. The matter can be seen even more clearly in the limiting case, that of an anhydrous salt in equilibrium with a saturated solution and the vapor thereof. Here there can be no question that we have a solid and a liquid phase coexisting, and that they do not give off the same vapor. With calcium chloride, and still more strikingly with the hydrates of ferric chloride, Roozeboom[1] has shown that the same hydrate can be in stable equilibrium with two different solutions, one containing more water than the crystals, the other less. As the vapor-pressures of the two solutions are not the same, it follows that at least one is different from the value for the hydrated salt, which is sufficient to prove the point. The case does not rest on this alone. We may reach the same conclusion in another way. If we add to a saturated solution of a hydrated salt a second salt having different ions, we shall have more of the first salt go into solution. The solution will now have a less vapor-pressure than before. If the vapor-pressure of the hydrated salt had been equal to the vapor-pressure of its saturated solution, it would be greater than that of the new solution, and the crystals would effloresce, no matter how small the added quantity of the second salt was. In general this is not the case, and I conclude that the vapor-pressure of a hydrated salt is not necessarily the same as that of the solution with which it is in equilibrium. It has been overlooked by every one except Roozeboom and van 't Hoff that in the system, salt, solution, and vapor, there are two kinds of equilibrium represented, the stable and the indifferent. A given solution can have only one vapor-pressure at a given temperature; the concentration of water vapor in equilibrium with an anhydrous or a hydrated salt may have any value between two limits. The reason for this difference is that the concentration of the solution can

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[1] Zeitschr. f. phys. Chem., 4, p. 34, 1889; *Ibid.*, 10, p. 486, 1892.

vary continuously, that of the hydrate cannot. The vapor-pressure of a system containing hydrate, water vapor, and a third phase will depend therefore on the nature of the third phase. The experiments of Roozeboom[1] show that this is so.[2] In Table III. I give his determinations of the vapor-pressures at which $CaCl_2 6 H_2O$ is in equilibrium with different phases, the pressures being in millimeters of mercury.

TABLE III.

Temperature.	0°	10°	20°	25°
$CaCl_2 6 H_2O$, solution, vapor . . .	1.944	3.456	5.616	6.696
$CaCl_2 6 H_2O$, $CaCl_2 4 H_2O\alpha$, vapor .	0.92	1.92	3.78	5.08
$CaCl_2 6 H_2O$, $CaCl_2 4 H_2O\beta$, vapor .	0.76	1.62	3.15	4.32

As will be seen, not only is the vapor-pressure of the saturated solution different from that when there is a solid phase present, but there is a marked difference between the values for the systems $CaCl_2 6 H_2O$, $CaCl_2 4 H_2O\alpha$, vapor, and $CaCl_2 6 H_2O$, $CaCl_2 4 H_2O\beta$, vapor. This discrepancy is a real one, being greater than the probable error of the measurements. The question suggests itself, in view of these facts, whether it is proper to speak of the vapor-pressure of a hydrated salt; in other words, whether it has a true vapor-pressure independent of the nature of the third phase. There is such a value as we may see from the following considerations: Suppose that water and the salt under consideration could form a continuous series of mix crystals, as is the case with the alums. For a given temperature and a given concentration of the solid phase the pressure would be definitely fixed, just as is the case when the equilibrium is between a liquid solution and its vapor. That value is the true vapor-pressure of that crystal. If we bring in discontinuity, we increase the range of pressures at which the hydrate can be in equilibrium, but we do not change the fact that one particular pressure differs from the others, because the equilibrium in that case is independent of the discontinuity in the solid phase. I define the true vapor-

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[1] Zeitschr. f. Chem., 4, p. 42, 1889.

[2] This has been overlooked by Nernst, Theor. Chem., p. 491.

pressure of a given hydrate at a given temperature as the pressure at which it would be in equilibrium if it were one term in a continuous series of mix crystals. This is probably the same as the vapor-pressure of the system containing hydrate, anhydrous salt, or lower hydrate, solution, and vapor in equilibrium, the number of the components in the solution not being limited.[1] If this be true, it follows that as yet only in the cases where the measurement has been made at the inversion temperature can we be sure that we have determined the true vapor-pressure of the hydrated salt, for there is no reason to assume that this value coincides with that usually measured for the equilibrium between hydrate, effloresced product, and vapor.

The fact that the saturated solution often has a greater vapor-pressure than the hydrated salt which crystallizes from it is of great interest as throwing light on some of the peculiarities which have been discovered in regard to the inversion temperature of salts. It is clear that if we add to a saturated solution enough of any substance to bring the vapor-pressure of the solution below that of the hydrated salt in respect to which the solution is saturated, the salt must effloresce. The simplest way to do this is to add a salt having no common ion. The only instance of this which I can now recall is the case cited by Meyerhoffer,[2] that the double salt $CuCl_2KCl$ crystallizes out of solutions containing acetic acid, instead of the double salt, $CuCl_2\ 2\ KCl\ 2\ H_2O$. As I shall have occasion to discuss the mechanism of this reaction more fully under another head, I will only point out that the hydrated double salt ceases to be stable as soon as, by the addition of acetic acid, the partial pressure of the water-vapor in equilibrium with the solution becomes less than the true vapor-pressure of the hydrated double salt. That this instance might not seem an isolated, abnormal case, I have made a few qualitative experiments on other hydrated salts, and have found the phenomenon to be entirely general.

Another means of obtaining the same result, namely dehydration, is to add a substance which increases the number of re-

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[1] Cf. Vriens, Zeitschr. f. phys. Chem., 7, p. 208, 1891.

[2] Zeitschr. f. phys. Chem., 3, p. 339, 1889.

acting weights in solution, though decreasing the solubility of the hydrated salt. This effect may be produced by a non-electrolyte in which the salt is insoluble, or by a salt having a common ion, though it by no means follows that either of these must do it. The dehydrating effect of alcohol on many salts with water of crystallization is too familiar to need more than a reference. That salts crystallize in a more or less completely dehydrated condition from solutions containing an excess of acid is also well known. This has been used as a method for obtaining salts having less crystal water than is normal at the temperature of the experiment.[1] This means that the inversion temperature of that particular hydrate in respect to the solution has been changed, and this phenomenon has been noticed often without any very satisfactory explanation having been given. The reaction

$$MgSO_4\,7\,H_2O = MgSO_4\,6\,H_2O + H_2O$$

takes place at 48°.2 when no other salt is present; at 47°.2,[2] if an excess of $K_2Mg(SO_4)_2\,6\,H_2O$ be present, and at 29°.8,[3] if the solution be also saturated in respect to potassium chloride. Loewenherz[4] has noticed that the inversion temperature is lowered to 25° if, to a saturated solution of magnesium sulfate, magnesium chloride be added in such quantities that the solution contains 73 units of anhydrous magnesium chloride to 1000 units of water, or if magnesium chloride and potassium chloride be added in such proportions as to give concentration of 62 units of $MgCl_2$ and 16 units of KCl per 1000 units of water. We have in all these cases the same phenomenon, addition of another salt or salts reducing the vapor-pressure of the solution below that of the hydrated salt, which thereupon effloresces. The difference in the effect produced by magnesium chloride and by Schönite is due chiefly to the greater solubility of the former, though the relative influence on the solubility of the magnesium sulfate is also a factor. The change of Schönite into potassium astrakanite, corresponding to the reaction

$$K_2Mg(SO_4)_2\,6\,H_2O = K_2Mg(SO_4)_2\,4\,H_2O + 2\,H_2O,$$

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[1] Cf. Ditte, Ann. chim. phys. (5), 22, p. 560.

[2] Zeitschr. f. phys. Chem., 12, p. 426, 1893.

[3] *Ibid.*, 13, p. 489, 1894.

[4] *Ibid.*, 13, p. 480, 1894.

occurs at 92° if there is an excess of potassium sulfate present, and at 72° in presence of an excess of the magnesium sulfate with six units of water.[1] If the solution is not saturated in respect to $MgCl_2\,6\,H_2O$, the inversion temperature may be made to lie anywhere between these two temperatures, depending on the amount of magnesium sulfate in solution. There is no doubt in my mind that still other inversion temperatures could be found by adding other salts to a saturated solution of Schönite. As is well known, $Na_2SO_4\,10\,H_2O$ changes into the anhydrous salt at about 33° if there is nothing else in solution. If an excess of

$$Na_2Mg(SO_4)_2\,4\,H_2O$$

be added, the inversion temperature falls to 26°, while an excess of NaCl and $MgSO_4\,7\,H_2O$ carries it down to 15°.[2] The double salts of copper and potassium chlorides have been studied by Meyerhoffer,[3] who found that the reaction which takes place is represented by the equation

$$CuCl_2\,2\,KCl\,2\,H_2O = CuCl_2KCl + KCl + 2\,H_2O.$$

This change takes place at 92° if the solution is saturated in respect to KCl; at 55° if saturated in respect to $CuCl_2\,2\,H_2O$. Here, as before, the greater solubility of the cupric chloride is the cause of this change in the stability of the hydrated double salt. This reaction differs from the others which we have considered in that we do not get a simple case of dehydration as we should expect, but have the formation of a new salt with separation of potassium chloride. The reason for this seems to be that the anhydrous salt $CuCl_2\,2\,KCl$ is unstable and goes over into the form $CuCl_2KCl$ and KCl. Why this should be so is not known. I have let the blue double salt effloresce over strong sulfuric acid, but the product seems to be the red double salt and potassium chloride. It would be very interesting to know whether double salts of this type, where the two components are held together by the water of crystallization, differ in any other properties from hydrated double salts which do not show this peculiarity.

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[1] Zeitschr. f. phys. Chem., 12, p. 417, 1893.

[2] *Ibid.*, 1, p. 176, 1887.

[3] *Ibid.*, 3, p. 336, 1889.

The cases which we have examined so far have all been alike in one respect, that the hydrated salt which it was proposed to make effloresce was stable below the inversion temperature. This is not necessary, and in astrakanite we have the reverse order of things.

$$MgSO_4\,7\,H_2O + Na_2SO_4\,10\,H_2O = Na_2Mg(SO_4)_2\,4\,H_2O + 13\,H_2O.$$

Here the double sulfate crystallizes out above 21°.5, the single salts below that temperature. Adding a salt which will increase the number of ions in solution will therefore raise the inversion temperature, while the addition of a salt which decreases the number of ions will lower it. In other words, we shall have our previous effects reversed. Both these cases have been realized by van 't Hoff.[1] In the presence of an excess of $MgCl_2\,6\,H_2O$ the inversion temperature is raised to 31°, while saturating the solution with sodium chloride produces the opposite effect, the inversion temperature becoming +5°. For the first time we get a marked effect, due to the different precipitating power of two salts. The addition of either magnesium or sodium chloride should cause a decrease in the solubility of the double salt; but in the first case the precipitation is so slight that the number of ions in solution is increased, and in the second it is so great that the vapor-pressure of the solution rises.

Having shown that in general the vapor-pressure of a partially effloresced salt is less than that of its saturated solution, it is worth while to consider whether the two can be equal except at the inversion temperature. In Table IV. I give some of Lescœur's measurements.[2] The pressures are in millimeters of mercury.

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[1] Zeitschr. f. phys. Chem., 1, pp. 170, 176, 183, 1887.

[2] Ann. chim. phys., (7), 2, p. 78, 1894.

TABLE IV.

	Pressure.		Temperature.
	Solution.	Salt.	
$BaBr_2 2 H_2O$	10.7	10.6	20°
$BaBr_2 2 H_2O$	124.0	124.0	60°
$MgBr_2 6 H_2O$	3.4	3.3	20°
$MgBr_2 6 H_2O$	166.0	166.0	100°
$CdBr_2 4 H_2O$	10.0	9.0	20°
$CdBr_2 4 H_2O$	122.0	124.0	60°
$BaI_2 6 H_2O$	8.4	8.4	20°
$BaI_2 6 H_2O$	58.0	60.0	60°
$MnBr_2 4 H_2O$	5.0	5.0	20°
$MnBr_2 4 H_2O$	202.0	200.0	100°

We have in all these cases equality between the two vapor-pressures, and that over a considerable range of temperature. A more interesting confirmation is furnished by Joannis[1] in his measurements of the vapor-pressure of saturated solutions of sodammonium and of the partially effloresced product.

TABLE V.

	Pressure.	Temperature.
1 g. NH_3Na + 1.669 g. NH_3	169.7 mm.	0°
1 g. NH_3Na + 0.460 g. NH_3	169.7	0°
0.971 g. NH_3Na + 0.029 g. Na	169.7	0°
0.487 g. NH_3Na + 0.513 g. Na	169.7	0°
0.108 g. NH_3Na + 0.892 g. Na	169.7	0°
0.043 g. NH_3Na + 0.957 g. Na	169.65	0°
1 g. NH_3Na + 0.46 g. NH_3	117.0	– 10°
0.7 g. NH_3Na + 0.30 g. Na	117.3	– 10°
0.39 g. NH_3Na + 0.61 g. Na	117.0	– 10°
0.19 g. NH_3Na + 0.81 g. Na	117.1	– 10°

The agreement is perfect, and as the compound is stable at +22°, the objection of Roozeboom that the measurements had been made in the neighborhood of the inversion temperature

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[1] C. r., 110, p. 238, 1890.

cannot be sustained. I see at present no theoretical reason why the dissociation-pressure of a hydrated salt may not be the same as that of its saturated solution, and I do not agree with Roozeboom when, after describing the usual diagram for the equilibrium between different hydrates and water, he says:[1] "Il en resulte que la tension de dissociation est toujours plus petite que celle de sa solution saturée, sauf dans le point C. Ainsi ce point represente la température et la pression unique ou il y a coexistence des deux corps solides avec la solution et la vapeur d'eau." At the inversion temperature there come together three vapor-pressures,[2] that of the hydrate, of its saturated solution, and of the saturated solution of the anhydrous salt, and all that can be predicted is that the vapor-pressure of the stable saturated solution is greater than that of the solution saturated in respect to the labile modification. How rapidly the curves for the true vapor-pressure of the hydrate and its saturated solution diverge, or whether they necessarily diverge at all, is a question which has no bearing on the inversion temperature. They may intersect before the inversion temperature is reached, in which case the salt melts and there is no formation of a new solid phase.

In speaking of the stable and the labile modifications, it must be kept in mind that these terms are to be reversed if we are considering the vapor-phase. When we refer to the solution, the more stable modification is the less soluble one. When we refer to the vapor-phase, it is the one having the lesser vapor-pressure. Below 33°, for instance, the saturated solution of anhydrous sodium sulfate has a smaller vapor-pressure[3] than the solution in equilibrium with the hydrated salt, and is therefore more stable in that respect. If we place the two saturated solutions in the two limbs of an inverted U-tube, water will distill from the one containing the hydrated salt into the other. We can go still further, and

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[1] C. r., 110, p. 135, 1890.

[2] If there are no other components, the dissociation curve intersects here. The true vapor pressure of the hydrate will always lie between the pressure of the saturated solution and the dissociation pressure.

[3] Meyerhoffer's diagram is wrong. (Phasenregel, p. 28.) His curves for the vapor-pressures of Na_2SO_4, solution, vapor, and of Na_2SO_4 10 H_2O, solution, vapor, if continued so as to represent the labile equilibria, are in contradiction with the facts.

say that if the system hydrated salt, anhydrous salt, vapor, has a greater vapor-pressure than the system anhydrous salt, solution, vapor, the hydrated salt will effloresce, and the water will condense in the beaker containing the saturated solution of the anhydrous salt. We shall thus have the spontaneous formation of the less stable system at the expense of the more stable. I tried to realize this with sodium sulfate at a temperature of about thirty degrees, and it looked once as if I had succeeded, but I cannot be certain of this. The great difficulty in carrying out the experiment is, of course, the spontaneous appearance of the more stable modification in the solution. It may be that this experiment is theoretically impossible for the reason that the vapor-pressure of the system hydrate, anhydrous salt, vapor, may be necessarily less than that of the saturated solution of the unstable modification. This is the case with the saturated solutions of $CaCl_2 4 H_2O\alpha$ and $CaCl_2 4 H_2O\beta$.[1] This would be very interesting if true. In that case Roozeboom would be entirely correct in the remarks of his which I have just quoted. While this may be true, it has not yet been shown by any one so far as I am aware.

While I was in Amsterdam, Professor van 't Hoff showed me a very pretty lecture experiment which consisted in putting clear pieces of crystallized calcium sulfate in mixtures of sulfuric acid and water of different proportions. In the solutions containing much sulfuric acid, the crystals became cloudy, and in those containing much water they remained clear. The concentration at which the first dehydration took place could be determined with great accuracy by the eye. The method in this form is adapted only to sulfates insoluble in water, and is therefore incapable of general application. This is easily remedied by bringing the crystals in contact with the vapor of the solution instead of with the liquid itself. In this way one can use any salt which forms clear crystals, and one can equally use any other drying agent. Theoretically there are objections to be made. For instance, it would not be proper to say that with sodium carbonate there was no formation of sodium sulfate; but this reaction runs so slowly that the experiment is ended long before this effect becomes noticeable.

[1] Zeitschr. f. phys. Chem., 4, p. 43, 1889.

This might not be the case were one to use strong hydrochloric acid as the drying agent. I have made a few measurements on copper and magnesium sulfates with rather surprising results. Frowein[1] found the vapor-pressure of partially effloresced copper sulfate to be equal to 10.9 mm. of mercury at 30°.2; I find that copper sulfate just begins to effloresce when placed over a solution containing 48 per cent of sulfuric acid by weight, the temperature being 30°. This corresponds to a vapor-pressure of about 13 mm.[2] of mercury, or over two millimeters more than the value found by Frowein. This is beyond the limits of experimental error, as my measurements are accurate to within one-half a per cent of H_2SO_4, while the value of 10.9 mm. corresponds to a solution containing 51.5 per cent of sulfuric acid by weight. The same thing was noticed with magnesium sulfate. At 30°, Frowein's measurements give for the vapor-pressure of partially effloresced $MgSO_4\,7\,H_2O$ the value (by interpolation) of 17.5 mm. Hg corresponding to the vapor-pressure of a solution containing 40.7 per cent HSO by weight. The direct experiment shows that magnesium sulfate effloresces over a 38 per cent solution of sulfuric acid, which has a vapor-pressure of 19.2 mm. As the vapor-pressure of an 84.5 per cent solution is only about 0.23 mm. at 30°, there is no appreciable error in assuming the whole vapor-pressure of sulfuric acid solutions at that temperature to be due to water-vapor. The experiments just cited force upon us the conclusion that the equilibrium between a hydrated salt and water-vapor is affected by the presence of other substances. This shows that the minute quantity of sulfuric acid present as vapor does not behave as a so-called "indifferent" gas, and the same will be true of alcohol vapor and of the vapors of all substances capable of forming a solution with water at that temperature of the experiment. This has never been recognized. Nernst[3] says: "Haben wir das Gleichgewicht zwischen Wasserdampf und wasserhaltigem Aether einmal untersucht, so ergibt umgekehrt die Bestimmung der Wassermenge, die einem krystallwasserhaltigen Salze von Aether entzogen wird, die Dissociationsspannung des Salzes."

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[1] Zeitschr. f. phys. Chem., 1, p. 5, 1887.

[2] Landolt and Börnstein's Tables, p. 65.

[3] Theoretische Chemic., p. 524.

Linebarger[1] has based a method of measuring vapor-pressures on this.

This method can give good results only in cases where the effects due to the other liquid fall within the experimental error. This seems to be the case with ether, which is not surprising, though I have little doubt that a careful series of determinations would show that the results from the indirect method were larger than those by direct measurement. This would certainly be the case if alcohol or methyl alcohol were taken.[2] The importance of this is that we can no longer assume that the same amount of work is done in compressing a given quantity of water-vapor from one volume to another in the two cases when we have the water-vapor alone and when we have alcohol-vapor present also, but work with a piston permeable to alcohol.

Since it is not necessarily true that a solid and a liquid phase when in equilibrium must have the same vapor-pressure, it seems worth while to ask whether two liquid layers in equilibrium must give off the same vapor. Ostwald has given a proof of Konowalow's Law, which I quote:[3] "Denken wir uns nämlich einen ringförmigen Hohlraum, Fig. 1, der bei *A* etwa eine gesättigte Lösung von Wasser in Äther, bei *B* eine solche von Äther und Wasser und in *C* den Dampf der Flüssigkeiten enthalte, so würde, falls der Dampf über *A* eine andere Spannung als bei *B* hätte, oder anders zusammengesetzt wäre, eine fortdauernde Destillation oder Diffusion von der einen Seite zur anderen stattfinden, ohne dass jemals ein Stillstand einträte, da auch die Flüssigkeiten sich durch Diffusion immer wieder ausgleichen würden. Wir hätten also ein Perpetuum mobile was unmöglich ist." This sounds most convincing; but let us examine this so-called "perpetuum mobile" a little more closely. For the purposes of argument, let us assume that the vapor given off by the ether layer contains more ether than the vapor given off by the water layer and that the second vapor contains more water than the first. Ether will therefore

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[1] Zeitschr. f. phys. Chem., 13, p. 500, 1894.

[2] I ventured to point out to Mr. Linebarger, nearly a year ago, this source of error; but he replied that the reasoning on which the method was based was free from hypothesis and as certain as the laws of thermodynamics.

[3] Lehrbuch, I., p. 644.

distill from *A* to *B*, and water from *B* to *A*. The water condensing at *A* will sink through the less dense ether layer; the ether which condenses at *B* will become saturated with water, and we shall have as the second step in the process three liquid layers, the solution of water in ether at *A*, the solution of ether in water at *B*, and an infinitely thin film of a solution of water in ether on top of the aqueous layer. Both free surfaces having the same composition, there is no need nor possibility of any further distillation if we neglect the effect due to gravity.[1] In other words, it is conceivable that we may have two liquid layers with different vapor-pressures and not assume the possibility of a perpetual-motion machine. Whether such a case really exists is an experimental problem, for which there are as yet no data. It is true that two liquid layers such as benzol and water, ether and water, have different boiling points, but this evidence is capable of another interpretation and is not conclusive. Of course, if it is shown that two liquid layers do not, as a rule, have the same vapor-pressure, that part of my argument on the difference between solvent and solute, which is based on the contrary assumption,[2] falls to the ground.

The results of this paper, most of which are contained implicitly or explicitly in Roozeboom's articles, may be summed up:

(1) Anhydrous salts are permanent till the pressure of the water-vapor in the gaseous phase becomes greater than the vapor-pressure of the saturated solution, after which they deliquesce.

(2) Hydrated salts deliquesce when the pressure of the water-vapor becomes greater than the vapor-pressure of the saturated solution, effloresce when it becomes less than the vapor-pressure of the system containing hydrated and anhydrous salt, and are permanent when the value lies between these limits.

(3) The vapor-pressure of a hydrated salt is usually less than the vapor-pressure of its saturated solution.

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[1] Professor Trevor pointed out to me some time ago that, assuming the two liquid layers had the same vapor-pressure when at the same level, the effect of gravity would cause distillation till the system was symmetrical and the two free surfaces at the same level. This experiment has since been tried in his laboratory with the predicted result.

[2] PHYSICAL REVIEW, III., p. 203, 1895.

(4) The vapor-pressure of a hydrated salt is affected by the nature of the effloresced salt.

(5) The true vapor-pressure of a hydrated salt is probably known in few cases.

(6) The equilibrium between a hydrated salt and water-vapor is affected by the presence of sulfuric acid.

(7) Two liquid layers in equilibrium need not have the same vapor-pressure.

May 1, 1895.

ON THE HEAT EFFECT OF MIXING LIQUIDS.

BY C. E. LINEBARGER.

