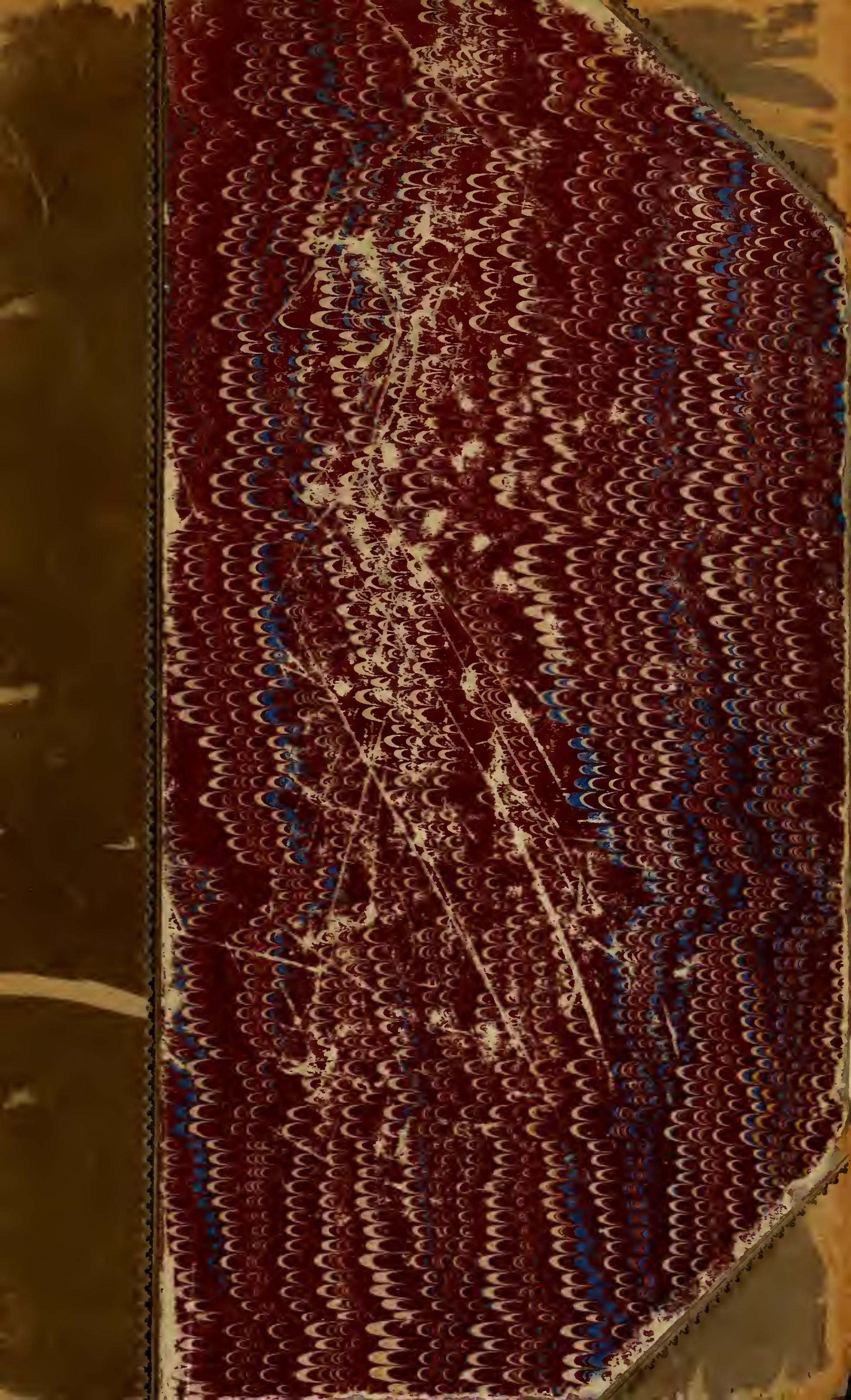

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CONDUCTED BY

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

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

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

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

J. B. Pinelli ad Mazonium.

ALERE FLAMMAM.

CONTENTS OF VOL. XXI.

(FIFTH SERIES).

NUMBER CXXVIII.—JANUARY 1886.

NUMBER CXXIX.—FEBRUARY.

NUMBER CXXX.—MARCH.

NUMBER CXXXI.—APRIL.

NUMBER CXXXII.—MAY.

Page

NUMBER CXXXIII.—JUNE.

PLATES.

THE
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[FIFTH SERIES.]

JANUARY 1886.

I. *On the Law of the Electromagnet and the Law of the Dynamo.* *By* SILVANUS P. THOMPSON, *D.Sc., B.A.*[*]

IT is remarkable, considering the vast amount of research that has been made, that authorities in physics are in so little agreement as to what the law of the electromagnet is. Upon the one topic that is all-essential to the electric engineer the professed physicist is either silent, or gives mathematical rules that are hopelessly wide of the observed facts, and based in most cases on no consistent theory. The expressions given by Weber[†] for the relation between the magnetizing force and the induced magnetism are an exception; but they are unmanageable in the extreme, and have led to no useful results. The expression given by Lamont[‡] is also based on a certain consistent theory, but it appears to be entirely unknown both to physicists and to electric engineers, and is to be found only buried in the depths of Lamont's own treatise. The two mathematical formulæ which are most often given in treatises on physics as representing the relation between the magnetizing current and the induced magnetism of the electromagnet are the following:—

Lenz and Jacobi's Formula.—According to the experiments of these early investigators (1839), the magnetism of the electromagnet is simply proportional to the strength of the current and to the number of turns of wire in the coil. This may be written as $m=kSi$,

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[*] Communicated by the Physical Society: read 14th November, 1885.

[†] Weber, *Elektrodynamische Maasbestimmungen*, p. 572. See also Maxwell, 'Electricity and Magnetism' (2nd edition), vol. ii. p. 78.

[‡] Lamont, *Magnetismus*, p. 41.

where i is the strength of the current, S the number of turns in the coil, k a constant depending on shape and quality of iron, and m the strength of the pole. Joule (1839) showed this rule to be incorrect, and that as the iron became saturated, m ceased to be proportional to Si.

Müller's Formula.—Müller gave an expression of the form:—

$$m = b \tan^{-1} \frac{Si}{a},$$

where b and a are constants, depending on the form, quantity, and quality of the core and on the form and disposition of the coils. Very similar formulæ have been used by Von Waltenhofen, Dub, Cazin, and Breguet. They are purely empirical, fail to represent the facts with accuracy, and have moreover the defect of not lending themselves conveniently to use in the equations of electromagnetic motors, dynamo-electric machines, and other kinds of electric machinery.

More recently another formula has been coming into use, and is known—for reasons which will presently appear—as Frölich's formula: it is written

$$m = \frac{i}{a+bi},$$

where a and b are again constants, b being the reciprocal of the maximum value of m. This formula, like the preceding, is a perfectly empirical expression not based in itself upon any physical theory, and it accords with the observed facts of the electromagnet better than any of the preceding formulæ. Frölich, who in 1878 was using merely Lenz and Jacobi's formula*, appears to have adopted this expression in 1880†, in consequence of the experiments which he had made with dynamo-machines. A similar formula had been used twenty-five years before by Robinson‡ to express the lifting-power of an electromagnet, and similar formulæ have been used by Oberbeck§, Fromme‖, Clausius¶, Ayrton and Perry**, and Rücker††.

Now it must be obvious that since almost the whole of

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* Frölich, *Die Lehre von der Elektricität und dem Magnetismus*, p. 237.

† Frölich, *Berl. Berichte*, Nov. 18, 1880, p. 973; also *Elektrotechnische Zeitschrift*, 1881, April, p. 139.

‡ Robinson, Trans. Roy. Irish Academy, vol. xxii. p. 1, 1855.

§ Oberbeck, *Pogg. Ann.* cxxxv. pp. 74–98, 1868.

‖ Fromme, *Pogg. Ann.* clv. p. 305, 1878.

¶ Clausius, *Wied. Ann.* xx. p. 367, 1883.

** Ayrton and Perry, Journ. Soc. Telegr. Eng. and Electr. xii. p. 317, 1883.

†† Rücker, Phil. Mag. ser. 5, xix. p. 463 (June 1885).

electric technology deals with the electromagnet and its applications, it is of utmost importance to know what the true law of the electromagnet is. If the technologist is left to the mercy of the physicist, he has to choose between formulæ that are based on physical conceptions and which are utterly unmanageable for his purpose, and formulæ that are purely empirical expressions and have no rational basis.

But the study of the modern dynamo-electric machine has brought us to a point that makes some decision a necessity. The entire action of the dynamo is dependent on the magnetizing action of the electric current, and the law of the dynamo is, in the very nature of things, not to be discovered, save by the discovery of the law of the electromagnet. It is indeed extraordinary that such able physicists as Mascart and Angot, Mayer and Auerbach, Schwendler, and Herwig sought in vain for the true law to connect the electromotive force of the dynamo with its speed, the resistance of its circuit, and the constants of its construction. Hopkinson came nearest to the mark when in 1879 he described the properties of the dynamo in terms of those of a certain curve, which we now call the characteristic curve of the machine; but he did not state the law of the dynamo algebraically, and apparently he accepted as true Weber's formula for the electromagnet.

But the law of the dynamo is now known, and expressions have been deduced which are found to agree with the utmost accuracy with the observed facts. The discovery is almost entirely due to Dr. Frölich*, whose papers, published at intervals from 1880 to 1885, are in their way already classical. The results first obtained by Frölich related exclusively to that form of dynamo in which the armature-coils and the field-magnet coils are both included in the main circuit—the series-dynamo—though they have been further extended by the present writer, and by others, including Frölich himself, to other forms of machine. A very brief résumé of Frölich's research will explain his method of arriving at the law.

His theory is based upon (1) Faraday's law of induction, (2) Ohm's law, (3) a curve, called by him the current-curve, expressing certain results of experiments made on the series-wound dynamo.

Following Faraday's principle, the induced electromotive force E will be proportional to the speed of the machine n and to a quantity M which Frölich calls the "effective magnetism," and which is itself proportional to the effective area of the

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* Frölich's chief papers are as follows:—*Berl. Berichte,* 1880, p. 978; *Elektrotechnische Zeitschrift*, vol. ii. p. 134 (1881); *ib.* vol. iii. pp. 69 and 113 (1882); *ib.* vol. iv. pp. 60, 67, and 71 (1883); *ib.* vol. vi. pp. 128, 139, 227 (1885).

armature-coils and to the intensity of the magnetic field. Writing this as an equation, we have

$$E = nM,$$

and, by Ohm's law,

$$E = i/R,$$

which gives us for the current i,

$$i = \frac{n}{R}M,$$

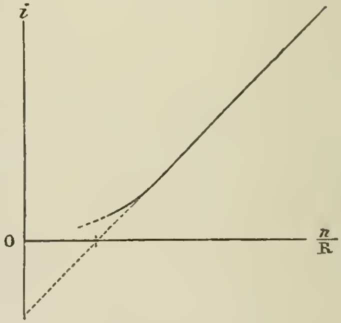
or

$$\frac{i}{M} = \frac{n}{R}.$$

Since M is itself a function of i, and not primarily of n or R, it is clear that i is itself a function of n/R, and we may write

$$\phi(i) = \frac{n}{R}.$$

This function Frölich set himself to investigate by pure experiment without making any hypothesis whatever. He determined the values of i at various speeds and with various resistances, and plotted out the results as a curve, values of i being taken as ordinates and values of n/R as abscissæ. This curve (see figure) he termed the "current-curve." It shows itself to be very nearly a straight line, which, however, does not pass through the origin. The portion which departs from the line is difficult of observation because it is only obtained when either n is very small or R very large, that is to say when the dynamo is scarcely able to excite its magnets. Neglecting this unstable state, and dealing only with that part of the curve which relates to the machine as it is when in action, it is clear that the relation between the two variables may be expressed as



$$bi = \frac{n}{R} - a,$$

where b and a are constants; giving us as the equation of the series-dynamo:—

$$i = \frac{1}{b}\left(\frac{n}{R} - a\right).$$

Substituting for n/R its equivalent i/M, Frölich then obtained from the law of the dynamo the following expression for the "effective magnetism":—

$$\mathrm{M} = \frac{i}{a+bi},$$

an expression which he himself appears, in his original paper, to have considered as a mere interpolation-formula. It is, however, this expression which is generally referred to as Frölich's formula for the electromagnet.

It was in 1883 that the author of this paper, in working at the problem of the dynamo, realized the significance of this result of Frölich's. He had been using as the fundamental law

$$\mathrm{E} = 4n\mathrm{AH}$$

to express the average value of the electromotive force developed by rotating in a uniform magnetic field of intensity H, an armature whose total effective area was A; and requiring a formula to connect H with the exciting current, he was considering the various equations of Müller, Weber, and others when he became aware that Frölich's expression furnished what was needed; and, finding it necessary for the case of compound-wound machines to express the excitation in terms of ampère-turns rather than of ampères, he rewrote the formula in the following way:—

$$\mathrm{H} = \mathrm{GS}i\frac{k}{1+\sigma\mathrm{S}i},$$

where, as before, Si is the number of ampère-turns, G a geometrical coefficient, k the coefficient of magnetic permeability in the initial stage, and σ a small saturation-coefficient dependent on the quantity and form as well as on the quality of the iron of the core.

Writing similarly $\mathrm{Z}i_s$ for the ampère-turns of a shunt-winding, the expressions for H became

$$\mathrm{H} = \mathrm{GZ}i_s\frac{k}{1+\sigma\mathrm{Z}i_s}$$

for shunt-wound machines, and

$$\mathrm{H} = \mathrm{G}(\mathrm{S}i \pm \mathrm{Z}i_s)\frac{k}{1+\sigma(\mathrm{S}i \pm \mathrm{Z}i_s)}$$

for compound-wound machines.

Inserting these values in the fundamental equation at once gave the following expressions:—

Series dynamo.

$$E=\frac{1}{\sigma}\left\{4nAGk-\frac{\Sigma R}{S}\right\}$$

$$i=\frac{1}{\sigma}\left\{\frac{4nAGk}{\Sigma R}-\frac{1}{S}\right\}$$

Shunt dynamo.

$$E=\frac{1}{\sigma}\left\{4nAGk-\frac{r_a r_s+Rr_s+Rr_a}{ZR}\right\}$$

Compound dynamo (at critical speed for regulation).

$$e=\frac{1}{\sigma}\left\{\frac{r_s(r_a+r\ \ )}{S(r_s+r_a)}-\frac{r_s}{Z}\right\}\text{(short shunt).}$$

or

$$e=\frac{1}{\sigma}\left\{\frac{r_s(r_a+r_m)}{S(r_s+r_a+r_m)}-\frac{r_s}{Z+S}\right\}\text{(long shunt),}$$

where r_a, r_m, r_s, and R are the resistances of armature, main-circuit coil, shunt-coil, and external circuit respectively, and e the difference of potentials at the terminals of the machine. These results were announced by the author at the Montreal meeting of the British Association, and were published by him in his volume on Dynamo-Electric Machinery, as was also the important proposition that the factor $\frac{1}{\sigma}$ (which may be called *the determinant* of the working power of the dynamo, since it appears in every one of the equations, both of current and electromotive force) is that number of ampère-turns which will reduce the effective permeability of the electromagnet, or rather of the magnetic circuit, to half its initial value. It will be seen that all these synthetical results were new, except that for the current of the series dynamo, which is identical with the expression that had been deduced by Dr. Frölich from the current-curve which represented his experimental results.

Since the publication of the author's treatise, Frölich has further elaborated the equations of the compound-wound machines; and a more generalized form has been deduced by Prof. Rücker in the masterly paper which he communicated to the Physical Society in March last, in which, however, he attributes to Frölich (I know not on what grounds) the general equation for the electromotive force of all kinds of dynamos. Frölich has also verified the adequacy of these formulæ by comparing results calculated from them with actual experiments on compound-wound machines. One example will suffice.

n.	R.	e obs.	e calc.	i obs.	i calc.
850	0·841	127	127	151·0	151·0
853	1·22	133	133	109·0	109·0
855	2·34	139	140	59·9	59·4
850	4·52	138	139	30·3	30·5
850	9·25	136	138	14·7	14·7
850	22·1	137	136	6·2	6·2
845	222·0	133	134	0·6	0·6

Such a series of results proves the law of the dynamo to be fully established. But if the law of the dynamo, so deduced from Frölich's empirical expression for the electromagnet, be true, *then*, to an equal degree of precision, *must the law of the electromagnet be itself true.*

But Frölich's expression is not the expression of any physical law: it is a mere interpolation-formula, destitute of rational significance. What then is the true law of induced magnetism? And how comes it that an expression devoid of physical significance so nearly expresses the physical law?

That question the author believes to have been already solved by a forgotten investigation of Lamont, published almost without note or comment in his *Handbuch von dem Magnetismus* in 1867. On p. 41 of that work he gives the following equation:—

$$m = \frac{a\text{M}x}{\text{M}+ax},$$

as a convenient first aproximation to another equation based on a new theory of induced magnetism. In the above equation x stands for the magnetizing force, m the induced magnetism, and M the maximum value of the latter. Writing Gk for a, Si for x, and σ for $\frac{a}{\text{M}}$, we at once get

$$m = \frac{\text{G}k\text{S}i}{1+\sigma\text{S}i},$$

which is the author's way of writing Frölich's equation.

The physical theory which led Lamont up to this result is of great interest, the more so since it has been revived during the current year in a more elaborate form by Bosanquet*, who has apparently been led thereto by an inde-

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* Bosanquet, Phil. Mag. ser. 5, xix. p. 85 (Feb. 1885).

pendent line of thought, and who has gone much further than Lamont in bringing in the additional consideration of the forces resisting the orientation of the molecules. Lamont's theory is, briefly, that the permeability of the iron diminishes as the permeation increases, being at every stage of the magnetization proportional to the deficit of saturation. He assumes that for every bar there is a certain maximum of magnetization, to which it could only attain under the influence of an infinitely great magnetizing force; and that the permeability of the bar is at every stage of the magnetization proportional to the difference between the actual magnetization and the possible magnetization. This is, in other words, as if in every bar there were room for only a certain limited number of magnetic lines of force, and that, when any lesser number have been induced in it, the susceptibility of the bar to the reception of additional lines is proportional to the room yet left for them in the bar. Lamont's theory is expressed as follows: Let the magnetism present at any stage be called m, and let the maximum magnetism be called M. Then the amount which the bar can still take up is $\mathrm{M}-m$; and it is to this that the permeability dm/dx is proportional. Here x may be understood, as itself proportional to the number of ampère-turns of the exciting current; and we may write

$$\frac{dm}{dx}=k\ (\mathrm{M}-m),$$

where k is a constant depending on the units employed, and on the initial value of the permeability of the magnetic circuit when $m=0$. Integrating we obtain

$$\mathrm{M}-m=\mathrm{A}\epsilon^{-kx},$$

where A is a constant of integration. But when $x=0$, $m=0$ also; whence $\mathrm{A}=\mathrm{M}$, giving

$$m=\mathrm{M}(1-\epsilon^{-kx}),$$

which is Lamont's formula.

Lamont also develops this expression in ascending powers of kx,

$$m=\mathrm{M}kx\left(1-\frac{kx}{1\,.\,2}+\frac{k^2x^2}{1\,.\,2\,.\,3}-\quad.\quad.\quad.\quad.\quad.\quad.\right),$$

and he then makes the remark that it may be approximately represented by the simpler, but empirical expression

$$m=\frac{a\mathrm{M}x}{\mathrm{M}+ax},$$

which is identical in form with the expression known as Frölich's. Now, writing k for a/M,

$$m=\frac{\mathrm{M}kx}{1+kx},$$

and expanding this in ascending powers, we get

$$m=\mathrm{M}kx(1-kx+k^2x^2- \quad . \quad . \quad . \quad . \quad . \quad .).$$

Neglecting the fourth and higher terms, it will be seen that the formulæ are very nearly equal for all small values of kx, and are identical for the value

$$kx=\frac{3}{5},$$

or when the actual magnetism has about ·456 of the value it would have under an infinite magnetizing force. For larger values of the magnetizing force the values of m calculated by the empirical formula are slightly greater than those calculated by the exponential formula.

None of these formulæ render any account of a phenomenon noticed in many cases where an electromagnet is magnetized with gradually ascending magnetic forces, namely, a concavity in the *early* part of the curve of magnetization, the permeability apparently becoming greater after a certain degree of magnetization has been attained. The researches of Chwolson and of Siemens seem to show that this apparent increase in the permeability (which is not observed with descending magnetic forces) is due to non-homogeneity, and to the resistance of some of the molecules to magnetization. Bosanquet's theory may be taken in connection with the recent observations of Rowland, Warburg, Ewing, and Hopkinson on this subject, which, however, is of no great importance here since the apparent maximum of permeability is attained in most cases at a much lower degree of magnetization than that at which the dynamo is actually worked.

The very close agreement between the observed values of current and potential of the dynamo and those calculated by the equations based upon Frölich's formula, proves that nowhere within the working range do the actual values of the magnetization differ sensibly from those calculated by the Frölich formula. That is to say this formula may be taken as *something more than a first approximation* to the true law of the electromagnet for all degrees of saturation of the magnets employed in practice, and may be taken as a first approximation for all degrees of saturation beyond that usually attained.

It is eminently desirable, in the face of these facts, that the imperfect formula of Lenz and Jacobi, as well as that of Müller, should henceforth disappear from the text-books of physics, and that instead thereof the true law of the electromagnet should be stated, either in the exponential form or in the simpler form that is found to be equally true within the range of saturation attained in practice.

II. *On* Prof. Himstedt's *Determination of the Ohm.*

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

AS there is still some discrepancy in the values of the ohm obtained by able workers using various methods, it seems desirable to put forward any criticisms that may suggest themselves, in the hope that the causes of disturbance may thus come to be better understood. I propose accordingly to make a few remarks upon the paper of Professor Himstedt, translated in your November number, not at all implying that his results may not be as good as any other, but rather in order to raise discussion on certain points which the author may be able to treat satisfactorily when he publishes a more detailed account of his work.

The leading feature in the method of Prof. Himstedt is the use of a commutator, or separator, by which the make- and break-induced currents are dissociated, one or the other passing in a stream at equal small intervals of time through a galvanometer, by whose aid their magnitude is appreciated. The instrument works with mercury contacts. When I first considered the methods available for the solution of this problem at Cambridge in 1880, I found ready to my hand an ingenious apparatus, contrived by Prof. Chrystall for this very purpose. The contacts were effected by metallic dippers, controlled by eccentrics, and passing in and out of mercury cups. What determined me against this method*, notwithstanding its obvious advantages in respect of sensitiveness, was the recollection of unavailing attempts of my own in 1870 to make satisfactory mercury contacts with dippers carried by electrically maintained tuning-forks. Even when silver was the metal employed, the contacts were uncertain, and no trustworthy galvanometer deflection could be obtained. It may be men-

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* I may remark that Brillouin used a commutator of this nature in his researches on the comparison of coefficients of induction: Thèses présentées à la Faculté des Sciences de Paris, 1882.

tioned, in passing, that the object was to obtain, through the galvanometer, a stream of charges of a condenser, separated from the discharges, with a view to the determination of v (the ratio of electrical units). Dippers in electrical connection with the body of the fork (and by means of a wire attached to the stalk with one pole of the condenser) were carried on both the upper and lower prongs. Underneath these, mercury cups were so arranged that the vibrating-fork was in contact with them alternately, but never with both at the same time. One of the cups was connected with the insulated pole of the battery and the other with the earth. The fork was driven by a current entirely insulated from it. It was found, however, that the contacts could not be made perfect, and the direct use of the fork was abandoned in favour of a commutator with platinum contacts driven by the fork*. This form of the apparatus is unsuitable as a separator of induced currents; and I was inclined to favour the observation of a single induced current with a ballistic galvanometer as carried out by Rowland, and afterwards by Glazebrook.

It is to be presumed that the contact difficulty has been overcome by Prof. Himstedt; and my principal reason for mentioning it is that I found it particularly capricious and insidious. The galvanometer indication would often remain steady for minutes together, and then suddenly change. It would be interesting to know whether Prof. Himstedt has met with any behaviour of this sort.

The next question that I wish to raise relates to the measurement by the galvanometer of a series of induced currents, each of short duration. On page 421 there is a reference to "cross magnetization" that I do not quite understand. I have myself† objected to the use of a ballistic galvanometer, on the ground of the tacit assumption that the needle at the moment of the impulse, when subject to a powerful cross-magnetizing force, retains its axial magnetization unaltered; but in the method of Prof. Himstedt the question assumes a different shape. In this case the needle stands in an oblique position, and we have to consider whether the axial magnetization does not alter under the action of a force having a *sensible axial component*‡. In all probability Prof.

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* "On the Determination of the Number of Electrostatic Units in the Electromagnetic Unit of Electricity," J. J. Thomson, Phil. Trans. 1883, p. 719.

† Phil. Trans. 1882, p. 670.

‡ "On a Permanent Deflection of the Galvanometer Needle, &c.," B.A. Report 1868. Phil. Mag. Jan. 1877. Chrystall, Phil. Mag. Dec. 1876.

Himstedt has considered this matter. It admits of a very simple test, all that is necessary being to deflect the needle into its oblique position with an external permanent magnet, and then to allow the induced currents to pass, *suppressing the interruption of the secondary contact.* Both make- and break-induced currents would then pass, whose mean value is zero ; and any deflection of the needle under these conditions would be a sign that its magnetism fluctuated and that the evaluation of either stream alone would be vitiated.

An interesting feature in Prof. Himstedt's work is the arrangement of the primary and secondary coils, of which the former is a long solenoid embraced by the latter. The fact that as regards the secondary the induction-coefficient depends sensibly upon the number of turns only, without regard to radius, is much in its favour. Any one who has had to do with the measurement of coils will appreciate too the advantage of reducing the primary to a single layer. There are, however, disadvantages in this arrangement which must be kept in sight. I will not dilate upon the use of a wooden core on which to wind the primary, though I should think it hardly safe. But assuming that there is no important uncertainty as to the value of R (the mean radius of the primary), though it should be remarked that it occurs in the formula as a square, nor in the data relating to the secondary, we have still to consider the factor K, expressive of the number of turns per unit length in the primary. So far as appears, the value of this quantity is obtained by simply dividing the whole number of turns, 2864, by the measured length, 135·125 cm. Now there is here a tacit assumption either that the wire is wound with perfect uniformity, or that we have to deal only with the mean value. The latter alternative is manifestly incorrect, since the central parts lying nearly in the plane of the secondary are necessarily more effective than the remoter parts. In point of fact the simplicity of this arrangement is more apparent than real, relating rather to calculation than to measurement, as I have already had occasion to remark* in connection with a somewhat similar use of a long solenoid in Mascart's determination of the electrochemical equivalent of silver. How far uniformity was attained in the present case I have no means of judging ; but where the successive turns are merely brought into contact with one another I should not expect a high degree of precision, if only because the thicknesses of the wire and silk are liable to vary. Again, it may be possible to verify the uniformity *a posteriori*, or to obtain

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* Phil. Trans. 1884, p. 413.

data for the calculation of a correction. But at any rate it seems misleading to exhibit the result as determined by the average number of turns per unit length, when it really depends also upon the ratios of the rates of winding at the various parts of the length.

Repeating that I throw out these remarks merely for purposes of discussion, I remain,

Your obedient Servant,

RAYLEIGH.

III. *A Note on the Electromotive Force of certain Tin Cells.*

By E. F. HERROUN, *of King's College, London.*[*]

HAVING failed to find any published account giving the electromotive force of cells consisting of *tin* in solutions of any of its salts, opposed to other metals in solutions of their corresponding salts, I thought that some measurements recently made by myself might be of interest to this Society as tending to complete the series of double-fluid cells already investigated and recorded by others.

The cells examined consisted of an outer containing-vessel of glass or glazed earthenware, in which was placed one of the metals in a solution of one of its salts, and an inner porous pot 8 centim. high containing the other metal in a solution of its corresponding salt. It will be seen that they were, therefore, similar in construction to the ordinary laboratory form of Daniell cell, and the standard employed in these experiments was a Daniell cell made up in exactly the same manner.

The solutions in the Daniell cell were copper and zinc sulphates of equal molecular strength as recommended by Dr. C. Alder Wright, the proportion being $1{\cdot}8\ M''SO_4$, $100\ H_2O$. The cell made up in this way was assumed to have an electromotive force of 1·08 volt, and it probably differed but little from this value.

Method of Measurement.

The measurements of the E.M.F. of the cells were made by the zero method of Latimer Clark, in which no polarization is possible when the adjustment is effected. The standard Daniell cell was used before and after each experimental cell in order to avoid error due to variation in the potential of the wire, resulting from changes in the E.M.F. or internal resistance of the third or polarizing battery, which consisted either of

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[*] Communicated by the Physical Society: read November 14, 1885.

two Daniell cells or a Fuller's bichromate. This precaution, however, was usually found to be superfluous, as the circuit of the third battery was only closed when an observation was being made, and its E.M.F. and internal resistance varied only within very small limits.

In order to ascertain if the E.M.F.'s measured were really due to the essential chemical changes occurring within the cell, it was usual, after making an observation with an experimental cell when first put up, to allow the cell to work for a short time on a circuit of a few ohms, so as to cause the surfaces of the metals to become dissolved and deposited upon respectively. The circuit was then opened, and after a short rest the E.M.F. was again determined. If this differed by little or nothing from the previous measurements it was considered to be the true value for that cell; if, on the contrary, there was an appreciable difference further measurements were made. By operating in this way it was found that copper plates (particularly electro-deposited metal) which had been exposed to the air, and had acquired a superficial film of suboxide, usually gave, when first put up, an E.M.F. somewhat in excess of their true value. After allowing the cell to send a current for a few minutes, the E.M.F. fell to the normal value, and thereafter remained sensibly constant. (*Vide* also Dr. Fleming, "Use of Daniell's Cell," Proc. Phys. Soc. vol. vii. p. 168.)

As such initial fictitious electromotive forces would affect to their full extent the results obtained by a method like that of Poggendorf or Latimer Clark, or in fact any method in which difference of potential and not the current is measured, it was thought well to control such measurements with one or two cells by using Wheatstone's method of adding a resistance to bring down the deflection of a galvanometer-needle through a given number of degrees. The results obtained by this means agreed remarkably with those found by the previously mentioned process.

In the calculations relating to the heat of formation of some of the salts, it has been taken as a mean value that the electrochemical equivalent of hydrogen is ·0001038 *, and that the Joule equivalent is $4{\cdot}16 \times 10^7$ ergs. From these numbers the factor which, multiplied into the heat, expressed in gramme-degrees, evolved by the displacement of the gramme equivalent of one metal by that of another, will give the electromotive force in volts, is found to be $4{\cdot}318 \times 10^{-5}$ or $4{\cdot}32 \times 10^{-5}$ nearly.

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* "On the Determination of Chemical Affinity in terms of Electromotive Force," by Messrs. Wright and Thompson, Phil. Mag. vol. xix. p. 7.

The electromotive forces of the following combinations have been measured :—tin and copper, zinc and tin, cadmium and tin, in solutions of their sulphates and chlorides; and zinc and tin in solutions of their iodides.

The stannous sulphate employed was obtained by the action of sulphuric acid with the aid of heat upon finely granulated tin, in presence of platinum or copper to aid the action. The solution of stannous sulphate contained some free sulphuric acid ; and in fact it appears to be impossible to prepare a neutral solution suitable for these experiments, as on dilution to the required strength it deposits a basic salt, the solution becoming acid. Moreover a nearly neutral solution of stannous sulphate when kept is easily acted on by atmospheric oxygen, becoming cloudy and finally depositing what is probably either a mixture of basic stannous sulphate and stannic hydrate, or a basic stannic sulphate (?). With free sulphuric acid present in the proportion of from 1 to 2 per cent., the solution was satisfactory, and the effect of the free acid is considered below. For similar reasons it was found necessary to operate with solutions of stannous chloride containing a small amount of free hydrochloric acid, and with stannous iodide containing free hydriodic acid.

The metallic tin employed as plates in these cells was chemically pure, it having been obtained by electrolysis of a pure solution of the sulphate. The electro-deposited metal was carefully fused and rolled into strips.

The copper plates employed had in all cases been well covered with the electro-deposited metal. The zinc used was a good specimen of commercially "pure" metal, and was amalgamated. The cadmium was fairly pure, and was covered with the electro-deposited metal.

Electromotive Force of Cells consisting of the Metals immersed in Solutions of their Sulphates.

I. *Zinc-Tin Sulphate Cell.*

A cell in which zinc in $\cdot 5\mathrm{ZnSO_4}, 100\ \mathrm{H_2O}$ is opposed to tin in $\cdot 5\mathrm{SnSO_4}, 100\ \mathrm{H_2O}$, *both* solutions containing about 1·5 per cent. $\mathrm{H_2SO_4}$, was found to have an E.M.F. of from ·519 to ·535 volt, the variation being due to two causes : (1) slight differences in the percentage of free $\mathrm{H_2SO_4}$, and (2) differences in the condition of the surface of the tin plate.

It is thus difficult to assign an exact value except between such limits ; but with solutions of the above strength, and with a tin plate covered with freshly deposited tin, the value of ·525 volt may be taken as a tolerably accurate average E.M.F. for this kind of cell.

It would, of course, be unphilosophical to assume that an *equality* in the amount of free acid present in each solution has the same effect as operating with neutral solutions ; but being unable to employ a neutral solution of stannous sulphate, the addition of an amount of sulphuric acid to the zinc solution equal to that present in the $SnSO_4$ solution was considered to be the fairest way of meeting the difficulty.

Increasing the amount of free sulphuric acid in the tin solution only has naturally the effect of lowering the E.M.F., so that with 5 per cent. H_2SO_4 the E.M.F. is not higher than ·49 volt.

Substituting a 10 per cent. solution of H_2SO_4 for the zinc sulphate, leaving the stannous sulphate unchanged, raises the E.M.F. to ·596 volt.

The effect of varying the strength of both solutions (keeping them of equal molecular strength) is the same in kind as that which occurs with the zinc-tin chloride cell, but is less marked. (See Zinc-Tin Chloride Cell.)

The heat of formation of stannous sulphate being unknown, it is impossible to compare the value ·525 volt with deductions from thermal data.

II. *Tin-Copper Sulphate Cell.*

A cell in which tin in $\cdot 5 SnSO_4, 100 H_2O$ is opposed to copper in $\cdot 5 CuSO_4, 100 H_2O$, containing from 1 to 2 per cent. H_2SO_4 in both solutions, was found to have an E.M.F. varying from ·56 to ·572 volt, according to the condition of the surfaces of the plates and the acidity of the solutions. The effect of increasing the proportion of free H_2SO_4 in the tin solution is to raise the E.M.F. of the cell, and it is, of course, opposite to the effect observed in a cell in which zinc displaces tin. The increase of free sulphuric acid equally in both tin and copper solutions also tends (at least through a certain range up to 3 or 4 per cent.) to slightly raise the E.M.F. ; and from this I conclude that with neutral solutions of the above strength, the value would not exceed, and would probably fall slightly below, ·56 volt. Preference would therefore be given to the minimum value ·56 instead of the mean value ·566.

Alteration of the strength of the solutions is complicated by the question whether such alteration involves a change in the percentage of contained acid or only of the salts employed. Increase of strength of the solutions as regards the salts only, is attended with a slight depreciation of the E.M.F. ; but if the addition of more salt causes an increase in the acidity of the tin solution, the effect is to heighten the E.M.F., so that these opposite effects may equal each other, or one may exceed the other, according to their relative magnitude.

Cells were set up in which tin in a solution of 20 per cent. H_2SO_4 (sp. gr. 1·141) was opposed respectively to tin in $\cdot 5SnSO_4$, $100\,H_2O$, containing $1\frac{1}{2}$ per cent. H_2SO_4, and to $\cdot 5CuSO_4$, $100\,H_2O$, and the following values obtained :—

Tin-tin sulphate cell.	·058–·062 volt.
Tin sulphuric-acid-copper sulphate cell.	·59 volt.

(It will be seen that the last-mentioned cell does not exceed the tin-copper sulphate cell (·566) by an amount equal to the tin-tin cell, the lower E.M.F. being probably due to an adverse E.M.F. resulting from diffusion into the comparatively strong sulphuric-acid solution.)

If the mean values assigned to the zinc-tin cell and the tin-copper cell are added together, they are found to exceed the zinc-copper cell, which they should theoretically equal

$$(\cdot 525+\cdot 566=1\cdot 091-1\cdot 08=\cdot 011 \text{ excess}).$$

This result confirms the opinion that for neutral solutions the value ·566 is probably too high for the tin-copper cell, and justifies the minimum value ·56 being taken as correct. This still gives a slight excess $1\cdot 085-1\cdot 08=0\cdot 005$, and in practice it is found that a zinc-tin cell and a tin-copper cell united in series actually give an E.M.F. slightly in excess of the zinc-copper cell. This difference may be due either to the different conditions of the surfaces of the two tin plates or to some less obvious cause ; but as it has been found to exist on several occasions in different cells, it can hardly be a mere coincidence.

III. *Cadmium-Tin Sulphate Cell.*

A cell set up with cadmium in $\cdot 5CdSO_4$, $100\,H_2O$, opposed to tin in $\cdot 5SnSO_4$, $100\,H_2O$, both containing about 1·5 per cent. H_2SO_4, was found to have an E.M.F. of ·189 volt.

In order to compare the summation with the zinc-tin cell, a determination of the zinc-cadmium sulphate cell was made (using $\cdot 5M''SO_4$, $100H_2O$), and it was found to have an E.M.F. of ·335 volt. (The value given by Messrs. Wright and Thompson for the zinc-cadmium cell where $m=\cdot 5$ and the solutions are *neutral* is ·361, which, correcting for difference of standard, gives $\frac{1\cdot 08}{1\cdot 114}\times\cdot 361=\cdot 349$ or somewhat higher.)

Adding together the values obtained we get $\cdot189+\cdot335=\cdot524$ volt for the zinc-tin cell, a result which shows a striking agreement with the average value previously given, viz. ·525.

The average E.M.F. of the cadmium-copper cell was also determined and found to be ·744, Messrs. Wright and Thompson finding ·753 for the same cell, which gives $\left(\frac{\cdot753\times1\cdot08}{1\cdot114}=\right)$ ·73 volt; or, in other words, my value for the cadmium-copper is as much above, as my zinc-cadmium is below, their estimate, both values adding up correctly,

$$\cdot73+\cdot349=1\cdot079,$$

and

$$\cdot744+\cdot335=1\cdot079.$$

This discrepancy is no doubt due to the fact that the solutions employed by me contained about 1·5 per cent. of free H_2SO_4 in order to keep the conditions uniform with the tin cells.

Subtracting the E.M.F. of cadmium-tin from that of cadmium-copper, we get the E.M.F. of tin-copper, thus:—

$$\cdot744-\cdot189=\cdot555 \text{ volt};$$

which accords fairly well with ·56, but is, as would be anticipated, somewhat less.

Cells the algebraic sum of whose E.M.F.'s should equal 1·08, the standard Daniell.

Zinc-tin-sulphate	+	tin-copper-sulphate.				
·525	+	·56			=	1·085.
Zinc-cadmium	+	cadmium-tin	+	tin-copper.		
·335	+	·189	+	·56	=	1·084.
Zinc-tin	+	cadmium-copper	–	cadmium-tin.		
·525	+	·744	–	·189	=	1·08.

Electromotive Force of Cells consisting of the Metals in Solutions of their Chlorides of Equal Molecular Strength.

I. *Zinc-Tin Chloride Cell.*

A cell set up with amalgamated zinc opposed to tin in solutions of their chlorides of the strength $\cdot5\,M''Cl_2, 100\,H_2O$, containing 1 per cent. HCl, gave an E.M.F. of ·544 to ·553 volt, mean $=\cdot549$ volt.

Diluting the solutions equally with distilled water causes a rise of E.M.F. up to about ·607 volt, but dilution with 1 per cent. hydrochloric acid causes a slight diminution of E.M.F. This and other facts render it probable that with this cell, and to a less extent with the zinc-tin sulphate cell, increase of solution-strength without increase in the percentage of contained acid is associated with a rise of E.M.F.; but that with a corresponding increase of acidity, with a fall of E.M.F. Thus it is that dilution with distilled water raises the E.M.F. not because the metallic salt is diluted, but because the free acid is more attenuated.

Mutatis mutandis the same remarks apply to tin-copper or other cells in which tin is the metal attacked (*i. e.* with constant acidity and increasing strength of solution the E.M.F. falls, but with increase of *both* the E.M.F. rises, or does not fall).

The heat of formation of zinc chloride and of stannous chloride being known, the theoretical E.M.F. is directly calculable.

$$[Zn, Cl_2, aq.] = 112840. \qquad [Sn, Cl_2, aq.] = 81140.$$

$112840 - 81140 = 31700$; half of which multiplied into $4{\cdot}32 \times 10^{-5}$ gives ·684 volt as the E.M.F. of zinc displacing tin from solution of its chloride, and the difference between the observed and calculated value is $\cdot 684 - \cdot 549 = \cdot 135$ volt. Or to employ the terminology of Messrs. Wright and Thompson, $-\cdot 135$ is the "*Thermovoltaic constant*" for tin in solution of its chloride for certain strengths of solution (near $\cdot 5\ MCl_2$, $100\ H_2O$).

II. *Cadmium-Tin Chloride Cell.*

A cell set up with electro-cadmium opposed to tin in solutions of their chlorides, $\cdot 5\ M''Cl_2, 100\ H_2O$, was found to give an E.M.F. of ·247 to ·262 volt and an average value of ·249 volt. The solutions used contained the same amount of free hydrochloric acid, namely about 1 per cent.

The heats of formation being $[Cd, Cl_2, aq.] = 96250$ and $[Sn, Cl_2, aq.] = 81140$ and their difference 15110 or 7555 per equivalent, the theoretical E.M.F. of cadmium displacing tin from dilute solutions of its chloride is ·326 volt, and the difference between this and the average observed value is ·077.

The E.M.F. of a zinc-cadmium chloride cell was also determined and found to be between ·291 and ·308 volt, giving an average of ·301 volt. This is below the value given by Messrs. Wright and Thompson, owing to the solutions used by me containing 1 per cent. free HCl, they giving for this cell ·329 volt, which becomes $\left(\frac{\cdot329 \times 1\cdot08}{1\cdot114} = \right)$ ·318 volt, allowing for difference of standard.

In reference to a point to which these authors* drew attention a short time ago, namely, that, although the heat evolved by displacing cadmium by zinc in solutions ·25 $CdCl_2$, 100 H_2O is greater than that evolved by the same substitution in the case of the sulphates, yet the E.M.F. of the zinc-cadmium *chloride* cell is materially less than that of the zinc-cadmium *sulphate* cell, my measurements afford direct confirmation, as the value given here for the average E.M.F. of the zinc-cadmium sulphate cell is ·335 volt and that for the zinc-cadmium chloride cell only ·301 volt, or a difference of ·034 volt, substantially the same as the difference given by them, viz. ·035.

III. *Electromotive Force of Zinc-Tin Iodide Cell.*

A cell set up with amalgamated zinc in ·25 ZnI_2, 100 H_2O opposed to tin in ·25 SnI_2, 100 H_2O, both solutions acidified with 1·5 per cent. of HI, was found to have an E.M.F. of from ·47 to ·49, averaging ·485 volt.

There being no thermal data at my disposal no comparisons can be drawn.

PM 21 (1886)

IV. *The Dynamo as a Generator and as a Motor. Some Analogies and Contrasts. By* W. M. Mordey, *Esq.*†

DURING the last few years an immense amount of attention has been given to everything relating to theory and practice of dynamo machines. So thorough has been the study of the problems connected with these machines, which are of a character to appeal both to the physicist and the practical constructor or engineer, that it is now not difficult to lay down, in a fairly complete form, the laws governing their action, and the rules and principles under which they should be constructed; although three or four years ago much confusion and uncertainty existed as to what was best in dynamo construction.

But in electric motors the case is very different. While it is easy to name physicists and constructors in considerable

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* Phil. Mag. vol. xvii. p. 378 (May 1884).

† Communicated by the Author.

numbers who hold clear and correct views on the subject of electric generators, it is by no means easy to find definite and correct explanations of what is right and what wrong in regard to the allied subject of electric motors.

And on no point does there appear to be greater uncertainty than on that of the analogies and the differences between the two machines. For instance, while it has been proved beyond question that in dynamos the most economical and best working conditions are obtained by employing field-magnets of great magnetic strength, and armatures which are relatively very weak magnetically, the only definite assertion within the writer's knowledge given with authority on this point, asserts exactly the contrary to be the case with motors, viz. that the fields should be relatively much lighter and weaker than the armatures*.

Again, what can be more striking than the great and known difference between dynamos and motors in respect to the very important matter of efficiency! Almost any modern generator will give a return in the form of electric energy of 90 per cent. of the mechanical energy expended in it, and a useful yield of over 80 per cent. in its external circuit. In the case of the best generators this is a considerable understatement of the working conditions. With electric motors, on the other hand, one has to be contented with a much lower efficiency. The energy supplied to them is severely taxed in the process of conversion. Motors frequently yield, as mechanical energy in a useful and available form, only 30 per cent., and seldom more than 60 per cent., of the electric energy absorbed.

The reversibility of the dynamo, or its ability to work either as generator or motor, has been spoken of as one of the most important discoveries of late years (the great physicist credited with the expression of this opinion having apparently overlooked the fact that Pacinotti made his famous machine as a *motor* in the first place). But the fact that a given machine which will work well and efficiently as a dynamo, will not work so economically when its action is reversed and it is made to act as a motor, is a proof that the reversal is accompanied by some radical change in its action. This difference, where it is noticed at all, is generally sought to be explained by an assertion or a supposition that having been designed and made for one purpose, it was therefore not suitable for the other. No satisfactory explanation, as far as the writer is aware, has been given of the cause of this lower efficiency

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* Profs. Ayrton and Perry, "Electromotors and their Government," Journ. Soc. Teleg. Eng. and Electricians, March 1883.

of motors, or, in other words, of how the missing power is expended. In what particulars a good motor should resemble a good dynamo, and in what they should differ from one another, are also interesting questions of great importance which await answers.

The writer having, with Mr. C. Watson—who is his assistant in the works of the Anglo-American Brush Electric Light Corporation—given some attention to the matter from a practical point of view, a great necessity was felt for some foundation on which to work, similar in character to the broad general principles which serve to guide the practical constructor of dynamo machines. In the search for such general principles, all those ways of considering the actions which depend on the idea of magnetic poles in the armature were abandoned, and the conclusion was arrived at that the armature should have no polar action whatever, that the iron of the armature should have only the function of a conductor of lines of force, and that the power of the motor should be due to the simple action between the lines of force of the magnetic field and the armature-wires conveying currents at right angles to those lines of force. This mode of regarding motor action is convenient on several grounds, and leads to certain conclusions, which, if correct, form substantial bases for practical construction. Thus the armature, instead of being, as hitherto, considered as a strong electromagnet placed in the field of another electromagnet, is to have its electromagnetic functions reduced as much as possible, or preferably suppressed altogether.

The field is to be very strong.

As with such an arrangement there is no polar effect in the armature except that due to the direct magnetic induction of the field-magnets, it follows that the maximum power is obtained with any given current when the brushes occupy an absolutely neutral position, or, in other words, when there is no " lead " and no distortion or rotation of the field. These conditions do away with the most troublesome and prolific cause of the sparking at the brushes, which is so often an objectionable feature of most electric motors.

But by working backwards in this way it was seen at once that the conditions which seemed to be best for a motor were precisely those which the would-be designer of a perfect dynamo would set before him as his goal.

Certain perfect analogies had been arrived at. In both dynamos and motors, according to this briefly sketched view:—

(1) The field should be a very strong, the armature a very weak electromagnet.

(2) In both generators and motors "lead," distortion, or displacement of brushes or of magnetic field is wrong, and is to be avoided by attention to (1).

Whatever "lead" there may be in either case, there is this difference, that in dynamos this "lead" is in the direction of rotation; in motors it is in the opposite direction, as the course of the current through the armature is reversed, but the field is the same.

(3) In both generators and motors absence of sparking at the brushes depends mainly on the conditions of (1) being complied with.

(4) Reversal of rotation. In neither generators nor motors is movement of the brushes necessary.

But having got so far, a little consideration suggested the probable existence of another analogy. Since a dynamo having the above theoretically perfect form and action, with a constant field would produce a constant electromotive force if run at a constant speed, independently of the load or amount of current generated, a motor constructed on the same principles and having a constant field, if supplied with energy at a constant difference of potential, should run at a constant speed, independently of load.

If this should prove to be a true analogy, a simple means of obtaining results of great use in the practical application of electricity would be obtained—results which have been sought in many directions, more or less complicated, without any great success.

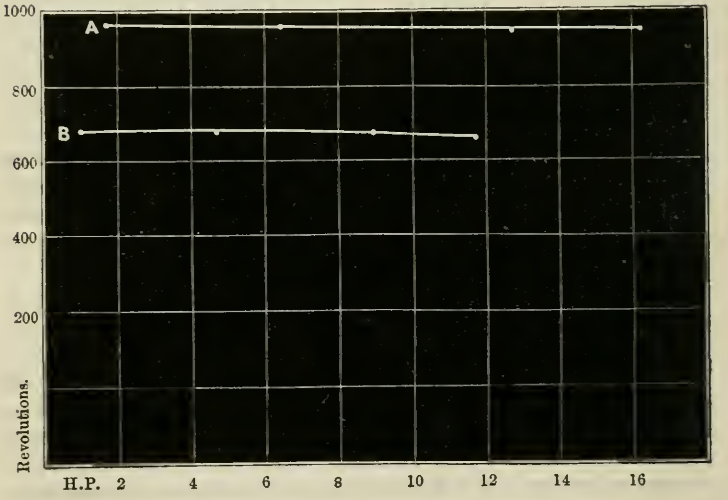
By permission of the Anglo-American Brush Electric Light Corporation experiments were carried out in the testing-room of their works, with a "Victoria" dynamo. The results ultimately obtained, which are given in the following tabulated account of the experiments, and in the curves plotted for them, show that this fifth analogy is as true as the preceding ones, a constancy of speed being obtained which was very remarkable —even when the load was increased, until much more than that which as a generator was usually considered the full working current was traversing the armature.

Two sets of readings were taken, working up to about the same current in each set, but with the potential-difference of the supply different in the two cases, as stated. The field was of the same strength throughout. The load consisted of another "Victoria" dynamo driven through a modified White's transmission-dynamometer, the work being varied as required by altering the external circuit of this dynamo.

Experiments with a D_2 "Victoria" Shunt Motor at Constant E.M.F.

Speed.	Current.	Difference of potential at terminals.	H. P.*	
975	36·3	140	1·8	Curve A. Maximum speed-variation 3 per cent.
965	66·5	,,	6·6	
948	97·1	,,	12·87	
945	130·8	,,	16·3	
680	29	100	1	Curve B. Maximum speed-variation 3 per cent.
677	61·4	,,	4·8	
675	102	,,	9·14	
660	125	,,	11·7	

Curves connecting *Speed* and *Work* of D_2 "Victoria" Shunt Motor. With supply at constant difference of potential.



At first it appeared that the counter electromotive force of the motor was dependent neither on speed nor strength of field, as the latter was constant and the former very nearly so, while the current rose with the work; but calculation showed that this was not the case, indeed it could not be so.

Let us call the counter electromotive force e, and the loss of potential caused by the resistance of the armature e_1, and the difference of potential at the terminals E. Then

$$e + e_1 = E.$$

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* Including an unascertained loss in transmission.

Calling the current C, and the resistance of the armature R, we know that

$$e_1 = \mathrm{CR};$$

The resistance of the armature of the motor in question was ·027 ohm, which we will call ·03 in order to make some allowance for the effect of heating.

In the first and last readings of the second set of tests (curve B) we have therefore the following conditions:—

Speed.	e_1.	e.
680	·87	99·13
660	3·75	96·25

Now

$$\frac{680 \times 96{\cdot}25}{660} = 99{\cdot}13.$$

From which it appears that the counter electromotive force was exactly proportional to the speed, as is to be expected where the field is constant and the magnetic distortion *nil.*

The other cases do not work out with the same accuracy. The results are, however, quite within the limits of error inseparable from the rather rough conditions of these workshop tests.

One other fact may be pointed out in connection with these tables of results and curves. In the case of dynamos working with a constant field, the output with the same current is almost exactly proportional to speed, as the E.M.F. is also simply proportional to speed. So with the motor, the speed is proportional to the E.M.F. of supply; and the work, with the same current in the two cases, is simply proportional to speed, therefore to E.M.F.

With regard to the theory alluded to above, that in a motor the fields should be much weaker and lighter than the armature, it may be pointed out that in this, as in the other points mentioned, there is a real analogy between motors and generators, inasmuch as, according to the views briefly expressed in this note, such a motor, although a bad one from most points of view, would have a certain advantage in that for its weight it would do a good deal of work. Similarly, dynamos may be, and have been built, which, although far from efficient and reliable, will give a large output for their weight. Their construction is, however, scarcely to be recommended on this ground, except, perhaps, under very exceptional circumstances; and they, as well as the motors constructed on the same lines, appear to be instances of a mistaken apprehension of elementary principles.

Having briefly traced the analogies between generators and motors thus far, the subject may be dismissed for the present with the remark that a further consideration of the matter serves only to reveal the fact that in almost every phase of their actions the two machines afford further opportunities of a direct comparison.

Turning now to the question of efficiency alluded to above, it is evident that there is some important cause of loss or waste of energy in electric motors which is absent in generators. This has always been a kind of *lacuna* in the explanations of the action of motors; and in order to localize the loss and to ascertain its cause, the several possible sources of waste were carefully considered. These are:—(*a*) Friction at the bearings, air-friction, and friction of the brushes against the commutator. (*b*) Loss of energy in heating the armature and field-conductors, and a certain loss due to self-induction. (*c*) Loss by the production of eddy-currents in the iron.

Now it is evident, especially with a generator or motor having the qualities sketched above, that at the same speed, and working with the same currents in its conductors, the losses under (*a*) and (*b*) must be identical, whether it be working as a generator or as a motor. And as with such conditions its efficiency as a motor is lower than as a generator, the cause of the loss must be sought under (*c*), *i. e.* the eddy-currents in a dynamo must be less than in a motor, all other conditions being the same. And such is the case, the explanation arrived at by the writer and Mr. Watson being a very simple one.

In a dynamo the rotation of the armature causes eddy-currents to be generated in the iron core, in the same direction as in the conductor proper with which the core is surrounded. Of course, as the armature is always more or less subdivided or laminated in a direction at right angles to the lines of force, any circulation of currents round the core is avoided; but local currents, which are aptly called eddies, are set up, and, taken as a whole, these eddy-currents on the outside of the core are in the same direction as the current flowing in the copper conductors.