Introductory.

THE wide-reaching analogy between gases and solutions, first clearly pointed out by van 't Hoff, has proven very fruitful when applied to the elucidation of the phenomena presented by solutions. The fact that the laws which have been established for gaseous matter are by a little extension applicable to dissolved matter has been of great service in getting at the nature of solution. While these laws are strictly true for gaseous and dissolved matter only in states of great rarefaction or dilution, they may, when properly modified, be employed in the investigation of gases or solutions of any degree of condensation. Especially is this true in the case of such substances as do not suffer molecular polymerization, for the complexity caused by the introduction of considerations relative to the association and dissociation of the molecules is in such cases not present. In the case of normal liquids, a close continuity may be expected, not only in the passage from the liquid to the gaseous state, but also in the properties of the two states, and such differences as may be found in the liquid state compared with the gaseous state may be accounted for by comparatively simple assumptions.

An important property of different portions of matter is their possible inter-diffusibility or miscibility with one another. A characteristic of the gaseous state is unlimited miscibility. All liquids which do not suffer any alteration in the size of their molecules on passing into the gaseous condition are also perfectly miscible; at least, no exception to this statement, so far as I know, has yet been found. Many associated liquids, however, do not mix in all proportions under certain conditions, but a certain degree of miscibility may always be observed, which, through changes in temperature and pressure, may become perfect. Solids, also, are not generally found to be capable of forming homogeneous mixtures under ordinary conditions; yet by suitable changes of these conditions, it is probable that they may be made to mix. Van der Waal's law — "All substances can mix with one another if subjected to sufficient pressure"[1] — is without doubt true of any system of bodies whatever, no matter what their state of aggregation; seeming contradictions must, and doubtless will, be cleared away by future experimentation.

To mix substances requires energy. The kinds of energy expended in effecting the mixing are principally heat, volume, and chemical energy; in the case of liquids and solids, surface and osmotic energy also come into play; in all but exceptional cases electrical energy and light energy play no part. When the sum of the volumes of the unmixed substances is equal to the volume of the mixture, the mechanical energy, which is mainly evident in the overcoming of the pressure of the atmosphere, is equal to zero, and in many cases the changes of volume that occur during the mixing are so slight that the concomitant changes of mechanical energy vanish in comparison with the quantities of other kinds of energy brought into action. Heat energy plays by far the most important *rôle* in the mixing of substances.

In nearly all work, both experimental and theoretical, on the heat changes occurring during solution, materials have been employed which can exhibit the phenomenon of saturation or a limited degree of miscibility, and only one side of the question is taken into account. In the case of aqueous solutions of salts, which have as yet received the most attention, the solution of the salt in the water is alone thought of, although it is just as proper to say that the water dissolves in the salt, as that the salt dissolves in the water. This view of the subject is probably due to the circumstance that the salt alone undergoes a change in its state of aggregation; it *becomes* liquid, while the water *remains* liquid. But in reality solution is just as truly reciprocal in this case as in the case of dissolving liquids in liquids. This last-named phenomenon

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[1] Die Continuität des gasförmigen und flüssigen Zustandes. Roth's German translation, p. 146.

—solution of liquids—has received but little attention, especially when the liquids are normal. But as normal liquids approximate closely to gases in their behavior, and as gases present the simplest phenomena, it may be expected that investigation of the thermal behavior of normal liquids will yield the simplest possible results, and give some indications as to the best means of getting a clear understanding of the general question of solution.

The object of this paper is, accordingly, the determination and discussion of the heat effect of mixing normal liquids.

Historical.

H. Sainte-Claire Deville[1] determined the "heat produced by twenty-five different mixtures of water and sulphuric acid." No experimental details are given, and the method employed is incapable of giving very accurate results. Deville believed that his data were in corroboration of certain theoretical views that he advanced, and, when the latter were subjected to some animadversions on the part of Jamin,[2] he protested energetically.[3] To this, Jamin[4] made a rather detailed reply, giving some experimental determinations of the changes of temperature occurring when alcohol and water are mixed, as corroborative of a theory of his own in contradiction to that of Sainte-Claire Deville. Still the latter was not convinced, and maintained his old opinions.[5] It is not necessary to enter into the consideration of the theoretical views advanced by these two scientists, as none of them have proven to be correct.

Favre[6] determined, by the mercury calorimeter, the heat effect of mixing, in several proportions, water with sulphuric acid, with alcohol, with acetic acid, and with glycerine; alcohol with glycerine, and with acetic acid; and acetic acid with sulphuric acid. His results showed that, in the mixing of these liquids, heat was either evolved or absorbed. As he puts it, having, as he did, the idea that solution was an example of a kind of chemical affinity: "Deux ordres d'actions semblent se produire simultanément et marcher de front; une action d'attraction réciproque des molecules hétéro-

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[1] Comptes Rendus, 50, p. 534, 1860.

[2] *Ibid.*, 70, p. 1309, 1870.

[3] *Ibid.*, 70, p. 1379, 1870.

[4] *Ibid.*, 71, p. 23, 1870.

[5] *Ibid.*, 71, p. 30, 1870.

[6] *Ibid.*, 50, p. 1150, 1860, and 51, p. 316, 1860.

gênes qui sont mises en contact et qui est accompagné d'un degagement de chaleur, et une action de diffusion qui produit un abaissement de température. Le nombre fourni par l'expérience est positive ou negative suivant que la première ou la seconde de ces actions predomine." His data cannot be well compared with later ones, as he has omitted to give the details necessary for a reliable comparison.

Bussy and Buignet[1] determined the changes of temperature brought about by mixing, in various proportions, alcohol with carbon bisulphide, chloroform, ether, and essence of terebenthine; water with acetic acid, and alcohol; ether with carbon bisulphide, essence of terebenthine, and chloroform; and carbon bisulphide with essence of terebenthine. The results of their experiments are similar to those obtained by Favre,[2] although his researches are not mentioned. This induced Favre[3] to call attention to his work, and, in so doing, to communicate some new results on the thermal effect of mixing water with methyl alcohol, and of mixing ethyl alcohol with methyl, amyl, and caprylic alcohols, as well as glycol. This claim of priority was recognized by Bussy,[4] who stated that he had been ignorant of the work by Favre, but that, anyhow, he had taken different liquids, of a simpler nature than Favre had.

In a subsequent paper, Bussy and Buignet[5] determined the specific heats of many of the mixtures, the change of temperature caused by the mixing of which they had previously observed,[6] thus permitting the calculation in heat units of the thermal effect.

Guthrie[7] determined, by rather a crude method, the changes of temperature occasioned by mixing alcohol with ether, carbon bisulphide, chloroform, and benzene; ether with carbon bisulphide, amylene, chloroform, and benzene; carbon bisulphide with amylene, chloroform, and benzene; amylene with chloroform, and benzene; and chloroform with benzene. The changes in the volume of these liquids, when mixed, were also measured, it being found that, when the mixing was accompanied with a rise of temperature,

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[1] Comptes Rendus, 59, p. 673, 1864, and Annales de chimie et de physique, (4), 4, p. 1, 1865.

[2] *loc. cit.*

[3] Comptes Rendus, 59, p. 783, 1864.

[4] *Ibid.*, 59, p. 785, 1864.

[5] *Ibid.*, 64, p. 330, 1867.

[6] *loc. cit.*

[7] Philosophical Magazine, (5), 18, p. 495, 1884.

contraction in volume occurred, while, when there was a fall in temperature, expansion took place. These generalizations are, however, based on too narrow a field of inquiry, and Guthrie's paper contains very little that is really novel, at least, along these lines.

W. Alexejew,[1] in summing up his work on the solubility of liquids in liquids, communicates some data as to the amount of heat absorbed in mixing benzene and aniline in several proportions. This he finds to be quite insignificant, and states in this connection: "Für ein Gemisch von 68.5 Proc. Benzol und 31.5 Toluol bei 14°, z. B. ist sie gleich −13.7 cal." As he states later that the possible error of a determination may amount to 5 cal., and as he does not give the absolute masses of the liquids taken, the absorption of heat given by him for this case may even be less than −8.7 cal.

Experimental Details.

Of the common methods of carrying out thermochemical measurements, the one in which use is made of a Bunsen's ice calorimeter has been preferred, mainly for the reasons that accurate results can be obtained with small quantities of material, and because it is unnecessary to know the specific heats of the liquids mixed.

The ice calorimeter employed was of rather large size, permitting of the introduction of about 15 c.c. of liquid. The amount of mercury expelled or drawn into the outer chamber by the formation or melting of ice was determined by weighing, as recommended by Schüller and Wartha;[2] indeed, the disposition of the apparatus was very similar to that adopted by these investigators, there being an outer cylindrical vessel filled with pure water, around the walls of which was a layer of ice, etc. The calorimeter was set in an ice box, and covered, with the exception of the top of the inner tube and the mercury tube, with clean snow or ice. The room in which the work was done was nearly all the time at the temperature of freezing water, and the temperature never rose above 5° or 6°.

After the calorimeter had been brought into normal working condition, it was found that the mercury was continually moving

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[1] Wiedemann's Annalen, 28, p. 322.

[2] *Ibid.*, 2, p. 359, 1877.

in one direction or the other, according to external conditions. As the amounts of heat evolved or absorbed by the mixing of non-associated liquids are generally quite small, it was necessary to keep strict account of this movement of the mercury; as the degree and direction of the movement changed very slightly in intervals of time long in comparison with the time occupied for the performance of an experiment, this could be done both easily and accurately in a way to be described later.

The cooling of the liquids to 0°, and their subsequent mixing, was accomplished as follows: A thin glass tube, closed at one end, and of such external diameter as to permit of its being slipped easily, but snugly, into the inner tube of the calorimeter, was taken of such length that about an inch of it projected out of the calorimetric tube. A pipette fitting easily into the above tube had its outlet directly below its cylindrical bulb, and was closed by means of a glass rod running axially up through the pipette and ground accurately into the outlet. A bit of thin rubber tubing was slipped over this glass rod and pushed down between the upper stem of the pipette and the rod, thus closing the pipette above. By means of a good cork the pipette was held within the tube mentioned at the beginning of this paragraph.

A rectangular piece of aluminium foil was for about two-thirds of its length cut into in several places on each side to near the middle, and the parts thus formed were so bent that, when the uncut portion of the foil was rolled into cylindrical shape and slipped over the lower part of the bulb of the pipette, where it was held securely by its own elasticity, they formed a number of small paddles, some directed upwards and some downwards. This stirring device proved to be very efficient, the mixing of two liquids being brought about rapidly and perfectly.

To make a determination, a certain amount of one liquid was drawn up into the pipette and weighed to 0.0001 gram. The other liquid was weighed in the tube, which was corked during the operation. The aluminium stirring contrivance was then slipped over the bulb of the pipette, and the latter passed into the tube, where it was held in place by a tightly fitting cork, and was so adjusted that its orifice would be above the level of the liquid after the mixing had been done, while the paddles reached to the bottom of the tube.

A weighed dish of mercury was always placed to catch the expelled mercury for exactly half an hour just before the tube and pipette with their contents were placed in the inner tube of the calorimeter; in this way a calorimeter correction was obtained just before the performance of an experiment. The weighed dish of mercury was then exchanged for an unweighed one, and the tube and pipette which had been standing in the ice box, so that they had already attained the temperature of 0°, were placed in the calorimetric chamber. In a half-hour or so a weighed dish of mercury was placed under the mercury tube, and the amount of mercury moved during another half-hour determined. Again a weighed dish of mercury was placed in position, and without delay the cork holding the pipette was lifted a little and its contents made to run out into the tube. The pipette was then tightly closed and moved around and a little up and down for a minute or so, in order to thoroughly mix the two liquids. The cork was again inserted in the tube and the whole left undisturbed for just half an hour. At the expiration of that time another weighed dish of mercury was substituted for the last one and left there for another half-hour, when the mercury vessel, as well as the tube and pipette, were removed. The amount of mercury moved during this last half-hour should, if the thermal equilibrium disturbed by the heat evolved or absorbed by the mixing of the liquids has reëstablished itself, and if there has supervened no change in the velocity of the movement of the mercury, be equal to the amount moved in the half-hour before the introduction of the liquids, and in the half-hour elapsing just before they are mixed. This was generally the case, the deviation always being very slight, and the average of these amounts was taken as the true correction to be applied.

All weighings were made with great care, since an error of one milligram entails an error of several hundredths of a heat unit. It is believed that the results of the experiments are accurate to within less than one-half of a calorie.

The calorimetric unit employed is defined by the amount of heat required to melt a volume of ice equal to that occupied by 0.01544 gram of mercury at 0°.

The liquids used as material for the investigation had all been carefully purified; in foot-notes are indicated the methods of purification and their boiling-points (uncorr.).

Experimental Results.

When a pair of liquids was taken for the determination of the heat effect of mixing them, about equal quantities of each were weighed out for the first estimation. If the thermal effect proved to be less than that capable of detection by the apparatus, commonly no other mixtures were examined, it having been found that the maximum heat effect was produced when the amounts of the liquids mixed were about the same. An evolution or absorption of heat might nevertheless have been found if other proportions had been investigated, although this is not very probable. Such mixtures as did not appear to exhibit any heat effect are given first. The minus sign before a number indicates an absorption of heat; the positive sign, an evolution of heat.

TABLE I.

HEAT EFFECT OF MIXING MONOCHLORBENZENE[1] AND TOLUENE.[2]

	I.	II.
Chlorbenzene	3.0028 g.	3.7715 g.
Toluene	4.3032	4.2190
Calorimeter correction in weight of mercury	−0.0013	−0.0014
Weight of mercury moved	−0.0018	−0.0020
Weight of mercury moved due to mixing liquids	−0.0005	−0.0006
Heat effect in calories	−0.032	−0.033

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[1] Commercial, chemically pure monochlorbenzene was distilled in fractions until nearly half of it boiled at 131°.8 to 131°.9, under a pressure of 757 mm. of mercury.

[2] The toluene had been fractionally distilled until more than a pound of it boiled constantly at 110°.1, under a pressure of 758 mm. of mercury.

TABLE II.

HEAT EFFECT OF MIXING MONOBROMBENZENE[1] AND TOLUENE[2]

	I.	II.
Brombenzene	4.9530 g.	1.1611 g.
Toluene	4.3680	7.3887
Calorimeter correction in weight of mercury	−0.0009	−0.0010
Weight of mercury moved	−0.0020	−0.0005
Weight of mercury moved due to mixing liquids	−0.0011	+0.0005
Heat effect in calories	−0.072	+0.032

TABLE III.

HEAT EFFECT OF MIXING ETHYL ETHER[3] AND TOLUENE[2]

Ether	6.9858	grams.
Toluene	3.7256	"
Calorimeter correction in weight of mercury	−0.0033	"
Weight of mercury moved	−0.0033	"
Weight of mercury moved due to mixing liquids	0.0000	"
Heat effect in calories	0.000	

TABLE IV.

HEAT EFFECT OF MIXING ETHYL IODIDE[4] AND TOLUENE[2]

Ethyl iodide	7.8668	grams.
Toluene	6.1445	"
Calorimeter correction in weight of mercury	−0.0130	"
Weight of mercury moved	−0.0129	"
Weight of mercury moved due to mixing liquids	+0.0001	"
Heat effect in calories	+0.006	

Since the freezing-point of benzene is higher than that of water, it was impossible to employ it in the ice calorimeter in the pure state; accordingly a mixture containing 97.37 per cent of the

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[1] Of about a pound fractionally distilled, nearly 150 grams were obtained, boiling at 154°.3 to 154°.5, under a pressure of 761 mm. of mercury.

[2] The toluene had been fractionally distilled, until more than a pound of it boiled constantly at 110°.1, under a pressure of 758 mm. of mercury.

[3] The ethyl ether had been washed repeatedly with water, dried over fused calcium chloride, and finally distilled from phosphoric anhydride. Almost the whole of it boiled at a constant temperature.

[4] Rectified over phosphoric anhydride, the ethyl iodide boiled at 72°.5, under a pressure of 757 mm. of mercury.

hydrocarbon and 2.63 per cent of monochlorbenzene was prepared, and it was with this mixture that the determination recorded in Table V. was made.

TABLE V.

HEAT EFFECT OF MIXING CHLORBENZENE[1] AND BENZENE.[2]

Mixture benzene and chlorbenzene	3.0208	grams.
Chlorbenzene	6.3470	"
Calorimeter correction in weight of mercury .	−0.0013	"
Weight of mercury moved	−0.0030	"
Weight of mercury moved due to mixing liquids	−0.0017	"
Heat effect in calories	−0.101	

The rest of the mixtures examined showed so appreciable thermal effects that several proportions of the liquids were mixed, and in the following tables are recorded the results. In order to obtain a uniform means of comparison, the quantities of liquids mixed are calculated in molecular per cents, and the amounts of heat increased so as to correspond to these masses. In this way, the numbers representing the amounts of heat change when certain numbers of gram-molecules are mixed, come out over a hundred times greater than those actually determined. Accordingly, it must be borne in mind that the units and tens of the numbers communicated have hardly any significance.

TABLE VI.

HEAT EFFECT OF MIXING ETHYL IODIDE[3] AND ETHYL ETHER.[4]

Grams C_2H_5.	Grams $C_4H_{10}O$.	Per cent C_2H_5I.	Molec. per cent C_2H_5.	Mercury moved.	Calorimeter correction.	Calories.	Cal. per mols.
2.4240	9.3465	20.595	10.955	−0.0110	0.0000	−0.71	− 632
8.3683	5.9185	58.573	40.146	−0.0053	+0.0125	−1.18	− 863
13.8745	5.2520	72.543	55.616	−0.0300	0.0000	−1.92	−1215

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[1] Commercial, chemically pure monochlorbenzene was distilled in fractions until nearly half of it boiled at 131°.8 to 131°.9, under a pressure of 757 mm. of mercury.

[2] Commercially pure benzene was treated with sulphuric acid to remove thiophene, fractionally crystallized to constant melting-point, viz. 5°.42, and distilled over sodium. Boiling-point was 80°.1, under a pressure of 757 mm. of mercury.

[3] Rectified over phosphoric anhydride, the ethyl iodide boiled at 72°.5, under a pressure of 757 mm. of mercury.

[4] The ethyl ether had been washed repeatedly with water, dried over fused calcium chloride, and finally distilled from phosphoric anhydride. Almost the whole of it boiled at a constant temperature.

TABLE VII.

HEAT EFFECT OF MIXING CARBON BISULPHIDE[1] AND TOLUENE.[2]

Grams C_7H_8.	Grams CS_2.	Per cent C_7H_8.	Molec. per cent C_7H_8.	Mercury moved.	Calorimeter correction.	Calories.	Cal. per mols.
1.6035	13.2050	10.829	9.117	−0.0420	+0.0080	−3.22	−1695
3.6267	12.4130	22.610	19.443	−0.0871	+0.0061	−6.00	−2971
6.8225	7.0721	49.101	44.350	−0.1105	+0.0095	−7.81	−4648
10.6800	1.8372	85.322	82.766	−0.0605	−0.0020	−3.80	−2701
10.5282	0.5040	95.518	94.517	−0.0050	+0.0065	−0.76	− 615

TABLE VIII.

HEAT EFFECT OF MIXING CHLOROFORM[3] AND TOLUENE.[2]

Grams C_7H_8.	Grams $CHCl_3$.	Per cent C_7H_8.	Molec. per cent C_7H_8.	Mercury moved.	Calorimeter correction.	Calories.	Cal. per mols.
0.6075	6.8166	8.182	10.375	+0.0708	−0.0010	+ 4.53	+ 7,101
2.8565	6.1682	31.562	37.560	+0.1962	−0.0038	+12.91	+15,669
2.1741	3.1679	40.698	47.120	+0.1215	−0.0072	+ 8.33	+16,493
6.0145	2.0438	74.637	79.264	+0.1108	−0.0038	+ 7.40	+ 8,996
7.0100	0.6445	91.619	93.406	+0.0110	−0.0030	+ 0.50	+ 636

TABLE IX.

HEAT EFFECT OF MIXING CARBON TETRACHLORIDE[4] AND TOLUENE.[2]

Grams C_7H_8.	Grams CCl_4.	Per cent C_7H_8.	Molec. per cent CCl_4.	Mercury moved.	Calorimeter correction.	Calories.	Cal. per mols.
0.4200	7.2987	5.441	8.785	−0.0080	−0.0042	−0.25	− 474
1.3662	6.9568	16.415	24.735	+0.0005	−0.0057	−0.41	− 666
3.7530	6.5552	36.408	48.937	+0.0050	−0.0114	+1.13	+1272
5.1212	4.2560	54.613	71.717	+0.0162	−0.0066	+1.51	+1504
6.0023	1.8523	76.418	84.434	+0.0070	−0.0066	+0.88	+1139
6.3920	0.8978	87.684	93.320	−0.0102	−0.0042	−0.32	− 419

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[1] The carbon bisulphide was dried over phosphoric anhydride and distilled over mercury; it boiled constantly at 46°.25, under a pressure of 756 mm. of mercury.

[2] The toluene had been fractionally distilled until more than a pound of it boiled constantly at 110°.1, under a pressure of 758 mm. of mercury.

[3] The chloroform had been fractionated to constant boiling-point, and was finally distilled over phosphoric anhydride; its boiling-point was 61°.3, under a pressure of 759 mm. of mercury.

[4] The sample had been fractionally distilled over phosphoric anhydride, and boiled at 76°.7, under a pressure of 754 mm. of mercury.

TABLE X.

HEAT EFFECT OF MIXING CARBON TETRACHLORIDE[1] AND CHLOROFORM.[2]

Grams CCl_4.	Grams $CHCl_3$.	Per cent CCl_4.	Molec. per cent $CHCl_3$	Mercury moved.	Calorimeter correction.	Calories.	Cal. per mols.
0.7632	11.9765	5.986	4.713	−0.0210	−0.0151	−0.45	− 369
1.3275	6.2995	16.649	14.053	−0.0302	−0.0190	−0.71	−1193
8.9100	5.2060	63.120	57.046	−0.0892	−0.0052	−5.42	−5353
12.5720	2.6480	82.599	78.643	−0.0750	−0.0213	−3.41	−3289
11.8203	1.6395	87.820	84.838	−0.0580	−0.0180	−2.59	−2786
11.3480	0.3600	97.199	96.072	−0.0364	−0.0152	−1.40	−1799

Discussion of Results.

In a paper "On the Vapor Tensions of Mixtures of Volatile Liquids,"[3] I have had occasion to discuss the mixing of liquids without the production of any appreciable thermal effect, in connection with considerations on their vapor tensions, and in this present paper more experimental data are given in corroboration of the views stated in that place. It may be added here, to what was said there, that it is not probable that absolutely *no* heat change occurs when certain liquids are mixed. The amount of heat evolved or absorbed is, however, so slight that it escapes detection; with more delicate instruments, no doubt, its amount could be ascertained.

In regard to whether heat will be evolved or absorbed in appreciable measure, there seems to be no criterion. Thus, it seems probable, if two liquids A and B each mix with another liquid C, without a measurable heat effect, that these two liquids will mix with one another without giving rise to any evolution or absorption of heat. This is, however, not the case, for both ethyl ether and ethyl iodide mix with toluene without a thermal change (Tables III. and IV.), and yet, when mixed with each other, give a not inconsiderable heat effect (Table VI.). A curious result is ob-

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[1] The chloroform had been fractionated to constant boiling-point, and was finally distilled over phosphoric anhydride; its boiling-point was 61°.3, under a pressure of 759 mm. of mercury.

[2] The sample had been fractionally distilled over phosphoric anhydride, and boiled at 76°.7, under a pressure of 754 mm. of mercury.

[3] Journal of the American Chemical Society, Vol. XVII., August, 1895.

tained with mixtures of chloroform, carbon tetrachloride, and toluene. When carbon tetrachloride and chloroform are mixed, heat is absorbed, and, indeed, the heat absorption reaches a maximum when about equal quantities of each liquid are mixed. The mixing of chloroform and toluene gives, on the other hand, an evolution of heat, attaining its maximum when about the same number of molecules of each liquid is taken. With mixtures of carbon tetrachloride and toluene, an entirely different behavior is found. If a small proportion of either of the liquids be added to the other, heat is absorbed; when, however, the proportions in which the liquids are mixed become more nearly equal, an evolution of heat is observed. This difference of behavior in the three liquids is enigmatical. Chloroform and carbon tetrachloride being so similar, both chemically and physically, it might be expected that they would behave more similarly, as regards their thermal effects, when mixed with toluene, a liquid which had shown itself to give very simple results when mixed with ether, ethyl iodide, etc. Our knowledge of the subject does not at present permit us to get at the secret of the affair.

When carbon bisulphide and toluene are mixed, heat is absorbed, no matter what the relative proportions of the two liquids, and the amount of heat is greater than that absorbed in the mixing of ethyl iodide and ether. This greater absorption of heat, occasioned by the mixing of the first two liquids, may be due to the fact that carbon bisulphide is slightly associated; and it is probable that heat is required to break up the associated molecules.

Influence of Temperature upon the Heat Effect of Mixing Normal Liquids.

It is of some interest to consider what influence a change of temperature exercises upon the amount of heat absorbed or evolved when liquids are mixed. It may be that the absolute amount of heat brought into play is different at various temperatures, and in some cases the mixing of liquids will occasion an evolution of heat at one temperature, and an absorption of heat at another. Certain energetical considerations will afford us a relation between the heat effects of mixing liquids at different temperatures and the specific heats of the mixed and unmixed liquids, and by its aid and comparison with experimental data on the specific heats of mixtures of liquids, we will obtain a definite answer to our question.

Let two liquids A and B be mixed at the temperature T_1, whereby a positive or a negative heat effect amounting to $\pm Q$ is occasioned; for the sake of simplicity, we will assume the heat effect to be positive, as such a supposition is in nowise a restriction to the generality of the results. The mixture is now heated to the temperature T_2, in which operation an amount of heat equal to $(T_2 - T_1)c_1$ is needed, c_1 representing the specific heat of the mixture in the temperature interval $(T_2 - T_1)$. At the temperature T_2 the two liquids are separated, the act of separation being accompanied by an absorption of heat amounting to Q_2. The separated liquids are now cooled down to the original temperature, when $(T_2 - T_1)c_2$ units of heat are given out, if c_2 represents the sum of the heat capacities of the liquids. As the cycle of operations is now completed, we may, in accordance with the law of the conservation of energy, form the following equation:

$$Q_1 + (T_2 - T_1)c_2 = Q_2 + (T_2 - T_1)c_1,$$

or (1)

$$C_2 - C_1 = \frac{Q_2 - Q_1}{T_2 - T_1}.$$

Accordingly the difference between the specific heats of the pure liquids and their specific heats when mixed is equal to the increase of the heat effect of mixing them per degree of rise of temperature.

Now it results from the experiments of J. H. Schüller,[1] of W. Alexejew,[2] and of F. L. Perrot,[3] that the difference between the specific heats of mixed and unmixed normal liquids is less than that due to unavoidable experimental errors; a normal liquid preserves its specific heat in mixture. From this experimental fact it follows that the first member of equation (1) is equal to zero in the case of mixtures of normal liquids, and hence the second member is equal to zero also. A change of temperature, then, has no appreciable influence upon the thermal effect of mixing normal liquids.

CHICAGO, January 24, 1896.

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[1] Pogg. Ann. Ergänzungsband, V., p. 210, 1871.

[2] Wiedemann's Annalen, 28, p. 322, 1886.

[3] Arch. des sciences physiques et naturelles, 32, pp. 145, 254, and 337, 1894.

THE INFLUENCE OF HEAT, OF THE ELECTRIC CURRENT, AND OF MAGNETIZATION UPON YOUNG'S MODULUS.

BY MARY CHILTON NOYES.

IN the PHYSICAL REVIEW for January–February, 1895,[1] an article was published describing a series of experiments which had been made in the physical laboratory of Cornell University, to determine the effect of temperature upon Young's modulus for a piano wire. An electric current was used as the source of heat, and a series of different temperatures employed. The experiments showed very clearly that Young's modulus for a piano wire decreases as the temperature is raised from 15° to 180° C., and that the decrease is nearly, if not exactly, proportional to the increase in temperature. The value of the thermal coefficient was likewise determined.

There were, however, other questions which were raised rather than settled by the experiments. When the wire was heated by an electric current through a helix surrounding it, the results were quite regular; but when the current was sent through the piano wire itself, results were obtained which were so irregular that no certain conclusions could be drawn from them. Some of them seemed to indicate that the current through the wire had a very perceptible effect upon the elasticity; others made it doubtful whether there was any effect aside from that due to the heat. It seemed desirable to conduct a series of experiments by the same general method, but so planned as to distinguish between the effects due to the heat, to the longitudinal magnetization, and to the electric current through the wire. For this purpose apparatus similar in all essential particulars to that used at Cornell, and described in the previous article, was arranged in the physical laboratory of Western Reserve University. A solid block of oak

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[1] PHYSICAL REVIEW, Vol. II., No. 10, p. 277.

of sufficient length was placed upon a stone pier which was isolated from the floor so as to avoid jars from other parts of the building. The wire was passed through a glass tube, attached to a support at one end, and passed over an Atwood wheel at the other. Every precaution was taken to avoid drafts of air or anything which would cause variation of temperature. A large cloth screen was placed between the apparatus and the hot-air register; the Atwood wheel was carefully covered with a cloth, and the wire at the other end was protected in a similar way.

When the wire was heated by a current through the helix around the tube, the temperature was determined by three thermometers placed inside the tube, but so arranged as not to touch it. Before using the thermometers, a table of corrections was made for them. To do this they were compared with a standard thermometer between 0° and 100°; the freezing and boiling points were determined; and the stems between 100° and 200° were calibrated by using a thread of mercury and comparing with the parts between 0° and 100°. The corrections so determined were applied to all the readings taken. When the wires were heated by a current through them, the temperatures were determined by the elongation, the coefficient of linear expansion being previously determined by noticing the elongation when the wires were heated by the current around them. Sometimes the highest temperature used in a series of observations was determined both by noticing the elongation when the wire was heated and the subsequent contraction after the current had stopped; the results usually agreed within a fraction of a degree. Some experimenters have found that an electric current through a wire produces a greater elongation than would be caused by the same temperature produced in some other way. The difference is, however, so small that it has not seemed necessary to take it into account in determining the temperatures.

The micrometer heads of the microscopes had fifty divisions; in all the readings half-divisions were used. It was found that 4080 half-divisions were equal to one millimeter. The diameters of the wires were measured by two or three micrometer wire gauges and the average results taken.

The wires were stretched by a weight equal to about one-half the breaking weight for twenty-four hours or longer before the first observations were made, and the maximum weight used in the determinations was a little less than the stretching weight. With the piano wires, the same weights were always used for the same kind of wire, so that the results obtained in the different experiments might be comparable. In determining the modulus, all the weight added was put on at once instead of using intermediate weights, as had been done in most of the previous work. The additional weight was always put on and taken off before the first reading was taken, and the readings were made as soon as possible after placing the weights. Usually the weight was put on and removed three times for one determination, so that the result was the average of six values; in many cases a larger number of observations was taken. The attempt was made to secure so steady a temperature that the readings before placing the weights and after removing them would not vary more than one or two half-divisions, but it was not always found possible to obtain this condition. If the variations were a little more, but all in the same direction and of the same amount, showing that the change in temperature was regular, it was thought that the average result could not be far wrong. The matter was tested by comparing the average result when there was a considerable, but regular, change in the readings with that obtained a little later with the same current but after the temperature had become steady; the results usually differed only about one-tenth of one per cent.

The wires were measured to one one-hundredth of a millimeter with a standard meter rule. In computing the moduli, this length was corrected for the elongation corresponding to each temperature employed.

With the first wire used, the elongation for one degree was found to be 0.01137 mm.; the length of the wire was 952.00 mm., making the coefficient of expansion 0.000012. The same coefficient was used in determining the change in the cross-section with change of temperature, and this correction was also used in making the calculations.

Experiment 1.

A piece of number six piano wire was used in this series of observations. It was heated alternately by the magnetizing current and by the current through the wire itself. The lowest weight used was 3.5 Kg., and the additional weight used to produce the elongation was 1.0 Kg. A number of observations made before the adjustments were sufficiently perfect to give concordant results were discarded.

Observations were first made with current through the magnetizing helix, then with current in the wire itself. The set with the current through the wire are somewhat irregular, but with a single exception are higher than those that had been previously obtained with the magnetizing helix. When the magnetizing current was again used, the values found fall between those of the first and second sets. A final set, with the current again through the wire, are more regular than the first set obtained in the same way, and are on the whole higher than any of the preceding sets.

The results show an increase from heating the wire alternately by the two methods; but there is little to indicate whether the effect is due to the heat alone, to the current, or to the magnetization.

In order to see if a continuation of the current would change the modulus, a number of determinations were made with an interval between the sets of observations, but making no change in the conditions. The results differed no more than the probable errors of observation.

Experiment 2.

Another piece of the same kind of wire as had been used in the previous experiment was adjusted and heated in a similar way, only the current through the wire was used first, and afterwards the magnetizing current. The following table gives the numerical results obtained, and (Fig. 1) represents them graphically.

TABLE I.

Current left to right, through wire.

No.	Date.	Temperature.	Elon. for 1 Kg.	No. of obs.	Modulus.
1	March 14	23°.5	1442.44	7	21,234
2	" 15	24°.9	1140.50	6	21,268
3	" 15	27°.2	1145.50	6	21,173
4	" 15	34°.1	1145.05	4	21,179
5	" 15	43°.2	1150.63	6	21,075
6	" 15	50°.3	1157.63	8	20,947
7	" 15	63°.6	1160.23	6	20,896
8	" 15	83°.0	1172.28	6	20,676
9	" 15	97°.9	1189.90	6	20,366
10	" 16	33°.8	1146.56	12	21,152
11	" 16	45°.8	1148.33	8	21,118
12	" 16	64°.9	1155.00	4	20,992
13	" 16	91°.4	1172.27	6	20,675
14	" 16	112°.7	1186.85	8	20,416
15	" 16	137°.1	1200.87	3	20,171

Current right to left, through wire.

16	March 18	27°.2	1131.98	5	21,426
17	" 18	76°.7	1158.67	12	20,920
18	" 18	93°.1	1172.36	8	20,672
19	" 18	116°.0	1191.90	4	20,328
20	" 18	157°.8	1209.15	4	20,028
21	" 18	183°.5	1231.42	10	19,654
22	" 19	77°.1	1155.40	4	20,979 (?)
23	" 19	95°.0	1176.47	6	20,599
24	" 19	111°.6	1182.01	8	20,500
25	" 19	123°.8	1186.58	10	20,418
26	" 19	150°.3	1198.60	8	20,207
27	" 19	166°.6	1209.78	8	20,014
28	" 20	13°.3	1134.07	6	21,394

Current right to left, through magnetizing helix.

29	March 20	28°.8	1134.78	8	21,373
30	" 20	37°.4	1140.03	7	21,272
31	" 20	42°.7	1140.50	8	21,262
32	" 20	50°.4	1142.59	10	21,223
33	" 21	33°.5	1134.66	8	21,374
34	" 21	51°.0	1139.20	8	21,286
35	" 21	68°.1	1153.45	4	21,018
36	" 21	85°.3	1157.50	3	20,939

TABLE I. (*continued*).

Current left to right, through magnetizing helix.

No.	Date.	Temperature.	Elon. for 1 kg.	No. of Obs.	Modulus.
37	March 22	39°.1	1137.76	8	21,315
38	“ 22	61°.5	1148.98	5	21,102
39	“ 22	86°.9	1154.60	6	20,993
40	“ 22	90°.3	1165.00	4	20,804
41	“ 22	105°.1	1169.03	6	20,728
42	“ 23	15°.6	1128.84	7	21,498

Current left to right, through wire.

No.	Date.	Temperature.	Elon. for 1 kg.	No. of Obs.	Modulus.
43	March 23	39°.9	1133.37	6	21,398
44	“ 23	58°.2	1137.53	4	21,315
45	“ 23	90°.5	1159.90	4	20,895
46	“ 25	77°.3	1147.70	8	21,120
47	“ 25	93°.4	1157.28	5	20,942
48	“ 25	150°.0	1199.63	6	20,188
49	“ 26	19°.8	1129.27	6	21,481
50	“ 26	34°.2	1138.87	6	21,295
51	“ 26	42°.5	1147.29	7	21,136
52	“ 26	51°.2	1139.35	4	21,282
53	“ 26	76°.2	1146.63	6	21,141
54	“ 26	92°.5	1155.68	8	20,971
55	“ 26	113°.9	1172.90	8	20,657
56	“ 26	150°.0	1202.32	10	20,143

$L = 954$ mm. at 18°. $Q = 0.16046$ sq. mm. at 18°. $P = 1$ Kg.

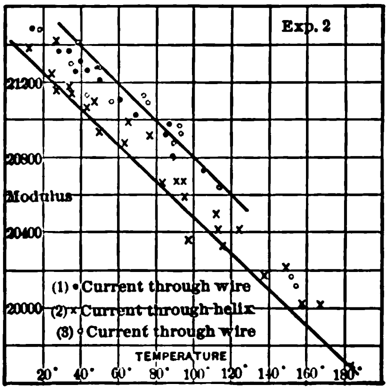

Fig. 1.

The values found for the first set of observations show a gradual increase in the modulus as the heating is repeated; some of the later values fall very nearly in the same line as those of the next set, which were obtained with the magnetizing current. Most of the final set, when the current was again sent through the wire, are higher than either of the preceding sets. There is the same progressive increase in elasticity with the alternate methods of heating that had been found in the preceding experiment.

Experiment 3.

A third piece of the number six piano wire was taken, and the same order used in the methods of heating as in the first experiment.

After a few readings had been obtained, it was discovered that the cloth used to protect the Atwood wheel from drafts of air touched the wire, making the results uncertain; hence the values for the first heating were rejected. The subsequent results were more regular than in either of the previous experiments, and the results obtained in the third and fourth sets fall almost exactly in the same line, which seems to indicate that the wire had reached a condition such that its elasticity would not have been much modified by further repetition of the heating or of the magnetization.

The three experiments all show that the elasticity of a piano wire is increased by heating it alternately by a magnetizing current and by a current through the wire itself. The fact that the order in which the two methods are used makes no essential difference in the result, makes it probable that the effect is due to the heat alone.

In this, as in several of the other experiments, both the magnetizing current and the current through the wire were reversed a number of times; no difference in the effect of the current could be detected. This fact furnishes additional evidence that neither the longitudinal nor the circular magnetization is the cause of the change in the elasticity.

Experiment 4.

A larger piano wire was used for this experiment in order to make it more certain that the results obtained did not depend upon any peculiarity in the particular specimen of wire employed. The results obtained are much the same as those that had been found with the smaller wire, but the increase in elasticity from the heating is less than in the other cases, and a condition in which a repetition of either form of heating produced no further change was sooner reached.

Experiment 5.

In order to determine with greater certainty whether heat alone was the cause of the increase in the modulus produced by alternating the two methods of heating, a double coil was so arranged that the current flowed through one part in one direction and the other part in the opposite direction, thus making it non-inductive. This coil was used for heating another piece of the number six wire. Figure 2 shows the results obtained by this method. There is the same kind of increase in elasticity with each alternation of the method of heating that had been found when using the magnetizing helix. The conclusion seems inevitable that the longitudinal magnetization at least has no appreciable effect upon the result.

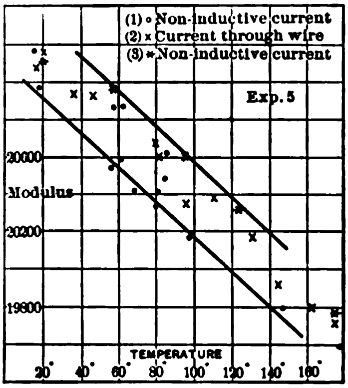

Fig. 2.

Experiment 6.

The results of each of the previous experiments showed a change in the modulus produced by repeated heating. It therefore seemed desirable to compare the moduli obtained with the different methods of heating applied to a wire that had already been heated and cooled so many times that further repetition of the treatment would produce no change in the elasticity. For this purpose a piece of the number six piano wire was placed in the tube inside the magnetizing helix, and was repeatedly heated by a current through the helix.

Some of the results obtained in the previous year indicated the possibility that repeated magnetization might modify the effects produced in a wire by a current through it. The plan of this experiment made it possible to test this point also.

After heating and magnetizing the wire a number of times, a series of values for the modulus was found when it was heated by the magnetizing current, and the following day a corresponding series when it was heated by a current through the wire itself. The results are plotted in Fig. 3. They all fall very close to a straight line, with no appreciable difference in the results obtained by the two methods of heating. These results show that if there is any difference in the effects produced upon the elasticity of a piano wire by magnetizing it longitudinally and circularly, that difference is too small to be detected with any certainty by this method of experiment.

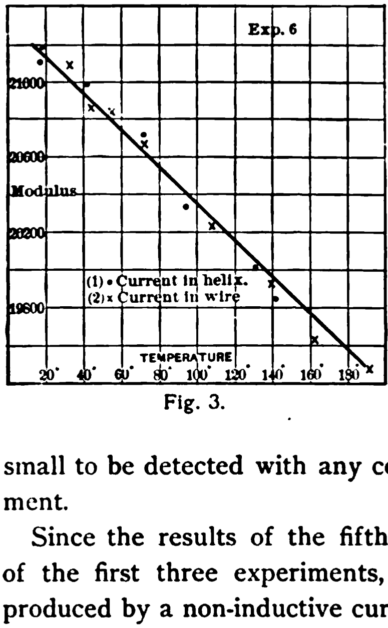

Fig. 3.

Since the results of the fifth experiment, compared with those of the first three experiments, showed that the heating effects produced by a non-inductive current and by a magnetizing current are the same, the proof seems conclusive that neither longitudinal magnetization nor a current through a wire produce any appreciable effect upon Young's modulus aside from that which is due to the accompanying heat.

From the results obtained in the first three experiments, it was computed that the permanent increase in elasticity due to repeated heating is about 1.45 per cent of the value found for the modulus by producing the line passing through the first set of results until it intersects the zero line. The corresponding change found in the fifth experiment is 1.90 per cent of the value at 0°; the greater increase may be due to the fact that higher temperatures were secured in this case with the current around the wire than had been used in the earlier experiments; the cooling took place much more slowly after stopping the current through the helix than when the current was through the wire itself; this more gradual cooling might easily account for the larger increase in elasticity.

The thermal coefficient was determined in connection with the different experiments by drawing lines which would correspond to the average decrease of the modulus with the increase of temperature, and comparing that decrease with the zero value corresponding to the final set of results. The average value found in this way from experiments 1, 2, 3, and 5, is 4.65 per cent for 100°. The value found in a similar way from the results of the sixth experiment is 4.55 per cent. This result is more probable than any of the others, since it is difficult to draw a line satisfactorily through the results obtained before the wires had been heated sufficiently to reach a permanent condition. Giving equal weight to the average of the four results and to the result of the sixth experiment, we get a value of 4.60 per cent for the thermal coefficient. This is a little smaller than the value found in the previous investigation already cited for the larger wire experimented with, but is just the same as that found for the smaller wire.

A few results which were obtained with this wire at temperatures ranging from 300° to 600°, showed a continued decrease in the modulus with the increasing temperature. The decrease was apparently at about the same rate as that found between 15° and 180°; but these high temperatures could not be determined with sufficient accuracy to be sure that the thermal coefficient remains constant.

Experiment 7.

A piece of the number six piano wire was annealed by heating it inside a glass tube, through which a current of coal gas was passing so as to prevent oxidation. The modulus of the wire was then determined when it was heated by the non-inductive current and by a current through the wire. Another piece of the same kind of wire was heated while covered with powdered charcoal, to prevent oxidation. The modulus was then determined when it was heated by the non-magnetizing current, by a current through the wire, and by a magnetizing current. The results, which were entirely analogous to those of the previous experiments, make it safe to conclude that with an annealed wire, as with the unannealed, there is no appreciable effect except that due to heat. The thermal coefficient is smaller for the annealed than for the unannealed wire, being only 3.4 per cent for 100°.

Experiment 8.

A piece of silver wire 0.48 mm. in diameter was used for this experiment. Young's modulus was determined when the wire was heated by a current through the non-inductive coil, and when it was heated by a current through the wire itself. Figure 4 shows the results. The observations are numbered so that the progressive change in the modulus may be traced more clearly. Comparing numbers 1, 4, and 7, we see an increase in the modulus each time the wire was heated. The still greater change between numbers 7 and 16 was probably due to the fact that in determining number 15 the wire was stretched beyond its elastic limit. All of the results from the sixteenth through the twenty-fourth are close to the same line. Between numbers 21 and 22 there was an interval of about a month during which the wire had remained unstretched; a comparison of results obtained before and after that time shows no appreciable change in the elasticity.

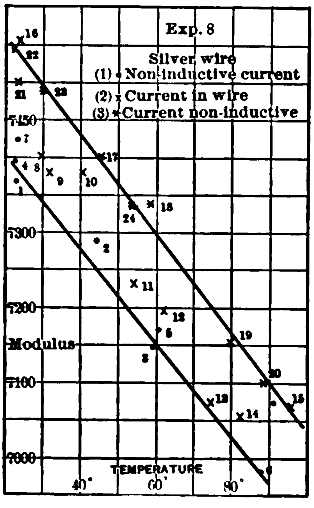

Fig. 4.

Number 15, and some of the other results obtained at the higher temperatures, are somewhat uncertain. No appreciable change in the elastic limit with the increase in temperature had been anticipated, and the weights chosen were those found suitable at the temperature of the room. It was found, however, that at about 80° the larger weight that had been used at the lower temperature, 2.9 Kg., slightly exceeded the elastic limit; and at 88° the heaviest weight that could be used was 2 Kg. These facts led to an investigation of the change in the elastic limit with change of temperature. The results obtained are shown in Fig. 5. Numbers 1 to 5 were obtained one day, and numbers 6 to 12 two or three days later, while number 13 was twenty-four hours after number 12. There was not time to contrive any very accurate method of determining the elastic limit that could be employed with the apparatus in use, and the results are not as definite as could be desired. They seem, however, to show plainly that the elastic limit decreases with increasing temperature, and also that between 20° and 115° the decrease is nearly, if not exactly, proportional to the increase in temperature. They also show a decrease in the elastic limit with the repeated heating and stretching.

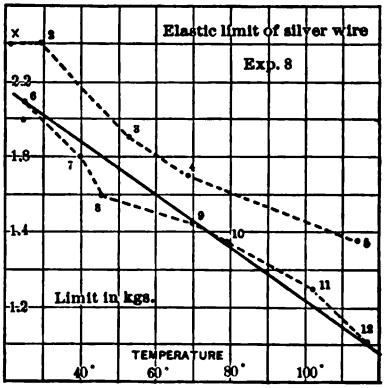

Fig. 5.

Determinations of the modulus made after numbers 5 and 13 in the elastic-limit series, gave the values 7605 at 23°, and 7954 at 25°. These values, and also number 16, previously referred to, show a permanent increase in the elasticity produced by stretching the wire beyond the elastic limit while that limit was temporarily lowered by heating.