In an electric motor, however, the eddy-currents and the currents in the copper conductor are in opposite directions; as, although the E.M.F. set up in the conductor is in the same direction in a motor as in a dynamo, the current in the former is forced through the armature in a direction contrary to the E.M.F., or opposite to its course in a generator. According to the laws of induction, therefore, it will be seen that while in a dynamo the two sets of currents, those in the iron and those in the conductor, tend to oppose and to reduce one another, in a motor they act in such a manner as to mutually assist each other. Thus, with the strength of field, the current in the conductor, and the speed the same in the two cases, it will be seen that in a motor the eddy-currents in the iron core of the armatures will be greater than in a generator, and therefore the heat-loss in the former will be more than in the latter. There is little doubt that this is the cause of the lower efficiency of motors than of generators; and it points to the advisability of giving even greater attention in the former to those principles which are well understood for the reduction or elimination of eddy-currents.

V. *Note on the Verification of Thermometers at the Freezing-Point of Mercury.* *By* G. W. Whipple, *B.Sc., F.R.A.S., Superintendent of the Kew Observatory*[*].

It is not many years since the operation of freezing mercury was considered a scientific feat, and a party of gentlemen were invited to the Kew Observatory to assist at the performance of the operation by the late Mr. R. Addams. That gentleman produced the solidified mercury by the action of ether upon carbonic acid gas in the solid form, and with his assistance considerable quantities of mercury were frozen, and a number of observations were made with carefully constructed thermometers, which gave the value for the melting-point of mercury which has since been accepted as the fixed point. Prof. Balfour Stewart communicated an account of these experiments to the Royal Society, in whose publications they will be found (Phil. Trans. 1863, pp. 425–435).

Since that date the determination of the low-temperature fixed point of thermometers has become a regular operation in the verification department of the Kew Observatory, and some eight or nine dozen instruments are compared in melting mercury annually, most of them being destined for use in Canada and other cold countries.

As the mode of making this comparison is not described in any readily accessible publication, we have frequently been requested to give an account of it, and have accordingly drafted this paper with a view of putting it on record.

The carbonic acid in its liquid form is purchased generally of Orchard, of High Street, Kensington, in the well-known

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[*] Communicated by the Physical Society: read November 14, 1885.

heavy iron bottles so familiar in lecture-rooms as recipients of compressed oxygen. A convenient quantity for the prosecution of an experiment is 200 gallons of gas, which weighs about 3 lb. The quantity of mercury operated upon is from 17 to 20 lb. By means of a common salt and ice freezing-mixture, the vessels, thermometers, mercury, and ether are all cooled down to about −10° C. beforehand.

The collecting-box being applied to the nozzle of the gas-receiver, the valve is unscrewed and gas allowed to escape through the apertures in the handles of the box for about a minute, during which time about 550 grains of solid carbonic gas are deposited in the form of snow.

The box being opened, the snow is removed with an ivory paper-knife and laid on the surface of the mercury previously placed in a wooden box well jacketed with felt. 2 oz. of ether is then poured over it, and the pasty mass forced under the surface of the mercury by means of a special wooden stirrer. The liberated gas and ether-vapour escaping through the mercury rapidly cool its temperature down, and a thin film of solid mercury forms on the top of the mass, which is immediately broken up by the stirrer. About six charges of acid snow and six fluid ounces of ether are usually necessary to convert the whole of the mercury into the finely granular mass of a pasty consistence.

It is considered inadvisable to freeze the mercury into a solid state, as then it becomes necessary to take it out of the box, and cut it up with shears into small lumps before the thermometers can be inserted into it, an operation which entails great loss of time and frozen mercury.

When the mass is in the semi-solidified condition the thermometers are plunged into it and allowed to fall to the requisite temperature—a well-verified standard being always placed in the bath at the same time and carefully watched during the progress of the comparison.

As soon as this standard is seen to begin to rise above the lowest point, the thermometers are taken out, and an additional quantity of snow and ether forced into the mercury until its temperature is again reduced, and the *feel* of the thermometer shows it has regained the proper consistency.

When the operation is properly and carefully performed, it is found that the work of comparison may be spread over from half an hour to forty minutes, a period which permits of more than 100 mercurial thermometers being read with the necessary exactitude. If the thermometers are ordinary alcohol or Rutherford minimums with large bulbs, only from thirty to forty can be compared at a time.

The operation might be continued for an indefinite period were a sufficient supply of liquefied carbonic acid available, but at Kew we usually find the 200-gallon bottle, which, as already referred to, contains about 3 lb. weight of gas at sufficient pressure to afford snow, adequate for our purpose.

The cost of the materials is as follows:—gas 19*s.* 2*d*; ether 1*s.* 2*d.*

We do not wish to claim any credit for the process above described, but only to bring before the Fellows of the Society a description of our *modus operandi* as a matter which may perhaps be of a little interest to some of them.

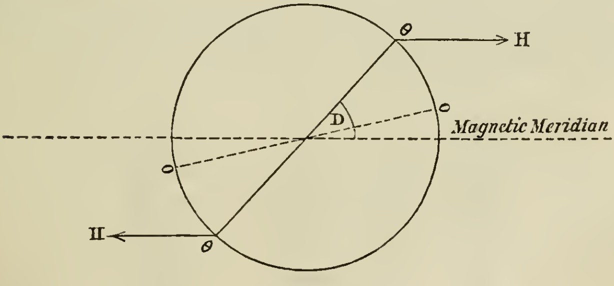
VI. *Note on the Calibration of Galvanometers by a Constant Current. By* T. MATHER, *Assistant in Physical Department, City and Guilds of London Central Institution**.

THE principle of the method to be described consists in measuring the turning moment exerted on the magnetic needle of the galvanometer by a constant current, when the needle and coils are in different relative positions.

Suppose the galvanometer is placed in any position in a uniform field, and that a suitable current be passed through it, which current we will take as our *unit* current. The needle will take up some position of equilibrium, say, at an angle D to the magnetic meridian, and at angle θ to the zero of the scale (fig. 1).

When in this position, the controlling couple is :: to sin D; and since this is balanced by the deflecting couple due to unit current, we see that this couple due to unit current, when the needle points to θ is also :: to sin D (fig. 1).

Fig. 1.



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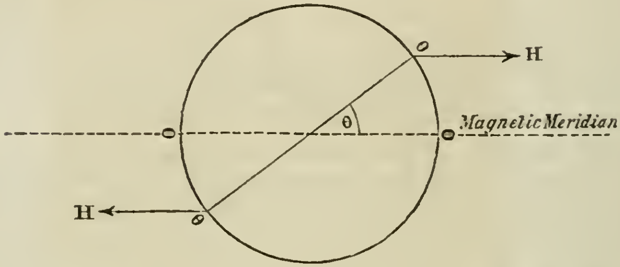
* Communicated to the Physical Society by Professor W. E. Ayrton, F.R.S.: read November 28, 1885.

But in the ordinary use of the instrument the line of zeros is in the magnetic meridian, and when the needle is deflected through angle θ the controlling couple is : : to $\sin\theta$. Hence the current required to produce this deflection θ when the galvanometer is used in the ordinary way, is $\frac{\sin\theta}{\sin D}$. For the currents must be proportional to the controlling couples, since the relative positions of the needle and coils are the same (fig. 2).

Fig. 2.



This being true for any deflection, the calibration-curve is got by plotting θ and $\frac{\sin\theta}{\sin D}$.

Of course the same strength of current must be used in determining the different values of D.

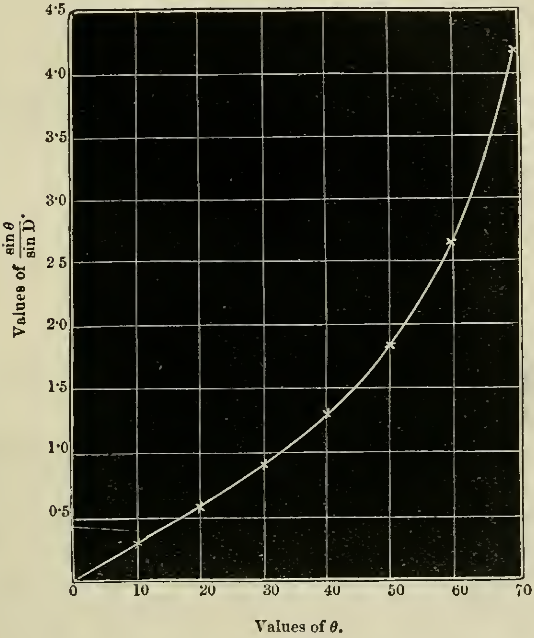
To measure the angle D corresponding to any θ, we have merely to break the circuit and observe the angle through which the needle moves before coming to rest in the magnetic meridian. θ is read off directly on the scale of the galvanometer when the current is passing.

Below are appended the results of a calibration obtained by this method, for which I have to thank Mr. Kilgour, a student of the Central Institution, who made the observations :—

θ.	D.	$\frac{\sin\theta}{\sin D}$.
10	34·8	·304
20	35·3	·592
30	32·2	·938
40	29·2	1·318
50	25·0	1·813
60	19·2	2·633
70	12·9	4·209

If θ and $\dfrac{\sin\theta}{\sin D}$ be plotted, we get the calibration-curve for that particular galvanometer (fig. 3).

Fig. 3.



In the foregoing Table the values of θ are integral numbers of degrees; but this is not at all necessary, for no fine adjustment, such as is required with sine-galvanometers, need be attempted. All that is needed is that the position of the needle, as indicated on the scale of the galvanometer, should be accurately noted before breaking the circuit to observe the corresponding D.

The method described above may be utilized as a ready means of testing whether a galvanometer, whose law is *supposed to be known*, does *actually* conform thereto. For if the law of the galvanometer is $C=f(\theta)$, then, on plotting $f(\theta)$ and $\dfrac{\sin\theta}{\sin D}$, a straight line should result.

In the case of tangent-galvanometers, where $f(\theta)=k\tan\theta$

(k being a constant), we have to plot $\frac{\sin\theta}{\sin \mathrm{D}}$ and $\tan\theta$ (*i. e.* $\frac{\sin\theta}{\cos\theta}$). Thus $\sin\theta$ is common to both variables; and hence, if we plot $\sin \mathrm{D}$ and $\cos\theta$, we should get a straight line if the galvanometer be really a tangent one.

About the law of sine-galvanometers there can be no question if the controlling field be uniform; and herein lies one great advantage of sine-galvanometers.

In "proportional" galvanometers, where the deflection is supposed to be proportional to the current, the curve obtained by plotting θ and $\frac{\sin\theta}{\sin \mathrm{D}}$ should be a straight line; or

$$\frac{\sin\theta}{\theta\sin \mathrm{D}} = \text{a constant},$$

if calculation be preferred.

It may be pointed out that, by choosing our unit current such that the maximum value of D is nearly 90°, the method admits of great sensibility.

The quantity of apparatus required to perform the calibration is reduced to a minimum, nothing but the galvanometer and a suitable current-generator being needed.

As described above, the angle D is measured by breaking the circuit and allowing the needle to come to rest in the magnetic meridian. This requires some time, if the needle is not dead-beat, and the observations could be greatly facilitated by the use of a fixed divided circle or pointer, by which D could be read off simultaneously with θ without breaking the circuit. If so arranged, the whole operation could be completed in a few minutes; but as the method is chiefly characterized by the fewness and simplicity of the apparatus required, it was thought undesirable to mar that simplicity by the addition of something not essential.

In conclusion, I desire to thank Professor Ayrton, F.R.S., for his kindness in suggesting the simple way of describing the method adopted in this note, and also for the statement of a problem which led to the results herein stated.

VII. *Some Thermodynamical Relations.*—PART II.

By WILLIAM RAMSAY, *Ph.D., and* SYDNEY YOUNG, *D.Sc.*[*]

IN a note at the conclusion of the first of this series of papers, it was stated that the absolute temperatures of certain nearly related bodies corresponding to equal vapour-pressures are constant at all pressures. Further investigation, however, has shown that although it is only in the case of nearly allied substances, such as chlorobenzene and bromobenzene, that the ratio of the absolute temperatures corresponding to the same vapour-pressure is a constant, whatever (within the limits afforded by experimental data) that pressure may be, yet a relation does exist between the ratios of the absolute temperatures of all bodies, whether solid or liquid and whether stable or dissociable, which may be expressed in the case of any two bodies by the equation

$$R' = R + c(t' - t),$$

where R is the ratio of the absolute temperatures of the two bodies corresponding to any vapour-pressure, the same for both ; R′ is the ratio at any other pressure, again the same for both ; c is a constant which may be 0 or a small + or − number ; and t' and t are the temperatures of one of the bodies corresponding to the two vapour-pressures

When $c=0$, $R'=R$, or the ratio of the absolute temperatures is a constant at all pressures ; and where c is greater or less than 0, its value may readily be determined either by calculation, or graphically by representing the (absolute) temperatures of one of the two bodies as ordinates, and the ratio of the absolute temperatures at pressures corresponding to the absolute temperatures of that body as abscissæ. It is found that in all cases the points representing the relation of the ratio of the absolute temperatures of the two bodies to the absolute temperatures of one of them fall in a straight line. This is illustrated in some of the examples which are brought forward to prove the truth of the law. It follows from this that, if we know accurately the vapour-pressures of one substance, we only require two, or, better, three, accurate determinations of the vapour-pressure of any other substance, at temperatures moderately far apart, in order to be able to calculate the vapour-pressure of that substance at any required temperature, or, rather, to calculate the temperature corresponding to any vapour-pressure within the limits of pressure comprised in the determinations of the standard substance.

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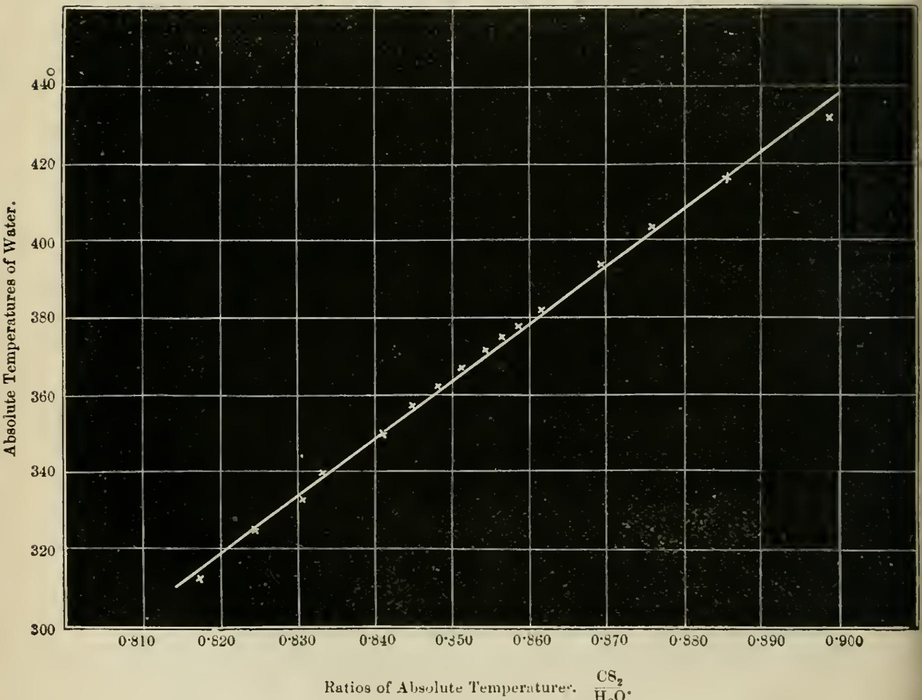
[*] Communicated by the Physical Society : read December 12, 1885.

In the examples which follow, the same substance has not always been taken as the standard; but generally, in the comparison of any two bodies, that one is taken as correct which is likely to have been the more accurately investigated. Twenty-two different bodies have been examined, and they are arranged in twenty-three couples. The absolute temperatures corresponding to definite vapour-pressures of a number of substances are given in the tables in a previous portion of this paper. For other substances, curves were drawn to represent the relation of temperature to pressure, and the temperatures corresponding to definite pressures read off.

1. *Ratios of the Absolute Temperatures of Water and Carbon Bisulphide at Definite Vapour-pressures.*—As an example of the method employed, the whole of the data are given in this case, and also a diagram showing how the value of *c* may be obtained graphically. The absolute temperatures of water corresponding to the definite vapour-pressures are taken to be correct, and are made the ordinates in fig. 1. The

Fig. 1.



abscissæ are the ratios of the absolute temperatures of carbon bisulphide to those of water at those vapour-pressures. As might be expected, some of the points representing the relation of the ratios of the absolute temperatures to the temperatures of water fall slightly to one or other side of the straight line drawn to pass through them. In order to find the error involved in these slight deviations from the straight line, points on the line itself corresponding to the same temperatures of water were read off, and these are given in the table as smoothed ratios. Lastly, the absolute temperatures of carbon bisulphide were calculated by multiplying those of water by the smoothed ratios; and the recalculated temperatures of carbon bisulphide are given together with the observed temperatures. It will be seen that the difference between the observed and recalculated temperatures is very small.

Pressures.	Absolute temperatures of water.	Ratios of absolute temperatures of CS_2 to those of H_2O.	Smoothed ratios.	Recalculated absolute temperatures of CS_2.	Observed absolute temperatures of CS_2.
millim.	°			°	°
50	311·3	·8161	·8160	254·0	254·05
100	324·7	·8245	·8242	267·6	267·7
150	333·1	·8301	·8296	276·3	276·5
200	339·6	·8339	·8338	283·2	283·2
300	348·9	·8403	·8400	293·1	293·2
400	356·0	·8448	·8449	300·8	300·75
500	361·7	·8485	·8483	306·8	306·9
600	366·5	·8517	·8519	312·2	312·15
700	370·7	·8545	·8545	316·8	316·75
800	374·45	·8567	·8571	320·9	320·8
900	377·8	·8589	·8590	324·5	324·5
1000	380·85	·8612	·8611	327·95	328·0
1500	393·2	·8695	·8692	341·8	341·9
2000	402·5	·8753	·8757	352·5	352·3
3000	416·5	·8852	·8850	368·6	368·7
5000	435·85	·8987	·8978	391·3	391·7

In the equation $R' = R + c(t' - t)$ the value of $c = ·0006568$. The greatest difference between the observed and recalculated temperatures is at the highest pressure (5000 millim.), and is only 0°·4.

2. *Water and Ethyl Alcohol.* $\frac{H_2O}{C_2H_6O}$. Temperatures of water taken as correct, and made the ordinates. $c = \cdot0000962$.

Pressures.	Ratios.	Smoothed ratios.	Absolute temperatures of Alcohol.	
			Recalculated.	Observed.
10	1·058	1·0527	270°·1	269°·25
50	1·0553	1·0553	295·0	295·0
100	1·0559	1·0567	307·3	307·5
150	1·0565	1·0574	315·0	315·3
200	1·0580	1·0580	321·0	321·0
300	1·0579	1·0589	329·5	329·8
400	1·0595	1·0596	336·0	336·0
500	1·0604	1·0602	341·2	341·1
600	1·0609	1·0606	345·55	345·45
700	1·0619	1·0610	349·4	349·25
800	1·0618	1·0614	352·8	352·65
900	1·0624	1·0617	355·8	355·6
1000	1·0626	1·0620	358·6	358·4
1500	1·0633	1·0632	369·8	369·8
2000	1·0648	1·0641	378·25	378·0
3000	1·0663	1·0655	390·9	390·6
5000	1·0675	1·0673	408·4	408·3
10000	1·0687	1·0701	435·15	435·7
15000	1·0701	1·0720	452·7	453·5
20000	1·0715	1·0735	466·2	467·1

The only noticeable differences between the observed and recalculated temperatures are at the three highest pressures and at 10 millim. With regard to the error at the low pressure, it may be mentioned that a number of careful determinations of the vapour-pressure of alcohol at low temperatures were made by Ramsay and Young by the still method (see note at end of paper), and that their results differed slightly from those of Regnault. At a pressure of 50 millim. the difference was only 0°·05, but at 10 millim. the absolute temperature found by them was 270°·25, which is practically the same as that recalculated by means of the equation

$$R' = R + c(t' - t).$$

3. *Ethyl Alcohol and Methyl Alcohol.* $\frac{C_2H_6O}{CH_4O}$. Temperatures of ethyl alcohol taken as correct. $c = \cdot0001603$.

Pressures.	Ratios.		Absolute temperatures of Methyl Alcohol.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.			°	°
10	*a* 1·0372	1·0475	256·5	259·0
10	*b* 1·0428	1·0473	257·9	
50	1·0424	1·0433	282·8	283·0
100	1·0424	1·0414	295·3	295·1
150	1·0406	1·0400	303·2	303·0
200	1·0392	1·0392	308·9	308·9
300	1·0384	1·0379	317·75	317·6
400	1·0371	1·0368	324·1	324·0
500	1·0358	1·0359	329·3	329·3
600	1·0346	1·0351	333·75	333·9
700	1·0335	1·0346	337·4	337·8
800	1·0339	1·0340	341·05	341·1
900	1·0334	1·0336	344·05	344·1
1000	......	1·0331	346·9	......
1500	1·0304	1·0314	358·5	358·9
2000	1·0297	1·0300	367·0	367·1
3000	1·0276	1·0280	380·0	380·1
5000	1·0256	1·0251	398·3	398 1

Two values are given for 10 millim.:—(*a*) the ratio calculated from Regnault's values, and (*b*) the ratio obtained by employing the recalculated temperature of ethyl alcohol. The only noticeable difference between the observed and recalculated temperatures is at a pressure of 10 millim.; and by taking the recalculated temperature of ethyl alcohol it is greatly reduced.

4. *Carbon Bisulphide and Ethyl Oxide.* $\frac{CS_2}{C_4H_{10}O}$. Temperatures of carbon bisulphide taken as correct. $c = \cdot0001621$.

Pressures.	Ratios.		Absolute temp. of Ethyl Oxide.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.			°	°
100	1·0284	1·0283	260·3	260·3
150	1·0298	1·0298	268·5	268·5
200	1·0306	1·0307	274·8	274·8
300	1·0324	1·0325	284·0	284·0
400	1·0335	1·0337	290·95	291·0
500	1·0344	1·0346	296·65	296·7
600	1·0353	1·0355	301·45	301·5
700	1·0361	1·0361	305·7	305·7
800	1 0372	1·0369	309·4	309·3
900	1·0371	1·0375	312·8	312·9
1000	1·0380	1·0380	316·0	316·0
1500	1·0408	1·0402	328·7	328·5
2000	1·0423	1·0420	338·1	338·0
3000	1·0451	1·0446	352·95	352·8
5000	1·0490	1·0484	373·6	373·4

In this series the greatest difference between the observed and recalculated temperatures is only 0°·2.

5. *Carbon Bisulphide and Ethyl Bromide.* $\frac{CS_2}{C_2H_5Br}$. Temperatures of carbon bisulphide taken as correct. $c = \cdot0001185$.

Pressures.	Ratios.		Absolute temperatures of Ethyl Bromide.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·0162	1·0172	249°·75	250°·0
100	1·0186	1·0188	262·8	262·8
150	1·0203	1·0199	271·1	271·0
200	1·0224	1·0206	277·5	277·0
300	1·0223	1·0218	286·9	286·8
400	1·0233	1·0228	294·05	293·9
500	1·0237	1·0234	299·9	299·8
600	1·0244	1·0241	304·8	304·7
700	1·0251	1·0247	309·1	309·0
800	1·0249	1·0251	312·9	313·0
900	1·0259	1·0256	316·4	316·3
1000	1·0263	1·0260	319·7	319·6
1500	1·0274	1·0276	332·7	332·8
2000	1·0280	1·0289	342·4	342·7
3000	1·0299	1·0308	357·7	358·0
5000	1·0327	1·0335	379·0	379·3

6. *Carbon Bisulphide and Ethyl Chloride.* $\frac{CS_2}{C_2H_5Cl}$. Temperatures of carbon bisulphide taken as correct. $c = \cdot0001050$.

Pressures.	Ratios.		Absolute temperatures of Ethyl Chloride.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
150	1·1118	1·1135	248°·3	248°·7
200	1·1136	1·1142	254·2	254·3
300	1·1152	1·1152	262·9	262·9
400	1·1164	1·1160	269·5	269·4
500	1·1164	1·1166	274·9	274·9
600	1·1174	1·1172	279·4	279·3
700	1·1181	1·1177	283·4	283·3
800	1·1178	1·1181	286·9	287·0
900	1·1186	1·1185	290·1	290·1
1000	1·1194	1·1189	293·15	293·0
1500	1·1210	1·1203	305·2	305·0
2000	1·1209	1·1215	314·1	314·3
3000	1·1224	1·1232	328·25	328·5
5000	1·1253	1·1256	348·0	348·1

7. *Chlorobenzene and Water.* $\frac{C_6H_5Cl}{H_2O}$. Temp. of water taken as correct. $c = \cdot000598$.

Pressures.	Ratios.		Absolute temperatures of Chlorobenzene.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
100	1·0579	1·0573	343°·3	343°·5
150	1·0625	1·0623	353·85	353·9
200	1·0654	1·0660	362·0	361·8
300	1·0711	1·0716	373·9	373·7
400	1·0753	1·0760	383·05	382·8
500	1·0788	1·0791	390·3	390·2
600	1·0819	1·0820	396·55	396·5
700	1·0845	1·0845	402·0	402·0

8. *Bromobenzene and Water.* $\frac{C_6H_5Br}{H_2O}$. Temp. of water taken as correct. $c = \cdot000609$.

Pressures.	Ratios.		Absolute temperatures of Bromobenzene.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·1156	1·1124	346°·3	347°·3
100	1·1220	1·1206	363·9	364·3
150	1·1255	1·1258	375·0	374·9
200	1·1284	1·1297	383·65	383·2
300	1·1344	1·1353	396·1	395·8
400	1·1388	1·1396	405·7	405·4
500	1·1427	1·1431	413·45	413·3
600	1·1460	1·1460	420·0	420·0
700	1·1489	1·1486	425·8	425·9
800	1·1516	1·1509	430·95	431·2

9. *Aniline and Water.* $\frac{C_6H_5NH_2}{H_2O}$. Temp. of water taken as correct. $c = \cdot000345$.

Pressures.	Ratios.		Absolute temp. of Aniline.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·2046	1·2048	375°·05	375°·0
100	1·2100	1·2094	392·7	392·9
150	1·2129	1·2124	403·85	404·0
200	1·2144	1·2145	412·45	412·4
300	1·2174	1·2176	424·8	424·75
400	1·2197	1·2201	434·4	434·2
500	1·2217	1·2221	442·1	441·9
600	1·2237	1·2239	448·55	448·5
700	1·2254	1·2253	454·2	454·25
800	1·2269	1·2266	459·3	459·4

10. *Methyl Salicylate and Water.* $\frac{C_6H_4(OH)CO\,O(CH_3)}{H_2O}$. Temperatures of water taken as correct. $c = \cdot000459$.

Pressures.	Ratios.		Absolute temperatures of Methyl Salicylate.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·3026	1·3008	404°·9	405°·5
100	1·3067	1·3069	424·35	424·3
150	1·3101	1·3107	436·6	436·4
200	1·3118	1·3136	446·1	445·5
300	1·3170	1·3179	459·8	459·5
400	1·3204	1·3212	470·35	470·05
500	1·3235	1·3239	478·9	478·7
600	1·3261	1·3260	486·0	486·0
700	1·3283	1·3280	492·3	492·4
800	1·3302	1·3298	497·95	498·1

11. *Bromonaphthalene and Water.* $\frac{C_{10}H_7Br}{H_2O}$. Temperatures of water taken as correct. $c = \cdot000612$.

Pressures.	Ratios.		Absolute temperatures of Bromonaphthalene.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
150	1·4587	1·4592	486°·05	485°·9
200	1·4623	1·4631	496·9	496·6
300	1·4689	1·4690	512·5	512·5
400	1·4733	1·4732	524·45	524·5
500	1·4766	1·4769	534·2	534·1
600	1·4797	1·4798	542·3	542·3
700	1·4823	1·4821	549·4	549·5
800	1·4846	1·4847	555·95	555·9

12. *Sulphur and Carbon Bisulphide.* $\frac{S}{CS_2}$. Temperatures of carbon bisulphide taken as correct. $c = -\cdot0006845$.