Experiment 9.

A piece of copper magnet-wire 0.64 mm. in diameter was heated by the same methods that had been employed with the silver wire. The results were somewhat affected by the application of unsuitable weights, but they sufficed for the computation of the thermal coefficient of the modulus.

It was found to be 13.3 per cent for 100°; whence

$$M_t = M_0(1 - 0.00133\,t).$$

The elastic limit was also determined at three temperatures. The results show a decrease which is proportional to the increase in temperature. (See Table III.)

The coefficient of linear expansion of the wire was determined when it was heated by using the non-inductive coil, and this coefficient was employed in determining the temperatures when heating by the other method. The coefficient found was 0.0000153. This is smaller than the coefficient usually given; the low value is probably due to the quality of the copper wire tested. The small value found for the modulus may perhaps be accounted for in a similar way.

Experiment 10.

A smaller piece of copper magnet-wire was used for this experiment. Its diameter was 0.50 mm. The following table gives the results that were obtained, and Figs. 6 and 7 represent them graphically.

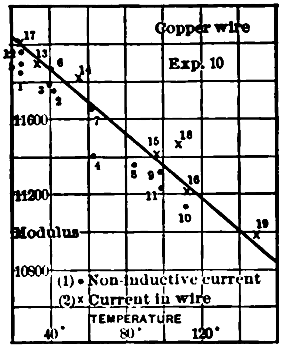

Fig. 6.

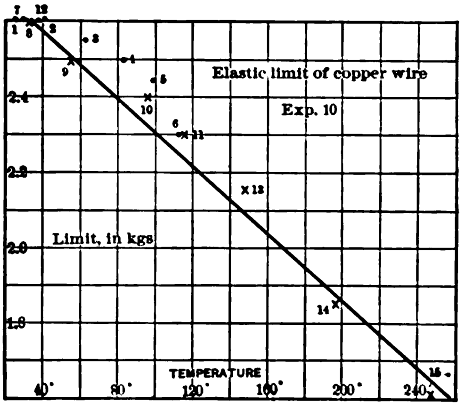

Fig. 7.

TABLE II.

Non-inductive Current.

No.	Date.	Temperature.	Elon. for 0.6 Kg.	No. of obs.	Modulus.	Elastic limit.	No. (Elastic limit series).
1	June 14	25°.5	983.60	6	11,841		
2	" 14	40°.8	990.73	6	11,754		
3	" 14	40°.2	988.56	10	11,780		
4	" 14	62°.8	1020.87	3	11,402		
5	" 15	24°.7	979.80	4	11,887	2.60 Kg.	1
6	" 15	40°.3	981.37	7	11,866	2.60	2
7	" 15	62°.9	998.84	7	11,653	2.55	3
8	" 15	82°.8	1025.80	4	11,345	2.50	4
9	" 15	97°.9	1027.29	7	11,327	2.45	5
10	" 15	111°.6	1045.30	4	11,129	2.30	6
11	" 15	98°.8	1036.30	6	11,228		
Current through wire.							
12	June 17	25°.1	973.93	6	11,959	2.6	7
13	" 17	33°.3	978.50	4	11,901	2.6	8
14	" 17	55°.0	984.30	6	11,827	2.5	9
15	" 17	96°.0	1019.76	5	11,409	2.4	10
16	" 17	112°.9	1036.77	6	11,218	2.3	11
17	" 17	25°.0	972.05	4	11,982	2.6	12
18	" 18	107°.0	1014.60	6	11,465		
19	" 18	149°.3	1057.33	6	10,994	2.15	13
20	" 18	188°.3	1146.63	6	10,132	1.85	14
21	" 18	248°.8	1050.09	9	9,209	1.60	15

$Q = 0.1998$ sq. mm. $L = 950.91$ at 25°.5. $P = 0.6$ Kg.

If we notice numbers 1, 5, 12, and 17, all of which were obtained at the temperature of the room, we see an increase in the elasticity after each time that the wire was heated, although the change from 12 to 17 was very slight. The increase may have been partly due to stretching the wire in determining the elastic limit, and not wholly to the heat; the irregularity of the values after the seventeenth is probably due to the same cause.

The results found for the elastic limit show a decrease which is very nearly proportional to the increase in temperature. As was found to be true with the silver wire, the elastic limit decreased slightly with repeated heating and stretching, while the elasticity was increased by the same treatment.

The following table gives a comparison of the results obtained with the copper wires tested in this and the preceding experiment:

TABLE III.

	1	2
Coefficient of Expansion	0.0000153	0.0000164
Thermal coefficient of elasticity	0.00133	0.000698
Modulus at 25°	10020	11980
Thermal coefficient of elastic limit . . .	0.0034	0.00165

As the table shows, the differences in all of the properties tested are very marked. The thermal coefficient of elasticity, and also of the elastic limit, are nearly twice as large in the first case as in the second. Such results serve rather to call attention to the wide variations in the properties of apparently similar specimens of wire than to fix the values of the coefficients determined.

Conclusion.

The following table gives a summary of results obtained from the experiments described in this article and the one previously published. The results for the piano wires are for temperatures ranging from about 15° to 180°, for the silver wire and the first copper wire the range was from 20° to 80° or 90°:

TABLE IV.

Kind of wire.	Diam.	Per cent of change in modulus for 100°.	Per cent of permanent change in modulus.	Per cent of change in elastic limit for 100°.
Piano wire	0.40 mm.	5.0		
Piano wire	0.26	4.6		
Piano wire	0.45	4.6		
Piano wire	0.49	4.3		
Average for piano wire . .		4.6	1.5	
Annealed piano wire . . .	0.45	3.4	1.27	
Silver wire	0.48	8.2	1.8	69.2
Copper wire	0.64	13.3		33.9
Copper wire	0.50	7.04	1.15	16.8

The results obtained show that neither magnetization nor an electric current through a wire produces any appreciable effect upon the size of Young's modulus aside from that which can be attributed to the accompanying heat. All the wires show a permanent increase in elasticity produced by heating them, the increase being greatest for the silver and least for the copper wire.

The thermal coefficient of elasticity is somewhat smaller for annealed than for unannealed piano wire. The values found for the thermal coefficients of silver and copper wire are much larger than those that have been found by others who have worked upon this subject.[1] Perhaps the weights which my method of experiment made necessary were heavier than those used by other experimenters; the thermal coefficient may be quite different for weights nearly as large as the elastic limit from what it would be with smaller weights.

The temporary effects of heat upon the elastic limit of silver and copper wires are very marked. In some electric circuits for which copper wire is employed, it has been found that the wire stretches much more during the summer than it contracts when the cold weather returns. This is doubtless because the elastic limit is so decreased by the summer heat that the weight of the wire between the points of support stretches it beyond this limit. The fact that copper wires vary so much in the effect of heat upon the elastic limit may need to be considered in selecting wires for telephone circuits or other purposes for which long wires are to be employed.

(These experiments were made under the direction of Professor Frank P. Whitman, and the paper was presented as part of a thesis for the degree of Ph.D.)

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[1] N. Katzenelsohn, Beiblätter XII., p. 307, 1888. H. Tomlinson, Pro. Roy. Soc., XL. p. 343, 1886.

A PHOTOGRAPHIC STUDY OF ARC SPECTRA. II.[1]

By Caroline Willard Baldwin.

II.

Metallic Spectra.

CERTAIN metals when introduced into the arc tend to obscure the band spectrum, *e.g.* Na, Li, K, Sr, Ba, Ca; while others, as Zn, Cd, Cu, Ag, give the band spectra with equal or increased brilliancy. In no case was the band spectrum entirely invisible, but it was so much weakened by the alkalies that it is not strange that in their presence the carbon bands were not detected by the bolometric measurements of Professor Snow.

In the ensuing paragraphs the results obtained by photographing the arc when cores of the carbons were filled with various alkalies are briefly described and tables of the lines are given.

Lithium Carbonate.

Lithium gives an almost homogeneous carmine-colored arc. The spectrum has much the same general appearance as the spectra from the outer sheaths of the arc, with the addition of the lithium lines, and at a very short distance from the center of the arc the band spectrum is entirely invisible. However, the bright groups are faintly visible in the photographs taken from the center of the arc.

Lithium does not materially affect the other metallic lines present in the ordinary arc spectrum. The lines which are most brilliant in the outer sheaths of the original arc are, with but few exceptions, the strong lines present when lithium is introduced. The carbon lines 3585.99, 3586.04, and 3590.52 are much fainter than in the yellow of the ordinary arc, and are not visible at

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[1] Concluded from the Physical Review, March–April, 1896.

all when the slit is at a little distance from the center of the image, while a line at 3583 is very sharp in all the photographs. The calcium lines 4299.14, 4302.68, 4318.80, 4425.61, 4435.86, and 4456.81 are stronger than in the yellow of the arc, being nearly as strong as 4307.91; but Ca 4527.17 is fainter in comparison to surrounding lines. Line 4527.17 is in fact hardly visible.

Lithium lines photographed.[1]

$\lambda = 2741.39$	$\lambda = 3794.9$	$\lambda = 3985.94$	$\lambda = 4602.37$
3232.77	3838.3	4132.44	4972.11
3670.6	3915.2	4273.44	6103.77
3718.9			

Sodium Nitrate.

When sodium is in the arc the flame is homogeneous and quite dense; the band spectrum is not so faint as when lithium is present, still it is much reduced in brilliancy. All of the calcium lines are strengthened. Calcium seems to have been present as an impurity in a number of the salts used. The *D*-lines were reversed both when the nitrate and chloride were used.

Sodium lines photographed.

$\lambda = 2512.23$	$\lambda = 4343.7$	$\lambda = 4546.03$	$\lambda = 5153.72$
2543.85	4390.7	4665.2	5670.40
2593.98	4393.7	4669.4	5675.92
2680.46	4420.2	4748.36	5682.90
2852.91	4423.7	4752.19	5688.26
3302.47	4494.3	4979.30	5890.19
3303.07	4500.0	4983.53	5896.16
4325.7	4542.75	5149.19	

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[1] The wave lengths of the metallic lines are taken from Kayser and Runge, Ueber die Spectrum der Elemente, with whose measurements the scale readings agreed quite accurately. These tables are not given to establish wave lengths, but to show which of the lines already catalogued were found in these photographs.

Potassium Chloride.

Potassium easily gives a long arc which is homogeneous and very clear, so as to be hardly visible between the carbons. It is of a less intense color than the arc of sodium or of lithium, and seems to be surrounded by a considerable mass of cooler vapor. The carbons are not at a very high temperature. The band spectrum is absent except very near the positive carbon. The strong metallic lines from the original arc are present. The metallic lines appear much as when sodium and lithium are used.

Potassium lines photographed.

λ = 3217.76	λ = 4047.36	λ = 4956.8	λ = 5112.68
3446.49	4870.8	4965.5	5782.67
3447.49	4943.1	5084.49	5802.01
4044.29	4952.2		

Calcium Chloride.

When calcium is in the carbons, they are as highly incandescent as carbons which contain no metallic salt. The heat of the arc does not seem to be so much diminished as in the preceding cases. The arc shows a more varied formation. There is a blue-violet center, which is decidedly blue near each carbon. This is surrounded by a dark part, while the outer sheath is of an orange tint. The dark part diminishes as the carbons become heated.

In the spectrum the strength of the bands is less affected than by the other metals yet studied; but their hazy appearance is removed, and the fine lines are more sharp. As soon as we pass into the outer sheath, the bands disappear with the exception of a slight indication of the one which terminates at $\lambda=3885$. The calcium lines remain exceedingly sharp and brilliant in the outer sheath.

As in the ordinary arc, the calcium lines 4581.66 and 4586.12, also lines of unknown origin near 4603., 4586., and 4581., are clearly seen at the negative carbon only, while lines at 4604. and 4576. are visible only at the positive carbon. Line 4226.91 was strongly reversed.

Calcium lines photographed.

λ = 2398.66
2995.06
2997.42
2999.76
3006.95
3140.91
3150.85
3158.98
3179.45
3181.40
3209.68
3215.15
3225.74
3344.49
3350.22
3361.92
3468.68
3474.98
3487.76
3623.15
λ = 3630.82
3644.45
3653.62
3706.18
3737.08
3933.83
3949.09
3957.23
3968.63
3973.89
4092.93
4095.25
4098.82
4226.91
4240.58
4283.16
4288.51
4299.14
4302.68
4307.91
λ = 4318.80
4355.41
4425.61
4435.13
4335.86
4454.97
4456.08
4456.81
4508.04
4509.89
4512.73
4527.17
4578.82
4581.66
4586.12
4685.40
4833.85
4847.22
4878.34
5041.93
λ = 5189.05
5260.58
5261.93
5262.48
5264.46
5265.79
5270.45
5349.66
5513.07
5582.16
5588.96
5590.30
5594.64
5598.68
5601.51
5603.06
5857.77
6102.99
6122.46

Strontium Oxide.

With strontium the arc has a pear-shaped purple center, the larger end of which rests on the positive carbon. The central part is bluish at each carbon. The outer sheath is of a brilliant red color, and the line between the two parts is very sharp and bright. The carbons are not very hot. They are, indeed, scarcely more than at a red heat. The effect on the spectrum is similar to that of calcium, and the same arrangement of lines at the positive and negative carbon is emphasized. The band spectrum is about as strong as when calcium is present, but it does not disappear quite so completely as in the outer sheaths of the arc.

The number of strontium lines in the vicinity of the bands tends to obscure their character.

Strontium lines photographed.

$\lambda = 2931.98$	$\lambda = 3547.92$	$\lambda = 4319.39$	$\lambda = 4784.43$	$\lambda = 5156.37$
3199.1	3628.62	4326.60	4812.01	5222.43
3200.4	3653.22	4338.00	4784.43	5225.35
3301.81	3705.88	4361.87	4812.01	5229.52
3307.64	3940.91	4412.82	4832.23	5238.76
3322.32	3969.42	4438.22	4855.27	5257.12
3330.15	3970.15	4480.96	4868.92	5451.08
3351.35	4030.45	4531.54	4869.41	5481.15
3366.43	4032.51	4607.52	4872.66	5486.37
3380.89	4077.88	4678.39	4876.35	5504.48
3464.58	4161.95	4722.42	4892.20	5522.02
3475.01	4215.66	4729.93	4962.45	5535.01
3477.33	4305.60	4742.07	4968.11	5540.28
3499.40	4308.49	4755.59	4971.85	5543.49
3504.70				

Barium Chloride.

When barium is present, the arc has a large round center, which shades from rose pink through lemon yellow to lime green at the edge. Next to each carbon it is of a brilliant lemon yellow color. The carbons are not very highly heated.

The barium lines come out easily, and are very strong; but the bands and all but the strongest lines in the original spectrum are so weak that they are almost invisible.

Barium lines photographed.

$\lambda = 2304.32$	$\lambda = 3662.62$	$\lambda = 4085.35$	$\lambda = 4407.10$	$\lambda = 4636.80$
2335.33	3664.76	4087.90	4413.96	4642.38
2596.89	3689.28	4110.46	4432.13	4673.69
2702.78	3701.87	4130.88	4467.36	4691.74
3281.96	3794.77	4132.60	4489.50	4700.64
3357.00	3861.87	4166.24	4493.82	4724.98
3420.48	3889.45	4179.57	4506.11	4726.63
3501.29	3891.97	4224.11	4523.48	4877.99
3525.23	3892.97	4239.91	4525.19	4900.13
3544.94	3900.54	4242.83	4554.21	4903.11
3577.79	3906.20	4264.45	4574.08	4934.24
3579.97	3910.04	4283.27	4579.84	4947.50
3586.64	3917.42	4323.15	4589.82	5424.82
3588.33	3935.87	4325.38	4591.88	5437.66
3593.58	3938.09	4333.04	4600.02	5519.37
3599.60	3993.60	4350.49	4605.11	5535.69
3611.17	3995.92	4359.80	4620.19	5777.84
3637.10	4079.56	4402.10	4628.45	5853.91

Zinc Chloride.

The band spectrum is better than was obtained under any other circumstances. The bands are greatly extended and very distinct. The arrangement of lines in different parts of the arc is especially marked in the flame spectra. All of the calcium and aluminium lines are very clear in the outer sheath of the arc and near the negative carbon. The bands cling closely to the positive carbon, but the zinc lines cross the arc with nearly equal brilliancy in all parts. Only the carbon bands are seen in the region having a wave length greater than $\lambda = 4862$.

The "grating effect" is continuous from $\lambda = 3400.$ to $\lambda = 5635$. The effect of the zinc seems to be to obscure all but the strongest of the other metallic lines, and to increase the intensity of the band spectrum.

Zinc lines photographed.

λ = 2802.11	λ = 3072.19	λ = 3515.26	λ = 4293.02
2823.27	3075.99	3572.90	4298.54
2833.13	3282.42	3671.71	4630.06
2863.43	3302.67	3683.63	4680.38
2873.39	3303.03	3740.12	4722.26
2913.63	3345.13	4019.75	4810.71
3018.50	3345.62	4058.02	5182.20
3035.93	3346.04	4101.94	

Cadmium Chloride.

The spectrum obtained when cadmium is present in the arc is similar to that with zinc.

Cadmium lines photographed.

λ = 2677.65	λ = 2961.64	λ = 3466.33	λ = 3981.92
2712.65	2980.75	3467.76	4306.98
2733.97	2981.46	3500.09	4413.23
2763.99	3081.03	3595.64	4662.69
2775.09	3133.29	3610.66	4678.37
2837.01	3252.63	3613.04	4800.09
2868.35	3261.17	3649.74	5086.06
2880.88	3299.11	3729.21	5154.85
2881.34	3403.74		

Copper.

Copper gives an arc which has a bluish-green center with bright green near the carbons. This is surrounded by a dark part, which is again enclosed by a yellow outer sheath.

The spectrum appears almost like that obtained from the center of the original arc, with the addition of the lines due to copper. The variation in brightness of certain lines at the positive and negative carbons is very noticeable, and is more easily observed owing to the fact that the copper lines are all strongest *about half-way between the carbons,* at which point they show a decided enlargement. In the band spectrum only the fine, grating-like lines are seen. The indications of the strong lines are seen at the negative carbon, while the lines of the band spectrum are strong for the whole width of the arc.

Copper lines photographed.

$\lambda = 3771.96$	$\lambda = 4123.38$	$\lambda = 4378.40$	$\lambda = 4674.98$
3860.64	4177.87	4397.42	4697.62
4003.18	4242.42	4415.79	4704.77
4010.96	4249.21	4480.59	5105.75
4015.80	4253.53	4507.62	5144.35
4022.83	4259.63	4509.60	5153.33
4056.80	4267.48	4513.39	5218.45
4062.54	4275.32	4531.04	5220.25
4063.50	4329.00	4539.98	5292.75
4073.28	4336.17	4587.19	5700.39
4080.70	4354.91	4651.31	5782.30

Silver.

The appearance of silver in the arc, and its effect upon the spectrum, are almost identical with that of copper.

Silver lines photographed.

$\lambda = 3280.80$	$\lambda = 3841.30$	$\lambda = 4055.44$	$\lambda = 4616.03$
3383.00	3907.63	4212.10	4668.70
3542.67	3914.47	4311.28	4678.04
3557.30	3940.30	4379.45	5209.25
3681.80	3943.10	4396.49	5465.66
3710.10	3981.87	4476.29	5471.72
3810.60	3991.90	4556.13	

REMARKS.

As has been noted in a previous paragraph, the lines of the ordinary arc which are strongest at the negative carbon increase in intensity in the outer sheaths, while the reverse is true with the lines from the positive carbon. When the metals K, Na, Li, Ba, Sr, and Ca are introduced, the lines from the positive carbon are weakened. The effect is most marked in the case of potassium. Barium reduces the carbon bands the most.

The metals Cu and Ag, from the group I. *b*, give the spectrum in about its normal condition, with the lines due to the especial metal added; while the metals Cd and Zn increase the intensity of the bands and diminish the strength of the metallic lines originally present near the negative pole.

It has been frequently observed by others who have worked with metallic spectra by this method, that it is necessary to have added resistance in the circuit which supplies the arc, when metals are used, in order to maintain a constant length of arc. The amount that had to be added in the course of these experiments varied very much with the different metals.

In a circuit of such electromotive force that 3 ohms resistance were necessary to give the ordinary arc its normal voltage (48 v), it was found that the following resistances would restore the arc to its proper condition:

Metal.	Resistance.	Metal.	Resistance.
Silver	3.1	Cadmium	5.8
Copper	3.8	Potassium	9.1
Zinc	5.6	Sodium	9.5
Barium	5.6	Lithium	9.7
Strontium	5.8	Calcium	9.9

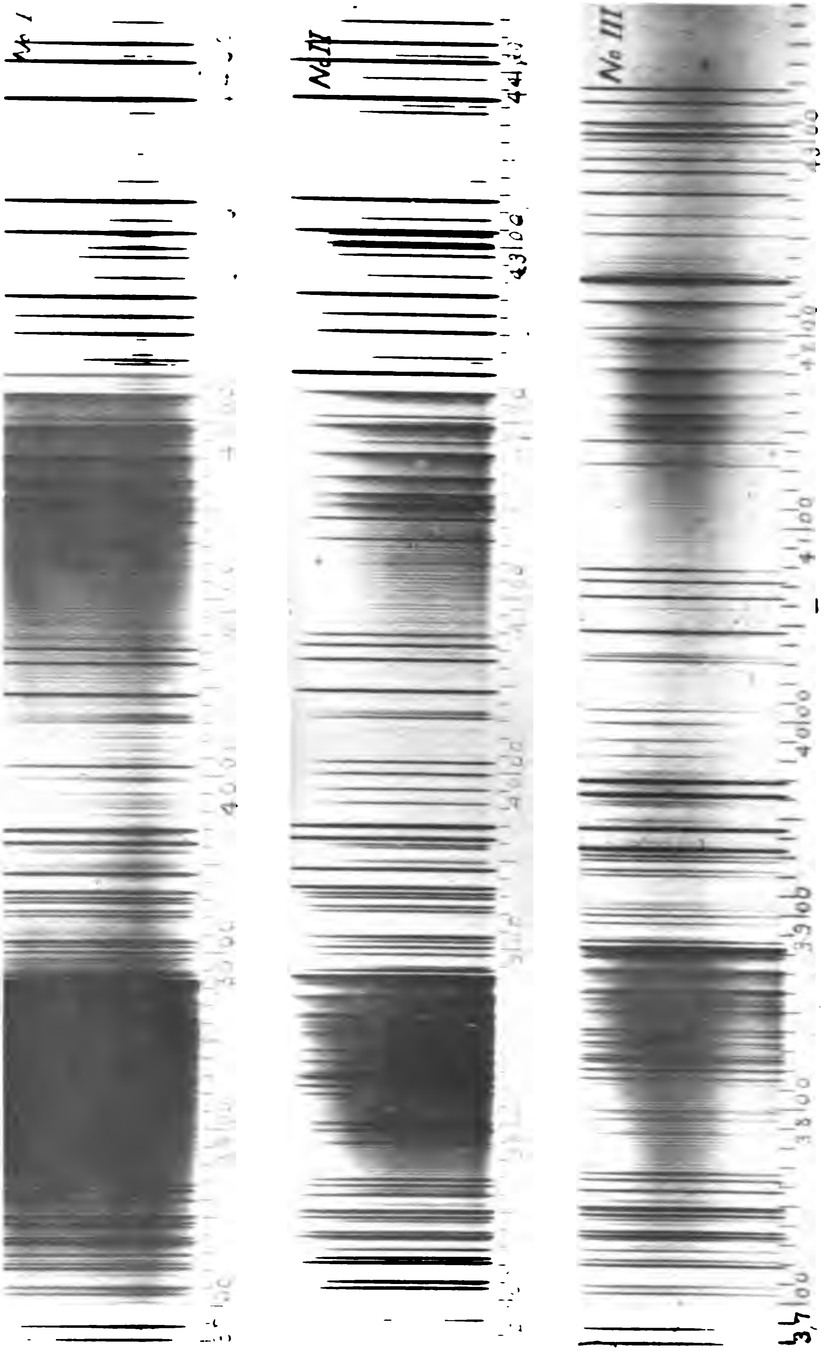
When the metals were used, the temperature of the carbons was apparently much less than with the pure carbon points. The temperature of the positive carbon was most affected, and it did not waste so rapidly in proportion to the negative as when no metallic salt was in the core.