Pressures.	Ratios.		Absolute temperatures of Sulphur.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
300	2·2783	2·2779	667°·9	668°·0
400	2·2733	2·2727	683·5	683·7
500	2·2681	2·2685	696·2	696·1
600	2·2650	2·2649	707·0	707·0
700	2·2607	2·2617	716·4	716·1
800	2·2588	2·2588	724·6	724·6
900	2·2558	2·2563	732·2	732·0
1000	2·2530	2·2540	739·3	739·0
1500	....	2·2444	767·4	......
2000	2·2373	2·2372	788·15	788·2
3000	2·2262	2·2262	820·8	820·8

The close agreement between the observed and recalculated temperatures of such a high-boiling substance as sulphur is very striking.

13. *Carbon Bisulphide and Ethylene.* $\frac{CS_2}{C_2H_4}$. Temperatures of carbon bisulphide taken as correct. $c = \cdot000274$.

Pressures.	Ratios.		Absolute temperatures of Ethylene.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·8212	1·8208	139°·5	139°·5
100	1·8242	1·8244	146·8	146·75
150	1·8263	1·8268	151·35	151·4
200	1·8283	1·8287	154·9	154·9
300	1·8325	1·8315	160·1	160·0
400	1·8339	1·8336	164·0	164·0

Here again the agreement is very remarkable, considering the difficulty of measuring very low temperatures accurately.

14. *Water and Oxygen.* $\frac{H_2O}{O}$. Temperatures of water taken as correct. $c = -\cdot0003932$.

Vapour-pressures of oxygen have been determined by

Olszewski and by Wroblewski, but their results do not agree well together. Olszewski measured his temperatures by means of a hydrogen-thermometer; Wroblewski by a thermopile. It was found that the curve showing the relation of temperature to pressure was very fairly regular when constructed from Olszewski's numbers, and the temperatures corresponding to definite pressures were therefore read from this curve. The temperature corresponding to a pressure of 9 millim. is a single observation by Olszewski. The temperatures corresponding to 50, 100, and 150 millim. are taken from Wroblewski's results.

Pressures.	Ratios.		Absolute temperatures of Oxygen.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.			°	°
9	4·5967	4·454	63·5	61·5
50	4·0534	4·349	71·6	76·8
100	3·9358	4·2845	75·8	82·5
150	4·0132	4·253	78·6	83·0
300	....	4·191	83·2	......
400	....	4·182	85·1	......
500	....	4·1405	87·4	......
600	....	4·120	89·0	......
700	....	4·1025	90·4	......
800	4·0701	4·090	91·6	92·0
1000	4·0732	4·064	93·7	93·5
1500	4·0536	4·0175	97·9	97·0
2000	4·0520	3·980	101·1	100·0
3000	3·9478	3·924	106·1	105·5
5000	3·8267	3·849	113·2	113·9
10000	3·7044	3·733	124·7	125·7
15000	3·6489	3·656	132·7	133·0
20000	3·6242	3·5975	139·1	138·1

It is hardly to be expected that the measurement of such extremely low temperatures could be very exact, and the difference of 2°·0 at an absolute temperature of about 60°, is not more than might be expected. It will be seen that the three temperatures given by Wroblewski differ considerably from those calculated from Olszewski's results.

The vapour-pressures of oxygen are given up to the critical point, at which the pressure is 38,600 millim., but those of water have only been determined up to 20,000 millim. The absolute temperatures of oxygen were therefore compared with those of alcohol, in order to find whether the value of *c* remains constant up to the critical point.

15. *Alcohol and Oxygen.* $\frac{C_2H_6O}{O}$. Temperatures of alcohol taken as correct. $c = -{\cdot}00040075$.

Pressures.	Ratios.		Absolute temperatures of Oxygen.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
300	...	3·940	83°·7	......
400	...	3·913	85·9	......
500	...	3·894	87·6	......
600	...	3·879	89·1	......
700	...	3·861	90·4	
800	3·8331	3·848	91·6	92°·0
1000	3·8332	3·824	93·7	93·5
1500	3·8123	3·780	97·8	97·0
2000	3·7800	3·7485	100·8	100·0
3000	3·7024	3·694	105·7	105·5
5000	3·5848	3·621	112·8	113·9
10000	3·4662	3·514	124·0	125·7
15000	3·4098	3·441	131·8	133·0
20000	3·3824	3·388	137·9	138·1
30000	3·3189	3·300	147·9	147·1
40000	3·2698	3·240	155·6	*154·2

The absolute temperatures of oxygen recalculated from the smoothed ratios with alcohol agree well with those calculated from the ratios with water. It was thought worth while to compare these temperatures with those of sulphur, oxygen being the most and sulphur the least volatile of all the substances examined.

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* The last pressure, 40,000 millim., is a little above the critical point, but sufficiently near to allow of the continuation of the vapour-pressure curve without sensible error. This was done instead of calculating the absolute temperature of alcohol corresponding to 38600 millim., the critical pressure of oxygen. It is to be remarked that the last two or three points representing the experimentally determined vapour-pressures of oxygen at the highest temperatures lie a little above the curve which was drawn. If more weight had been given to these points, the agreement between the observed and recalculated numbers would have been much closer. Thus Olszewski gives 154°·2 as the absolute temperature at the critical pressure 38600 millim., whereas from the curve this would be the temperature at 40000 millim. If the curve were raised so as to pass through the point representing the observed critical pressure and temperature, the exterpolated temperature would become 155°·3, or only 0°·3 lower than that recalculated from the smoothed ratio.

In any case, the agreement seems to be close enough to show that the equation $R' = R + c\,(t' - t)$ holds good up to the critical point.

16. *Sulphur and Oxygen.* $\frac{S}{O}$. Temperatures of Sulphur taken as correct. $c = -\cdot 0001652$.

Pressures.	Ratios.			Absolute Temperatures of Oxygen.				
	From observed temperatures.	From mean of recalculated temperatures.	Smoothed.	*a.* From $\frac{H_2O}{O}$.	*b.* From $\frac{C_2H_6O}{O}$.	*c.* Mean of *a* & *b*.	From $\frac{S}{O}$.	Observed.
millim. 300	...	8·005	8·005	83°·2	83°·7	83°·45	83°·45	...
400	...	7·9965	7·980	85·1	85·9	85·5	85·7	...
500	...	7·955	7·957	87·4	87·6	87·5	87·5	...
600	...	7·9395	7·9395	89·0	89·1	89·05	89·05	...
700	...	7·921	7·9245	90·4	90·4	90·4	90·4	...
800	7·876	7·910	7·910	91·6	91·6	91·6	91·6	92°·0
1000	7·904	7·887	7·8875	93·7	93·7	93·7	93·7	93·5
1500	7·9155	7·847	7·840	97·9	97·8	97·85	97·9	97·0
2000	7·882	7·808	7·8055	101·1	100·8	100·95	101·0	100·0
3000	7·780	7·750	7·7525	106·1	105·7	105·9	105·9	105·5

It will be seen that the temperatures of oxygen recalculated from those of sulphur, when $c = -\cdot0001652$, agree remarkably well with the mean of the temperatures recalculated from the ratios with water and alcohol.

17. *Acetic Acid and Water.* $\frac{C_2H_4O_2}{H_2O}$. Temperatures of water taken as correct. For liquid acetic acid $c = \cdot0003186$; for solid acetic acid $c = -\cdot000852$.

In the 'Philosophical Transactions,' Part 2, 1884, it was shown experimentally by Ramsay and Young that the vapour-pressures of solid acetic acid were lower than those of the liquid acid at the same temperature, and curves were constructed showing the relation of temperature to pressure for both the solid and the liquid acid. The absolute temperatures corresponding to definite pressures were read from these curves. For pressures below 5 millim. the vapour-pressures of water adopted by Regnault were not employed, the values calculated from his empirical formula representing the relation of temperature to pressure of water between 0° and 100° being probably more correct.

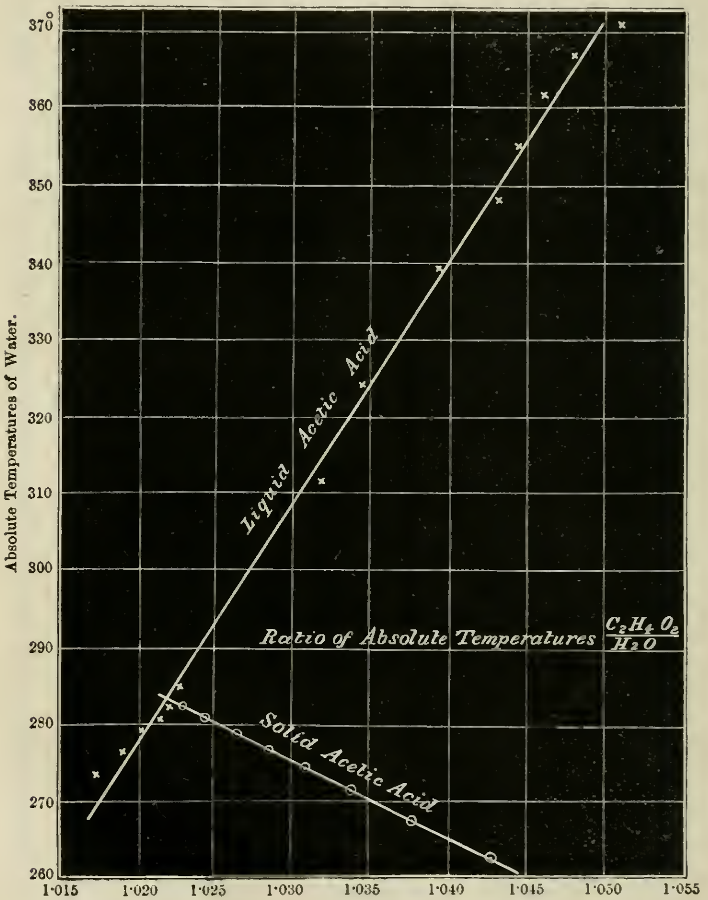
a. Liquid Acetic Acid and Water.

Pressures.	Ratios.		Absolute temperatures of Acetic Acid.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
5	1·0175	1·0188	279°·35	279°·01
6	1·0193	1·0195	282·2	282·14
7	1·0202	1·0202	284·6	284·64
8	1·0212	1·0209	286·8	286·91
9	1·0219	1·0215	288·8	288·88
10	1·0222	1·0220	290·55	290·6
50	1·0311	1·0305	320·8	321·0
100	1·0345	1·0347	336·0	335·9
150	1·0369	1·0375	345·6	345·4
200	1·0392	1·0395	353·0	352·9
300	1·0426	1·0424	363·7	363·75
400	1·0447	1·0447	371·9	371·9
500	1·0455	1·0465	378·5	378·15
600	1·0478	1·0480	384·1	384·0
700	1·0506	1·0495	389·05	389·45
b. Solid Acetic Acid and Water.				
2	1·0423	1·0422	272·9	272·89
3	1·0372	1·0374	277·15	277·10
4	1·0335	1·0335	280·15	280·14
5	1·0306	1·0307	282·6	282·60
6	1·0284	1·0284	284·7	284·67
7	1·0264	1·0261	286·3	286·37
8	1·0244	1·0244	287·8	287·8
9	1·0226	1·0226	289·1	289·08

The differences between the recalculated and observed absolute temperatures of solid acetic acid are extremely minute. If the vapour-pressures of water given by Regnault were employed, the value of *c* would be slightly altered, and in that case the agreement would not be quite so close, the greatest difference amounting to 0°·15.

The results for both the solid and the liquid acid are shown in the diagram (fig. 2).

Fig. 2.



Dissociating Substances.

Five of these bodies have been examined, three liquid and two solid. In all of them the value of c is constant, while in the case of nitrogen peroxide, when compared with water it is $=0$, or at any rate it is a very small number.

18. *Nitrogen Peroxide and Water.* $\frac{N_2O_4}{H_2O}$. Water taken as correct. $c=0$.

Pressures.	Ratios.		Absolute temperatures of N_2O_4.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
100	0·7884	0·790	256°·5	256°·0
150	0·7899	"	263·15	263·1
200	0·7895	"	268·3	268·1
300	0·7908	"	275·6	275·9
400	0·7904	"	281·25	281·4
500	0·7904	"	285·75	285·9

Considering the nature of the substance, these differences may probably be considered within the limits of experimental error.

19. *Chloral Ethyl-alcoholate and Water.* $\frac{CCl_3CH\left\{\begin{matrix}OH\\OC_2H_5\end{matrix}\right.}{H_2O}$.

Temperatures of water taken as correct. $c=-{\cdot}0005119$.

Pressures.	Ratios.		Absolute temperatures of Chloral Ethyl-alcoholate.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·0729	1·0728	334°·0	334°·0
100	1·0659	1·0659	346·1	346·1
150	1·0619	1·0615	353·6	353·7
200	1·0545	1·0582	359·4	358·1
300	1·0530	1·0535	367·6	367·4
400	1·0500	1·0499	373·8	373·8
500	1·0470	1·0470	378·7	378·7

20. *Chloral Methyl-alcoholate and Water.* $\frac{CCl_3CH\left\{\begin{matrix}OH\\ OCH_3.\end{matrix}\right.}{H_2O}$

Temperatures of water taken as correct. $c = -{\cdot}0005392$.

Pressures.	Ratios.		Absolute temperatures of Chloral Methyl-alcoholate.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·0639	1·0641	331°·25	331°·2
100	1·0573	1·0570	343·2	343·3
150	1·0532	1·0546	351·3	350·8
200	1·0486	1·0489	356·2	356·1
300	1·0439	1·0439	364·2	364·2
400	1·0402	1·0400	370·2	370·3

The last two substances examined are solid throughout, and, at the higher temperatures at any rate, dissociate completely on being converted into vapour.

21. *Ammonium Chloride and Water.* $\frac{NH_4Cl}{H_2O}$. Temperatures of water taken as correct. $c = -{\cdot}0006667$.

Pressures.	Ratios.		Absolute temperatures of NH_4Cl.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.				
50	1·6855	1·6809	523°·3	524°·7
100	1·6717	1·6720	542·9	542·8
150	1·6650	1·6664	555·1	554·6
200	1·6587	1·6620	564·4	563·3
300	1·6546	1·6560	577·8	577·3
400	1·6514	1·6511	587·8	587·9
500	1·6478	1·6475	595·9	596·0
600	1·6453	1·6441	602·6	603·0

The determinations of the vapour-pressures and temperatures of volatilization of ammonium chloride were attended with great difficulties, and the agreement between the calculated and observed temperatures is as near as could be expected. The volatilizing-point at the atmospheric pressure, calculated from the equation $R' = R + c(t' - t)$, would be 338°·6 C., which agrees well enough with the temperature found by experiment.

22. *Ammonium Carbamate and Water.* $\frac{CO\left\{\begin{matrix}NH_2\\ ONH_4\end{matrix}\right.}{H_2O}$. Temperatures of water taken as correct. $c = -\cdot000696$.

Pressures.	Ratios.		Absolute temperatures of Ammonium Carbamate.	
	From observed temperatures.	Smoothed.	Recalculated.	Observed.
millim.			°	°
10	0·9529	0·9510	270·4	270·9
50	0·9313	0·9321	290·2	289·9
100	0 9221	0·9230	299·7	299·4
150	0·9159	0·9170	305·45	305·1
200	0·9122	0·9126	309 9	309·8
300	0·9060	0·9061	316·15	316·1
400	0·9017	0·9011	320·8	321·0

It is thought that these twenty-two examples, including twenty-one different bodies—solid, liquid, stable, and dissociable—are sufficient to prove that the equation $R' = R + c(t' - t)$ is applicable to all classes of bodies, and that by the determination of the constant c, which involves only a small amount of experimental work, it becomes possible to calculate the vapour-pressures of any substance, assuming those of water or some other body to be accurately known, within the limits of pressure included in the experimental determinations of the standard substance.

It should be pointed out that those dissociable substances which have been investigated, are either, as in the case of ammonium carbamate and chloride and the compounds of chloral, wholly or almost wholly dissociated on their passage into the gaseous state at the temperatures of observation, or the amount of dissociation is very small, as with nitric peroxide. Until reliable data are obtained, it is perhaps premature to make any complete statement in reference to the behaviour of dissociable bodies.

On the Vapour-Pressures of Mercury.

It will have been observed in the tables in Part I. of this series of papers that mercury appears to differ from all the other substances examined, inasmuch as the values of $\frac{dp}{dt} \cdot t$, when compared with either water or carbon bisulphide, are not even approximately constant at different pressures, but rise steadily and somewhat rapidly. Again, the absolute temperatures of mercury cannot be calculated from those of water by means of the equation $R'=R+c(t'-t)$, for if Regnault's data are correct, c is not a constant. There appeared, however, to be good reason to believe that Regnault's values were not reliable, and he himself admits that great difficulties were experienced in the investigation of this substance.

It was, therefore, considered desirable to attempt a redetermination of the vapour-pressures of mercury with the greatest possible accuracy at a few temperatures. This has been accomplished, and the results are fully described in Trans. Chem. Soc. Jan. 1886. It will be sufficient here to mention that new determinations were made at the boiling-points of methyl salicylate and of sulphur under atmospheric pressure (220° and 450° approximately). Two other determinations at the boiling-point of bromonaphthalene under atmospheric and reduced pressure (280° and 270°), described in the Trans. Chem. Soc. xlvii. p. 640, and four determinations of the boiling-point of mercury under atmospheric pressure by Regnault (*Mémoires de l'Académie,* xxi. p. 230), were also made use of in the calculations.

On comparing the absolute temperatures of water with those of mercury at these five pressures, it was found that the value of c in the equation $R'=R+c(t'-t)$ was constant, and that mercury did not form an exception to the law, which has been proved to hold good for all the other substances examined.

By making the absolute temperatures of mercury ordinates, and the ratios of the absolute temperatures of mercury to those of water at the same pressures abscissæ, and drawing a straight line through the five experimentally-determined points, the value of c was ascertained, and vapour-pressures of mercury were calculated for each 5°, from 270° to 520° C. It should be mentioned that slightly different results were obtained when the absolute temperatures of water were made the ordinates; but within the limits of temperature just mentioned, the difference was unimportant.

With the absolute temperatures of mercury as ordinates, the value of c is ·0004788.

The values of $\frac{dp}{dt}\cdot t$ for mercury were then determined; for the most part by the method of tangents, but between 150 and 700 mm. from the vapour-pressures calculated for each degree of temperature, and were compared with those of water and of carbon bisulphide. The results are given in the following table :—

Pressure.	$\frac{dp}{dt}$.	*t*.	$\frac{dp}{dt} \cdot t$.	Water made =1·000	Carbon bisulphide made = 1·000
millim.		°			
10	0·350	457·3	160	0·866	
50	1·405	508·5	714	0·850	1·057
100	2·506	534·2	1339	0·833	1·046
150	3·54	550·97	1950	0·843	1·061
200	4·47	563·44	2519	0·835	1·061
300	6·25	582·21	3639	0·834	1·061
400	7·85	596·44	4682	0·827	1·055
500	9·40	608·03	5715	0·827	1·055
600	10·91	617·87	6741	0·829	1·060
700	12·34	626·48	7731	0·824	1·057
800	13·75	634·0	8717	0·829	1·059
900	15·01	641·0	9621	0·814	1·037
1000	16·37	647·2	10595	0·818	1·049
1500	22·38	673·1	15064	0·811	1·038
2000	28·33	693·0	19633	0·816	1·064
3000	38·61	723·1	27919	0·804	1·071
5000	56·90	765·6	43562	0·800	1·059

It will be seen that the agreement with carbon bisulphide is extremely close throughout, and that with water the variation is not greater than with some of the other substances examined. The variations from constancy in the reduced values of $\frac{dp}{dt} \cdot t$ will be considered in Part III.

Note.—Reference has been made to the vapour-pressures of alcohol at high and low temperatures determined by ourselves. The data are contained in a paper presented to the Royal Society in May 1885. The vapour-pressures of dissociable substances are given in a paper read before the Royal Society in November 1885. Neither of these papers is as yet published.

PM (Jan. 1886)

VIII. *Some Notes by* Professors AYRTON, *F.R.S., and* JOHN PERRY, *F.R.S., on* Dr. Lodge's *Paper on The Seat of the Electromotive Forces in a Voltaic Cell*[*].

THE value of the historical part of Dr. Lodge's paper can hardly be overrated. A fair share of credit has been given in it to all experimenters on Contact Forces, and his description of the different kinds of apparatus used by the various investigators is very clear and very helpful, but we certainly object to the unproved assumption running all through

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[*] Communicated by the Authors.

his paper, that there is a *primâ facie* absurdity in acknowledging a considerable difference of potentials between two metals such as zinc and copper in contact with one another.

He says that all the apparent differences of potential which have been measured in air are due to an air-effect; and when these same differences of potentials are obtained by measurements in gases quite different from air, he still says that they are due to an air-effect, and even that when they are obtained from measurements made in a fairly good vacuum, they are still due to air-effects. In fact, he considers that he has such good reason for concluding that the existence of a large contact-potential difference between metals is absurd, and he boldly puts forward the view that if measurements were made in the most perfect vacuum hitherto obtained in the laboratory, and if the results were still the same (as they probably would be) they would still be due to air-effects. Now, when it is borne in mind that all the experimental evidence is in favour of the existence of a real large contact-potential difference between metals, it is quite evident that our most important duty is to examine the basis of the strong reason which has caused Dr. Lodge to discard direct experimental results, for it is this strong reason which has caused him to enter into elaborate explanations as to the attraction between gases and metals.

We will first dispose of that part of Dr. Lodge's paper which is not debatable, viz. the seat of the E.M.F. in a voltaic circuit. So far from differing from Dr. Lodge on this point, we believe that we are in agreement; and we hope to prove that this seat of the E.M.F. in a voltaic circuit has really nothing whatever to do with the potential-difference between zinc and copper in contact. In fact, Dr. Lodge's paper has not got quite its proper title. The subject to which the greater part of his paper is devoted is a debatable one, but it is quite a different subject from that of the seat of the E.M.F. in a voltaic cell. In considering this latter subject we shall, for brevity's sake, regard the small Peltier effect as non-existent. Formerly, any cause of flow of electricity was called an E.M.F., and hence in stating Ohm's law, E.M.F. and potential-difference were used indifferently. But when we adopt, as everybody does nowadays, the exact definition of Clerk Maxwell, we must be more careful; and when we adopt the much more guarded definition of E.M.F. of Dr. Lodge, we must be particularly careful. This definition of Dr. Lodge is given in two quotations from Clerk Maxwell; and the definition is not merely the definition of E.M.F., but is the definition of the seat of the E.M.F. *The seat of the E.M.F. in any circuit* *is the place at which the circuit receives or gives up energy as distinct from heat due to resistance, and the amount of the E.M.F. is measured as the amount of energy which enters the circuit per unit of electricity passing that place.* Now it is not possible with such a definition of E.M.F. as this, to give any answer to Dr. Lodge's question different from the one he has himself given. The seat of the E.M.F. is practically defined to be the place where the chemical action goes on. It follows, therefore, that the place where the chemical action goes on is the seat of the E.M.F. The answer is given in the definition, and the definition is merely a partial statement of Sir William Thomson's result—that the E.M.F. of a voltaic circuit can be calculated from the chemical action going on.

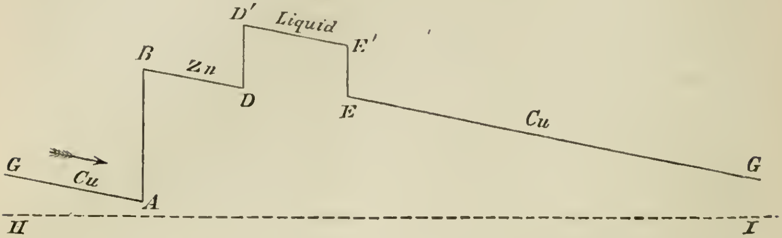
The important subject, however, taken up in Dr. Lodge's paper is, as we have already stated, quite a different one. He finds strong reasons for believing that there cannot be a considerable difference of potential between zinc and copper in contact. In fact, a large difference of potential is to him logically absurd, and he devotes the paper to speculations as to how experiments could have misled Sir William Thomson and others into believing such an absurdity. The absurdity is so obvious to Dr. Lodge, that it might have struck him, perhaps, that Sir William Thomson might also have seen it. However, as Dr. Lodge has the opinions of Clerk Maxwell and many others on his side, the question is a fair subject for debate, and we shall endeavour to show that our notions on the subject do not lead to any absurdity. With his definition of E.M.F. we have never stated that there is such an E.M.F. due to contact between zinc and copper. We deny that there is such contact E.M.F., but we do say there is contact-difference of potential. We do not say that what has been measured may not be to some, even to a large extent, due to air-effect: indeed, in our third paper on the Contact Theory of Voltaic Action, in Part I. of the Phil. Trans. for 1880, we drew especial attention to the possibility of air-effects, and we showed, exactly as Dr. Lodge now shows, that our measurements gave no indication as to whether there is or is not an air-effect. But we contend that no such air-effect has ever been observed, and until it is observed we cannot admit that there is strong reason for believing in its existence, especially since we shall prove that all the phenomena of contact-action can be rigorously explained without the necessity of resorting to any air-action.

Dr. Lodge says that if electricity rises in potential from copper to zinc, there must be a supply of energy from some outside source at the place of contact. We ask him why he should make such an assumption. Putting on one side the question as to what is exactly meant by electricity rising in potential at a point, or by the potential inside a wire through which a current is flowing, we are willing for the sake of his argument to assume that in taking a unit of electricity from a point in a section of the wire to the outside and from that through the dielectric, and from that into the wire to a point in another section, the work that must be done is the same for any points in the sections as Dr. Lodge assumes, and to take that work as the measure of the difference of potential between these two sections; and still we ask him why we must assume that, when electricity rises in potential suddenly at a place in a circuit, energy must come in from the outside to enable the electricity to rise in potential? Suppose we grant that electricity gains in potential-energy in flowing from copper to zinc, do we know so much of an electric current as to assert that when the electricity gains potential-energy it does not lose an equivalent quantity of some other kind of energy? Why may we not assume, for example, that electricity loses tension-energy in passing from copper to zinc, so that if it gains potential-energy it loses tension-energy. From that point of view, part of the function of the liquid in the cell would be taking electricity from the zinc to the copper inside the cell, giving it tension-energy, and this tension-energy is converted into potential-energy when the electricity passes in the outer part of the circuit from copper to zinc.

But, indeed, there is no need to assume the existence of a tension-energy. Why should we assume that work must be done by outside agents at a place in raising electricity from potential A to potential B? By definition work will be done if we take electricity through the dielectric from A to B, but it does not follow that an outside source must do work in carrying electricity from A to B through the wire itself. We know so little of what is really meant by the electric current, and the mechanical analogies which have been put forward from time to time are so imperfect, not even excluding the beautiful form that Prof. Poynting has given to Clerk Maxwell's analogy, that we like to fall back upon the oldest and simplest one, which is that, when electricity is flowing in a wire, at one end it is being continually thrust in, and at the other end it is in consequence continually being thrust out, just for the same reason that electricity tries to come to the outside of bodies—repulsion of electricity by electricity. Hence in the case of a copper wire one end of which is joined to the copper plate of a battery and the other to the zinc plate, electricity is being pushed into the copper wire at the end where it is connected with the copper plate, and at the other end is pushed out of the wire into the zinc plate. If at the zinc end, electricity can only get away by rising in potential, then it rises in potential, but the energy, which there becomes potential-energy, comes from the battery, and it is not necessary to get a supply of energy from any outside source.

Of course this is only an analogy, but when we speak of electricity flowing in a wire, we are using an analogy which is derived from electrostatic and hydraulic phenomena to explain a phenomenon of an electrokinetic kind. The idea of a tension-energy in electricity as distinct from a potential-energy may be objected to as being new and unnecessary, but in spite of our very exact knowledge of mechanics we have the same sort of difficulty in many mechanical arrangements unless we assume the existence of a tension-energy. For example, suppose you have a winding-engine and a long endless inextensible rope passing over pulleys, horizontal in places, vertical in places, and coming back to the engine again, and at one place there is a weight being lifted. Now work is being done on that weight in lifting it. But energy does not come from the outside into the circuit there; it comes from the winding-engine; it comes somehow through the rope. Energy disappears at the winding-engine and appears as work done in the weight being lifted. In what form is it before it is converted into potential-energy? The energy is conveyed. In what form is it when it is in the rope? We really do not know, or, rather, we have not given a name to it. But if we must give a name to it, it is tension-energy. We know that there is a difference in the tension of the rope above and below the weight which is being lifted. Difficulties of this kind are really due to the fact that the notion of conveyance of energy from one point to another has not yet been co-ordinated with the ordinary exact definition of energy. The energy which we usually speak of as being possessed by a portion of matter, or as existing at a particular place, is really possessed by a much larger system.

The analogy, however, which Dr. Lodge has used for showing, as he considers, the absurdity of our position, is the hydraulic one, but even with the analogy, when properly interpreted, no such absurdity is found to exist. In fact the explanation mentioned by Dr. Lodge in his paper as having come through one of us from Sir William Thomson, but which must really be regarded as having come from ourselves, as we think that Sir William has probably his own distinct method of looking at the matter, has been misapprehended by Dr. Lodge.



Suppose we have a circuit of pipes, G A B D D′ E′ E G, whose development is shown in the figure, the two ends of the figure G and G being the same point in the real circuit; the pipes to be of uniform section, and to rise suddenly in level from A to B and from D to D′, and to fall from E′ to E, and there being a uniform rate of fall from B to D, D′ to E′, and from E through G to A. H I may be any datum-level. Let us suppose that there is a continuously acting pump in the part D′ E′, causing incompressible fluid, such as water, filling the pipes to flow continuously. Mechanical energy is given to the pump from some outside source, and the energy reappears at various places in the circuit. Thus, for example, between A and B the water rises in level. A pound of water at B has more energy than a pound of water at A, and its increase of energy is h foot-pounds, if the difference of level is h feet between B and A. It has really gained energy. What has it lost? Pressure, certainly; but pressure is not a form of energy. We know that in a steady frictionless stream

$$\frac{v^2}{2g}+2{\cdot}3\,p+h$$

remains constant, if v is the velocity in feet per second, and p the pressure in pounds per square inch, and h height in feet above datum-level. As $\frac{v^2}{2g}$ is the kinetic energy of a pound of water in foot pounds, and h is its potential-energy, one is tempted to call $2{\cdot}3\,p$ also a form of energy—pressure-energy; but we have just as much and no more right to call it so, than to speak, as we did, of tension-energy in electricity. We can see that pressure conditions are not in themselves a source of energy, by imagining incompressible fluid, like water, filling a closed vessel at great pressure, and then imagining an orifice to be made, when, of course, the water is no longer subjected to great pressure. But 2·3 p enters into the expression and is familiarly spoken of as a form of energy when the stream is *steady*—when there is a continuously acting pump somewhere in the circuit. In fact, then, we see that when a pound of water rises in level from A to B it receives h foot-pounds of energy if h is the difference in level, and it receives no energy from an outside source at A B ; energy disappears in the pump, and work is done between A and B. Now just as difference of potential in electrical things is measured as the work which must be done, on unit of electricity, in taking it from one point A to another B *through the dielectric*, so the difference of level between A and B represents the work done on a pound of water in taking it from A to B *through the air*. And just as the water in being raised from D to D′ gains energy *without any work being done on it from an outside source*, so we may consider that electricity in passing from copper to zinc may gain potential-energy *without there being any external source of energy at the junction.*

The preceding is even more than an analogy. There is a tendency for electricity to leave copper and enter zinc at the junction, which we are now prevented from calling the E.M.F. of contact, but which we may call contact-force. It is measured as the difference of potential established between two metals which are in contact. There is no contact-force in a piece of copper or in a piece of zinc. The contact-force is analogous with pressure in water. There is a sudden rise in level in the pipe from A to B which corresponds with a sudden rise of potential from copper to zinc. There is a consequent diminution of pressure from A to B which corresponds with the contact-force at the junction. There is no contact-force in a copper wire; and hence it is necessary to give to the pipe such an inclination that the potential-energy lost by the water in flowing along the pipe shall be equal to the energy given out in friction. In the voltaic circuit, similarly, the fall of potential-energy is known to be equal to the heat produced in overcoming resistance.

The analogy may be carried still further, for we may obtain the representation of thermoelectric effects. Suppose the water to be slightly compressible, then maintaining any vertical parts of the pipe at different constant temperatures will help or oppose the action of the pump in the circuit. Thus, not using a pump, let there be an endless pipe, rising suddenly from A to B, horizontal from B to C, falling suddenly from C to D, and horizontal from D to A. Imagine this filled with a slightly compressible fluid, and that the limb

C D is permanently kept at a higher temperature than A B, there will be a steady flow maintained in the direction A D C B A. If the limb A B is the higher in temperature, the flow will be in the direction A B C D A. Strictly speaking, we ought to consider the fluid in the endless tube to be one which changes the law connecting its density and temperature at a critical point, like water at 4° C.

To be quite correct, let what we have called "tension" in a metal a, at the absolute temperature t, be denoted by ${}_tP_a$; and the increase of potential from a to a metal b, as measured inductively, by ${}_tV_{ab}$, then the E.M.F. of a thermoelectric circuit of two metals, a and b, whose junctions are at temperatures t_1 and t_2, is

$$E = {}_{t_2}V_{ab} - {}_{t_1}V_{ab}.$$

The Peltier effect at a junction is

$${}_t\Pi_{ab} = {}_tP_b - {}_tP_a - {}_tV_{ab},$$

where

$${}_tV_{ab} = (k_b - k_a)t\{T_{ab} - \tfrac{1}{2}t\} + C_b - C_a,$$

and

$${}_tP_a = \tfrac{1}{2}k_a t^2 + C_a.$$

k_a and C_a are constants peculiar to the metal a, and T_{ab} is a constant peculiar to the two metals a and b.

Hence

$${}_t\Pi_{ab} = t\frac{d}{dt}\cdot {}_tV_{ab},$$

or the Peltier effect is proportional to the product of the absolute temperature into the rate of change of contact-potential difference with temperature. Consequently, *although the amount of heat generated when a unit current is sent through a junction for a second is the measure of the coefficient of the Peltier effect, this coefficient is in no sense a measure of the contact-potential difference existing at the junction.*

This really disposes of Dr. Lodge's fundamental argument —the argument, in fact, on which his whole objection to the large contact-potential difference at the junction of metals is based; for he *assumes* that in all cases where there is a considerable difference of potential at a junction, heat or cold must be developed when a current flows across that junction. He states, what is quite true and well known, that practically no heat is developed when a current flows from zinc to copper across the junction; therefore he concludes that there can be no contact-potential difference at this junction like three-quarters of a volt. But if, as we have proved, the coefficient of the Peltier effect is *not* a measure of the contact-potential difference, but of the product of the absolute temperature into the rate of variation with temperature of the contact-potential difference, it follows that the smallness of the Peltier effect does not require that the contact-potential difference must be also small.

We have endeavoured to experiment on this rate of variation of the contact-potential difference with temperature ; and in the discussion on Dr. Lodge's paper before the Society of Telegraph Engineers and Electricians, we gave a number of hitherto unpublished results which we had obtained on this subject. The apparatus we employed was the same as that which Dr. Lodge described as being used by us in our former experiments on contact-potential difference, and with it we measured the contact-potential difference of hot and cold mercury and of hot mercury and cold iron, hot mercury and cold copper, also for hot mercury and cold platinum, in each case for various differences of temperature. The results obtained were large (amounting in the case of mercury and iron to as much as 3 volts for about 16° C. difference of temperature), and not small, as might have been expected from the preceding equation and the smallness of the coefficient of the Peltier effect. We explained, however, that the very large potential-differences we obtained were probably due to *invisible* films of oxide on the surface of the warm mercury, which probably existed in spite of the fact that every effort was made to remove this oxide by distilling the mercury between every two sets of experiments ; and we showed that in such cases the summation law does not hold true—that is to say, the E.M.F. of a combination is not equal to the algebraical sum of the various potential-differences at the contacts, *measured inductively*, and which we have always found to be true in other cases when the experiments were conducted with as much care as was devoted to those made with hot mercury. For example, we found that

Copper at 16° C., with *clean* mercury at 16° C., had a contact-difference of 0·308 volt ;
Mercury at 16° C., with mercury at 26° C., had a contact-difference of 0·75 volt ;
Mercury at 26° C., with copper at 16° C., had a contact-difference of $-1·5$ volt.

Therefore, if these numbers represented the true contact-potential differences, a thermopile consisting of two pieces of cold copper at 16° C., dipping into two vessels of mercury, one of which was warmed up to 26° C., and which were joined together by a syphon-tube containing mercury, ought to have an E.M.F. of half a volt. But, as was to be anticipated, we found experimentally that no such E.M.F. could be obtained with such a thermopile, unless there were an oxide present at the hot junction separating two of the metals, and thereby introducing a high resistance.

Contrasting these results with those given in our papers read before the Royal Society (and which prove conclusively that when a cell is formed of a number of substances, solid or liquid, at the same temperature, its E.M.F. is equal to the algebraical sum of the various contact-potential differences, *measured inductively*, in air, of each of the pairs of substances in contact in the cell), we are justified in concluding that when layers of oxides or their salts are formed on the surfaces of the substances employed, as in Mr. Brown's experiments, the measured potential-differences do not represent the true contact-potential differences of the substances employed.

We are not disposed to think that Dr. Lodge has discovered any striking coincidence between measured chemical heats of combination and those heats as calculated on his theory. Such coincidence as he has discovered is not more wonderful than that the electro-positivity of the metals should be in the order of their tendencies to combine with oxygen ; there can be no doubt that an exceedingly important advance in the sciences of Chemistry and Electricity will be made by the philosopher who explains this and the twenty other coincidences of a like nature which have been discovered. We are quite sure, too, he would regard the seeming coincidences which he has discovered as trivial, had he not at the beginning made up his mind that the existence of contact-difference of potential was absurd, and that what we and many others have measured are due to air-effects.

We are in the habit of using the expression "difference of potentials between two points" as meaning, in *Electrokinetics*, the *Electrostatic* difference of potentials between two copper wires, coming from the points. This practice is very convenient; and there can be no objection to it, so long as we do not imply that it is always the same as the *Electrostatic* difference of potentials between the points. Now it seems to us that Dr. Lodge, in following this convenient custom, has fallen into the error of imagining that what he has been in the habit of calling "difference of potential" is really the same as "*Electrostatic* difference of potential." Indeed, we believe that the root of the whole difficulty which prevented Clerk Maxwell, and which now prevents Dr. Lodge, from seeing the position of the contact theorists, lies in their defining potential in a new way not recognized in Electrostatics. Clerk Maxwell's electromagnetic theory is so perfect in itself that no one thinks of attacking it; and we very much wish that we had the leisure to show, what we feel might probably be shown, that throughout his mathematical work, when he speaks of difference of potentials it is not necessary to assume that he speaks of electrostatic difference of potential.

Dr. Lodge, in his reply to remarks made during the discussion at the Society of Telegraph Engineers and Electricians, was kind enough to mention the fact that we had drawn Prof. Poynting's equipotential surfaces and lines of flow of energy as they must be drawn in practice, most of them lying like successive sleeves in an infinitely shallow space round all the conductors in a voltaic circuit, if we are to follow Maxwell in assuming a considerable difference of potential between air and metals. As Dr. Lodge has stated, we have also drawn these surfaces and flow-of-energy lines on our own assumption of no air-effect and considerable contact-differences of potential. Dr. Lodge did not, however, refer to the very much more interesting curves which we have drawn as the energy-lines from a primary voltaic or thermoelectric circuit whose current is altering just in such a way as to keep the current in a secondary circuit constant. Suppose it is the E.M.F. of the primary which is altering, it is very interesting to see how the lines of flow of energy sweep over the primary circuit, their parts which cut the secondary remaining unaltered. But now, suppose the total E.M.F. of the primary to be less than 1 volt, and imagine that Prof. C. Maxwell and Prof. Poynting and Dr. Lodge were right in their idea of a considerable difference of potential between air and metals, it will be found that no line of flow of energy can connect the primary and secondary circuits, since all the equipotential surfaces of the primary will lie infinitely close to the conductors of which it is composed, and yet it cannot be doubted that the secondary circuit receives energy from the primary.

For the purpose of evading all difficulties which might be due to our taking different numbers to represent possible contact-differences between the parts of a voltaic circuit and air, let us test Prof. Poynting's deduction from Maxwell's theory in another way. Assume that there is a voltaic circuit completely enclosed in a hermetically-sealed metallic case; and let us suppose that, just before sealing-up, we set up differences of potentials of many thousands of volts between the voltaic circuit and its case, and that it is in our power at any instant to cause any regular change of current in the voltaic circuit by means of mechanism enclosed by the case. Now let there be, outside the case, a secondary circuit, and let the primary enclosed circuit have its current diminished at such a rate that a constant current is maintained for a short length of time in the secondary by induction. We know quite well that such an inductive effect might take place, and that the energy of the secondary circuit must somehow come from the primary; and it must be remembered that it need not have been by a diminution of the primary current, but an increase of the primary current, that this induction takes place. We cannot see how it is possible that Prof. Poynting's electro-potential surfaces can proceed from the primary so as to pass through the secondary circuit; we can, however, imagine that, instead of equipotential surfaces, such as we speak of in Electrostatics, if we speak of a series of surfaces cutting the lines of electrical displacement at right angles, then an explanation becomes quite possible. In fact, it seems to us that if Prof. Poynting's views are logically deducible from Maxwell's theory, it is necessary to assume that Maxwell's differences of potential are essentially different from electrostatic difference of potentials.

September 3, 1885.

Note added December 14, 1885.

Since these notes of our remarks made in the discussion on Dr. Lodge's paper were sent to the Editors at the beginning of September, a paper on Contact Electricity has been read by Dr. Hopkinson before the British Association, and has appeared in the Philosophical Magazine. We are glad to see that Dr. Hopkinson, who has entered so fully into the energy equations, not only for Sir William Thomson's view, but also for that of Prof. Maxwell and Dr. Lodge, has come to the same conclusions as ourselves.

We leave our formulæ on page 58 of these Notes as they were written in April last, following Prof. Maxwell's lettering; but for the sake of those who may have studied that part of Dr. Hopkinson's paper which refers to Sir William Thomson's theory, it is well to state that

he uses $f(t)$ where we use ${}_tV_{ab}$,
„ $F(t)$ „ „ ${}_t\Pi_{ab}$,
„ $\phi(t)$ „ „ tk_a,
„ $\psi(t)$ „ „ tk_b.

IX. *On the Integration of Partial Differential Equations of the Third and Higher Orders.* *By* ROBERT MOON, *M.A., Honorary Fellow of Queens' College, Cambridge**.

THE following method of deriving the first integrals, where such integrals exist, of the equation

$$\mathrm{R}\frac{d^3z}{dx^3}+\mathrm{S}\frac{d^3z}{dx^2\,dy}+\mathrm{T}\frac{d^3z}{dx\,dy^2}+\mathrm{U}\frac{d^3z}{dy^3}=\mathrm{V}\quad .\quad .\quad (1)$$

(R, S, T, U, V being functions of x and y only), and of developing the conditions under which alone the equation will admit of such integrals, is capable of being extended to Partial Differential Equations of the higher orders involving two independent variables.

Assume (1) to be satisfied by

$$f(xyrst)=0,\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad (2)$$

where r, s, t respectively have their usual values.

Differentiating (2) with respect to x and y, we get

$$0=f'(r)\frac{d^3z}{dx^3}+f'(s)\frac{d^3z}{dx^2\,dy}+f'(t)\frac{d^3z}{dx\,dy^2}+f'(x),$$

$$0=f'(r)\frac{d^3z}{dx^2\,dy}+f'(s)\frac{d^3z}{dx\,dy^2}+f'(t)\frac{d^3z}{dy^3}+f'(y),$$

$$\therefore\ \frac{d^3z}{dx^3}=-\frac{f'(s)}{f'(r)}\frac{d^3z}{dx^2\,dy}-\frac{f'(t)}{f'(r)}\frac{d^3z}{dx\,dy^2}-\frac{f'(x)}{f'(r)},$$

$$\frac{d^3z}{dy^3}=-\frac{f'(r)}{f'(t)}\frac{d^3z}{dx^2\,dy}-\frac{f'(s)}{f'(t)}\frac{d^3z}{dx\,dy^2}-\frac{f'(y)}{f'(t)},$$

the substitution of which in (1) gives

$$\begin{aligned}0=&-\mathrm{R}\frac{f'(s)}{f'(r)}\frac{d^3z}{dx^2\,dy}-\mathrm{R}\frac{f'(t)}{f'(r)}\frac{d^3z}{dx\,dy^2}-\mathrm{R}\frac{f'(x)}{f'(r)},\\&-\mathrm{U}\frac{f'(r)}{f'(t)}\frac{d^3z}{dx^2\,dy}-\mathrm{U}\frac{f'(s)}{f'(t)}\frac{d^3z}{dx\,dy^2}-\mathrm{U}\frac{f'(y)}{f'(t)},\\&+\mathrm{S}\frac{d^3z}{dx^2\,dy}+\mathrm{T}\frac{d^3z}{dx\,dy^2}-\mathrm{V},\end{aligned}$$

in order to which we must have the coefficients of $\frac{d^3z}{dx^2\,dy}$,

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* Communicated by the Author.

$\frac{d^3z}{dx\,dy^2}$ separately $=0$; therefore

$$0=\mathrm{R}\cdot\frac{f'(s)}{f'(r)}+\mathrm{U}\cdot\frac{f'(r)}{f'(t)}-\mathrm{S}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$0=\mathrm{R}\cdot\frac{f'(t)}{f'(r)}+\mathrm{U}\cdot\frac{f'(s)}{f'(t)}-\mathrm{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$0=\mathrm{R}\cdot\frac{f'(x)}{f'(r)}+\mathrm{U}\cdot\frac{f'(y)}{f'(t)}+\mathrm{V}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Eliminating $f'(s)$ between (3) and (4), we have

$$\frac{\mathrm{R}}{\mathrm{U}}\cdot\frac{f'(t)}{f'(r)}=\frac{\mathrm{U}\cdot\frac{f'(r)}{f'(t)}-\mathrm{S}}{\mathrm{R}\cdot\frac{f'(t)}{f'(r)}-\mathrm{T}},$$

$$\therefore\ \frac{\mathrm{R}^2}{\mathrm{U}}\cdot\overline{\frac{f'(t)}{f'(r)}}\Big|^2-\frac{\mathrm{RT}}{\mathrm{U}}\frac{f'(t)}{f'(r)}=\mathrm{U}\cdot\frac{f'(r)}{f'(t)}-\mathrm{S};$$

or, putting $\frac{f'(t)}{f'(r)}=\alpha$, and arranging,

$$0=\mathrm{R}^2\alpha^3-\mathrm{RT}\alpha^2+\mathrm{US}\alpha-\mathrm{U}^2, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

an equation the adoption of each of the three roots of which gives us

$$0=f'(t)-\alpha f'(r), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where α is a function of x and y only.

The auxiliary equations for the solution of (7) by Lagrange's method are

$$0=dr+\alpha dt, \quad 0=ds, \quad 0=dx, \quad 0=dy;$$

the integration of which gives

$$c=r+\alpha t, \quad c_1=s, \quad c_2=x, \quad c_3=y.$$

Hence we have

$$f(xyrst)=f_a\{xy\,s(r+\alpha t)\}=f_a(xy\,s\,\mu) \text{ suppose,}$$

where $\mu=r+\alpha t$: and f_a is an arbitrary function.

Substituting in (3) the value of f thus derived; since

$$f'(s)=f_a'(s)+f_a(\mu)\frac{d\mu}{ds}$$

$$=f_a'(s), \quad \text{since } \frac{d\mu}{ds}=0,$$

and

$$f'(r)=f_a'(\mu)\frac{d\mu}{dr}=f_a'(\mu);$$

we shall get

$$0=\mathrm{R}\frac{f_a'(s)}{f_a'(\mu)}+\frac{\mathrm{U}}{\alpha}-\mathrm{S},$$

or

$$0=f_a'(s)+\frac{\mathrm{U}-\mathrm{S}\alpha}{\mathrm{R}\alpha}f'(\mu);$$

which is a linear equation between the partial differential coefficients of the first order of the function $f_a(xys\mu)$.

The auxiliary equations for the solution, by Lagrange's method, of this last equation are

$$0=d\mu-\frac{\mathrm{U}-\mathrm{S}\alpha}{\mathrm{R}\alpha}ds,\quad 0=dx,\quad 0=dy,$$

whence we get

$$f=f_a(xys\mu)=f_b\left\{xy\left(\mu-\frac{\mathrm{U}-\mathrm{S}\alpha}{\mathrm{R}\alpha}s\right)\right\}=f_b\{xy\mu_1\}\text{ suppose,}$$

where

$$\mu_1=\mu-\frac{\mathrm{U}-\mathrm{S}\alpha}{\mathrm{R}\alpha}s=r+\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha}s+\alpha t,$$

and f_b is an arbitrary function.

Observing that the equation

$$f=f_b(xy\mu_1)$$

gives

$$f'(r)=f_b'(\mu_1)\frac{d\mu_1}{dr}=f_b'(\mu_1),$$

$$f'(t)=f_b'(\mu_1)\frac{d\mu_1}{dt}=\alpha f_b'(\mu_1),$$

$$f'(x)=f_b'(x)+f_b(\mu_1)\frac{d\mu_1}{dx}$$

$$=f_b'(x)+f_b'(\mu_1)\cdot\left\{s\cdot\frac{d}{dx}\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha}+t\cdot\frac{d\alpha}{dx}\right\},$$

$$f'(y)=f_b'(y)+f_b'(\mu_1)\left\{s\cdot\frac{d}{dy}\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha}+t\cdot\frac{d\alpha}{dy}\right\},$$

the substitution in (5) of the above value of f gives us

$$0=\mathrm{R}\frac{f_b'(x)}{f_b'(\mu_1)}+\frac{\mathrm{U}}{\alpha}\frac{f_b'(y)}{f_b'(\mu_1)}+\mathrm{V},$$

$$+\mathrm{R}\left\{s\cdot\frac{d}{dx}\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha}+t\frac{d\alpha}{dx}\right\}+\frac{\mathrm{U}}{\alpha}\left\{s\cdot\frac{d}{dy}\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha}+t\cdot\frac{d\alpha}{dy}\right\};$$

or,

$$0=\mathrm{R}\alpha f_b'(x)+\mathrm{U}f_b'(y)+\mathrm{V}\alpha f_b'(\mu_1),$$
$$+s\left\{\mathrm{R}\alpha\frac{d}{dx}\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha}+\mathrm{U}\frac{d}{dy}\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha}\right\}f_b'(\mu_1),$$
$$+t\left\{\mathrm{R}\alpha\frac{d\alpha}{dx}+\mathrm{U}\frac{d\alpha}{dy}\right\}f_b'(\mu_1).$$

But s and t can only appear in this last equation as parts of the symbol μ_1 or $r+\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha}s+\alpha t$: hence the coefficients of s and t in the last equation must separately $=0$: or we must have

$$0=\mathrm{R}\alpha\frac{d\alpha}{dx}+\mathrm{U}\frac{d\alpha}{dy},$$
$$0=\mathrm{R}\alpha\frac{d}{dx}\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha}+\mathrm{U}\frac{d}{dy}\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha};$$

which are the conditions to be satisfied in order that the given equation may admit of a first integral: and which being satisfied, we shall have for the final and complete determination of f the equation

$$0=\mathrm{R}\alpha f_b'(x)+\mathrm{U}f_b'(y)+\mathrm{V}\alpha f_b'(\mu_1).$$

We may take as the auxiliary equations for the solution of this last,

$$0=\mathrm{R}\alpha dy-\mathrm{U}dx : 0=d\mu_1-\frac{\mathrm{V}\alpha}{\mathrm{U}}dy;$$

from the first of which we may always derive

$$\mathrm{F}(x, y)=c, \text{ a constant.}$$

By means of this last equation we may always eliminate x from $\frac{\mathrm{V}\alpha}{\mathrm{U}}$. Let $\mathrm{F}_1(y, c)$ be the result of such elimination; then the second auxiliary equation will stand,

$$0=d\mu_1-\mathrm{F}_1(y, c)dy;$$

whence we derive

$$\text{const.}=\mu_1-\int\mathrm{F}_1(y, c)dy,$$

c having to be regarded as constant in the integration. Hence we get finally for the first integral of (1),

$$\mu_1-\int\mathrm{F}_1(y, c)dy=\phi\{\mathrm{F}(x, y)\},$$

or

$$r+\frac{\mathrm{S}\alpha-\mathrm{U}}{\mathrm{R}\alpha}s+\alpha t=\int\mathrm{F}_1(y, c)dy+\phi\{\mathrm{F}(x, y)\},$$

where ϕ is an arbitrary, and F, F_1 are *definite* functions; and where $F(xy)$ is to be substituted for c after the integration indicated in the last equation has been effected.

If it is proposed to integrate the equation

$$R\frac{d^4z}{dx^4}+S\frac{d^4z}{dx^3\,dy}+T\frac{d^4z}{dx^2\,dy^2}+U\frac{d^4z}{dx\,dy^3}+V\frac{d^4z}{dy^4}=W, \quad (8)$$

putting

$$\frac{d^3z}{dx^3}=r,\quad \frac{d^3z}{dx^2\,dy}=s,\quad \frac{d^3z}{dx\,dy^2}=t,\quad \frac{d^3z}{dy^3}=u;$$

and assuming (8) to be satisfied by $f(x\,y\,r\,s\,t\,u)=0$, proceeding in the same manner we shall find the conditions to be satisfied in order that (8) may have a first integral will be the three equations

$$0=R\alpha\frac{d\alpha}{dx}+V\frac{d\alpha}{dy},$$

$$0=R\alpha\frac{d}{dx}\frac{S\alpha-V}{R}+V\frac{d}{dy}\frac{S\alpha-V}{R},$$

$$0=R\alpha\frac{d}{dx}\frac{R\alpha-U}{V}+V\frac{d}{dy}\frac{R\alpha-U}{V};$$

where $\alpha=\dfrac{f'(U)}{f'(r)}$ is one of the roots of the equation

$$0=R^3.\alpha^4-R^2U.\alpha^3+RTV.\alpha^2-SV^2.\alpha+V^3;$$

and the first integral, when these conditions are satisfied, will be

$$r+\frac{S\alpha-V}{R\alpha}.s+\frac{U-R\alpha}{V}.\alpha t+\alpha u=\int F_1(y,c)dy+\phi\{F(x,y)\},$$

where $F(xy)=c$ is the integral of the equation

$$0=R\alpha dy-Vdx;$$

and $F_1(y,c)$ denotes the result of the elimination of x from the quantity $\dfrac{W\alpha}{V}$ by means of the equation $F(xy)=c$; c being treated as constant, or as $F(xy)$, in the manner indicated in the preceding case.