It might be thought that the changes observed were due to the fact that the temperature is not high enough to render all the lines visible. This view would be strengthened if the lines of metals which require the highest temperature for fusing and vaporization were strongest in those parts of the arc which are hottest. But this does not seem to be the case, for although K, Na, and Li, metals of low melting points, are strengthened at the negative carbon, so also are Ba, Sr, and Ca, which have relatively high melting points. The Cu and Ag lines extend across the arc with nearly even intensity, and the same is true of Zn and Cd.

It does not seem that the diminished intensity of the carbon bands in the presence of certain metals can be wholly due to the density of the gases of the flame; as there is no direct relation between the amount of weakening of the bands and the density of the metallic vapor. Neither does the change seem to depend in any simple way upon the atomic weight of the metals. Barium and potassium obscure the bands most; and they are respectively the highest and lowest in atomic weight of the metals studied.

There are many reasons for believing that there is an electrolytic action in the arc. This belief is strengthened by the fact that the metallic lines appear at the negative carbon, and the carbon bands are strongest at the positive. It is also true that the metals K, Na, Li, Ba, Sr, Ca, which are highly electropositive, are more strengthened at the negative carbon than are Cd, Zn, Cu, Ag, which are less positive.

In studying the effect of the metals upon the lines of the original spectrum, we may consider the need of increased resistance in the outer circuit to be due to diminished resistance of the arc, or to a change in the counter electromotive force. In the former case, the list of resistance given should have the same order as the resistance of the various metallic vapors. The arrangement, however, is not that of the respective metals as we know them at ordinary temperatures.



C. W. BALDWIN ARC SPECTRA.

SUMMARY.

(1) The spectrum obtained from the electric arc is not the same for all parts of the arc and the surrounding flame. On the contrary, there is a decided difference in the spectrum of the several sheaths. The difference is largely due to a fading out of the carbon bands and of all lines from the positive carbon, and an increase of intensity in the outer sheath of those lines which are most brilliant near the negative carbon. Certain lines and bands which are invisible in the center are seen in the outer part of the flame.

(2) The total number of metallic lines diminishes rapidly, as we explore the arc from the center outwards.

(3) When the spectrum is changed by the introduction of metals into the carbons, it is observed that the more positive metals, such as K, Na, Li, and Ba, Ca, Sr, greatly weaken, but do not destroy, the characteristic band spectrum of the arc. The lines which are most affected by these metals are those which in the ordinary spectrum are strongest near the *positive carbon.*

Certain metals, as silver and copper, do not materially alter the original arc spectrum, while others, as zinc and cadmium, affect the lines near the *negative carbon,* and thus give the band spectrum, which is no longer obscured by the metallic lines usually present, an unwonted brilliancy.

The causes of the phenomena are not easily discovered, but it is hoped that the points brought out in this paper may throw some light upon the intricacies of this complex problem.

MINOR CONTRIBUTIONS.

A Method for the Use of Standard Candles in Photometry.

By Clayton H. Sharp.

THE fundamental assumption on which is based all American and English practice in the use of candles as a standard of light in photometry is that the intensity of light emitted by a candle is, within certain arbitrary limits, proportional to the rate at which the material of the candle is consumed. Supposing this assumption to be in a measure justifiable, we could scarcely imagine it to be rigorously exact. The purity and hygrometric state of the air, which Liebenthal [1] has recently shown to have such a large influence on the intensity of the Hefner light, can scarcely be of inappreciable influence on the candle flame.[2]

But no matter how nearly this assumption approximates to the true state of affairs, the fundamental and inevitable difficulty with this definition of the light unit still remains. It is this: what we ought to know is not the mean rate of consumption during the period over which the measurements extend, but the rate at the instant at which a photometer setting is made. Since it is impracticable to determine this quantity, the mean rate has been used for correcting observations.

That this cannot be a proper method of procedure on the assumption made, is shown by a study of the enormous and quick variations to which the quantity of light emitted by a candle is subject. Curves [3] showing these instantaneous variations have been obtained by the use of a sensitive bolometer which, when exposed to the radiation of a candle flame, would respond to every change in the intensity of that radiation. It is quite

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[1] Liebenthal, "Ueber die Abhängigkeit der Hefnerlampe und der Pentanlampe von der Beschaffenheit der umgebenden Luft."

Elektrotechnische Zeitschrift, XVI., p. 655, 1895.

Zeitschrift für Instrumentenkunde, 15, p. 147.

Electrical World Digest, XXVI., p. 220 and p. 500, 1895.

[2] For evidence confirming this statement see an article by John Methven read before the Southern District Association of Gas Engineers and Managers, London Gas World, 1889, p. 572. A translation into German will be found in Dingler's Polytechnisches Journal, 1890, Vol. 277, p. 276.

[3] Sharp and Turnbull, "A Bolometric Study of Light Standards," Physical Review, Vol. II., p. 1. This article will be referred to frequently.

possible that a series of photometric settings should be made in such a way that their mean would give a value considerably lower than the mean ordinate of an intensity curve covering all the time between two weighings of the candle.

Moreover, in the bolometric investigation it was found that corrections to the mean ordinates of the various curves for deviations from the normal rate of consumption did not serve to reduce these ordinates to a common value; or, in other words, that the energy radiated was not proportional to rate. Since the radiant efficiency of a candle flame does not change with its size, — provided that it does not smoke, — this would be true for luminous radiation as well as for total radiation. This is in accord with the observations of Tyndall[1] and the results of von Jolly, who showed that on a mountain summit candles have a shorter flame and diminished intensity, with the same rate of consumption.

Recognizing these facts, the German photometrists have insisted that the flame height is the significant factor, and that candle measurements should be made only with a standard height of flame. They would clean the wick of the candle, wait until the flame height becomes normal, and then set the photometer.[2]

There are certain objections to this method of procedure although it undoubtedly gives better results than the English practice. In the first place, it must be a time-wasting and patience-trying operation. Moreover, it is very doubtful if snuffing the wick of a standard candle is an allowable operation, since the shape of the flame depends on the particular curl which the wick assumes, and is normal only when the wick has its natural curl.

A more desirable method would be to measure, at the instant the photometer setting is made, the height of the candle flame; then, knowing a relation between the height of the flame and the intensity of light emitted, to reduce the instantaneous intensity to the intensity at normal flame height.

The first question then becomes: Does any definite relation exist between these quantities? Giroud has shown that the slender, pointed flame

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[1] Tyndall, "Heat as a Mode of Motion." Also Dr. Frankland, Philosophical Transactions, 1861.

[2] In the original directions for the proper use of the German Vereinskerze, however, it is stated that snuffing is unallowable, and that measurements should be made only when the quietly burning flame has reached a height of 50 mm. See "Beschluss der Versammlung des Vereines des Gas- und Wasserfachmänner Deutschlands," etc. Dingler's Polytechnisches Journal, 206, p. 329. This is a reprint from the Journal für Gasbeleuchtung und Wasserversorgung, 1872, Nov. 12.

On the other hand, see the report of a committee of the Verein von Gas- und Wasserfacmännen as transcribed in La Lumière Électrique, 34, p. 178. Here snuffing the wick is recommended. See also Krüss' book, Elektrotechnische Photometrie.

of his bec-bougie varies at the rate of about 2 per cent per millimeter, the relation between flame height and intensity being nearly linear. Liebenthal[1] has drawn curves (see Fig. 1) showing this relation in the case of the Hefner lamp and of the English standard candle. For the former the relation is approximately linear for small variations and shows for variations between 35 mm. and 45 mm., 2.6 per cent per millimeter. The two English candle curves are practically straight lines for all ordinary variations, and show 2.1 per cent and 1.9 per cent per millimeter respectively, for variations between 40 mm. and 50 mm.

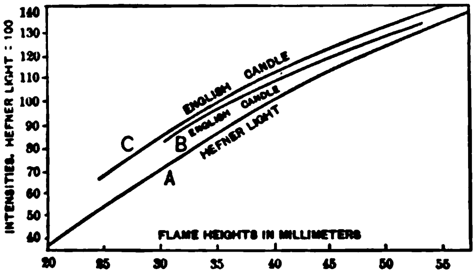

Fig. 1.

Curves by Liebenthal.

The present experiments were suggested by the results of the bolometric tests of candles. They were undertaken first for the purpose of investigating this relation between flame height and intensity, and, second, to determine whether the use of this relation would not make it possible to get more consistent results than can be obtained by correcting for rate of consumption.

Two methods were employed to determine the flame height-intensity ratio. In the first method the intensity of the radiation of the candle was measured by the bolometer in the way previously described. To measure the height of the flame, a long camera was constructed, having its lens and ground-glass plate at a fixed distance from each other. The ground-glass plate was graduated empirically to read directly in millimeters the height of objects focussed upon it. The candle was placed on a pan attached to a spiral spring of such a length that its elongation would be just equal to the length of the candle. By this arrangement the top of the candle was kept at a constant height above the floor, and when once the image of the base of the flame had been accurately adjusted on one of the lines of the camera screen (to facilitate which the screen was capable of a slight vertical movement), it remained there during a considerable period of time. Hence, to measure the height of the flame at any instant, it was necessary only to glance at the image of the *top* of the flame and to note its position on the screen. It will be noticed that this camera device is, to a certain extent, a modification of Krüss' optical flame measure which has been in use a

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[1] Liebenthal, "Photometrische Untersuchungen über die von Hefner-Altensck'sche Lichteinhert," Elektrotechnische Zeitschrift, 9, p. 96, 1888.

number of years. Extended to take in the bottom of the flame, and combined with the spring balance, it enables measurements to be made with great quickness, and with a sufficient degree of accuracy, by an observer who is located so far from the flame as to leave it entirely undisturbed by his movements.

The magnifying power employed was about two, and heights were measured only to 0.5 mm. Greater closeness of measurement was deemed unnecessary on account of the ill-defined nature of the base and tip of the flame. The actual base of a candle flame is difficult to observe, on account of the small quantity of light which it emits. The procedure adopted was to set on the line of demarkation between the charred and uncharred portions of the wick, since this was found usually to mark the base of the flame. In case a close inspection of the candle showed the base of the flame to be slightly above this point, a further adjustment of the screen was made.

In order to insure great steadiness of the flame, the candle was placed in a roomy, well-ventilated box having a glass window. Having put the candle in position before the bolometer, and having adjusted the camera properly, the bolometer screen was raised and simultaneous observations were made of galvanometer deflections and flame heights. These readings were corrected for any change in sensitiveness of the bolometer and any drift of the galvanometer needle, and were plotted, using flame heights and galvanometer deflections as coördinates.

In the second method a Lummer-Brodhun photometer was used. At one end of a photometer bar 200 in. long was placed a 110-volt glow-lamp. This was maintained at a voltage of 100 by means of a storage battery. Being run at low efficiency, its color was about the same as that of a candle, and its change in candle power during the time it was in use was too small to be detected.

At the other end of the bar was the candle, supported by its adjusted spring. The candle was always placed so that the curl of the wick was perpendicular to the axis of the bar.[1] The arrangement for measuring flame heights is shown in Fig. 2, which represents a projection of the apparatus on a horizontal plane. *B* is the photometer bar, *C* the candle, *M* a mirror placed behind the candle in such a way as to reflect the rays from it through the lens *L*, which projected them on a graduated screen *S* placed immediately behind the bar. The mirror was carried on a movable support so as to admit of an adjustment of focus.

This arrangement was adopted, since by its use one observer could do

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[1] For the variation of the intensity of candle as a function of the azimuth of the plane of the wick, see Methven, *loc. cit.;* also an article by Sugg, in the Journal for Gas Lighting, which is reprinted in the Scientific American Supplement, No. 484, p. 7726.

all the work. The method was simply to make a rather quick photometer setting, and then instantly to note the position of the top of the flame on the screen, reading the position of the photometer afterwards.

In some of the earlier measurements a kerosene lamp with an Argand burner similar to the ordinary student-lamp burner was used as a secondary standard. The upper part of the chimney was covered by a closely fitting cylinder of ferrotype iron in such a way that the top of the flame was entirely hidden. This furnished a very steady source of light after it had been burning long enough for the parts to become thoroughly warmed, and its intensity was unaffected by slight adjustments of the height of the flame, provided only that the flame was always high enough. Unfortunately, its intensity varied enough from day to day to make its indications unreliable without a daily calibration, and it was replaced by the more convenient and accurate glow-lamp. Observations of variation of intensity with flame height are not affected by this fact.

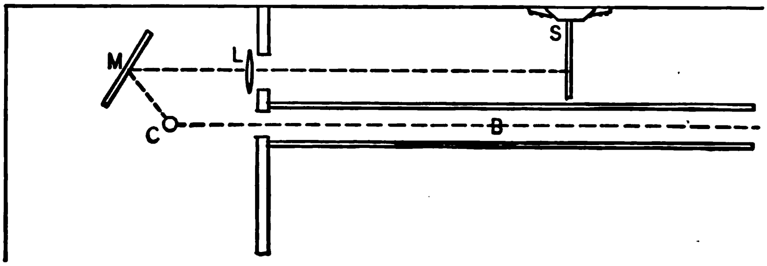

Fig. 2.

Arrangement of Photometer.

The observations were treated in the following manner: The various observed values of flame height were collected in such a way that heights of 41.0 mm., 41.5 mm., and 42.0 mm., formed one group; 42.5 mm., 43.0 mm., and 43.5 mm., another, etc. The mean height of each group was found, and also the mean bar-reading corresponding to it. The candle power of the standard was found by taking the mean of all the heights and bar-readings, and reducing, by means of an approximate correction, to a standard flame height of 45 mm. Using this value for the intensity of the glow-lamp, the intensity of the candle corresponding to each group was computed. By means of a curve plotted from these values the percentage variation per millimeter of flame height was determined.

In order to find the relative accuracy of this and of the ordinary method of using candles, the following observations were made: A candle burning normally was weighed by the "method of transits," was transferred to the spring balance, and ten or more photometer settings made — the flame heights also being noted. The candle was then weighed again, and another group taken. A number of such sets of observations were made on several days, and since the glow-lamp was used as a reference standard, these sets are comparable with each other.

The mean value of the candle power of the glow-lamp given by each of these sets of observations was corrected for rate in the ordinary way, and was also corrected by reducing from the mean flame height to the standard height of 45 mm., using the mean value of the relation between intensity and flame height as determined from all the observations, both bolometric and photometric. The deviation of each value obtained for the candle power of the glow-lamp from the mean value obtained from all the observations was computed, and this deviation was reduced to per cent. A comparison of the percentage deviations given by the two methods shows their relative accuracy, while the absolute values of the percentages show the error which one is liable to make in using candles in either of the two ways.

Table I.

Flame height (mm.).	Galvanometer deflection.	Flame height (mm.).	Galvanometer deflection.	Flame height (mm.).	Galvanometer deflection.
48.0	29.0	44.0	26.7	43.0	25.8
48.5	29.5	45.0	27.5	44.0	27.0
49.5	30.3	45.5	28.3	Wick of candle cleaned.	
48.0	29.2	43.5	27.0		
47.0	28.2	43.5	27.0	55.0	37.2
47.5	28.8	44.5	27.5	46.5	30.6
45.5	27.5	44.5	27.5	47.5	31.3
46.5	28.0	45.0	28.3	48.0	32.0
46.5	28.2	44.5	27.7	49.0	32.7
46.5	28.0	43.5	26.5	49.0	32.6
45.0	27.0	43.5	27.0	49.5	32.8
45.5	27.6	43.0	26.5	50.5	33.7
45.5	27.8	42.5	26.0	50.0	33.0
44.5	26.5	43.5	26.8	50.0	33.0
42.0	25.8	42.5	25.5	50.0	33.2
43.0	26.8	43.5	26.0	49.0	32.6
43.0	26.0	44.0	26.3	47.0	30.4
43.5	26.7	43.5	26.0	48.5	30.0
44.0	26.8	43.5	26.2	48.5	31.0
44.5	27.1	44.0	26.7	47.0	30.0
44.5	27.2	44.5	27.0	46.5	30.0
43.5	26.4	44.0	26.8	46.5	30.0

Table II.

Flame height (mm.).	Photometer bar.	Flame height (mm.).	Photometer bar.	Flame height. (mm.).	Photometer bar.
45.5	702	41.5	713	53.0	686
46.5	699	43.0	707	48.0	700
48.0	700	43.0	708	48.5	695
49.0	693	44.0	706	46.0	704
51.5	690	44.0	707	45.0	708
53.0	697	45.0	705	44.0	707
44.5	709	44.0	709	44.0	711
46.0	705	44.0	710	46.0	707
49.0	694	43.0	713	43.0	713
46.0	699	45.0	708	46.0	708
48.0	698	End of	wick	44.5	710
48.0	693	cut	off.	44.0	711
49.0	691	40.0	712	46.0	711
45.5	700	44.0	708	45.5	708
44.0	707	47.0	698	46.0	712
45.5	699	48.0	696	42.5	716
48.0	697	50.0	693	42.0	715
46.0	698	54.0	688	43.0	715
46.5	696	53.0	688	44.0	714
45.0	700	51.0	693	45.0	711
45.0	701	50.0	694		

Table III.

Bolometric.	Per cent.	Photometric.	Per cent.	Photometric.	Per cent.
1894. Nov. 29 . .	2.2	1895. July 27 . . .	3.3	1895. Dec. 3 E	2.3
Dec. 5 . . .	2.7	Oct. 30 . . .	3.4	F	
1895. Feb. 23, I.	2.2	Nov. 1 I.	3.3	G	
II.	2.5	II.	3.3	H	
III.	3.2	Nov. 6 I.	2.2	Dec. 4 I	2.6
March 21, I.	3.1	II.	2.7	J	
II.		Nov. 27 I.	2.7	K	
Oct. 4 . . .	2.7	II.	2.9	L	
		Dec. 2, A.M., A	2.7	M	
		B		N	
		Dec. 2, P.M., C	2.8		
		D			
Mean . . .	2.7	D′		Weighted mean of all	2.7

Table IV.

Name of group of observations.	Rate (grams per hour).	Flame height (mm.).	C. P. of glow-lamp uncorrected.	C. P. corrected for rate.	C. P. corrected for flame height.	Deviation from mean corrected for rate.	Deviation from mean corrected for height.	Percentage deviation. Rate.	Percentage deviation. Height.
								%	%
A	7.601	43.0	6.11	5.99	5.78	+0.35	+0.04	+ 6.0	+0.7
B	8.320	45.15	5.785	6.20	5.80	+0.56	+0.06	+ 9.8	+1.0
C	6.981	44.95	6.01	5.41	6.00	−0.23	+0.26	− 4.25	+4.5
D	8.100	46.1	6.09	6.35	6.25	+0.71	+0.51	+12.6	+8.7
E	7.157	46.4	5.52	5.09	5.73	−0.55	−0.01	− 9.8	−0.2
F	7.863	44.7	5.67	5.74	5.62	+0.10	−0.12	+ 1.6	−2.1
G	8.030	44.8	5.72	5.91	5.69	+0.27	−0.05	+ 4.8	−0.9
H	7.330	44.05	5.80	5.47	5.66	+0.17	−0.08	+ 3.0	−1.4
I	8.422	44.3	5.65	6.13	5.54	+0.49	−0.20	+ 8.5	−3.5
J	7.271	47.1	5.35	5.02	5.65	−0.62	−0.09	−11.0	−1.6
K	7.367	46.15	5.50	5.22	5.67	−0.42	−0.07	− 7.6	−1.2
L	7.440	45.6	5.64	5.41	5.73	−0.23	−0.01	− 4.25	−0.2
M	7.137	42.3	6.00	5.52	5.56	−0.12	−0.18	− 2.3	−3.2
N	7.301	44.2	5.79	5.45	5.67	−0.19	−0.07	− 3.5	−1.2
Means, disregarding signs	7.594	44.9	5.76	5.64	5.74	0.36	0.125	6.35	2.16
Nov. 6, I.		45.5	5.60		5.68		−0.09		−1.6
II.		46.3	5.79		6.00		+0.23		+4.0
Nov. 11		43.1	6.17		5.85		−0.08		−1.4
Nov. 12, I.		44.1	5.87		5.73		−0.04		−0.7
II.		42.9	6.20		5.85		−0.08		−1.4
Dec. 2, D′		49.3	5.36		5.99		+0.22		+3.8
Means of all, disregarding signs		45.0	5.78		5.77	Last six only.	0.123		2.14

Results.

Table I. gives a characteristic set of data obtained by the use of the bolometer, 1894, March 21. Table II. is a similar set of photometric data obtained 1895, November 6. The data of Table I. and Table II. are shown reduced and plotted in Fig. 3 and Fig. 4 respectively. Table III. gives values found for the variation in intensity of candles expressed in per cents per millimeter. Table IV. shows, in the way described above, the comparative accuracy of the two methods of reducing candle observations. Figure 5 shows plots obtained from groups of observations designated by *A*, *B*, *C*, · · · *N*. Figure 6 shows plots from three successive sets of bolometric observations.

An inspection of the tables and curves will show that while the relation between flame height and intensity is a fairly definite one for any given group of observations, there is a considerable range of variation in the values for it as obtained from different groups. Moreover, the relation sometimes changes during one burning of the candle. Figure 6 illustrates this peculiarity in that there is a group of points marked ⊡ which lie considerably below the line plotted to represent all the observations; and that the slope of the flame height-intensity curve plotted from the points

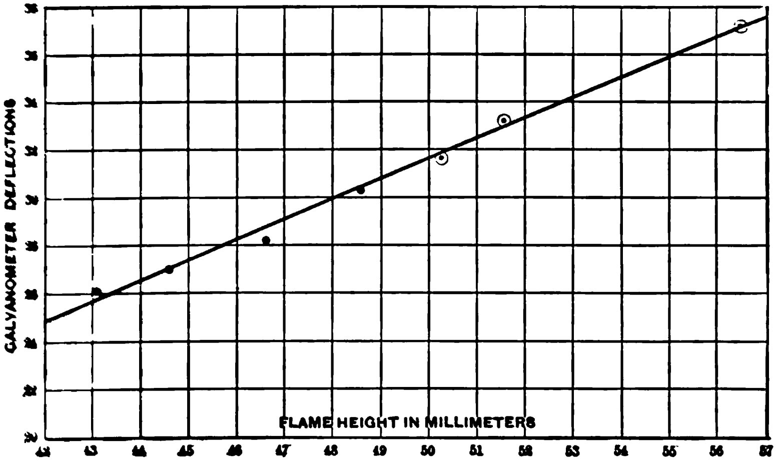

Fig. 3.

Bolometer Curve.

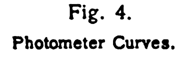

Fig. 4.

Photometer Curves.