If the equation to be integrated is

$$R\frac{d^5z}{dx^5}+S\frac{d^5z}{dx^4\,dy}+T\frac{d^5z}{dx^3dy^2}+U\frac{d^5z}{dx^2\,dy^3}+V\frac{d^5z}{dx\,dy^4}-W\frac{d^5z}{dy^5}=Z. \quad (9)$$

Putting r, s, &c., for the differential coefficients $\dfrac{d^4z}{dx^4}$, $\dfrac{d^4z}{dx^3\,dy}$,

&c., and assuming (9) to be satisfied by $f(xyrstuv)=0$, we shall find the conditions of (9) having a first integral to be the four following equations, viz. :—

$$0=\mathrm{R}\alpha\frac{d\alpha}{dx}+\mathrm{W}\frac{d\alpha}{dy},$$

$$0=\mathrm{R}\alpha\frac{d}{dx}\frac{\mathrm{S}\alpha-\mathrm{W}}{\mathrm{R}}+\mathrm{W}\frac{d}{dy}\frac{\mathrm{S}\alpha-\mathrm{W}}{\mathrm{R}},$$

$$0=\mathrm{R}\alpha\frac{d}{dx}\frac{\mathrm{RT}\alpha^2-\mathrm{SW}\alpha+\mathrm{W}^2}{\mathrm{R}^2}+\mathrm{W}\frac{d}{dy}\frac{\mathrm{RT}\alpha^2-\mathrm{SW}\alpha+\mathrm{W}^2}{\mathrm{R}^2},$$

$$0=\mathrm{R}\alpha\frac{d}{dx}\frac{\mathrm{V}-\mathrm{W}}{\mathrm{W}}+\mathrm{W}\frac{d}{dy}\frac{\mathrm{V}-\mathrm{R}\alpha}{\mathrm{W}};$$

where $\alpha=\frac{f'(v)}{f'(r)}$ is one of the roots of the equation

$$0=\mathrm{R}^4\alpha^5-\mathrm{R}^3\mathrm{V}.\alpha^4+\mathrm{R}^2\mathrm{UW}.\alpha^3-\mathrm{RTW}^2.\alpha^2+\mathrm{W}^3\mathrm{S}.\alpha-\mathrm{W}^4;$$

and the solution, when such exists, will be

$$r+\frac{\mathrm{S}\alpha-\mathrm{W}}{\mathrm{R}\alpha}.\mathrm{S}+\frac{\mathrm{RT}.\alpha^2-\mathrm{SW}.\alpha+\mathrm{W}^2}{\mathrm{R}^2\alpha^2}.t+\frac{\mathrm{V}-\mathrm{R}\alpha}{\mathrm{W}}.\alpha u+\alpha v$$
$$=\int\mathrm{F}_1(yc)dy+\phi\{\mathrm{F}(x,y)\};$$

where $\mathrm{F}(xy)=c$ is the integral of

$$0=\mathrm{R}\alpha dy-\mathrm{W}dx;$$

and $\mathrm{F}_1(y,c)$ is the result of eliminating x from the quantity $\frac{\mathrm{Z}\alpha}{\mathrm{W}}$ by means of the equation $\mathrm{F}(xy)=c$.

Pursuing the same method, I have already (in effect) shown in the pages of the Philosophical Magazine that the condition of the equation

$$\mathrm{R}\frac{d^2z}{dx^2}+\mathrm{S}\frac{d^2z}{dx\,dy}+\mathrm{T}\frac{d^2z}{dy^2}=\mathrm{V} \quad . \quad . \quad . \quad (10)$$

admitting of a first integral, in other words of its being integrable by Monge's method, is that we have

$$0=\mathrm{R}\alpha\frac{d\alpha}{dx}+\mathrm{T}\frac{d\alpha}{dy};$$

where α satisfies the equation

$$0=\mathrm{R}\alpha^2-\mathrm{S}\alpha+\mathrm{T};$$

and when this holds, the first integral of (10) will be

$$p+\alpha q=\int\mathrm{F}_1(yc)dy+\phi\{\mathrm{F}(xy)\},$$

where $F(xy)=c$ is the integral of $0 = R\alpha dy - Tdx$; and $F_1(yc)$ is the result of elimination of x from the quantity $\frac{V\alpha}{T}$ by means of $F(xy)=c$.

The adoption, in the case of equations of the second order, of the method of this paper not merely gives us the first integrals resulting by Monge's method, where such exist, but develops explicitly the conditions of their existence. It does more: for to the carrying out of Monge's method it is essential that the coefficients R, S, T, V should either be functions of x and y only, or of p and q only; whereas the method above set forth equally gives the first integrals where they exist, and the conditions of their existence, when R, S, &c. are functions of x, y, p, q; the only advantage of the restriction of the coefficients to being functions of x and y only, being that it enables us to carry further the development of the results when the coefficients R, S, &c. are expressed by general symbols.

The same remarks hold when the method is applied to equations of a higher order than the second; when R, S, &c. may involve, in addition to x and y, any differential coefficients of an order lower than that of the equation to be integrated; although when R, S, &c. are so made up, the cases in which first integrals exist will probably be very rare.

6 New Square, Lincoln's Inn,
July 20, 1885.

P.S.—The law of formation of the equations in α will be seen by considering the case of equation (9), in which R and W are the initial and terminal coefficients of the left side of the equation. Here the 1st, 2nd, 3rd, and 4th coefficients of the equation in α will be multiplied by R^4, R^3, R^2, R; and the 3rd, 4th, 5th, and 6th by W. W^2, W^3, W^4 respectively. Each of the terms from the 2nd to the 5th, both inclusive, will involve one other factor, viz. V, U, T, S respectively, *i. e.* the coefficients of (9) intermediate to R and W taken in reverse order.

The late Mr. Boole showed that the fact of the general equation of the second order admitting of a first integral of the form $u=\phi(v)$, where u and v are definite functions, and ϕ is arbitrary, is conditional: but his method fails to develop the conditions.

X. *Saturation of Salt-solutions.*—PART II. *By* W. W. J. NICOL, *M.A., D.Sc., F.R.S.E., Lecturer on Chemistry, Mason College, Birmingham.*[*]

SECTION I.

IN my paper[†], of which this is a continuation, I endeavoured to show that the solubility of a salt in water is dependent on the difference between the molecular volume of the salt in dilute solution and that in the saturated solution, compared with the difference between this last volume and that in the solid state. Thus, the greater the cohesion of the salt the less its solubility, and *vice versâ*. The adhesion of the water to the salt is also a factor in solution; the greater the adhesion the more soluble the salt. In very dilute solutions, when once the salt is dissolved the cohesion of the salt is practically *nil*; for the molecules encounter one another so rarely that no appreciable number are in collision at any one time. As the concentration of the solution increases the collisions of salt molecules become more frequent, and their cohesion asserts itself more and more, as shown by the gradual increase of the mean molecular volume of the salt in solution. Finally, when the cohesion of the salt and the adhesion of the water to the salt are in equilibrium the solution is saturated.

It is this gradual increase of the mean molecular volume[‡], from that in the most dilute solutions to that at the point of saturation, that forms the subject of the present paper.

In the course of the work connected with the other papers that I have published on solution, I had accumulated a great number of data dealing with the density and molecular volume of various solutions of numerous salts, and in the instances

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[†] Communicated by the Author.

Phil. Mag. June (Suppl.), 1884.

[‡] By mean molecular volume is meant the apparent volume of any one molecule of salt present in the solution, the volume of water being assumed constant. It is Thomsen's $\frac{r}{n}$; thus

$$\text{Mol. vol. of solution} = \frac{1800+n(\text{M.W.})}{\delta};$$

$$r = \frac{1800+n(\text{M.W.})}{\delta} - 1800;$$

$$\frac{r}{n} = \text{mean molecular volume};$$

$$(\text{M.W.}) = \text{molecular weight of the salt in grammes.}$$

where the lists were complete was struck by the regular increase of the mean molecular volume with the concentration, and that this increase was a gradually decreasing quantity. In order to study this point more closely I tried to find interpolation formulæ that would express with satisfactory accuracy the molecular volumes of solutions containing various amounts of different salts.

The most satisfactory form of formula I found to be

$$\text{M.V.} = 1800 + n\alpha + n^2\beta - n^3\gamma,$$

where α, β, and γ are constants depending on the salt; therefore

$$r = n\alpha + n^2\beta + n^3\gamma,$$

$$\frac{r}{n} = \alpha + n\beta - n^2\gamma.$$

The following tables I., II., III., and IV. contain the found and calculated values for NaCl, KCl, $NaNO_3$, and KNO_3, in solutions of strengths varying from 1 molecule up to the saturated solution. The last column in each table contains the molecular volume with which each successive molecule enters into solution, a point to which I shall return later.

The agreement between the found and calculated results is on the whole good except in two cases, the saturated solutions of NaCl and KCl, where the difference reaches 0·15 per cent. and 0·2 per cent. respectively. That this is the case will not surprise any one, for density determinations of *saturated* solutions are carried out only with the greatest difficulty, and are apt to be too low, thus rendering the molecular volume too high.

TABLE I. NaCl.

n.	M.V. found.	M.V. calculated.	Δ.	$\frac{r}{n}$.	
1	1817·5	1817·4	−0·1	17·4	
2	1836·3	1836·1	−0·2	18·0	18·7
3	1856·0	1855·9	−0·1	18·6	19·8
4	1876·2	1876·6	+0·4	19·2	20·7
5	1897·4	1898·1	+0·7	19·6	21·5
6	1918·8	1920·0	+1·2	20·0	21·9
7	1940·9	1942·2	+1·3	20·3	22·2
8	1963·6	1964·5	+0·9	20·6	22·3
9	1986·1	1986·6	+0·5	20·7	22·1
10	2009·2	2008·4	+0·8	20·8	21·8
11	2032·7	2029·6	+3·1	20·9	21·2
12		2050·0		20·8	20·4

$\alpha = 16·634$. $\beta = 0·7711$. $\gamma = 0·0351$.

TABLE II. KCl.

n.	M.V. found.	M.V. calculated.	Δ.	$\frac{r}{n}$.	
1	1827·7	1827·8	+0·1	27·8	
2	1857·1	1856·8	−0·3	28·4	29·0
3		1886·8		28·9	30·0
4	1917·8	1917·6	−0·2	29·4	30·8
5	1949·8	1948·8	−1·0	29·8	31·2
6		1980·3		30·1	31·5
7	2010·9	2011·8	+0·9	30·3	31·5
8		2043·1		30·4	31·3
8·38	2058·7	2054·7	−4·1		30·7
9		2073·8		30·4	

$\alpha=27·103$. $\beta=0·738$. $\gamma=0·041$.

On the supposition that the general formula

$$\frac{r}{n}=\alpha+n\beta-n^2\gamma$$

accurately expresses the mean molecular volume of the salt in a solution containing n molecules, it follows that the form of the corresponding curve is that of a parabola. There is, therefore, this relation between the constants β and γ, namely that $\frac{\beta}{2\gamma}$ expresses the apex of the parabola. But, as will be seen from Table V., $\frac{\beta}{2\gamma}$ also expresses the solubility of the salt in molecules per 100 water-molecules. Only the first half of the parabola is met with in nature; a further addition of salt, were it possible, would produce contraction.

TABLE III. $NaNO_3$.

n.	M.V. found.	M.V. calculated.	Δ.	$\frac{r}{n}$.	
1		1828·9		28·9	
2	1858·9	1859·0	+0·1	29·5	30·1
2·5	1874·4	1874·5	+0·1	29·8	
5	1955·0	1955·5	+0·5	31·6	
17		2380·6		34·2	
18		2415·1		34·2	34·5
18·45	2430·2	2430·5	+0·3	34·2	
19		2448·9		34·2	33·8

$\alpha=28·3$. $\beta=0·65$. $\gamma=0·018$.

TABLE IV. KNO_3.

n.	M.V. found.	M.V. calculated.	Δ.	$\frac{r}{n}$.	
1	1839·1	1839·0	−0·1	39·0	
2	1879·6	1879·3	+0·2	39·9	40·8
3		1921·7		40·6	41·9
4	1963·5	1964·2	+0·7	41·1	42·5
5	2006·7	2006·2	−0·5	41·2	42·0
5·63	2032·9	2032·4	−0·5	41·3	
6		2047·4		41·2	41·2

$\alpha=37·82$. $\beta=1·254$. $\gamma=0·114$.

TABLE V.

Salt.	β.	γ.	$\frac{\beta}{2\gamma}$.	Solubility.
$NaCl$	0·771	0·035	11·0	10·99
KCl	0·738	0·041	9·0	8·38
$NaNO_3$	0·650	0·018	18·1	18·45
KNO_3	1·254	0·114	5·5	5·63

The above relationship of the two constants β and γ appeared to me most singular and at the same time most interesting if it proved to be of universal occurrence. In order to test this point to some extent, I prepared solutions of $BaCl_2$ and $Sr(NO_3)_2$ each of three different strengths—one $n=0·5$, another nearly saturated, and the third intermediate in strength, and determined their densities at 20° C. The results thus obtained are given in Table VI. along with the values of β and γ for $BaCl_2$, $LiCl$, and $CaCl_2$ calculated from the data given by Gerlach*.

TABLE VI.

	$BaCl_2$.	$Sr(NO_3)_2$.	$BaCl_2$†.	$LiCl$†.	$CaCl_2$†.
β	1·515		1·0465	0·1768	0·5243
γ	0·1275		0·0739	0·0028	0·0116
$\frac{\beta}{2\gamma}$	5·95	13·06	7·08	31·0	22·5
Solubility ...	6·19	12·06	6·07	32·0	22·3

† Gerlach (*loc. cit.*). $t°=15°$ C.

In these cases, too, the agreement between the found and

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* *Spec. Gew. d. Salzlösungen*, 1859.

calculated solubility is satisfactory; I need hardly add that but a slight alteration in the value of γ would largely affect $\frac{\beta}{2\gamma}$, that is the calculated solubility, while it would have little influence on the value of

$$\text{M.V.} = 1800 + na + n^2\beta - n^3\gamma.$$

The theoretical bearing of the above is still more interesting. Saturation ensues at the apex of the parabola when the value of $a + n\beta - n^2\gamma$ is practically the same for any two values of n which lie closely together; that is, at a point at which the further addition of a small quantity of salt would be unattended by change in the mean molecular volume; but as a positive change is produced by *cohesion*, and a negative change by *adhesion*, it is evident that at this point the *cohesion* and *adhesion* are in equilibrium, as I pointed out three years ago.

The point at which saturation would theoretically take place can be calculated as follows:—

On the supposition that the molecular volume with which the last molecule enters into solution is the same as the mean molecular volume of the molecules already present, then

$$(na + n^2\beta - n^3\gamma) - [(n-1)a + (n-1)^2\beta - (n-1)^3\gamma]$$
$$= a + n\beta - n^2\gamma,$$

when

$$n = 1, \text{ or } n = \frac{\beta + \gamma}{2\gamma}.$$

The value $n = 1$ is of course beside the question, but the other solution shows that saturation is complete when $n = \frac{\beta + \gamma}{2\gamma}$. Experiment gives $n = \frac{\beta}{2\gamma}$ approximately.

The last columns in Tables I., II., III., and IV. contain the values for the first half of the above equation and will make this clearer.

SECTION II.

Saturation in a Solution containing two Salts.

In the former paper I described experiments on the molecular volumes of saturated solutions of two salts containing the same base or the same salt radical. I showed that in three cases out of the four examined, the resulting solution possessed a volume equal to that calculated on the supposition that each salt possessed the molecular volume it possesses in a saturated solution of itself alone ; and I concluded from this that each salt dissolved in the solution independently of the other. I also showed that the water was not shared between the two salts equally, nor in the ratio of their solubilities when separate, but that, as a general rule, the more soluble salt had its solubility increased to a greater extent than that of the less soluble salt. At that time I was not in a position to enter more fully into this subject, but a recent paper by Rüdorff* has furnished data by means of which I hope to be able to advance one step further towards the solution of this difficult question.

The results obtained by Rüdorff are as follows :—

(α) *Double salts (well defined).*—When one or other of the constituents of a double salt is added to a saturated solution of such a salt, it is found that precipitation of the double salt ensues, and if excess be added the *whole* of the double salt is precipitated, the merest trace only remaining in solution.

The salts experimented with were :—Ammonium alum, cadmium ammonium sulphate, nickel ammonium sulphate.

(β) *Double salts* (*ill defined*).—By this I mean salts which, being isomorphous, are able to crystallize out from solution, forming mixed salts the constituents of which bear no definite relation to one another, or else crystallize together in definite proportions : the distinguishing character between this class and those in class (a) being their isomorphism.

In this case also either of the salts is able to expel the other from its saturated solution, prepared by treating a mixture of the two salts with water insufficient to dissolve the whole quantity of either salt present ; but this precipitation is only partial, never complete as in class (a).

Ammonium alum and ferric ammonium alum ; cadmium ammonium sulphate and copper ammonium sulphate; ammonium and lithium sulphates; ammonium and lithium chlorides; sodium and cadmium sulphates; sodium and zinc sulphates; potassium and silver nitrates ; sodium and silver nitrates; nitrate and sulphate of sodium ; sodium and ammonium sulphates.

This complete or partial driving out of solution of the one salt by the other is readily explained by the theory of solution proposed by me some years ago. It has been concluded from the experiments of Berthelot and others† that, in the majority of cases, double salts do not exist, as such, in solution ; but that it is only at the moment of crystallization that the union

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* Wiedemann's *Annalen*, xxv. p. 626.

† Naumann, *Thermochemie*. p. 335.

of the constituents forming the double salt takes place. A saturated solution of a double salt is therefore not necessarily saturated to either of its constituents, but may be able to dissolve more of one or other of the salts. As the amount, however, of this salt increases, there arrives a point at which the solution has become so rich in this salt (B), that any one molecule of the other salt (A) may be regarded as being in contact with a molecule of B. Aggregation or combination to form the double salt (AB) is then possible, and the solution is then saturated for the double salt, and crystallization ensues, proceeding *pari passu* with the addition of B, and resulting in the complete expulsion from the solution of A in cases where the attraction between A and B exceeds the cohesion of either A or B; while, on the other hand, if this be not the case, the expulsion is only partial. This is strongly supported by the definite character and stability of the salts which are completely expelled, and the instability of those which are only partially driven out of solution. The question is, however, complicated by our total ignorance of the nature and amount of the attraction of the various salts for water, which, as I have previously pointed out (*loc. cit.*), plays an important part in determining the proportions in which the various salts dissolve.

Rüdorff makes the following generalizations from the results of his experiments :—

Salts divide themselves into three groups according to their behaviour when dissolved in pairs (no double decomposition being possible).

First.—Salts which form with one another definite (*wohlgeformten*) double salts. Total expulsion of the double salt by one or other of the constituents.

Second.—Salts which are isomorphous in pairs, which either form double salts or crystallize together in mixtures. Partial expulsion by excess of either salt.

Third.—Salts which neither form double salts nor are isomorphous. The saturated solutions of pairs of these salts are stable and unaffected by excess of either.

By keeping these three groups of salts fully in view it will be possible to arrive at a satisfactory knowledge of the laws governing the behaviour of salts belonging to the third group, for in this case alone is the problem one relating purely to solution.

XI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xx. p. 212.]

December 2, 1885.—Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. "On some Borings in Kent.—A Contribution to the Deep-seated Geology of the London Basin." By W. Whitaker, B.A., F.G.S., Assoc. Inst. C.E.

Seven deep borings in the eastern part of Kent were described, all of them reaching to the Gault. The chief one is at Chatham Dockyard, where, after passing through the whole thickness of the Chalk, the Gault was found to be 193 feet thick; whilst the Lower Greensand was only 41 feet, and was underlain by Oxford Clay, a formation not before known in Kent.

These facts involve the thinning of the Lower Greensand from 200 feet at the outcrop a few miles to the south, and the entire loss of the whole of the Wealden Series, which, further south, exists in great force, the Weald Clay being 600 feet thick, or perhaps more, and the Hastings Beds 700 feet or more.

Still further south, in the central part of the Wealden district, there are outcrops of the Purbeck Beds, whilst the Subwealden boring continues the series downwards. We have thus an addition to the beds wanting at Chatham of some 400 feet of Purbeck and Portlandian, of over 1100 feet of Kimeridgian, and of nearly 500 feet of Corallian &c. In a section of 32 miles, therefore (the distance between the Subwealden and the Chatham borings), we have a thinning of beds to the extent of over 3400 feet, or at the average rate of about 100 feet in a mile.

This northerly thinning agrees with the facts that have been brought before us from other deep borings in and near London; but the Chatham boring is the first in the London Basin in which a Middle Jurassic formation has been found. The teaching of the deep borings, as a whole, is that north of the Thames older rocks rise up beneath the Cretaceous beds, whilst on the south newer rocks come in between the two.

The question of the finding of the Coal-measures beneath parts of the London Basin seems to admit of a hopeful answer, whilst the lesson of the deep borings as regards water-supply is that there is small chance of getting water from the Lower Greensand at great depths underground.

It would be well if underground exploration could be conducted on a systematic plan, with proper regard to both topographical and geological considerations, and not left any longer to the chance work of people in search of water.

2. "Note on some recent openings in the Liassic and Oolitic Rocks of Fawler in Oxfordshire, and on the arrangement of those rocks near Charlbury." By F. A. Bather, Esq.

The river Evenlode rises in the Lower Lias of the Vale of Moreton, traverses the range of Oolites, and joins the Isis opposite Wytham Mill. Lias is exposed to about three quarters of a mile below Fawler, where Great Oolite is brought down by a fault; and in the Geological Survey map Lower Lias is brought down the valley to within half a mile of Charlbury Railway Station.

In this paper the author gives reasons for believing that the distribution of the different beds constituting the Lias in the Evenlode Valley do not agree with the Geological Survey map, nor with Prof. Hull's description, recent sections and borings made for clay, used in brick- and pottery-making, having exposed Lower-Lias clay in a brick-yard at Fawler, marlstone and Upper-Lias clay in a neighbouring coombe, and in a long section 100 yards north of the brick-yard Inferior Oolite comes in upon the Upper-Lias clay. On examining the banks of the Evenlode, north of Charlbury, it was found that clays referred in the Survey map to Lower Lias are really Upper Liassic, being above the Marlstone, sections of which are exposed near Culsham Bridge.

It was shown how these corrections in the mapping of the ground are explained by the section along the line of the Evenlode and by the dips of the beds.

XII. *Intelligence and Miscellaneous Articles.*

EXPERIMENTAL PROOF OF THE LAW THAT BOTH ELECTRICITIES ARE DEVELOPED AT THE SAME TIME AND IN THE SAME QUANTITIES, FOR PYROELECTRICITY. BY E. DORN.

THAT both electricities are produced in equal quantities in all cases of electrical excitation is a principle generally admitted, though the experimental proofs are not numerous.

It appeared to me desirable therefore to prove the above principle for Pyroelectricity, particularly as here an apparently paradoxical case occurs.

If a crystal of tourmaline is warmed at one end and then rapidly passed through the flame, it is first found to be almost entirely unelectrical. As it cools somewhat, considerable disengagements of electricity occur which are occasionally *of the same kind at both ends.*

The above principle requires that the same kind of electricity occur in equal quantity on the lateral faces, or in the interior of the crystal.

A test is furnished by the principle, that a quantity of + electricity in the interior of a shell-shaped conductor would induce − electricity on its inner, and + electricity on its outer side, whatever was the distribution of the original + electricity.

If the tourmaline, after being heated, is brought inside a conducting but insulated hollow body, an electrometer connected with the latter should show no signs of electricity as the crystal cools.

The arrangement of the experiment was as follows:—A brass cylinder, 4 centim. in height and 2 centim. in diameter, was supported on a rod of shellac, and had a lid which could be lifted off by means of an insulating rod of shellac. A third rod of shellac was fixed to the under surface of the lid, and in it was fused a thin brass wire which was wrapped round the tourmaline.

The tourmaline used was of a green colour, very transparent, fractured on both sides, and for a length of 2·05 centim. weighed 1·59 grm.

One pair of quadrants of the electrometer was put to earth. A volt was represented by a deflection of about 2·5 centim. on the scale, at a distance of 130 centim., which was sufficient for the present purpose. It was more important that the insulation of the one pair of quadrants should be good, and that it should not receive a charge from the movable part of the electrometer, or from the air in the room, than that the electrometer should be very sensitive. These conditions were more than sufficiently satisfied. For when electricity was imparted to the insulated pair of quadrants, the deflection only sank in forty minutes from 14·0 to 13·3; and, further, after insulation for three quarters of an hour without charge, there was a deflection of 0·4 centim.

The shellac rod which supported the cylinder also insulated well; for after being connected with the insulated pair of quadrants, the deflection sank in eleven minutes from 32·2 to 30·4.

The capacity of the insulated pair of quadrants was found in several experiments to be about seven times as great as that of the cylinder.

In the experiments the second pair of quadrants, from which a wire passed to the cylinder, was connected with that to earth.

The lid with the crystal was raised, the latter heated in one end of the flame of a Bunsen burner or spirit-lamp, again brought into its place, and the connection with the two pairs of quadrants rapidly broken.

However the heating was arranged, no deflection was ever obtained which exceeded the uncertainty of the instrument, although the quantities of electricity developed were often considerable, and were frequently of the same kind at both ends.

From a long series of experiments I select the following.

When the crystal was heated at one end, and after a minute removed from the cylinder, the proof plane applied to the crystal and then to the insulated pair of quadrants showed negative electricity at both ends, the deflections at the top and bottom being 3·0 and 7·50 centim. respectively.

In another case there was no apparent electricity at one end, while that of the lower sent the image out of the field.

If the duration of heating was somewhat greater, and the crystal remained longer in the cylinder, there was on the top positive, and on the bottom negative, and of such strength that often, on raising the lid with the crystal, the luminous image disappeared from the scale, which is simply explained by the fact that part of the electricity induced on the cylinder is removed with the lid.—Wiedemann's *Annalen*, November 10, 1885.

A NEW FORM OF ABSORPTION-CELL.

BY ARTHUR E. BOSTWICK.

The writer has devised and used the cell described below for the purpose of obtaining the absorption-spectra of liquids which have but little selective absorption, and which would therefore have to be used ordinarily in large quantities.

The cell is a rectangular box about six inches long by three broad and three in height. The bottom and the two ends are of pine wood, covered with shellac, and the two sides are of ordinary looking-glass, cemented to the wood, so that the box is water-tight. The reflecting surface of the looking-glass is turned inward, and at each of two diagonally opposite corners the amalgam is scraped away so as to make a vertical slit about two millimetres in width. One of these is placed close to the spectroscope-slit, and through the other a parallel beam of light is admitted. It is evident that the box may be so placed that the beam will be internally reflected in it a number of times, depending upon the angle between the two, and will finally pass through the second slit into the spectroscope. The length of its path through the cell may therefore be varied indefinitely by turning the latter, and is limited only by the decrease in intensity caused by general absorption—not only in the liquid, but also at each reflection.

A solution of bichromate of potash, so weak that a test-tube full of it was of a barely perceptible yellow colour and showed no absorption at all when held before the spectroscope-slit, when placed in this cell, absorbed the whole upper end of the spectrum, the F line being scarcely visible. In this case sunlight was used, the beam being reflected six times, and having a path whose length inside the cell was about two feet. With mirrors of polished metal the result might be even better, since the absorption in the glass would be eliminated. In this case however the number of liquids which could be used in the cell would be somewhat limited. —Silliman's *American Journal*, December 1885.

ON THE COOLING OF A WIRE WHEN STRETCHED. BY E. DORN.

A steel wire about 0·7 millim. in diameter is clamped at the top, while to the lower end is fixed a scale-pan in which weights can be placed. Round two adjacent places of the principal wire a thin German silver and a steel wire are wound, the ends of which are connected with the galvanometer in such a way that a thermo element (steel-argentan) is formed. When weights are placed in the pan the galvanometer shows a cooling, and a warming when they are removed. With a Wiedemann's galvanometer, which was almost dead-beat, arranged for objective representation, with lamp, lens, and scale, I got a deflection of several centimetres. The places of contact of the heterogeneous metals must be protected from air-currents by means of felt.—Wiedemann's *Annalen*, vol. xxvi. p. 334.

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XIII. *Bars and Wires of varying Elasticity.*

By C. CHREE, *B.A., King's College, Cambridge*[*].

IF m and n denote the elastic constants as used in Thomson and Tait's 'Natural Philosophy,' and no bodily forces act on the mass, then the equations of motion or of equilibrium of an elastic isotropic solid referred to cylindrical coordinates may be written in the form [†]

$$(m+n)r\frac{d\delta}{dr} - n\frac{d\mathfrak{C}}{d\theta} + n\frac{dr\mathfrak{B}}{dz} = \rho r\frac{d^2u}{dt^2}, \quad . \quad . \quad . \quad (1)$$

$$-n\frac{d\mathfrak{A}}{dz} + \frac{m+n}{r}\frac{d\delta}{d\theta} + n\frac{d\mathfrak{C}}{dr} = \rho\frac{d^2v}{dt^2}, \quad . \quad . \quad . \quad . \quad (2)$$

$$-n\frac{dr\mathfrak{B}}{dr} + n\frac{d\mathfrak{A}}{d\theta} + (m+n)r\frac{d\delta}{dz} = \rho r\frac{d^2w}{dt^2}. \quad . \quad . \quad (3)$$

The displacements being as usual denoted by u, v, w, the symbols used above are given by

$$\delta \equiv \frac{du}{dr} + \frac{u}{r} + \frac{1}{r}\frac{dv}{d\theta} + \frac{dw}{dz}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\mathfrak{A} \equiv \frac{1}{r}\frac{dw}{d\theta} - \frac{dv}{dz}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\mathfrak{B} \equiv \frac{du}{dz} - \frac{dw}{dr}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\mathfrak{C} \equiv \frac{1}{r}\frac{d\,.\,vr}{dr} - \frac{1}{r}\frac{du}{d\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

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[*] Communicated by the Author.

[†] *Cf.* Lamé, *Leçons d'Elasticité*, p. 184, noticing change of notation, and of sign in (5), (6), and (7).

In considering the strains, stresses, and surface-conditions we may employ Thomson and Tait's notation and results, looking upon the radius vector through any point as the axis of x at that point. Thus the strains are

$$\left.\begin{aligned} &e=\frac{du}{dr}; \quad f=\frac{u}{r}+\frac{1}{r}\frac{dv}{d\theta}; \quad g=\frac{dw}{dz}; \\ &a=\frac{dv}{dz}+\frac{1}{r}\frac{dw}{d\theta}; \quad b=\frac{dw}{dr}+\frac{du}{dz}; \quad c=r\frac{d\frac{v}{r}}{dr}+\frac{1}{r}\frac{du}{d\theta}. \end{aligned}\right\} \quad (8)$$

These present no difficulty if it be noticed that the axes of x, as above defined, at adjacent points are inclined at an angle $d\theta$.

The corresponding stresses are

$$P=(m-n)\delta+2ne; \quad Q=(m-n)\delta+2nf; \quad R=(m-n)\delta+2ng;$$
$$S=na; \; T=nb; \; U=nc. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

For the surface-conditions, denoting by λ, μ, ν the cosines of the inclination of the normal at the point to the radius vector, to the perpendicular to the radius vector in the cross section, and to the axis of z respectively, we have*

$$\left.\begin{aligned} &\lambda P+\mu U+\nu T=\text{component of surface-force along radius vector}, \\ &\lambda U+\mu Q+\nu S=\text{component perpendicular to above in cross section}, \\ &\lambda T+\mu S+\nu R=\text{component parallel to axis of } z. \end{aligned}\right\} \quad . \; (10)$$

For a right circular cylinder, whose axis is axis of z, we have on the curved surface,

$$\mu=0=\nu, \quad \lambda=1;$$

on the flat end,

$$\lambda=0=\mu, \quad \nu=1.$$

Thus for a right circular cylinder exposed to no surface-forces we must have

$$\left.\begin{aligned} &P=U=T=0 \text{ on the curved surface}, \\ &T=S=R=0 \text{ on the flat ends}. \end{aligned}\right\} \quad . \; (11)$$

Let us consider first the case of a right circular isotropic cylinder, whose axis is taken as axis of z, fixed at the end $z=0$, and exposed to tensions or pressures on its other end symmetrically distributed about the axis. Then obviously $v=0$ throughout, and u and w are independent of θ; thus (2) is identically satisfied, and (1) and (3) much simplified. Supposing these terminal forces independent of the time, the

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* See Thomson and Tait's 'Natural Philosophy,' §§ 662 and 734.

cylinder will remain at rest if originally so. Differentiate (1) with respect to r, and (3) with respect to z; then using the above simplifications we get

$$\frac{d^2\delta}{dr^2}+\frac{1}{r}\frac{d\delta}{dr}+\frac{d^2\delta}{dz^2}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Substituting in (1) the value of $\mathfrak{B}$ from (6), we find

$$r\frac{d^2u}{dz^2}-r\frac{d}{dr}\frac{dw}{dz}=-\frac{m+n}{n}r\frac{d\delta}{dr}.$$

Substituting for $\frac{dw}{dz}$ from (4), this becomes

$$\frac{d^2u}{dr^2}+\frac{1}{r}\frac{du}{dr}-\frac{u}{r^2}+\frac{d^2u}{dz^2}=-\frac{m}{n}\frac{d\delta}{dr}. \quad . \quad . \quad . \quad (13)$$

By a similar method we obtain from (3),

$$\frac{d^2w}{dr^2}+\frac{1}{r}\frac{dw}{dr}+\frac{d^2w}{dz^2}=-\frac{m}{n}\frac{d\delta}{dz}. \quad . \quad . \quad . \quad (14)$$

If A, B, C denote constants, obvious solutions of (12), (13), (14) agreeing with the identity (4) are

$$\left.\begin{aligned}\delta&=2\mathrm{A}+\mathrm{B},\\ u&=\mathrm{A}r,\\ w&=\mathrm{B}z+\mathrm{C}.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Referring to (8) and (9), we see that the corresponding stresses are

$$\left.\begin{aligned}&\mathrm{P}=2m\mathrm{A}+(m-n)\mathrm{B},\\ &\mathrm{R}=2(m-n)\mathrm{A}+(m+n)\mathrm{B},\\ &\mathrm{Q}=\mathrm{S}=\mathrm{T}=\mathrm{U}=0.\end{aligned}\right\} \quad . \quad . \quad . \quad (16)$$

If the cylindrical surface be free from forces, we see from (11) that P is zero, and therefore from (16),

$$\mathrm{A}=-\frac{m-n}{2m}\mathrm{B}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and therefore

$$\mathrm{R}=\frac{n}{m}(3m-n)\mathrm{B}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

If, then, $\frac{n}{m}(3m-n)=\mathrm{M}$, and $\frac{m-n}{2m}=\sigma$, and if F denote the traction, or negative pressure, exerted over the end section of the cylinder per square unit of surface, corresponding to the above solution, we see from (10) that

$$\mathrm{F}=\mathrm{MB},$$

whence

$$B=\frac{F}{M}; \quad A=-\frac{\sigma}{M}F. \quad . \quad . \quad . \quad . \quad . \quad . \qquad 19)$$

Thus this is the solution for a uniform normal tension or pressure. M is Young's modulus, and σ the ratio of lateral contraction to longitudinal expansion.

Suppose, now, that the cylinder consists of successive portions, or layers, of different isotropic materials, all of the same circular cross section when undisturbed, the planes of separation being all perpendicular to the axis of the cylinder. Let one end $z=0$ be fixed, and a uniform tension or pressure be applied over the other.

Then obviously the internal equations of equilibrium for any one layer, whose elastic constants are m and n, are given by (12), (13), and (14), and thus will be satisfied by a solution of the form (15). Also, in order that the cylindrical surface be free from forces, a relation of the form (17) must exist between the A and the B of each layer.

Now suppose that, starting from the fixed end, the suffixes 1, 2, 3, ... i refer to the successive layers, and that z_1, z_2 ... denote the undisturbed distances from that end of the successive surfaces of separation. It is clear that at a surface of separation the values of w and of R, *cf.* (10), for the adjacent layers must be equal. The latter consideration gives

$$M_1B_1=M_2B_2=\ldots,=M_iB_i=F\,; \quad . \quad . \quad . \qquad (20)$$

the former,

$$\left.\begin{array}{r} B_1z_1+C_1=B_2z_1+C_2, \\ B_2z_2+C_2=B_3z_2+C_3, \\ \cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \\ B_{i-1}z_{i-1}+C_{i-1}=B_iz_{i-1}+C_i. \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

Further, if we suppose the initial end of the first layer held, $w_1=0$ when $z=0$, $\therefore C_1=0$. Thus if s denote the suffix of a typical layer, we get

$$B_s=\frac{F}{M_s}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

$$C_s=F\left[z_1\left(\frac{1}{M_1}-\frac{1}{M_2}\right)+z_2\left(\frac{1}{M_2}-\frac{1}{M_3}\right)+\ldots+z_{s-1}\left(\frac{1}{M_{s-1}}-\frac{1}{M_s}\right)\right].$$

Or, if l_1, l_2, ... denote the lengths, when undisturbed, of the successive layers,

$$C_s=F\left[\frac{l_1}{M_1}+\ldots+\frac{l_s}{M_s}-\frac{z_s}{M_s}\right]. \quad . \quad . \quad . \quad . \qquad (23)$$

Thus

$$w_s = \mathrm{F}\left[\frac{l_1}{\mathrm{M}_1}+\dots+\frac{l_s}{\mathrm{M}_s}-\frac{z_s-z}{\mathrm{M}_s}\right]. \quad . \quad . \quad . \quad . \qquad (24)$$

The total extension of the cylinder is thus

$$w = \mathrm{F}\Sigma_{s=1}^{s=i}\left(\frac{l_s}{\mathrm{M}_s}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (25)$$

In any given layer, $\dfrac{-\dfrac{du}{dr}}{\dfrac{dw}{dz}}$ is $= -\dfrac{\mathrm{A}}{\mathrm{B}} = \sigma$, and depends only on the elastic properties of the layer considered.

No assumption has been made as to the thickness of the layers or the law of variation in the elastic properties; thus the previous results will be true when we suppose the layers to become indefinitely thin, and the difference between the elastic constants of consecutive layers to be indefinitely diminished. Proceeding to the limit, we can deduce the solution for a cylinder whose constitution varies gradually from one end to the other, so that the elastic constants are continuous functions of z the distance from the fixed end. Thus, in such a cylinder at a distance z from the fixed end,

$$\left.\begin{aligned} u &= -\frac{\sigma}{\mathrm{M}}\,\mathrm{F}r, \\ w &= \mathrm{F}\int_0^z \frac{dz}{\mathrm{M}}, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (26)$$

where σ and M are supposed to be known functions of z. In the most general case $\frac{1}{\mathrm{M}}$ might be expanded in a series of sines and cosines by Fourier's method, and the above integration effected. If the variation be such that, expanded in a convergent series of ascending powers of z,

$$\frac{1}{\mathrm{M}} = \frac{1}{\mathrm{M}_0}(1+\gamma_1 z+\gamma_2 z^2+\dots). \quad . \quad . \quad . \quad . \quad . \qquad (27)$$

we get

$$w = \frac{\mathrm{F}z}{\mathrm{M}_0}\left\{1+\frac{1}{2}\gamma_1 z+\frac{1}{3}\gamma_2 z^2+\dots\right\} \quad . \quad . \quad . \qquad (28)$$

It is to be remarked that, if a now denote the radius of the cylinder, the increase in radius $-\frac{\sigma}{\mathrm{M}}\mathrm{F}a$ is different for the different materials, or for different sections of the continuously varying material. Since, however, σ is a proper fraction, and

M a very large number in ordinary units (*e.g.* for steel about 21×10^8 C.G.S. units), this will not cause any appreciable variation in radius unless for cylinders of very large cross section. However, in a cylinder of very large cross section formed of layers of widely different materials exposed to a severe tension or pressure, this tendency to a separation at the edges at the junction of successive layers would become noticeable.

We shall next consider the torsion of a right circular cylinder. Considering it first as uniform and isotropic, regard u and w as vanishing, and v as independent of θ. Then, for equilibrium, (1) and (3) are identically satisfied, and (2) becomes

$$\frac{d^2v}{dr^2}+\frac{1}{r}\frac{dv}{dr}-\frac{v}{r^2}+\frac{d^2v}{dz^2}=0, \quad . \quad . \quad . \quad . \quad (29)$$

a solution of which is

$$v=\mathrm{D}r+\mathrm{E}rz, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where D and E are constants.

This contributes no term to δ, and the consequent stresses are

$$\mathrm{T}=0=\mathrm{U}, \text{ and } \mathrm{S}=n\mathrm{E}r.$$

This gives over every cross section the couple

$$\int 2\pi r^2 \mathrm{S} dr=\frac{n\pi \mathrm{E}a^4}{2},$$

denoting by a the radius of the cross section.

Thus if G denote the couple of torsion applied at the one end, the other being held, we get

$$\mathrm{G}=\frac{n\pi \mathrm{E}a^4}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

From (11) we see that the above solution satisfies the conditions over the cylindrical surface.

Suppose, now, the cylinder composed, as before, of a series of layers of different isotropic materials. The internal equations for the equilibrium of each layer will be satisfied by a solution of the form (30). From the equations (10), applied at the surface separating two adjacent materials, we get the value of S the same for both; and supposing the surfaces of these materials not to slip over one another, the values of v must also agree there. Employing the same notation as in the previous case, putting $\mathrm{D}_1=0$, as the one end is supposed fixed, we get

$$n_1\mathrm{E}_1=n_2\mathrm{E}_2=\ldots=\frac{2\mathrm{G}}{\pi a^4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

$$\left.\begin{array}{l} E_1 z_1 = E_2 z_1 + D_2, \\ E_2 z_2 + D_2 = E_3 z_2 + D_3, \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ E \quad z_{i-1} + D_{i-1} = E_i z_{i-1} + D_i, \end{array}\right\} \quad . \quad . \quad (33)$$

where G denotes the couple of torsion about the axis applied at the second end of the cylinder.

We thence get for a typical layer of suffix s,

$$E_s = \frac{2G}{\pi a^4} \frac{1}{n_s},$$

$$D_s = \frac{2G}{\pi a^4} \left\{ \frac{l_1}{n_1} + \ldots + \frac{l_s}{n_s} - \frac{z_s}{n_s} \right\};$$

and the solution,

$$v = \frac{2Gr}{\pi a^4} \left\{ \frac{l_1}{n_1} + \ldots + \frac{l_s}{n_s} - \frac{z_s - z}{n_s} \right\}. \quad . \quad . \quad (34)$$

Thus, at the second end the displacement is

$$v = \frac{2Gr}{\pi a^4} \Sigma_{s=1}^{s=i} \left(\frac{l_s}{n_s} \right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

These results are also obviously true when we pass to the case when the material of the cylinder varies continuously after the fashion already considered; for this case, at a distance z from the fixed end,

$$v = \frac{2Gr}{\pi a^4} \int_0^z \frac{dz}{n}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

while the stress is given by

$$S = \frac{2Gr}{\pi a^4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

The vibrations of an elastic cylinder of the kind whose equilibrium we have already considered may be treated in the same method.

As regards the torsional vibrations, the ordinarily accepted equations are perfectly satisfactory, as they satisfy the surface-conditions without making any assumption as to the cross section of the bar being small compared to the length; thus, in applying them to a bar formed by successive layers, no error can possibly be introduced by regarding the layers as thin. Thus, the results afterwards obtained for the torsional vibrations are more to be relied on than those obtained for the longitudinal, which, however, as being best known, we shall first consider.

For the longitudinal vibrations of a uniform bar, we shall assume the ordinarily accepted equation*

$$\frac{d^2w}{dz^2}=\frac{\rho}{\mathrm{M}}\frac{d^2w}{dt^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

the axis of the bar being taken for axis of z. This equation is obtained on the hypothesis that the cross section is very small compared to the length, though it is generally supposed to apply to bars of moderate cross section. The consequent solution satisfies the conditions over a free or fixed end of the bar, but not those over the cylindrical surface. The results we shall obtain for a bar of two or three materials, each layer being of a length great compared to the diameter of the cross section, are thus just as satisfactory as those ordinarily accepted. We do not think either that, in extending the results to a continuously varying bar, we introduce any appreciable error, as the principle that the lateral displacements are very small compared to the longitudinal at distances from a fixed end, great compared to the diameter of the bar, is not affected. Assuming in (38) $w \propto \cos kt$, we get

$$\frac{d^2w}{dz^2}+\frac{k^2\rho}{\mathrm{M}}w=0\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

whence, if A and B be constants, and α^2 stand for $\frac{k^2\rho}{\mathrm{M}}$, we get

$$w=\cos kt(\mathrm{A}\cos\alpha z+\mathrm{B}\sin\alpha z). \quad . \quad . \quad . \quad (40)$$

If we neglect u, we thus have

$$\frac{du}{dz}+\frac{dw}{dr}=0, \text{ and therefore } \mathrm{T}=0.$$

Thus the only stresses existent in the solid are

$$\mathrm{R}=(m+n)\frac{dw}{dz}=(m+n)\alpha(-\mathrm{A}\sin\alpha z+\mathrm{B}\cos\alpha z)\cos kt, \;. \;(41)$$

$$\mathrm{P}=(m-n)\frac{dw}{dz}=(m-n)\alpha(-\mathrm{A}\sin\alpha z+\mathrm{B}\cos\alpha z)\cos kt. \;. \;(42)$$

The surface-conditions over the cylindrical surface, whether circular or not, would require P to be zero, which, save for the altogether exceptional case $m=n$, it is not in general. This is the defect we referred to above; but it will not modify the following results to a greater extent than those ordinarily accepted for a bar of one material.

At a fixed end of the bar we have $w=0$, at a free $\mathrm{R}=0$ and so $\frac{dw}{dz}=0$; thus the natural periods of vibration of a free-

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* See Lord Rayleigh's 'Sound,' vol. i. § 150, putting M for q.

free bar, of a fixed-free bar, or of a fixed-fixed bar are at once deducible. They are respectively given by the equations $\sin \alpha l=0$, $\cos \alpha l=0$, $\sin \alpha l=0$.

Suppose, now, that the bar consists of two different isotropic elastic solids, the surface of separation being the plane $z=l_1$, and the whole length l_1+l_2. Let the suffix 1 refer to the first material, 2 to the second. Then, from previous remarks on a similar case in the equilibrium problem, it is obvious that for the first material we may take the solution

$$w_1=(\mathrm{A}_1 \cos \alpha_1 z+\mathrm{B}_1 \sin \alpha_1 z) \cos kt,$$

where

$$\alpha_1^2=\frac{k^2\rho_1}{\mathrm{M}_1};$$

and for the second,

$$w_2=(\mathrm{A}_2 \cos \alpha_2 z+\mathrm{B}_2 \sin \alpha_2 z) \cos kt,$$

where

$$\alpha_2^2=\frac{k^2\rho_2}{\mathrm{M}_2};$$

for it is clear that if the bar is not to break up, the two portions must have the same frequency of vibration.

At the surface of separation, the normal to which is $0z$, we must have $w_1=w_2$, and $\mathrm{R}_1=\mathrm{R}_2$, *cf.* (10);

$$\left.\begin{aligned}\therefore\ \mathrm{A}_1 \cos \alpha_1 l_1+\mathrm{B}_1 \sin \alpha_1 l_1&=\mathrm{A}_2 \cos \alpha_2 l_1+\mathrm{B}_2 \sin \alpha_2 l_1,\\ (m_1+n_1)\alpha_1(-\mathrm{A}_1 \sin \alpha_1 l_1+\mathrm{B}_1 \cos\alpha_1 l_1)&=(m_2+n_2)\alpha_2(-\mathrm{A}_2 \sin \alpha_2 l_1\\ &\qquad+\mathrm{B}_2 \cos \alpha_2 l_1);\end{aligned}\right\} \quad (43)$$

whence we get

$$\left.\begin{aligned}\mathrm{A}_2=\mathrm{A}_1&\left\{\cos \alpha_1 l_1 \cos \alpha_2 l_1+\frac{m_1+n_1}{m_2+n_2}\frac{\alpha_1}{\alpha_2}\sin \alpha_1 l_1 \sin \alpha_2 l_1\right\}\\ +\mathrm{B}_1&\left\{\sin \alpha_1 l_1 \cos \alpha_2 l_1-\frac{m_1+n_1}{m_2+n_2}\frac{\alpha_1}{\alpha_2}\cos \alpha_1 l_1 \sin \alpha_2 l_1\right\};\\ \mathrm{B}_2=\mathrm{A}_1&\left\{\cos \alpha_1 l_1 \sin \alpha_2 l_1-\frac{m_1+n_1}{m_2+n_2}\frac{\alpha_1}{\alpha_2}\sin \alpha_1 l_1 \cos \alpha_2 l_1\right\}\\ +\mathrm{B}_1&\left\{\sin \alpha_1 l_1 \sin \alpha_2 l_1+\frac{m_1+n_1}{m_2+n_2}\frac{\alpha_1}{\alpha_2}\cos \alpha_1 l_1 \cos \alpha_2 l_1\right\}.\end{aligned}\right\} \cdot \quad (44)$$

If there are normal forces applied uniformly over the ends, forcing the vibration whose frequency is $\frac{k}{2\pi}$, we can determine A_1 and B_1 by equating R to the applied forces at either end. For the various kinds of free vibration we can eliminate $\mathrm{A}_1 : \mathrm{B}_1$ and get a resulting equation giving the frequency.

Thus, for a free-free bar, $R=0$ when $z=0$ and when $z=l_1+l_2$, $\therefore B_1=0$, and

$$-A_2 \sin \alpha_2(l_1+l_2)+B_2 \cos \alpha_2(l_1+l_2)=0\,;$$

whence, after a simple reduction, we get

$$(m_1+n_1)\alpha_1 \tan(\alpha_1 l_1)+(m_2+n_2)\alpha_2 \tan(\alpha_2 l_2)=0. \quad . \quad (45)$$

For a fixed-free bar, $w=0$ when $z=0$. and $R=0$ when $z=l_1+l_2$, and we get

$$\tan(\alpha_1 l_1)\tan(\alpha_2 l_2)-\frac{m_1+n_1}{m_2+n_2}\,\frac{\alpha_1}{\alpha_2}=0. \quad . \quad . \quad (46)$$

For a fixed-fixed bar, $w=0$ when $z=0$ and when $z=l_1+l_2$, whence we get

$$(m_2+n_2)\alpha_2 \tan(\alpha_1 l_1)+(m_1+n_1)\alpha_1 \tan(\alpha_2 l_2)=0. \quad . \quad (47)$$

Remembering that $\alpha_1=k\sqrt{\frac{\rho_1}{M_1}}$ and $\alpha_2=k\sqrt{\frac{\rho_2}{M_2}}$, we see these are the equations giving the frequency in the three standard forms of longitudinal vibration. Putting $m_1=m_2$ &c., we deduce the ordinary results for a uniform bar.

We would specially remark that from (45) and (47) it follows that the frequency of the corresponding vibrations in the free-free and fixed-fixed conditions are no longer the same; while from (46) it follows that the frequency of the fixed-free vibrations depends on which end is fixed. Thus, if a fixed-free bar be reversed, the pitch is altered. This might prove a delicate test of the uniformity of material in a bar of strictly uniform cross section.

From (46) we see that if $(m_1+n_1)\alpha_1<(m_2+n_2)\alpha_2$, then

$$\cos(\alpha_1 l_1+\alpha_2 l_2)>0, \quad \text{and} \therefore k\left[l_1\sqrt{\frac{\rho_1}{M_1}}+l_2\sqrt{\frac{\rho_2}{M_2}}\right]<\frac{\pi}{2};$$

while if $(m_1+n_1)\alpha_1>(m_2+n_2)\alpha_2$, then

$$k\left[l_1\sqrt{\frac{\rho_1}{M_1}}+l_2\sqrt{\frac{\rho_2}{M_2}}\right]>\frac{\pi}{2}.$$

Thus the arrangement giving the highest pitch consists in fixing that end for which $(m+n)\sqrt{\frac{\rho}{M}}$ is greatest. Thus, if the materials differ only in density, the pitch is highest when the densest material is at the fixed end. Since $M=\frac{n}{m}(3m-n)$, we may infer, as a general rule, that if the two materials have the same density, the highest pitch is obtained when the material which possesses the largest elastic constants, or greatest elasticity, is at the fixed end.

By the same method, we find for the frequency of vibration in three materials forming portions of a bar of lengths l_1, l_2, l_3, writing $(m+n)\alpha = \mathrm{N}$ for shortness,

Free-free,

$$\frac{\mathrm{N}_2}{\mathrm{N}_1}\cot(\alpha_1 l_1)\cot(\alpha_2 l_2) + \frac{\mathrm{N}_2}{\mathrm{N}_3}\cot(\alpha_2 l_2)\cot(\alpha_3 l_3) + \frac{\mathrm{N}_2{}^2}{\mathrm{N}_1\mathrm{N}_3}\cot(\alpha_1 l_1)\cot(\alpha_3 l_3) = 1;$$

Fixed-free,

$$\frac{\mathrm{N}_2}{\mathrm{N}_1}\tan(\alpha_1 l_1)\tan(\ {}_2 l_2) + \frac{\mathrm{N}_3}{\mathrm{N}_1}\tan(\alpha_1 l_1)\tan(\alpha_3 l_3) + \frac{\mathrm{N}_3}{\mathrm{N}_2}\tan(\alpha_2 l_2)\tan(\alpha_3 l_3) = 1; \qquad (48)$$

Fixed-fixed,

$$\frac{\mathrm{N}_1}{\mathrm{N}_2}\cot(\alpha_1 l_1)\cot(\alpha_2 l_2) + \frac{\mathrm{N}_3}{\mathrm{N}_2}\cot(\alpha_2 l_2)\cot(\alpha_3 l_3) + \frac{\mathrm{N}_1\mathrm{N}_3}{\mathrm{N}_2{}^2}\cot(\alpha_1 l_1)\cot(\alpha_3 l_3) = 1.$$

There is no difficulty, except the length of the expressions, in extending the method to four or more materials. The resulting frequency-equations obviously will follow each a law which might be established inductively, so that the form for each of the three types for any number i of materials might be at once written down. Any difficulty would be purely trigonometrical, and in the free-free and fixed-fixed types would be much lessened by the interchangeability of the ends.

The relations (43) or (44) may clearly be regarded as relations between the constants of any two successive materials. They were established independently of any assumption as to the difference in constitution of consecutive layers. We may therefore, remembering our previous hypothesis, regard them as in the limit applicable to a continuously varying material. Thus, writing z for l &c., and putting $\alpha_2 = \alpha_1 + \frac{d\alpha}{dz}dz$ &c., when we proceed to the limit we easily find

$$(m+n)\alpha\frac{d\mathrm{A}}{dz} = \left[-\frac{\mathrm{A}}{2}(1-\cos 2\alpha z) + \frac{\mathrm{B}}{2}\sin 2\alpha z\right]\frac{d\ (m+n}{dz} - \alpha(m+n)\mathrm{B}z\frac{d\alpha}{dz}, \quad . \quad . \quad (49)$$

and

$$(m+n)\alpha\frac{d\mathrm{B}}{dz} = \left[\frac{\mathrm{A}}{2}\sin 2\alpha z + \frac{\mathrm{B}}{2}(1-\cos 2\alpha z)\right]\frac{d\alpha(m+n)}{dz} + \alpha(m+n)\mathrm{A}z\frac{d\alpha}{dz}. \quad . \quad . \quad (50)$$

Combining these two we should get, to determine A or B, a differential equation of the second order. To solve this in all its generality might be a very difficult process; but when the variation in the bar is small, an approximate solution is easily obtained. We should only have to regard A and B as constants when multiplied by $\frac{d\alpha}{dz}$ and $\frac{d\alpha(m+n)}{dz}$, *i.e.* on the right-hand side of the above equations, and $(m+n)\alpha$ as constant on the left-hand side. The variables m, n, &c. being expanded in Fourier's series, there would be only simple integrations to carry out.