[illegible] s materially different from that obtained from other groups [illegible] this may be due to a change in the shape of the wick. The [illegible] is not absolutely constant does not vitiate the pro- [illegible] candle observations; for since the deviations of flame height from 45 mm. is seldom more than 10 per cent, if our assumed value for this relation is in error by as much as 20 per cent, our reduced value for candle power would be in error by no more than 2 per cent.

Table IV. shows that the mean deviation from the mean of observations corrected in this way is a little over 2 per cent, and that fourteen out of twenty values were in error by 2.1 per cent or less. In the case of corrections for rate, the mean deviation is over 6 per cent, while but one out of fourteen values deviated by less than 2 per cent, and only four by less than 4 per cent.

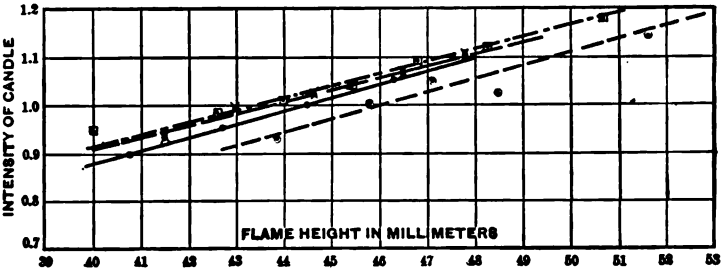

Fig. 5.

Photometer Curve.

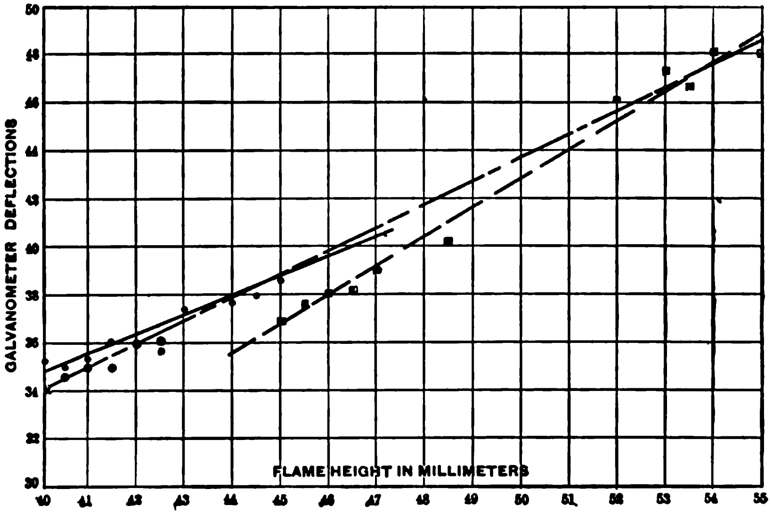

Fig. 6.

Bolometer Curve.

In other words, by correcting for flame height an error of less than 2 per cent may reasonably be expected, and the probability of making an error greater than 4 per cent is small; while in correcting for rate, errors of 8 per cent and 9 per cent are of common occurrence.

The values corrected for rate might, perhaps, be more consistent if the rule were followed to reject all observations in which the rate fell below 114 or above 126 grains per hour. Similarly, the errors in the values corrected for flame height might be smaller if observations made at extreme flame heights were to be rejected. Indeed, it is one of the chief advantages of the method that the observed flame height furnishes a criterion for the rejection of any observation which is regarded as doubtful. In this discussion, however, in order to be equally fair to both methods, no observations have been rejected.

The results of these photometer observations confirm fully those obtained by the use of the bolometer in determining the variations of light standards, and show very conclusively that the fundamental assumptions on which the bolometric tests were based, were entirely justifiable. If we compute from Table IV. the mean value of the flame height-intensity ratio, as determined by the bolometer, we find that it is just the same as the mean value from *all* the observations.

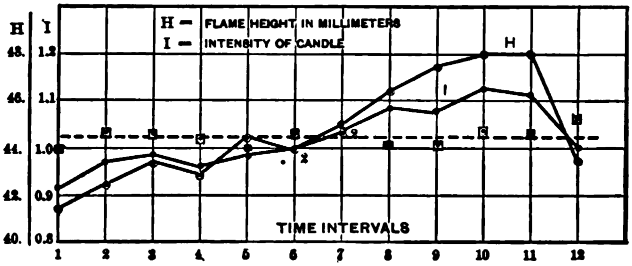

Fig. 7.

Variation of flame-height (H) and intensity (I) of English candles. Dotted line shows intensity reduced to standard flame-height.

In the "Bolometric Study of Light Standards" it was shown that the English candle is subject to sudden variations in intensity which are sometimes as large as 15 per cent. Many of these sudden drops were noticed while making the photometer observations, and they all had the same characteristics as are shown by the bolometer curves. Figure 7 shows a group of these observations — group F in the tables. Assuming that the time intervals between the various photometer settings were equal, points were plotted showing the relation between intensity of the candle and time and between flame height and time. It will be seen at once that the two curves are of very similar characters. The flame height gradually increased, and with it the intensity, until, when the height of 48 mm. had been reached, there was a sudden drop, the change in intensity amounting to 12 per cent.

These curves evidently show in an imperfect way variations precisely similar to those which are so faithfully reproduced by the galvanometer needle. In view of these qualitative and quantitative results, it would seem to be impossible to doubt the reliability of the bolometer as an instrument for making such tests.

Another interesting consequence of these candle measurements is the very careful standardization of the glow-lamp. Its intensity has been measured in terms of the Hefner light also, and by this means a good determination has been made of the candle power of the Hefner light. This result, together with previous determinations of the same ratio, appears in Table V.

TABLE V.

Observer.	Hefner. / English candle.
Sharp, candles reduced for rate	0.872
Sharp, candles reduced for flame height	0.892
Sharp and Turnbull, integration of energy curves [1]	0.941
Violle	0.98
Reichsanstatl investigations, mean value [2]	0.876
Netherland Photometry Commission [3]	0.921
S. Schiele, mean value [4]	0.881

The value 0.94 is taken from curves made in the bolometer tests, and rests on the assumption that the radiant efficiencies of the candle and Hefner flames are equal. Since the Hefner flame is distinctly redder in color than the candle flame, its radiant efficiency is probably smaller, and consequently the value 0.94 is too large. A difference in the radiant efficiencies of the two sources of less than 0.2 per cent would serve to bring

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[1] *Loc. cit.*

[2] This is the mean of a long series of determinations made by different observers at different times, using candles from various sources. The measurements were taken at normal flame height of 45 mm. See "Beglaubigung der Hefnerlampe"; Zeitschrift für Instrumentenkunde, 13, p. 257.

[3] An abstract in German by Krüss will be found in the Journal für Gasbeleuchtung und Wasserversorgung, 1894.

[4] Schiele, Report of Committee on the Comparison of the Hefner lamp and German and English candles, Journal für Gasbeleuchtung und Wasserversorgung, Band 32, 1889, p. 757; also Dingler's Polytechnisches Journal, 274, p. 540. The measurements were made at normal flame height of 45 mm.

this value down to 0.88. The preponderance of evidence in favor of the value 0.88 is very great. It is probably true that the very best way we have at the present time of determining candle power is to use the Hefner lamp and then to reduce by the use of this ratio.

The writer desires in conclusion to express his obligations to Mr. C. P. Matthews for timely assistance in making some of the above observations.

CORNELL UNIVERSITY, ITHACA, N.Y.,
January, 1896.

THE GRAPHICAL REPRESENTATION OF MAGNETIC THEORIES.

By HAROLD N. ALLEN.

THE induction theory of magnetism, introduced by Faraday, is now looked upon by all physicists as correct. The older theory which assumes the existence of magnetic fluids covering the ends of the magnet is in some cases mathematically simpler, and is for this reason often made use of. This, however, is apt to breed confusion as to the true nature of the induction or polarization in any given case. The difficulty Tyndall experienced in accepting Faraday's views as to diamagnetism, is accounted for by the fact that he was thinking in terms of the fluid theory, while Faraday was considering the magnetic polarization in the diamagnetic substance.

The object of this paper is to insist again upon the distinction between these two theories, and at the same time to consider some points in the induction theory itself. A number of diagrams will be described which illustrate the different aspects of the induction theory. They show how the molecules of the magnet are supposed to be polarized, and how this polarization is continued in the surrounding ether. The tubes of force, or "polarization tubes," and the equipotential surfaces are drawn in each case according to Maxwell's method. The figures must be revolved about the horizontal axis, so that the lines drawn will trace out, some the bounding surfaces between the tubes, and others the equipotential surfaces.

It has been found convenient to give the name polarization tube to a tube of force consisting of a bundle of 4π induction tubes. The polarization at any point is measured by the number of polarization tubes passing through a square centimeter of a surface, which cuts them at right angles, just as the induction is measured in the same way by means of the induction tubes.

If D_m is the magnetic polarization,
B_m the magnetic induction,
H_m the magnetic field intensity,

the following relations will hold:

$$D_m = \frac{B_m}{4\pi} = \frac{\mu H_m}{4\pi}.$$

A polarization cell or energy cell is a portion of the medium bounded on the sides by the walls of a polarization tube, and at the ends by two equipotential surfaces, differing from one another in value by unity. It is possible to regard each of these cells as containing half a unit (erg) of energy. This energy is to be regarded as in some way directed along the lines of force, as the energy of a bullet is directed along the line of its flight, or the energy of rotation of a fly-wheel is directed along its axis.

The length of the cell in a uniform field being

$$\frac{1}{H_m} = \frac{\mu}{4\pi D_m} = -\frac{dn}{dV_m},$$

and the area of its section being $\frac{1}{D_m}$,

the volume will be $\frac{\mu}{4\pi D_m^2}$.

Thus the density of the directed energy is $2\pi D_m^2$ in a medium of unit permeability.

According to one statement by Maxwell, the energy density in a medium of permeability μ is $\frac{2\pi D_m^2}{\mu}$. Ampère's theory of magnetism, however, implies, as will be shown, a much larger energy density than this.

In the first part of his treatise, Maxwell seems practically to assume that the polarization in a paramagnetic substance is made up of two parts, the polarization of the iron molecules or the intensity of magnetization I, and the polarization of the ether which occupies the same space $= D' = \frac{H'}{4\pi}$, where H' is the field intensity in the substance; that is, in a long uniform crevice, the direction of which coincides with that of the induction tubes.

Thus the total polarization is

$$D_m = \frac{H'}{4\pi} + I,$$

or

$$D_m = D' + I,$$

or in more familiar terms,

$$B_m = H' + 4\pi I.$$

The two polarizations are regarded as being superimposed, so that in some way they occupy the whole of the same space at the same time.

In Diagram II., Fig. 1, are shown the equipotential surfaces and polarization tubes produced, when an infinite cylinder of constant permeability, $\mu = 2$, is placed with its axis parallel to a uniform field of force $H = 1$.

Diagram I., Fig. 1, is a representation of the field before the introduction of the cylinder. The polarization tubes in these diagrams are bounded by the cylinders generated by the horizontal lines when the figure is rotated about AB. The line CD traces out the surface of the paramagnetic cylinder. The equipotential surfaces in the cylinder are simply continuations of those in the outside field. The polarization tubes are twice as numerous in the cylinder as outside.

Half of the tubes are supposed to pass through the ether, just as if the iron were not present; the other half go through the iron molecules, which are supposed to fill out the whole volume of the cylinder.

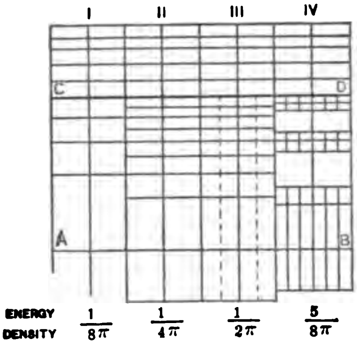


Fig. 1. Half size.

The energy density in the air is $\frac{1}{8\pi}$, in the iron $\frac{1}{4\pi}$. The polarization is $\frac{1}{4\pi}$ in the air, and $\frac{1}{2\pi}$ in the cylinder.

Maxwell does not say anything about the energy density according to Ampère's theory of elementary current magnets. From the nature of the case any exact determination seems impossible, but some idea can be obtained by making certain assumptions with regard to the distribution of the elements, and supposing that the amount of conducting material is very small.

Suppose that the cylinder is saturated, and that all the elements are set at right angles to the field of force. In order to obtain a minimum value for the directed energy density we will assume that the elementary magnets consist of thin wires of infinite conductivity, bent into square or hexagonal circuits, which, for the sake of simplicity, are taken as arranged regularly in long lines side by side so as to form square or hexagonal magnetic solenoids. These latter are to fit together so as to leave only very narrow cracks between them. The permeability of the ether between the conductors and of the conductors themselves is unity.

Then the polarization inside each solenoid due to the currents in the elementary circuits is I, and to this must be added D', the polarization which would exist there if the iron were not present. Thus the total polarization is $D = D' + I$. In the very narrow cracks between the solenoids the polarization is D', the same as that in the space outside, and the distance between the equipotential surfaces is $\frac{1}{4\pi D'}$. The equipotential surfaces in the cracks are then simply continuations of the plane equipotential surfaces in the air around the iron. The energy density in the crack is $2\pi D'^2$. The distance between the equipotential surfaces inside the solenoids is $\frac{1}{4\pi D}$, and this is to the distance in the outside field in the ratio $D' : D$.

The density of the energy directed parallel with the field inside the solenoid is $2\pi D^2$.

Since the cracks are very narrow, this will be the density of the directed energy in the iron.

With an induction of 20,000 lines per square centimeter, this gives about 16,000,000 ergs per cubic centimeter, or about four-tenths of a calorie.

An attempt is made to represent the equipotential surfaces and polarization tubes according to this hypothesis in Diagram III., Fig. 1. The full vertical lines represent equipotential surfaces, both within and without the iron, while the dotted lines are additional equipotential surfaces inside the solenoids. $\mu = 2$, $B' = 1$, $D' = \frac{1}{4\pi}$, $D = \frac{1}{2\pi}$. Energy density in air $= \frac{1}{8\pi}$, in iron $= \frac{1}{2\pi}$, or twice as great as in Diagram II. Length of polarization cell in air and in cracks = one centimeter, length in solenoids = half a centimeter.

It is certain that the elementary circuits do not fill out the space in this way. If they did, the induction would soon reach a limit, beyond which it could not rise. For each of the elementary circuits is a perfect conductor, and on being turned round so that its axis is parallel to the field, will prevent any additional lines from passing through it, if there is an increase in the field.

The facts of saturation seem to indicate that the space guarded from the entrance of external lines by the elementary magnets is very small.

The molecules of magnetized iron are in all probability distributed very irregularly, but the problem can be simplified by assuming that they form long solenoids when the iron is saturated, and that these solenoids only occupy $\frac{1}{n}$th of the whole volume. The following results can be deduced.

The polarization D'' inside these solenoids remains constant from the moment they are formed, the current in the elementary magnets decreasing as the external field increases.

The average polarization of a cubic centimeter of the iron is

$$D = \frac{1}{n} D'' + \frac{n-1}{n} D'.$$

The quantity known as intensity of magnetization is defined by the equation

$$D = D' + I.$$

Thus

$$I = \frac{D'' - D'}{n},$$

or I diminishes after the constant value of D'' has been reached, the diminution being $\frac{1}{n}$th of the increase of D'. If n is large, this diminution will be small, and I will be fairly constant through a large range if $n = 100$.

The amount of energy in a cubic centimeter will be

$$\frac{2\pi}{n} D'^2 + \frac{2\pi(n-1)}{n} D''^2.$$

Taking certain results of Ewing on induction in iron in high magnetic fields and making $n = 100$, the amount of energy in one cubic centimeter is found to be 45 calories. This may perhaps be regarded as a maximum value.

In Diagram IV., Fig. 1, the condition of a portion of a very long cylinder in a uniform field $H = 1$ is indicated, on the assumption that $n = 2$, and μ the ratio between the average polarization of the paramagnetic substance and that in the intermolecular spaces is also two. The polarization outside the cylinder is $\frac{1}{4\pi}$, while the average polarization inside is $\frac{1}{2\pi}$, as in the two former cases.

One half of the space is occupied by the solenoidal molecular chains, which are represented in the figure, suitably divided by the polarization tubes and equipotential surfaces. These are of course much nearer together inside the solenoids than outside.

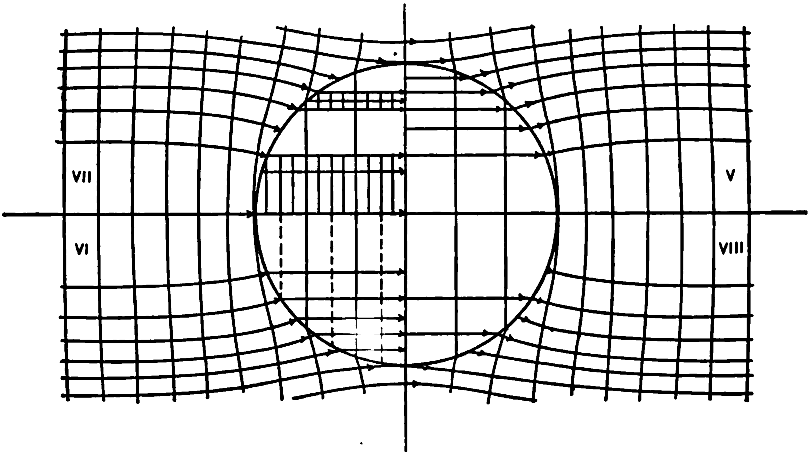
The polarization inside the solenoids is $\frac{3}{4\pi}\cdot$ Each of the cells shown, the volume of which is 4π c.c. outside the solenoids, and $\frac{4\pi}{9}$ c.c. inside, contains half an erg of energy; so that the energy density outside the solenoids is $\frac{1}{8\pi}\cdot$ Inside it is $\frac{9}{8\pi}$, and the average energy density in the cylinder is $\frac{5}{8\pi}$, as against $\frac{1}{8\pi}$ in the surrounding field, $\frac{1}{2\pi}$ inside the cylinder of Diagram III., and $\frac{1}{4\pi}$ in Diagram II.

Diagram V., Fig. 2, shows the result, according to the ordinary induction theory, of placing a sphere of radius 4 and permeability 2 in a unit field $B' = 1$. Inside the sphere are shown the equipotential surfaces $V' = -\frac{3B'x}{\mu + 2}$ which are $\frac{4}{3}$ cm. apart. At right angles to these run the tubes of polarization, which are bounded by the cylindrical surfaces traced out by the horizontal lines, when the figure is revolved about the horizontal diameter of the sphere. Of these there are

$$D = \frac{B}{4\pi} = \frac{3\mu B'}{4\pi(\mu + 2)} = \frac{3}{8\pi} \text{ per square centimeter.}$$

Hence through the 16π square centimeters of the equatorial plane there pass six of these polarization tubes, while in the original field, before the sphere was introduced, four tubes passed through the same area.

The polarization tubes outside the sphere are continuous on the surface with those inside, and at a distance from the sphere they become identical with those due to the field $H' = B' = 1$. The intensity of magnetization is $\frac{3}{16\pi}$, and the polarization of the ether in the sphere is also $\frac{3}{16\pi}$, making a total polarization of $\frac{3}{8\pi}$ in the sphere as compared with $\frac{1}{4\pi}$ in the air at a distance. The energy density is only $\frac{9}{64\pi}$ in the sphere, while it is $\frac{1}{8\pi}$ in the original field.



Energy density in $V = \frac{9}{64\pi}$, $VI = \frac{9}{32\pi}$, $VII = \frac{27}{64\pi}$, $VIII = \frac{9}{128\pi}$.

Fig. 2. Half size.

Diagram VI., Fig. 2, shows the same problem treated so as to represent Ampère's theory, the molecular circuits being supposed to fill out the whole volume, as is also the case in Diagram III., Fig. 1. The dotted lines represent equipotential surfaces inside the solenoids, but not in the narrow cracks between them.

The energy density is twice as great as in the former case, being

$$2\pi D^2 = \frac{9}{32\pi}.$$

In Diagram VII., Fig. 2, the molecular chains or solenoids are only supposed to occupy one-third of the volume of the sphere.

In reality of course these solenoids must be supposed to be very narrow in comparison to their length, and the difficulty observed in the diagram, with regard to the connection between the tubes inside the sphere and those outside, does not occur.

If these solenoids could exist without the presence of the external field, they would send tubes back in the negative direction through the empty spaces between them, so that the polarization in these spaces when the external field is present is only $\frac{3}{16\pi}$, whereas in the distant parts of the external field it is $\frac{1}{4\pi}$. Inside the molecular solenoids the polarization is $\frac{3}{4\pi}$. The total flow of polarization through the sphere is the same in Diagrams V., VI., and VII. The energy density in the sphere is in this last case $\frac{27}{64\pi}$, or 50 per cent greater than in Diagram VI.

Diagram VIII., Fig. 2, shows a sphere of insulating material, the dielectric constant of which is unity. The electrical density on its surface is

$$\sigma = \frac{3}{16\pi}\cdot\cos\theta.$$

The sphere is suspended in a uniform electrostatic field $B'_e = 1$, so that the line $\theta = 0$ points along the direction of the field.

Outside the sphere the electrostatic equipotential surfaces and polarization tubes are geometrically identical with the magnetic lines in the previous cases. Within the sphere the equipotential surfaces are identical with those of Diagram V.

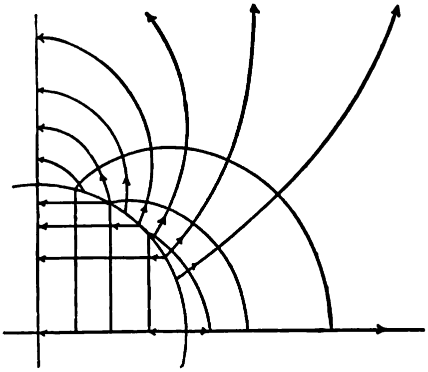


Fig. 3. Half size.

The electrostatic field intensity inside the sphere is only $\frac{3}{4} H'$, and the polarization is $\frac{3}{16\pi}$. The energy density is only $\frac{9}{128\pi}$. Three of the six tubes which come to the surface of the sphere on the negative side end in the three units of negative electricity distributed over that side, while three of the six tubes that start from the positive side, have their origin in the three units of positive electricity on that side. The remaining three tubes from the external field pass through the sphere.

The reason for the fact that the field in the sphere is smaller than that at a distance, is of course that the given electrical distribution would, if acting by itself, produce inside the sphere a field in the negative direction, as indicated in Fig. 3, the field intensity being $-\frac{1}{4}H'$. This is the "demagnetizing effect of the ends" of which we hear when instead of electric charges "free magnetisms" are supposed to exist on the surface of the sphere. It seems as though it would be almost worth while to treat all problems in which this mathematical method is simplest by means of the electrostatic analogy. That is, never to speak of free magnetism, but to work out the electrostatic problem, and to state that the required magnetic field is mathematically the same as the electrostatic field, wherever the permeability is unity.

While there may be nothing very new in what precedes, it is hoped that the diagrams with their explanations may prove of some use to those who, like the author, have experienced difficulty in keeping the different magnetic theories clearly separated.

UNIVERSITY OF NEBRASKA.

ON THE ALTERNATING CURRENT DYNAMO.

By W. E. GOLDSBOROUGH.

CONSIDER the case of a simple alternator having but one armature coil that rotates in a magnetic field of uniform intensity about an axis at right angles to the direction of the lines of force. If successive instants of time during one revolution of the coil are counted from the instant that the coil passes a line drawn through its axis of rotation and perpendicular to both the axis of rotation and the direction of the magnetic flux, the value of the induction piercing the coil at any instant during one cycle is expressed by the equation

$$N = N_{\max} \cos \omega t, \qquad (1)$$

in which $N_{\max}$ equals that portion of the flux that passes through the coil at the instant the plane of the coil is at right angles to the direction of the lines of force, and ω represents its angular velocity. The instantaneous value of the E.M.F. generated in the coil will be, by Faraday's law,

$$e = -\frac{dN}{dt} = \omega N_{\max} \sin \omega t = E \sin \omega t, \qquad (2)$$

since its maximum value $E = \omega N_{\max}$. (3)

If the coil is closed through a circuit of resistance R', inductance L' and capacity C', the resistance and inductance of the coil itself being R

and L respectively, a current i will begin to circulate, and we can write the equation of E.M.F.'s of the circuit in the form

$$e=(R+R')i+(L+L')\frac{di}{dt}+\frac{\int idt}{C'}.$$

From this expression we can derive the equation of the current in terms of the constants of the circuit and the maximum value of the E.M.F. developed in the coil and obtain

$$i=\frac{E}{\sqrt{[R+R']^2+\left[\frac{1}{C'\omega}-(L+L')\omega\right]^2}}$$

$$\sin\left\{\omega t-\tan^{-1}\left[\frac{1}{C'_1\omega(R+R')}-\frac{(L+L')\omega}{R+R'}\right]\right\} \qquad (4)$$

which expresses the instantaneous value of i as soon as a condition of cyclic stability has been attained.

Equations (1), (2), and (4) are the general equations that cover the working of alternating current dynamos; they have been subjected to graphical analysis, the results of which are exhibited in Fig. 1, and are discussed in the following paragraphs:

Suppose a circuit in which the inductance is zero, the capacity infinite, and the resistance variable, to be subjected to the influence of a simple harmonic E.M.F. that is generated by an alternator having a constant armature inductance for all values of armature current, a constant field excitation and a constant speed. Under these conditions, the virtual value of the E.M.F. at the brushes of the alternator just before the circuit is closed will be

$$\bar{E}=\omega N_{\max}\div\sqrt{2}, \qquad (5)$$

which is represented by the vector OA in the figure. The vector ON is laid off at right angles to OA to represent the value of the M.M.F. producing $N_{\max}$. It is drawn 90° in advance of the E.M.F. it induces in accordance with the relation exhibited in equations (1) and (2). At the time of closing the circuit, suppose the external variable non-inductive resistance to have a value R', and that the constant armature resistance has a value R, and the constant armature inductance a value L. Then the equation of the current will assume the form

$$i=\frac{E}{(\sqrt{R+R')^2+L^2\omega^2}}\sin\left[\omega t-\tan^{-1}\frac{L\omega}{R+R'}\right] \qquad (6)$$

and its virtual value $$\bar{I}=-\frac{\bar{E}}{\sqrt{(R+R')^2+L^2\omega^2}}, \qquad (7)$$

which we can represent[1] by the vector OB_0 lagging $\tan^{-1}\dfrac{L\omega}{R+R'}$ degrees behind OA. This armature current will react upon the magnetizing forces

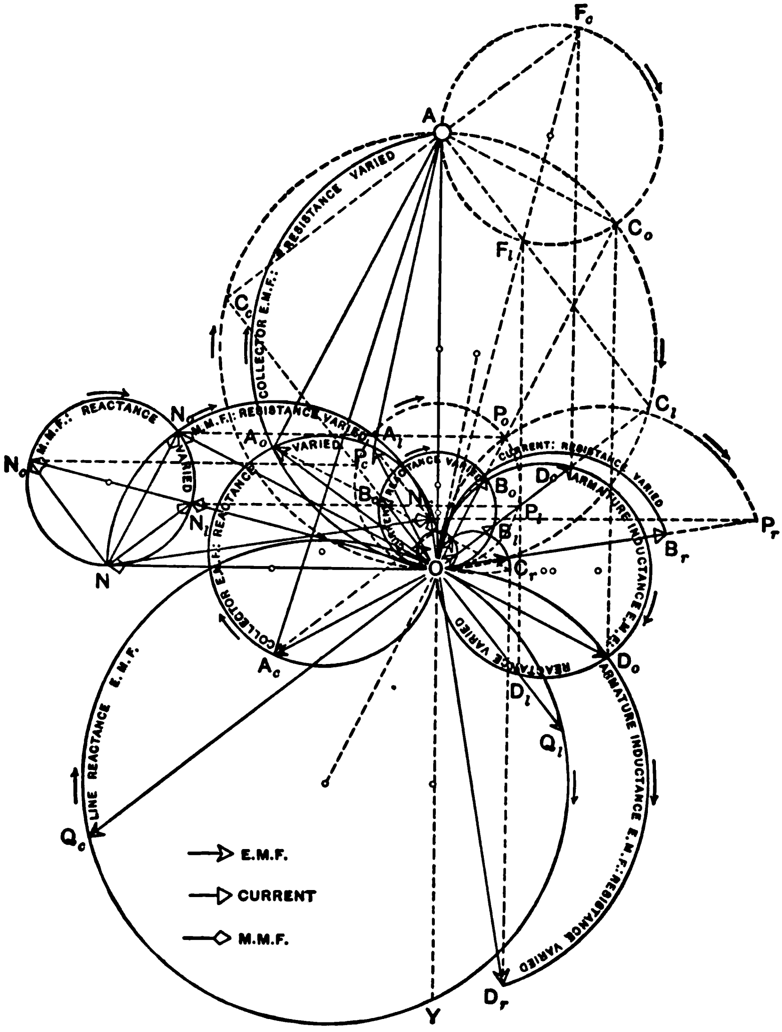


Fig. 1.

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[1] The subscript letter (*o*) refers to the initial condition.
The subscript letter (*r*) refers to changes in the line *resistance*.
The subscript letter (*l*) refers to changes in the line *inductance*.
The subscript letter (*c*) refers to changes in the *capacity* of the line.

due to the constant field excitation, and by virtue of the inductance of the armature will produce an M.M.F. in phase with itself which is represented by the vector NN_0, drawn parallel to the current vector from the positive extremity of ON. This armature M.M.F. sets up a cyclic magnetization developing a counter E.M.F. OD_0 lagging 90° behind the current, and there is a loss of effective E.M.F. due to the armature resistance that is shown by the short E.M.F. vector in phase with OB_0; therefore the total loss of E.M.F. in the armature will be the resultant of these two vectors or OA_0. The effective E.M.F. that overcomes the resistance of the non-inductive external circuit will be the vector A_0A, since it completes the E.M.F. triangle on OA and is in phase with the current OB_0. The total effective E.M.F. (OC_0) that overcomes the total ohmic resistance $(R+R')$ of the circuit, is due to the cyclic magnetization set up by the M.M.F. vector ON_0. ON_0 is the resultant of ON and NN_0, and as shown by the geometry of the figure, it is 90° in advance of the current, and therefore of A_0A, as it should be. The projection of NN_0 on ON is the component of the armature M.M.F. that acts against the field magnetization, *i.e.* it is *a measure of the armature reaction*. The projection of NN_0 on OA is likewise a measure of the cross-magnetizing action of the armature.

Having constructed the initial diagram, we can now follow out what takes place when the resistance of the external circuit is varied. Suppose R' is reduced to a value R_r. The current vector head B_0 will move out along the semicircle OB_0B_r until equilibrium is again established in the circuit by the current reaching its maximum possible value under the new conditions.[1] The vectors OA and ON retaining their positions, all the other vectors involved will reach their final values corresponding to the new current by following the arcs of the circles passing through their positive extremities to the positions designated by the common subscript letter (r). The correctness of the variations indicated can be readily verified by an inspection of the geometry of the figure in connection with equation (7).

In the present case, R' has been reduced to zero; in other words, the subscripts (r) indicate what takes place when a machine whose armature inductance is large, as well as constant, is short-circuited. A_0 moves up to A, and the E.M.F. at the brushes is zero. The current assumes an angle of lag of almost 90° behind the total internal armature E.M.F. OA, the *armature reaction* almost counterbalances the M.M.F. of the fields, and the resultant M.M.F. ON_r is just sufficient to develop the E.M.F. OC_r that overcomes the resistance of the armature.

Returning to the initial conditions, suppose we increase the value of L' from zero to some value L_t, *i.e.* suppose we introduce inductance into

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[1] See Bedell and Crehore's Alternating Currents, p. 223.

the external circuit. The virtual value of the current will then be expressed by the equation

$$\bar{I}=\frac{\bar{E}}{\sqrt{(R+R')^2+(L+L_l)^2\omega^2}}, \tag{8}$$

and it will lag behind the internal E.M.F. $\bar{\text{E}}$ or OA by an angle

$$\phi=\tan^{-1}\left(\frac{L+L_l}{R+R'}\omega\right). \tag{9}$$

Referring to the figure, the new positions assumed by the variable vectors, owing to the introduction of L_1, are designated by the subscript letter (l). The current will decrease and its vector head move along the circle $OB_cB_0B_lO$ until a state of equilibrium exists between the forces involved. The E.M.F. that overcomes the resistance and inductance of the armature will decrease also and move to the position OA_l, its vector head following the circle $OA_cA_0A_lO$, and the E.M.F. at the collector rings will first decrease and then increase to a final value A_lA. The introduction of inductance into the external circuit brings the E.M.F. at the collector rings and the total internal E.M.F. (OA) more nearly into phase; it however causes a lag angle F_lOB_l to be introduced between the collector E.M.F. and the current. The inductance E.M.F. of the armature decreases along the circle $OD_cD_0D_lO$ to a value OD_l, and the inductance E.M.F. of the external circuit increases from zero along the circle YQ_cOQ_lY to a value OQ_l. The resultant M.M.F. will be ON_l, and it is seen that while the armature reaction has remained very nearly constant, the cross-magnetizing effect has been reduced about fifty per cent.

From our initial conditions as indicated by the subscript letter (o), we can also study the effects produced by the introduction of capacity into the external circuit. If the value of C' is reduced from infinity to some value C_c, the virtual value of the current will change to

$$\bar{I}=\frac{\bar{E}}{\sqrt{(R+R')^2+\left(\frac{1}{C_c\omega}-L\omega\right)^2}}, \tag{10}$$

and the angle between OA and the current will have a value

$$\phi=\tan^{-1}\left[\frac{1}{(R+R')\,C_c\omega}-\frac{L\omega}{(R+R')}\right]. \tag{11}$$

In consequence of this change the current vector will assume the position OB_c, and the other variable vectors will move to their corresponding positions shown by the subscript letter (c). The current in its new position is not only in advance of the E.M.F. (A_cO) at the brushes, but is also in advance of the E.M.F. OA, since it has moved from B_0 to a maximum value when passing OA, and then decreased in value.[1]

The collector E.M.F., on the other hand, steadily increases as the capacity decreases, till it reaches a value A_cA much greater than the open circuit E.M.F. of the machine. A resonant effect comes into play here after the capacity of the line neutralizes the inductance of the armature that is very well illustrated by the figure; the line A_cA will be a maximum when it passes from A through the center of the circle $OA_cA_0A_1O$, and will represent the greatest difference of potential that can possibly exist between the brushes so long as R and R' remain unchanged in value. This rise in potential is due to the current being in *advance of the vector* OA, for the position of the armature M.M.F. vector is also advanced, and NN_c increases the total flux in the air gap instead of diminishing it. The cross-magnetizing action of the armature, however, remains approximately the same.

The introduction of capacity into the line causes the inductance E.M.F. of the armature to move to the position D_c, and the reactance E.M.F. of the external circuit to decrease through zero and then increasing, assume a position Q_cO, considerably in advance of the collector E.M.F., and 90° in advance of the current OB_c.

The arrows indicate the relative direction of motion of the vectors as the resistance is varied from infinity to zero, or as the reactance is carried from zero capacity to an infinite inductance.

By following out a similar line of constructions the effects produced by variations of the armature inductance can be studied, and by successively varying the resistance, inductance, capacity, and frequency constants, and constructing corresponding diagrams, a large variety of problems involving the simultaneous variation of several terms can be successfully treated.

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[1] See Bedell and Crehore's Alternating Currents, p. 297.

NEW BOOKS.

A New View of the Origin of Dalton's Atomic Theory: A Contribution to Chemical History, together with Letters and Documents concerning the Life and Labours of John Dalton, now for the first time published from Manuscript in the Possession of the Literary and Philosophical Society of Manchester. By HENRY E. ROSCOE and ARTHUR HARDEN. 8vo, pp. x+191. London and New York, Macmillan & Co., 1896.

The happy discovery, in the rooms of the Literary and Philosophical Society of Manchester, of a number of manuscript volumes in the handwriting of John Dalton, has thrown a new light upon the genesis of his ideas. The precious documents comprise an extensive series of laboratory notes, beginning with the year 1802, and continuing to Dalton's latest years, bound in twelve volumes, as well as lecture notes of six lectures delivered in 1810 by Dalton at the Royal Institution, London. The laboratory note-books contain an almost unbroken record of the experimental work conducted in the rooms of the Manchester Society, and which supplied him with the materials embodied in his great work, *A New System of Chemical Philosophy.*

It has hitherto been supposed that it was the experimental discovery of the law of combination in multiple proportions that led Dalton to conceive of the chemical combination of atoms having definite weights, the atomic theory being thus adopted to explain the facts ascertained by chemical analysis. But an examination of the newly found papers shows that Dalton approached the atomic theory from a physical standpoint, he being an adherent of the Newtonian doctrine of the atomic constitution of matter.

The first part of the volume contains details of the evidence on which the above conclusion is founded; this is followed by a short epitome of Dalton's daily laboratory notes from 1802 to 1808, and by a discussion of the successive series of numbers given by Dalton as representing the atomic weights of the elements. The following table of atomic weights was written out Sept. 6, 1803, and is probably the earliest constructed:

Ult. at hydrogen	1.00	Ult. at nitrous oxide	13.66
" oxygen	5.66	" nitric acid	15.32
" azot	4.00	" sulphur	17.00
" carbon (charcoal)	4.50	" sulphurous acid	22.66
" water	6.66	" sulphuric acid	28.32
" ammonia	5.00	" carbonic acid	15.80
" nitrous gas	9.66	" oxide of carbone	10.20

Chapter V. contains letters written and received by Dalton; among the latter are a few from Berzelius, Thomas Thomson, and Davy. The book is well printed, and the facsimiles of Dalton's MS. add to the interest of a valuable contribution to the history of chemistry. There is no index.

H. CARRINGTON BOLTON.

A Laboratory Course in Experimental Physics. By W. J. LOUDON and J. C. MCLENNAN. 8vo, pp. 302. Macmillan & Co., 1895.

A little more than a quarter of a century ago, the first laboratory guide-book in physics was published in Leipzig. The author was Friedrich Kohlrausch, and his *Leitfaden* is still a standard for most of the teachers of physics who have studied in Germany. But the book is so solid, so compact, that the elementary student who has no supplementary instructions is sure to be discouraged by its use, whether he employs the German edition or the English translation. It was natural, therefore, after laboratory methods had become generally introduced, that new guide-books should come forth to compete for popular favor, such as the well-known manuals by Pickering, Stewart, and Gee, and Glazebrook and Shaw. At present, we may safely look for one or more new ones each year.

Every such guide-book is the outcome of the author's own experience and necessities, and is published in the belief that its sphere of usefulness may extend beyond the laboratory for which it was primarily intended. It would be interesting to examine statistical returns, if such were available, with a view to ascertaining to what extent any such book is systematically employed in any laboratory with which the author has no immediate connection. The case is quite different from that of a class text-book, in which lessons are assigned for which the student is held responsible, or which is assumed as the accompaniment of a systematic course of lectures. In every college, a course of practical laboratory exercises in physics is given as the needful preparation for subsequent work of investigation; and a majority of the students never advance beyond this prescribed course in manipulation. Most generally this work is done under the supervision of an instructor who has but little leisure, and each exercise is undertaken by the students in rotation. The immediate object of a laboratory manual is, therefore, to economize the students' time and the instructor's labor. Instead of giving the same oral instruction, in succession, to scores of students, it is best to write out what the student needs, and let this specific instruction, on paper or cardboard, be found with the apparatus to which it refers. The expenditure of breath and of patience is thus reduced to a minimum. Such instruction-cards can be so prepared as to leave room for the exercise of ingenuity and thought on the part of the student; but such directions as they convey must be explicit, and adapted to the exact apparatus which the student is about to handle.

No two laboratories are alike in equipment. Whatever is written for one will be found, for any other, to be lacking in many indispensable details, and overburdened with much unavailable material. A variety of laboratory manuals must be at hand for reference-books, but not one of them can alone be a satisfactory guide. Most of them will receive but scant attention from the ordinary student if his instruction-cards have been well prepared. He will frequently consult tables of constants, and, in studying out the construction of an unfamiliar instrument, printed descriptions are often valuable. But such a description is quite as apt to be found in a dealer's catalogue, or a comprehensive text-book, as in any one of an assortment of laboratory guide-books.

Every laboratory instructor, therefore, finds it necessary to write his own guide-book, either in part or in whole. In doing so, he will naturally consult other guide-books, but adopt none. The volume by Loudon and McLennan is, doubtless, well suited for the students in the Toronto laboratory, where the collection of expensive and historical apparatus is evidently uncommonly fine. Part I. is devoted to an elementary course in which very excellent instructions are given for the standard beginner's exercises, such as measurements of length, volume, and density; but no discussion or guidance is offered regarding the measurement of mass. Quite probably, the students for whom the book was prepared receive training in the chemical laboratory, and thus acquire some familiarity with the use of the physical balance before beginning physical laboratory work. If so, this removes the necessity for teaching anything about the sensibility of the balance, and the precautions required for accurate weighing; but, for other laboratories, such an omission in a guide-book is serious. Exercises are provided for the testing of Boyle's law, the determination of capillary constants, specific heat, and heat of fusion, and quite a number in relation to mirrors, lenses, and photometry.

Part II. is a more advanced course devoted to work in acoustics, heat, magnetism, and electricity, followed by an appendix on the determination of gravity, and on the torsion-pendulum. The portion devoted to acoustics is exceptionally large, more than half as much as that assigned to electricity. It includes theoretical discussion and quantitative work in relation to pitch and musical quality, harmonic motion, optical methods of tuning, and several methods of measuring the velocity of sound. The Toronto laboratory is evidently well provided with König's best apparatus, including such pieces as the expensive Helmholtz outfit for synthesis, and Regnault's contrivance for studying the velocity of sound in gases. What is more remarkable is that this apparatus is actually used, instead of being kept merely on display for historical purposes. Of late years, acoustics has been so generally relegated to the background, to make room for electricity, that the exhibition of serious interest in it, in an American college, is a refreshing evidence of scientific courage and unselfish zeal.

The list of advanced experiments in heat covers considerable ground, and implies the possession of such instruments as Favre and Silbermann's calorimeter, and Regnault's apparatus for hygrometry, specific heat of gases, and energy of change of state. These may be legitimately regarded as laboratory luxuries. Access to them is impossible for perhaps a majority of those who read the book. Important as was the work of these distinguished physicists, it may be questionable whether the exact duplication of such historic apparatus is now really to be desired in a student-laboratory. If the student undertakes similar research, the outlay would, perhaps, better be spent in the construction of appliances due to his own adaptation of means to ends. In the repetition of what is historic, there should be wide room for variation.

The section assigned to electricity and magnetism is made unnecessarily diffuse by the introduction of much material that is better introduced in a lecture course of general instruction. It is fair to assume that elementary definitions, such as that "two magnetic poles of the same kind repel," are unnecessary for the student who is at all fit to enter the physical laboratory. There is, possibly, room for difference of opinion about the extent to which qualitative observation may be accepted in lieu of quantitative measurement in the student-laboratory, but there are few, to-day, who think that even the simplest laws of nature should be rediscovered by elementary students. The last thirty pages of the section contain an excellent exposition of methods in the electrical laboratory; but, of the preceding sixty pages, the greater part belongs more properly to the general text-book than to the laboratory guide.

Throughout the book, it may be said that the discussion of general principles has occupied space that would better have been devoted to precautions for securing accuracy, and to the consideration of numerical examples. As an aid to those who prepare their own laboratory instruction-cards, this volume will be found very useful, and it is a welcome addition to the laboratory book-shelf; but, as a practical guide to the ordinary student, in an ordinary laboratory, its usefulness will be less wide than one may naturally wish on account of its general attractiveness.

W. LECONTE STEVENS.

A Primer of the History of Mathematics. By W. W. ROUSE BALL. 8vo, pp. 146. Macmillan & Co., 1895.

Of all sorts and conditions of books that fall to the lot of the reviewer, one of this kind is the most difficult to fairly judge. One cannot say that it is unscientific, for it makes no pretensions to be otherwise; neither can one say that it is wanting in seriousness, for it will at once assert that seriousness is the farthest from its thoughts. If you assert that it gives no adequate view of mathematics of this century, it replies that that is not its humble mission, and, if you say that it wastes its pages in story-telling, it at once retorts that it caters to readers who must be brought to better things by just that diet. And the critic who sets his "five wits on the stretch" to demolish the work at the stroke of the pen finds himself helplessly repeating, "Is one mocked by an elf?" before he has fairly begun.

The fact is, for what the work pretends to be, it is well written, and may be called a decided success. A *multum in parvo*, it supplies, at a trifling expense, a handbook that will serve the purposes of elementary students and teachers who cannot afford the more elaborate and expensive treatises.

The first thing liable to impress the reader unfavorably is the apportionment of matter. Forty per cent of the pages have to do with mathematics before the Renaissance, and one-seventh of the work is devoted to the mediæval period, both being entirely disproportionate allowances. But when it is considered that this is a handbook for students who are reading the mere elements of the subject, and that these elements were largely developed before the Renaissance, the fault seems less prominent.

Nevertheless, it cannot be denied that here is the real weakness of the book, and the more one considers it the more serious it becomes. One feels that a line apiece to familiar names like Monge, Carnot, and Poncelet, and not a syllable for Möbius, fits hardly with a page on Roger Bacon, and a considerable setting forth of tradition about Thales, Pythagoras, Archimedes, and other worthies. And when one reads the further gossip, interesting but not very valuable, about Kepler's trouble with his first wife, and his method of courting his second, and about Tartaglia, Lagrange, Laplace, and others, he wonders if, after all, the elementary reader might not be better served by the mention of a few of the many familiar names which are omitted. As examples of names, almost every one of which finds place in text-books of quite an elementary grade, and for which readers of the *Primer* will seek information in vain, the following may be mentioned: Argand, Galois, Horner, Wilson, Plücker, Gudermann, Bezout, Vandermonde, Sarrus, Cramer, Landen, Malfatti, Matthew Stewart, Arbogaste, Mascheroni, L'Huilier, Maupertuis, Gergonne, Quetelet, Bellavitis, Clifford, with many others.

Furthermore, out of all proportion to the importance of their contributions are the apportionments between certain individuals. Jordanus gets fifteen times as much space as De Moivre, Roger Bacon eighteen times as much as Roger Cotes, and Regiomontanus twenty times as much as Poncelet. While Pacioli gets two pages, Von Staudt gets a quarter of a page; while Pascal gets three pages and a half, and certainly deserves generous treatment, Cayley, Riemann, and Steiner get along with half a page each.

The mathematics of the present century can hardly expect any generous treatment in a work of this nature. But such common names as those of Brianchon and Feuerbach in elementary geometry, or Lobachevsky and Bolyai in the non-Euclidean, or those of the creators of the recent geometry of the triangle, — Lemoine, Brocard, Tucker, and others; or Klein, Fuchs, Hermite, and Sylvester, — since living writers are not wholly excluded; or Clebsch and Hesse, — one cannot reconcile the omission of typical names like these, representing movements more or less familiar to all, with the presence of names of lesser note.

Of course, the work has its share of misprints, which is merely another way of saying that it is still in its first edition. Among them are: *iscosahedron* (p. 7); *octrahedron* (p. 7); δύναμίς (p. 32); 1621, for 1620, as the date of Harriot's death (p. 68); 1576, for March 5, 1574–5, as the date of Oughtred's birth (p. 68); improper spacing between the E's and F's in the index, etc. These dates are all right in the second edition of the author's larger history, and so are manifestly misprints here.

There are also some chronological errors which cannot be so easily explained away. That Abel's theorem was "written in 1828" is true, but it was not first written in that year. It was in Abel's possession as early as 1825, the year in which he first went to Paris, and it was made public in 1826. In cases of uncertainty of date, the author usually and commendably resorts to the word "about" or "*circa*"; but, in the case of Girard, he says "1590–1633," though each date is quite uncertain; similarly, for several other dates, including that of Lord Brouncker's birth, which, unless Mr. Ball has found some new documentary evidence, is also quite doubtful. Documentary evidence suggests the case of the date of Briggs's birth. The author and, rather strangely, Cantor, who is usually very exact in details, give 1556. The older writers all give that date, some with a *circa*. Since Whittaker's sketch in the *Dictionary of National Biography*, in which it is stated that Briggs was born "in February, 1560–1, according to the entry in the Halifax parish register," the recent encyclopedias have adopted this date. It would be interesting to know if there is longer any doubt about the matter. A rather strange error which has run through each edition of the larger work, and which now appears in the *Primer*, is the statement that "the only regular polygons which can be constructed by elementary geometry are those of which the number of sides is $2^m(2^n + 1)$, where m and n are integers, and $2^n + 1$ is a prime." This excludes the pentedecagon, and, unless zero be reckoned an integer, the triangle, pentagon, and others.

It must be confessed, however, that the essential features of criticism are, largely, matters of judgment which depend upon the point of view. It is doubtful if any one else would have succeeded better in the selection of matter, or would have presented the subject in as happy a style as that which characterizes all of Mr. Ball's contributions to the history of mathematics.

DAVID EUGENE SMITH.

MICHIGAN STATE NORMAL SCHOOL, YPSILANTI.

Étude Analytique et Graphique des Courants Alternatifs. Par F. BEDELL et A. C. CREHORE. Traduit par J. BERTHON, Ingénieur des Arts et Manufactures. 8vo, pp. 261. Éditeur, Georges Carré, 3 Rue Racine, Paris, 1895.

Theorie der Wechselströme in analytischer und graphischer Darstellung. Von Dr. FREDERICK BEDELL and Dr. A. C. CREHORE. Uebersetzt von ALFRED H. BUCHERER. 8vo, pp. 266. Berlin, Julius Springer, and München, R. Oldenbourg, 1895.

Perhaps the best proof that the theoretical work of American scientists is gaining recognition abroad is the fact that American treatises are now being translated into the Continental languages. That a mathematical work, even though pertaining to practical applications, should be deemed worthy of translation into the French and German languages, already rich in works of this nature, and particularly upon the alternating current, must be gratifying to the authors; for though perhaps not the birthplace of the alternating current, the Continent may justly be looked upon as the fatherland of the commercial applications. Both translations follow the original very closely, the intention evidently being to give the original authors full credit for their work. On many points there may arise a divergence of opinion, as, for instance, when the translators choose for the word *medium* the German *mittel* and the French *milieu*, while medium in German and medium in French express the English meaning of medium exactly. Professor Foeppl, a German authority on electro-mathematics, uses the word *medium* in his theoretical demonstrations, while, on the other hand, Mr. Vashy, the well-known French theorist, uses *milieu*. Mr. Bucherer adopts the English style of denoting the arc of tangent by tang^{-1}, instead of the more common German arc-tang, while Mr. Berthon seems to prefer the latter denomination. Drs. Bedell and Crehore followed Mr. Steinmetz's example in denoting $\sqrt{-1}$ by j instead of i, which is of importance in a treatise like the one under consideration, where the instantaneous value of the current, usually denoted by i, occurs so frequently. Mr. Bucherer seemed to be more radical in his views, and accepted the given hint, while Mr. Berthon avoids committing himself by clinging throughout to $\sqrt{-1}$. When it comes to the solution of the linear differential equations for the current, Mr. Bucherer follows the authors verbally, naturally omitting the references to Johnson's *Differential Equations* Mr. Berthon hesitated to follow this practice, which seems creditable, as Johnson's book is not known to any extent in France and Germany; he pronounces the American authors' method somewhat "peculiar," and applies a method commonly taught in Continental treatises of analysis, avoiding even a repetition of the solution by using a different one on each occasion. In the second part of the book, the graphical treatment, the originality of the American authors is strictly preserved. The careful work of the translators, and the original merit of the treatise, should ensure a hearty reception to the work which naturally must add to the appreciation and regard for American works in general.

F. J. DOMMERQUE.

Computation Rules and Logarithms, with Tables of Other Useful Functions. By S. W. HOLMAN. pp. xlv + 73. Macmillan & Co., 1896.

In the selection and arrangement of the material for this book, the author has shown exceeding care. The attention given by him to correctness in mechanical detail, adds not only to the pleasing effect produced by the book, but also to its efficiency and the facility with which it may be used. The logarithms (4 and 5 place) and other tables have been arranged with reference to rapidity in their use with minimum mental effort, type and spacing being selected with this end in view.

The first portion of this book gives directions for the rejection or retention of significant figures and other computation rules and directions for the use of the tables.

B.

A Text-book of Gas Manufacture. For students. By JOHN HORNBY. pp. xii + 261. London, George Bell & Sons, 1896. (*Received.*)

INDEX TO VOLUME III.

A.

- Absorption of heat experiment, 10.
- Admittance in oscillating currents, 341.
- Air effect in polarization, 96.
- Allen, H. N., The graphical representation of magnetic theories, 470.
- Alternating current:
  - An experimental study of inductive phenomena in, *Millis*, 351.
  - Galvanometer for photographing, *Hotchkiss and Millis*, 49.
  - Dynamo, *Goldsborough*, 477.
  - When the electromotive force is of a zigzag wave type, *Rimmington*, 100.
  - Ångström, K., On a simple method of photographically registering the infra-red energy spectrum, 137.
- Appleton, J. H., *Eli W. Blake*, 226.
- Arago's explanation of polarization by emission, 85.
- Arc spectra, A photographic study of, *Baldwin*, 370, 448.
- Austin, L. W., On a new form of water battery, 309.

B.

- Baldwin, Caroline W., A photographic study of arc spectra, 370, 448.
- Ball, W. W. R., *A Primer of the History of Mathematics*, 487.
- Bancroft, W. D.:
  - On ternary mixtures, 21, 114, 193.
  - Solids and vapors, 401.
  - The chemical potential of the metals, 250.
- Barium spectrum, 452.
- Battery, water, On a new form of, *Austin and Thwing*, 309.
- Bauer, L. A., On the secular motion of a free magnetic needle, II., 34.
- Bedell, F.:
  - *Étude Analytique et Graphique des Courants Alternatifs*, 489.
  - Holman's *Computation Rules and Logarithms, with Tables of Other Useful Functions*, 490.
  - *Theorie der Wechselströme in analytischer und graphischer Darstellung*, 489.
- Blake, E. W., *Appleton*, 226.
- Bolton, H. C., Roscoe and Harden's *A New View of the Origin of Dalton's Atomic Theory*, 483.
- Book Reviews:
  - A Laboratory course in experimental physics, *Loudon and McLennan*, 484.
  - A new view of the origin of Dalton's atomic theory, *Roscoe and Harden*, 483.
  - A primer of the history of mathematics, *Ball*, 487.
  - A text-book of gas manufacture, *Hornby*, 491.
  - American Association for the Advancement of Science, 226.
  - Analytical chemistry, *Menschutkin*, 400.
  - Computation rules and logarithms, with tables of other useful functions, *Holman*, 490.
  - Crystallography, a treatise on the morphology of crystals, *Story-Maskelyne*, 395.
  - Electric waves, *Hertz*, 234.
  - Electricity and magnetism, *Nipher*, 397.
  - Elementary lessons in electricity and magnetism, *Thompson*, 78.
  - Elementary mensuration, *Stevens*, 400.
  - Elements of the mathematical theory of electricity and magnetism, *Thompson*, 393.

Book Reviews (*continued*):
  - Elements of physics, I., *Nichols and Franklin*, 400.
  - Étude Analytique et Graphique des Courants Alternatifs, *Bedell and Crehore*, 489.
  - Grundzüge der Matematischen Chemie, *Helm*, 152.
  - Hydrodynamics, *Lamb*, 390.
  - Industrial photometry, *Poiaz*, 317.
  - Mechanics, *Glazebrook*, 239.
  - Mechanics and hydrostatics, *Glazebrook*, 400.
  - Notes on the nebular theory, *Stanley*, 399.
  - Oberflächen- oder Schillerfarben, *Walter*, 319.
  - Ostwald's Klassiker der exacten Wissenschaften, 154.
  - Polyphase motors, *Thompson*, 316.
  - Popular science lectures, *Mach*, 158.
  - Principien der mechanik, *Hertz*, 73.
  - Principles of physics, *Daniell*, 311.
  - Proceedings of the Electrical Society of Cornell University, 152.
  - Solution and electrolysis, *Whetham*, 315.
  - Standard methods in physics and electricity criticised, *Naber*, 160.
  - Steam and the marine steam engine, *Yeo*, 180.
  - The Herschels and modern astronomy, *Clerke*, 319.
  - Theorie der Wechselströme in analytischer und graphischer Darstellung, *Bedell and Crehore*, 489.

Briggs, L. J., On the electrolytic conductivity of concentrated sulphuric acid, 141.

Bruère, Alice H., A comparison of two concave Rowland gratings, 301.

Buckingham, E., Helm's *Grundzüge der Mathematischen Chemie*, 152.

Bunsen's ice calorimeter, 422.

C.

Cadmium spectrum, 453.

Calcium spectrum, 450.

Candles in photometry, A method for the use of standard, *Sharp*, 458.

Capacity in oscillating currents, 340.

Cauchy's formulæ for metallic reflection, 181.

Chemical potential of the metals, *Bancroft*, 250.

Child, C. D.:
  - The resistance of tinfoil as changed by electric waves, 387.
  - Thermal conductivity of copper, II., 1.

Clerke, Agnes M. *The Herschels and Modern Astronomy*, 319.

Color phenomena, A new apparatus for the study of, *von Hardroff*, 306.

Colored lights, on the photometry of differently, and the "Flicker" photometer, *Whitman*, 241.

Concentration, its effect on E. M. F. of a cell, 264.

Conductivities and viscosities, 332.

Conductivity, Electrolytic, of concentrated sulphuric acid, *Guthe and Briggs*, 141.

Conductivity of copper, Thermal, II., *Quick, Child, and Lanphear*, 1.

Conductivity of metallic wires in different dielectrics, *Sanford*, 161.

Cooley, L. C., Daniell's *Principles of Physics*, 311.

Copper spectrum, 454.

Copper, Thermal conductivity of, II., *Quick, Child, and Lanphear*, 1.

Crehore, A. C.:
  - *Étude Analytique et Graphique des Courants Alternatifs*, 489.
  - Experiments with a new polarizing photo-chronograph, as applied to the measurement of the velocity of projectiles, 63.
  - *Theorie der Wechselströme in analytischer und graphischer Darstellung*, 489.

Croker, F. B., Nipher's *Electricity and Magnetism*, 397.

Current, dynamo, On the alternating, *Goldsborough*, 477.

Currents, oscillating, Notes on the theory of, *Steinmetz*, 335.

D.

Daniell, *Principles of Physics*, 311.

Deliquescence, 403.

Demagnetization factors for cylindrical rods, *Mann*, 359.

Dielectrics, Variation in electric conductivity of metallic wires in different, *Sanford*, 161.

Discharges in oscillating currents, 344.

Dissociation theory, the relation of freezing-points to, 284.

Dommerque, F. J.:
- Bedell and Crehore's *Étude Analytique et Graphique des Courants Alternatifs*, 489.
- *Theorie der Wechselströme in analytischer und graphischer Darstellung*, 489.

Durand, W. F., Yeo's *Steam and the Marine Steam Engine*, 80.

Dynamo, Alternating current, *Goldsborough*, 477.

E.

Elastic limit, 447.

Electric current, influence of, upon Young's modulus, *Noyes*, 432.

Electrolytic conductivity of concentrated sulphuric acid, *Guthe and Briggs*, 141.

Electro-motive force of a cell, 250.

Engine cylinder, variation of temperature of, 60.

F.

"Flicker" photometer, On the photometry of differently colored lights and, *Whitman*, 241.

Fluid pressure, experimental demonstration of a law of, *Humphreys*, 71.

Foley, A. L., The surface tension of liquids, 381.

Franklin, W. S., *Elements of Physics*, I., 400.

Freezing-points of dilute aqueous solutions, *Loomis*, 270, 293.

Fresnel's formulæ for vitreous reflection, 177. [181.

Fresnel's formulæ for metallic reflection,

Frost, E. B., Stanley's *Notes on the Nebular Theory*, 399.

G.

Galvanometer for photographing alternating current curves, *Hotchkiss and Millis*, 49.

Gill, A. C., Story-Maskelyne's *Crystallography, a Treatise on the Morphology of Crystals*, 395.

Glazebrook, R. T.:
- *Mechanics*, 239.
- *Mechanics and Hydrostatics*, 400.

Goldsborough, W. E., On the alternating current dynamo, 477.

Gratings, A comparison of two Rowland's concave, *Bruère*, 301.

Guthe, K. E., On the electrolytic conductivity of concentrated sulphuric acid, 141.

H.

Harden, A., *A New View of the Origin of Dalton's Atomic Theory*, 483.

Heat effect of mixing liquids, *Linebarger*, 418.

Heat, influence of, upon Young's modulus, *Noyes*, 432.

Hefner light, 469.

Helm, G., *Grundzüge der Mathematischen Chemie*, 152.

Hertz, H.:
- *Die Principien der Mechanik*, 73.
- *Electric Waves*, 234.

Hicks, W. M., Lamb's *Hydrodynamics*, 390.

Holman, S. W., *Computation Rules and Logarithms, with tables of other useful functions*, 490.

Hornby, J., *A Text-Book of Gas Manufacture*, 491.

Hotchkiss, H. J., A galvanometer for photographing alternating current curves, 49.

Humphreys, W. J., Experimental demonstration of a law of fluid pressure, 71.

Hydrate of sulphuric acid, electrolytic properties of, 149.

I.

Incandescent solid and liquid surfaces, A study of the polarization of the light emitted by, *Millikan*, 81, 177.

Inductance of oscillating currents, 339.

Inductive phenomena in alternating current circuits, An experimental study of, *Millis*, 351.

Infra-red energy spectrum, On a simple method of photographically registering, *Ångström*, 137.

Impedance of oscillating currents, 339, 343.

Iron wires, On the changes in length produced by magnetization, *More*, 210.

J.

Jackson, D. C., Thomson's *Elementary Lessons in Electricity and Magnetism*, 78.

L.

Laboratory at Lille, The new Physics, *Nichols*, 232.

Lamb, H., *Hydrodynamics*, 390.

Lanphear, B. S., Thermal conductivity of copper, II., 1.

Lawrence, H. E., Glazebrook's *Mechanics*, 239.

Light emitted by incandescent solid and liquid surfaces, A study of the polarization of, *Millikan*, 81, 177.

Lille, The new Physics Laboratory at, *Nichols*, 232.

Linebarger, C. E., On the heat effect of mixing liquids, 418.

Liquids, On the heat effect of mixing, *Linebarger*, 418.

Lithium spectrum, 448.

Locke, J., Translation of Menschutkin's *Analytical Chemistry*, 400.

Loomis, E. H., On the freezing-points of dilute aqueous solutions, 270, 293.

Loudon, W. J., *A Laboratory Course in Experimental Physics*, 484.

M.

Mach, E., *Popular Science Lectures*, 158.

Mackenzie, A. S., Mach's *Popular Science Lectures*, 158.

Magnetic Theories, The graphical representation of, *Allen*, 470.

Magnetization:
  Its influence on Young's modulus, *Noyes*, 432.
  On the changes in length produced in iron wires by, *More*, 210.

Mann, C. R., Demagnetization factors for cylindrical rods, 359.

McLennan, J. C., *A Laboratory Course in Experimental Physics*, 484.

Menschutkin, N., *Analytical Chemistry*, 400.

Merritt, E., Naber's *Standard Methods in Physics and Electricity Criticised*, 160.

Metals, The chemical potential of, *Bancroft*, 250.

Metallic spectra, 448.

Millikan, R. A., A study of the polarization of the light emitted by the incandescent solid and liquid surfaces, 81, 177.

Millis, F. E.:
  A galvanometer for photographing alternate current curves, 49.
  An experimental study of inductive phenomena in alternating current circuits, 351.

Mixtures, Ternary, *Bancroft*, 21, 114, 193.

Moore, B. E., On the viscosity of certain salt solutions, 321.

More, L. T., On the changes in length produced in iron wires by magnetization, 210.

N.

Naber, H. A., *Standard Methods in Physics and Electricity Criticised*, 160.

von Nardroff, E. R., A new apparatus for the study of color phenomena, 306.

Needle, Secular motion of a free magnetic, II., *Bauer*, 34.

Nichols, E. L.:
  Elements of Physics, I, 400.
  Palaz's *Industrial Photometry*, 317.
  Walter's *Die Oberflachen- oder Schillerfarben*, 319.
  Clerke's *The Herschels and Modern Astronomy*, 319.
  The new Physics Laboratory at Lille, 232.

Nipher, F. E., *Electricity and Magnetism*, 397.
Noyes, Mary C., The influence of heat, of the electric current, and of magnetization upon Young's modulus, 432.

O.

Oscillating currents, Notes on the theory of, *Steinmetz*, 335.

P.

Palaz, *Industrial Photometry*, 317.
Patterson, G. W., and M. R., Translation of Palaz's *Industrial Photometry*, 317.
Photo-chronograph as applied to the measurements of the velocity of projectiles, *Crehore and Squire*, 63.
Photographic study of arc spectra, *Baldwin*, 370, 448.
Photographically registering the infra-red energy spectrum, *Ångström*, 137.
Photographing alternate current curves, *Hotchkiss and Millis*, 49.
Photometer, "Flicker," On the photometry of different colored lights and, *Whitman*, 241.
Photometry:
  A method for the use of standard candle in, *Sharp*, 458.
  Of different colored lights and the "Flicker" photometer, *Whitman*, 241.
Pitch for the human voice, The limits of, *Stevens*, 230.
Polarization of the light emitted by incandescent solid and liquid surfaces, A study of, *Millikan*, 81, 177.
Polarizing photo-chronograph as applied to the measurements of the velocity of projectiles, *Crehore and Squire*, 63.
Potassium spectrum, 450.
Potential, Chemical, of the metals, *Bancroft*, 250.
Pressure, Fluid, experimental demonstration of a law of, *Humphreys*, 71.
Projectiles, Polarizing photo-chronograph as applied to the measurements of the velocity of, *Crehore and Squire*, 63.
Pupin, M. I., Thomson's *Elements of the Mathematical Theory of Electricity and Magnetism*, 393.

Q.

Quick, R. W., Thermal conductivity of copper, II., 1.

R.

Reflection,
  Fresnel's formulæ for, 177.
  Cauchy's formulæ for, 181.
Resistance of tin-foil as changed by electric waves, *Child*, 387.
Rimmington, E. C., Alternating currents when the electromotive force is of a zigzag wave type, 100.
Rods, Demagnetization factors for cylindrical, *Mann*, 359.
Roscoe, W. E., *A New View of the Origin of Dalton's Atomic Theory*, 483.
Rowland's gratings, A comparison of two concave, *Bruère*, 301.
Ryan, H. J., Thompson's *Polyphase Motors*, 316.

S.

Salt solutions, On the viscosity of, *Moore*, 321.
Sanford, F., Variation in electric conductivity of metallic wires in different dielectrics, 161.
Secular motion of a free magnetic needle, *Bauer*, 34.
Self-induction, Experimental study of, 351.
Sharp, C. H., A method for the use of standard candles in photometry, 458.
Sheldon, S., Whetham's *Solution and Electrolysis*, 315.
Silver spectrum, 454.
Smith, D. E., Ball's *A Primer of the History of Mathematics*, 487.
Snow, B. W., Ostwald's *Klassiker der exacten Wissenschaften*, 154.
Sodium spectrum, 449.
Solids and vapors, *Bancroft*, 401.
Solution of liquids in liquids, 21.

Solutions, certain salts, On the viscosity of, *Moore*, 321.

Solutions, dilute, aqueous, On the freezing-points of, *Loomis*, 270, 293.

Spectra, arc, A photographic study of, I., *Baldwin*, 370, 448.

Spectrum, the infra-red, On a simple method of photographically registering, *Ångström*, 137.

Squier, G. O., The photo-chronograph as applied to the measurement of the velocity of projectiles, 63.

Standard candles in photometry, *Sharp*, 458.

Stanley, W. F., *Notes on the Nebular Theory*, 399.

Steinmetz, C. P., Notes on the theory of oscillating currents, 335.

Stevens, F. H., *Elementary Mensuration*, 400.

Stevens, W. L.:
  Loudon and McLennan's *A Laboratory Course in Experimental Physics*, 484.
  The limits of pitch for the human voice, 230.

Story-Maskelyne, N., *Crystallography, a Treatise on the Morphology of Crystals*, 395.

Strontium spectrum, 451.

Sulphuric acid, concentrated, On the electrolytic conductivity of, *Guthe and Briggs*, 147.

Surfaces, incandescent solid and liquid, A study of the polarization of the light emitted by, *Millikan*, 81, 177.

Surface tension of liquids, *Foley*, 381.

T.

Temperature:
  Co-efficient of copper wire, 2.
  Its influence on the heat effect of mixing normal liquids, 430.

Tension of liquids, Surface, *Foley*, 381.

Ternary mixtures, *Bancroft*, 21, 114, 193.

Thermal conductivity of copper, II., *Quick, Child, and Lanphear*, 1.

Thomson, J. J., *Elements of the Mathematical Theory of Electricity and Magnetism*, 393.

Thompson, S. P.:
  Elementary Lessons in Electricity and Magnetism, 78.
  Polyphase Motors, 316.

Thwing, C. B., On a new form of water battery, 309.

Tin-foil, Resistance of, as changed by electric waves, *Child*, 387.

Transformer, Oscillating currents, 348.

U.

Uranium glass, Polarization of light from, 97.

V.

Vapors and solids, *Bancroft*, 401.

Voice, The limits of pitch for, *Stevens*, 230.

Viscosity of certain salt solutions, *Moore*, 321.

W.

Walter, B., *Die Oberflächen- oder Schillerfarben*, 319.

Wave type, Alternating currents when the electromotive force is of a zigzag, *Rimmington*, 100.

Waves, electric, The resistance of tin-foil as changed by, *Child*, 387.

Webster, A. G.:
  Hertz's *Die Principien der Mechanik*, 73.
  Hertz's *Electric Waves*, 234.

Whetham, W. C. D., *Solution and Electrolysis*, 315.

Whitman, F. P., On the photometry of different colored lights and the "Flicker" photometer, 241.

Wires, metallic, in different dielectrics, Variations in electric conductivity of, *Sanford*, 161.

Y.

Yeo, John, *Steam and the Marine Steam Engine*, 80

Young's modulus, Influence of heat, of the electric current, and of magnetization upon, *Noyes*, 432.

Z.

Zinc spectrum, 453.