As a special and very interesting case, we may suppose the constitution of the bar to vary regularly from one end to the other. Thus, let us assume

$$\left.\begin{aligned} \rho &= \rho_0(1+\sigma' z), \\ m &= m_0(1+pz), \\ n &= n_0(1+qz); \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (51)$$

where ρ_0, m_0, n_0 are the values at the end $z=0$, while σ', p, q are constants so small that terms in $(\sigma' l)^2$ &c. may be neglected.

Thus,

$$\left.\begin{aligned} &\mathrm{M} = \frac{n}{m}(3m-n) = \mathrm{M}_0\left\{1 + z\frac{n_0 p + (3m_0-2n_0)q}{3m_0-n_0}\right\}, \\ &\alpha = k\sqrt{\frac{\rho}{\mathrm{M}}} = \alpha_0\left[1 + \frac{z}{2}\left\{\sigma' - \frac{n_0 p + (3m_0-2n_0)q}{3m_0-n_0}\right\}\right], \\ &\text{and} \\ &(m+n)\alpha = (m_0+n_0)\alpha_0\left[1 + \frac{z}{2}\left\{\sigma' \right.\right. \\ &\qquad\qquad \left.\left. + \frac{p(6m_0^2-3m_0 n_0-n_0^2) - qm_0(3m_0-5n_0)}{(m_0+n_0)(3m_0-n_0)}\right\}\right] \end{aligned}\right\} \quad (52)$$

For shortness write these in the form

$$\left.\begin{aligned} \alpha &= a_0(1+\mathrm{K}z), \\ (m+n)\alpha &= (m_0+n_0)\alpha_0(1+\mathrm{H}z), \end{aligned}\right\} \quad . \quad . \quad . \quad (53)$$

where the values of K and H are those of the last expressions. Employing these values in (49) and (50), with the simplifications obtained by writing A_0 for A &c. in the coefficients of small terms, we get

$$\frac{d\mathrm{A}}{dz} = \frac{\mathrm{H}}{2}\left\{-\mathrm{A}_0(1-\cos 2\alpha_0 z) + \mathrm{B}_0\sin(2\alpha_0 z)\right\} - \mathrm{KB}_0\alpha_0 z.$$

$$\frac{d\mathrm{B}}{dz} = \frac{\mathrm{H}}{2}\left\{\mathrm{A}_0\sin 2\alpha_0 z + \mathrm{B}_0(1-\cos 2\alpha_0 z)\right\} + \mathrm{KA}_0\alpha_0 z.$$

Introducing the proper constants, we find

$$A = A_0 - \frac{H}{2}\left\{ A_0\left(z - \frac{\sin 2\alpha_0 z}{2\alpha_0}\right) - B_0\frac{(1-\cos 2\alpha_0 z)}{2\alpha_0} \right\} - \frac{K}{2}B_0\alpha_0 z^2, \quad . \quad . \quad (54)$$

$$B = B_0 + \frac{H}{2}\left\{ A_0\frac{(1-\cos 2\alpha_0 z)}{2\alpha_0} + B_0\left(z - \frac{\sin 2\alpha_0 z}{2\alpha_0}\right) \right\} + \frac{K}{2}A_0\alpha_0 z^2. \quad . \quad . \quad (55)$$

For a free-free bar, $R=0$ when $z=0$ and when $z=l$; therefore

$$B_0 = 0, \text{ and } -A\sin\alpha l + B\cos\alpha l = 0.$$

Neglecting smaller terms as usual and putting $B_0=0$, the latter equation may be written

$$A\sin\alpha_0 l + A_0 K\alpha_0 l^2\cos\alpha_0 l = B\cos\alpha_0 l.$$

Introducing the above values of A and B, putting $B_0=0$, we get

$$\sin\alpha_0 l\left\{1 - \frac{H}{2}\left(l - \frac{\sin 2\alpha_0 l}{2\alpha_0}\right)\right\} + K\alpha_0 l^2\cos\alpha_0 l$$
$$= \cos\alpha_0 l\left\{\frac{H}{2}\left(\frac{1-\cos 2\alpha_0 l}{2\alpha_0}\right) + \frac{K}{2}\alpha_0 l^2\right\}.$$

Remembering that the terms in H and K are very small, we get as a first approximation,

$$\sin\alpha_0 l = 0, \text{ or } \alpha_0 l = i\pi.$$

As a second approximation, substituting $\frac{i\pi}{l}$ for α_0 in the smaller terms, we get

$$\sin\alpha_0 l + \frac{Kl}{2}i\pi(-1)^i = 0.$$

If we suppose $\alpha_0 l = i\pi - \epsilon$, where ϵ is very small, we thus have

$$\left.\begin{aligned} \epsilon &= i\pi\frac{Kl}{2}; \\ \therefore \alpha_0 &= \frac{1\pi}{l}\left(1 - \frac{Kl}{2}\right), \\ \text{and} \quad k &= \frac{i\pi}{l}\sqrt{\frac{M_0}{\rho_0}}\left(1 - \frac{Kl}{2}\right). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (56)$$

The frequency of the fundamental tone of the bar corresponds to $i=1$, and the overtones to the consecutive integral values of i. Thus, to the present degree of approximation, the overtones of a free-free bar of the kind here considered are strictly harmonics of the fundamental tone.

Referring to (53) for the law of variation of α or of $\sqrt{\frac{\rho}{\mathrm{M}}}$ we see that

$$k=\frac{i\pi}{l}\sqrt{\frac{\mathrm{M}'}{\rho'}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

where M′ and ρ' are the values of these quantities when $z=\frac{l}{2}$, *i. e.* at the middle point of the bar. Thus, the whole series of tones is the same as for a uniform bar whose material is the same as that of the given bar at its central cross section.

If we suppose the material of the bar at the end $z=0$ known, and from this knowledge the pitch calculated, then the real pitch will be higher or lower than the calculated according as K is negative or positive, *i. e.* according as $\frac{n_0p+(3m_0-2n_0)q}{3m_0-n_0}-\sigma'$ is positive or negative.

Thus, if the density increase from that end while the elastic properties remain constant, the calculated pitch is certainly too high. Since m_0-n_0 is positive for any known material, if we suppose p and q to be of one sign, the calculated pitch is too low if the density be uniform, while the elasticity increases from the known end. If the density and elasticity both increase or both diminish from the known end, the result depends on the relative amounts of variation, and also on the relation between p and q. If we suppose $q=p$ (*i. e.* all elastic properties to alter at the same rate and in the same direction), the calculated pitch is too low if $p-\sigma'$ be positive. In this case we may say :—

"If the elasticity and the density of a free-free bar vary both directly with the distance from one end, the tones produced by the bar are harmonics of the fundamental, and the pitch of each is higher or lower than the pitch as calculated from the material at that end according as the ratio of the elasticity to the density increases or decreases."

For a fixed-fixed bar we get, pursuing similar methods, exactly the same result as above in (56) for the free-free bar. Thus the overtones in this case also are harmonics of the fundamental, and are identically the same as those of the free-free bar ; and the results as to the variation of density and elasticity obtained above apply without modification.

For a fixed-free bar,

$$\mathrm{A}_0=0, \text{ and } -\mathrm{A}\sin\alpha l+\mathrm{B}\cos\alpha l=0\,;$$

whence, following the same method as for the free-free bar, we get as a first approximation,

$$\cos \alpha_0 l = 0 \, ;$$

and as a second,

$$\cos \alpha_0 l = \sin \alpha_0 l \left(\frac{\mathrm{H}}{2\alpha_0} + \frac{\mathrm{K}\alpha_0 l^2}{2} \right) ;$$

or, putting $\alpha_0 l = (2i+1)\frac{\pi}{2}$ in the small terms,

$$\alpha_0 l = (2i+1)\frac{\pi}{2} - \eta,$$

where

$$\eta = (2i+1)\frac{\pi}{2}\left\{ \frac{\mathrm{K}l}{2} + \frac{2\mathrm{H}l}{\pi^2(2i+i)^2} \right\} ;$$

$$\therefore k = \frac{(2i+1)\pi}{2l}\sqrt{\frac{\mathrm{M}_0}{\rho_0}}\left\{ 1 - \frac{\mathrm{K}l}{2} - \frac{2\mathrm{H}l}{\pi^2(2i+1)^2} \right\} \quad . \quad . \quad (58)$$

The overtones are thus in this case not strictly harmonics of the fundamental. In the higher overtones this defect becomes very small, but in the lower it is very noticeable. Consequently in a fixed-free bar of the nature here considered the musical character of the note will be decidedly inferior. This fact might prove a good criterion of the isotropic nature of a bar of strictly uniform cross section, especially when taken along with the absence of this defect in the same bar in the free-free or fixed-fixed vibrations. Noticing that, if the suffix l refer to the end $z = l$ of the bar,

$$\alpha_l = \alpha_0(1 + \mathrm{K}l),$$

we find that if the bar be reversed, the equation for the frequency is

$$k = \frac{2i+1}{2l}\pi\sqrt{\frac{\mathrm{M}_0}{\rho_0}}\left\{ 1 - \frac{\mathrm{K}l}{2} + \frac{2\mathrm{H}l}{\pi^2(2i+1)^2} \right\} . \quad . \quad (59)$$

Thus, if the fixed end become the free, the pitch of every tone, especially the lower tones, is altered. This, again, would supply a delicate test of the isotropic nature of the bar. From the value of H we see that, if the elastic properties be constant throughout the bar, the pitch is highest when the densest end is fixed; while if the density be constant, the effect of reversing the bar depends on the values of $p : q$ and of $m_0 : n_0$. Since $m_0 - n_0$ is positive for any substance that can properly be termed an elastic solid, the coefficient of p in H is always positive, and algebraically much greater than that of q, which may be positive or negative. Thus, as a general rule, the pitch will be highest when the most elastic end is fixed. If, however, the rigidity n alone vary, and m_0 be greater than $\frac{5}{3}n_0$ (*i. e.* $\frac{m_0-n_0}{2m_0}>\frac{1}{5}$), the pitch is highest when the least rigid end is fixed. For the special case $q=p$ we have $2\mathrm{H}=\sigma'+p$; this signifies that, to get the highest pitch, we must fix that end for which the product of the elasticity into the density is greatest.

Again, the pitch of the fundamental tone is higher or lower than that calculated from the material at the fixed end according as $\pi^2\mathrm{K}+4\mathrm{H}$ is negative or positive. When $q=p$, it is easily seen that

$$2(\pi^2\mathrm{K}+4\mathrm{H})=\sigma'(\pi^2+4)-p(\pi^2-4)\,;$$

so in this case the calculated pitch is too low or too high according as $p(\pi^2-4)-\sigma'(\pi^2+4)$ is positive or negative.

The torsional vibrations of a right circular isotropic cylinder are obtained by putting $u=0=w$, and assuming v independent of θ. Thus (1) and (3) are identically satisfied, and (2) becomes

$$\frac{d^2v}{dr^2}+\frac{1}{r}\frac{dv}{dr}-\frac{v}{r^2}+\frac{d^2v}{dz^2}=\frac{\rho}{n}\frac{d^2v}{dt^2}. \quad . \quad . \quad . \qquad (60)$$

If we assume $v \propto r$, this becomes

$$\frac{d^2v}{dz^2}=\frac{\rho}{n}\frac{d^2v}{dt^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (61)$$

while the accompanying stresses all vanish except $\mathrm{S}=n\frac{dv}{dz}$. Thus the conditions over the cylindrical surface are identically satisfied, while by taking $\frac{dv}{dz}=0$ over a free terminal section we leave no stresses there. In this case, then, the conditions in the interior and at the surface may be simultaneously satisfied, and the theory of the vibrations so deduced is perfectly satisfactory.

If we suppose n substituted for M, the internal equations for the torsional vibrations are identical with those we assumed for the longitudinal, while the conditions at a fixed or a free end are exactly the same, interchanging v and w. Again, at a surface $z=l$, separating two different materials, the surface-conditions are $v_1=v_2$ and $n_1\frac{dv_1}{dz}=n_2\frac{dv_2}{dz}$. Thus the methods to be employed in the corresponding cases are identical; while the occurrence of only one elastic constant n, the rigidity, simplifies the case of the torsional vibrations. We shall therefore merely state the results for the several problems analogous to those of the longitudinal vibrations.

Let $\beta^2=\frac{k^2\rho}{n}$; then for the vibration-frequency $\frac{k}{2\pi}$ in the following cases we have

Bar of two materials.

$$\left.\begin{array}{l}\text{Free-free,}\\ \qquad n_1\beta_1\tan(\beta_1 l_1)+n_2\beta_2\tan(\beta_2 l_2)=0;\\ \text{Fixed-free,}\\ \qquad \tan(\beta_1 l_1)\tan(\beta_2 l_2)-\frac{n_1\beta_1}{n_2\beta_2}=0;\\ \text{Fixed-fixed,}\\ \qquad n_2\beta_2\tan(\beta_1 l_1)+n_1\beta_1\tan(\beta_2 l_2)=0.\end{array}\right\}\quad . \quad . \quad . \quad (62)$$

Bar of three materials.

$$\left.\begin{array}{l}\text{Free-free,}\\ \frac{n_2\beta_2}{n_1\beta_1}\cot(\beta_1 l_1)\cot(\beta_2 l_2)+\frac{n_2\beta_2}{n_3\beta_3}\cot(\beta_2 l_2)\cot\beta_3 l_3)\\ \qquad\qquad +\frac{(n_2\beta_2)^2}{n_1 n_3\beta_1\beta_3}\cot(\beta_1 l_1)\cot(\beta_3 l_3)=1;\\ \text{Fixed-free,}\\ \frac{n_2\beta_2}{n_1\beta_1}\tan(\beta_1 l_1)\tan(\beta_2 l_2)+\frac{n_3\beta_3}{n_1\beta_1}\tan(\beta_1 l_1)\tan(\beta_3 l_3)\\ \qquad\qquad +\frac{n_3\beta_3}{n_2\beta_2}\tan(\beta_2 l_2)\tan(\beta_3 l_3)=1;\\ \text{Fixed-fixed,}\\ \frac{n_1\beta_1}{n_2\beta_2}\cot(\beta_1 l_1)\cot(\beta_2 l_2)+\frac{n_3\beta_3}{n_2\beta_2}\cot(\beta_2 l_2)\cot(\beta_3 l_3)\\ \qquad\qquad +\frac{n_1 n_3\beta_1\beta_3}{(n_2\beta_2)^2}\cot(\beta_1 l_1)\cot(\beta_3 l_3)=1.\end{array}\right\}\quad (63)$$

Bar varying continuously but slowly after the law

$$\rho=\rho_0(1+\sigma' z),\quad n=n_0(1+qz),$$

where terms of order $(\sigma' l)^2$, $(ql)^2$ may be neglected.

[Here we have merely to write $\sigma'+q$ for 2H and $\sigma'-q$ for 2K in the corresponding previous problems.]

Free-free,

$$k=\frac{i\pi}{l}\sqrt{\frac{n_0}{\rho_0}}\left(1-\frac{\sigma'-q}{4}\,l\right);\quad . \quad . \quad . \quad . \quad . \quad (64)$$

Fixed-free,

$$k=\frac{2i+1}{2l}\,\pi\sqrt{\frac{n_0}{\rho_0}}\left\{1-\frac{\sigma'-q}{4}\,l-\frac{(\sigma'+q)l}{\pi^2(2i+1)^2}\right\}. \quad (65)$$

Fixed-fixed, same as fixed-free.

Thus in the fixed-fixed and free-free bars the overtones are harmonics of the fundamental, and the frequency is the same as for a uniform bar whose material is identical with that at the central cross section of the bar. In both cases the pitch is higher or lower than that calculated from the material at one end, according as the ratio of the rigidity to the density increases or diminishes with the distance from that end.

In the fixed-free bar the overtones are not in general harmonics of the fundamental, though the defect becomes very small in the higher overtones. The actual pitch of any tone is higher or lower than that calculated from the material at the fixed end, according as

$$q\{\pi^2(2i+1)^2-4\}-\sigma'\{\pi^2(2i+1)^2+4\}$$

is positive or negative, i denoting the number of the overtone. Thus the pitch is always higher if the density diminish and the rigidity do not decrease; it is always lower if the rigidity diminish and the density do not also diminish. If both density and rigidity increase, the pitch is higher or lower than the calculated, according as the proportional variation in rigidity to that in density is greater or less than $\dfrac{\pi^2(2i+1)^2+4}{\pi^2(2i+1)^2-4}$; the reverse being the case if both diminish. For the fundamental tone the determining ratio is $\dfrac{\pi^2+4}{\pi^2-4}$.

If the bar were reversed,

$$k=\frac{2i+1}{2l}\pi\sqrt{\frac{n_0}{\rho_0}}\left\{1-\frac{\sigma'-q}{4}l+\frac{(\sigma'+q)l}{\pi^2(2i+1)^2}\right\}; \quad . \ (66)$$

so the pitch is altered by reversion.

To get the highest pitch, fix the end for whose material the product of the density into the rigidity is the greater.

There are several practical applications which might be made of the preceding results. Several of these have been suggested in passing, so we shall only briefly consider them. It is obvious that from (25) and (35) we can deduce the mean values of Young's modulus, and of the rigidity between the fixed end and any determinate cross section of a wire by observing the displacements w or v at that cross section. This may be done at a whole series of cross sections, while the wire is subjected to the same forces of tension or of torsion throughout its entire length, applied as in the ordinary experiments. We should thus be able to determine the law of variation of the modulus of elasticity, or of the rigidity to any required degree of accuracy throughout a considerable length of one and the same wire. The results might be employed to determine the degree of uniformity in the structure of the wire, or they might be used to determine the effect on the elastic properties of certain modifications in the nature of the wire. Thus one definite length of the wire might be heated to any required temperature, while adjacent portions were by cold water or ice kept at a low temperature, then (24) or (34) would indicate the effect either on the modulus of elasticity or on the rigidity, allowance being made for direct expansion by heat. So, again, observations made after part of a wire exposed for some time to a definite high temperature had cooled, would indicate the consequent modification of the elastic structure. Or, again, an electric current might be run through a definite portion of the wire, while the rest was exposed to no such influence, any heating-effect being avoided by surrounding the whole wire with cold water if necessary. By clamping the wire at different points, select portions might be subjected to severe strain, while the rest was free from strain; then removing this strain and observing the values of w or v at different points in the wire, now exposed to one and the same force of tension or torsion, the modification by strain of the elastic properties might be deduced. Other applications will suggest themselves.

The advantage of this method is that in every case the same wire is dealt with and the uniformity of its original structure may previously have been tested. Further, there is no comparison of results deduced from experiments in which any variation of the mode of application of the forces of tension or of torsion may have occurred. In two sets of experiments, even with the same wire, there is always risk of error through variation in the suddenness with which the stresses are applied. Again, if, as usual, the whole of the wire experimented on has been subjected to certain modifications, it can seldom, if ever, be restored exactly to its original condition, so that one experimental comparison cannot be repeated with accuracy, and in considering the effect of other physical changes a continually increasing modification in structure is introduced; whereas in the single wire locally and definitely modified, a comparison may be instituted between any given portion and an unmodified portion subjected to the same stress, neglecting or allowing for the weight of the intermediate portion in the case of tension. In many cases also it would be much easier to modify only a comparatively short portion of a long wire; and from the preceding results the difference between the observations made, on a given length of the wire, before and after the modification, would accurately disclose the change of state in the small modified portion.

The results obtained from the consideration of the torsional vibrations are applicable to circular bars of any cross section, but those from the longitudinal only to bars of small cross section. From a separate consideration of the torsional and longitudinal fixed-free vibrations, of a thin circular bar, a discrimination might be made between the effects on the modulus of elasticity and on the rigidity due to definite physical changes.

By heating up the bar at one end, making that the fixed or free end, and employing (58) and (59) or (65) and (66), considerable insight might be gained into the structure. Then allowing the bar to cool and repeating similar observations, the residual effect after any interval might be determined. As to the advantages of determining modification of physical properties by observations on a single bar, remarks similar to those already made will apply.

By the test of reversion we can also select for our experiments a bar originally of great isotropy.

XIV. *The Winding of Voltmeters.* *By* Professors W. E. Ayrton, *F.R.S.*, *and* John Perry, *F.R.S.*[*]

I. THE use of voltmeters for measuring the potential-difference existing between the mains in electric light circuits, and for enabling us to maintain this potential-difference constant, is so wide in its possible application, that it is unnecessary to dwell on the importance of voltmeters giving accurate indications. Indeed, the sensibility of an incandescent lamp is so great (the light, as we have shown in a previous communication to this Society[†], being in many cases proportional to the cube of the potential-difference minus a constant), that it is necessary that voltmeters should record with great accuracy the potential-difference, as well as quickly indicate any changes that from time to time take place in this potential-difference.

It is therefore desirable to consider what are the most important errors in commercial voltmeters as at present constructed, and how these errors may be practically diminished or altogether removed. They are:—

1. An error arising from the sensibility of the voltmeter varying with its resistance, and therefore with its temperature. This change of temperature is due partly to the variation of the temperature of the room and partly to the coils of the

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[*] Communicated by the Physical Society: read June 13, 1885.

[†] "The most Economical Potential-Difference to employ with Incandescent Lamps," Proc. Phys. Soc. vol. vii. p. 40 [Phil. Mag. [5] vol. xix. p. 304 (April 1885)].

instrument becoming heated by the passage of the current through them.

2. An error arising from the sensibility of the instrument being temporarily varied by external magnetic disturbance.
3. An error arising from certain types of voltmeters altering in sensibility so that their constants vary from time to time.
4. An error arising from the volt standards employed by different makers of voltmeters differing several per cent. from one another.

The variation in the resistance of a voltmeter produced by changes of temperature of the room can of course be made very small by winding the instrument with German-silver wire, or better with platinum-silver, or, best of all, with wire made of platenoid, or it may be made absolutely nought by use of an outside resistance of carbon; or, lastly, if the voltmeter be simply wound with copper wire, this error, although large, can be accurately allowed for if the temperature of the voltmeter be known. But the error arising from the heating of the voltmeter by the passage of the current through it is much more difficult to allow for, as this rise of temperature of the instrument will be unknown. Hence it is important to reduce this error to a minimum, and it does not at all follow that the employment of German-silver wire or even platenoid wire will effect this result; indeed we have already given, in a previous communication made to this Society*, general reasons showing that German silver is undesirable to be used in the winding of voltmeters. When, however, the diameter of the coil of the instrument exceeds a certain limit, it would appear that German-silver wire might be better for the outer coils: hence the following investigation has been made for the purpose of ascertaining whether in an instrument of the size of our Solenoid, or Long-Range Voltmeter, any portion of the coil should be wound with German-silver wire, and if so, how large a portion, also what should be the law of variation of sectional area of the copper and German-silver wire with the diameter of the convolution in which it is wound, so that the heating-error produced by the passage of the current through the voltmeter shall be a minimum.

Although the dimensions of the instrument adopted in the following investigation are those of this special form of voltmeter, the mode of considering the problem will apply equally well to any other galvanometer used as a voltmeter, or to the

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* "Direct-reading Electro-Measuring Instruments, and a Non-Sparking Key," Proc. Phys. Soc. vol. vi. p. 69 [Phil. Mag. [5] vol. xvii. p. 304 (April 1884)].

fine wire coil of an Ohm-meter, Powermeter, and Ergmeter, or indeed in any case where it is desired to produce a given magnetic effect with a minimum error due to heating. It is only necessary to consider the case of a cylindrical coil of internal radius r_0 and external r_1 and length l, as it is easy to extend our reasoning to a coil of any other shape and dimensions.

II. At a place in the coil at a distance r from the axis let the cross section of the wire be x, let ρ be the specific resistance of the material, and γ the rate at which ρ increases with temperature; x, ρ, and γ being functions of r. For simplicity of calculation we shall neglect the volume of the insulating material. Let one spire of radius r produce a magnetic effect of the amount

$$\mathrm{KC}r^d, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

C being the current, and d having in almost all instruments a value which lies between the limits -1 and 0. Also let

$$x = x_0 r^a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\rho = \rho_0 r^b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\rho\gamma = \rho_0 \gamma_0 r^c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In a layer of wire of thickness δr there are $\frac{l\,\delta r}{x}$ spires of wire, and the resistance of the layer is

$$\frac{2\pi r \rho l}{x^2}\delta r, \quad \text{or} \quad \frac{2\pi r \rho_0 r^b l}{x_0^2 r^{2a}}\delta r, \quad \text{or} \quad \frac{2\pi \rho_0 l r^{1+b-2a}}{x_0^2}\delta r;$$

so that the whole resistance of the coil is evidently

$$\mathrm{R} = \frac{2\pi\rho_0 l}{m x_0^2}\left(r_1^{\,m} - r_0^{\,m}\right) \text{ if } m = 2 + b - 2a. \quad . \quad . \quad (5)$$

The magnetic effect of the spires in the thickness δr is

$$\mathrm{KC}r^d l\frac{\delta r}{x} \quad \text{or} \quad \frac{\mathrm{KC}l}{x_0} r^{d-a}\delta r,$$

so that the whole magnetic effect of the coil is

$$\mathrm{M} = \frac{\mathrm{KC}l}{x_0 n}\left(r_1^{\,n} - r_0^{\,n}\right) \text{ if } n = d - a + 1. \quad . \quad . \quad (6)$$

We shall now assume that we can, by introducing thin strips of copper among the windings, give the same ease of cooling to unit volume of the wire everywhere; that is, after the current has flowed for some time, that the increase of temperature at any point is proportional to the rate at which current heat is produced per unit volume. Now

$$\mathrm{C}^2\frac{2\pi\rho_0}{x_0^2} r^{1+b-2a}\, l\delta r \quad \text{or } \mathrm{C}^2\,\frac{\rho_0}{x_0^2} r^{b-2a}\,.\,2\pi r l \delta r$$

is the rate at which heat is produced in a layer of thickness δr.

This rate is $\frac{\rho_0}{x_0^2} r^{b-2a}$ times the volume of the layer. Therefore the rate at which heat is produced *per unit volume* is $C^2 \frac{\rho_0}{x_0^2} r^{b-2a}$: therefore, by hypothesis, the increase of temperature is proportional to $C^2 \frac{\rho_0}{x_0^2} r^{b-2a}$.

The increase of resistance of this layer is the resistance of the layer multiplied by γ times the increase of temperature, and is therefore proportional to

$$\frac{2\pi\rho_0 l r^{1+b-2a}}{x_0^2}\,\delta r\,.\,\gamma\,.\,\frac{C^2\rho_0}{x_0^2}\,r^{b-2a},$$

or to

$$\gamma\frac{C^2\rho_0^2}{x_0^4}\,r^{1+2b-4a},$$

where $\gamma=\gamma_0 r^{c-b}$, and the whole increase of resistance is proportional to

$$\int_{r_0}^{r_1}\gamma_0 C^2\,\frac{\rho_0^2}{x_0^4}\,r^{1+b+c-4a}\,dr,$$

or

$$\gamma_0\,\frac{C^2\rho_0^2}{p x_0^4}\,(r_1^p-r_0^p),\text{ if } p=2+b-4a+c; \quad . \quad . \quad (7)$$

so that the fractional change of resistance is proportional to

$$\frac{\gamma_0 C^2\rho_0^2}{R x_0^4 p}\,(r_1^p-r_0^p). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Now regarding M as constant, and substituting for C and R from (6) (5) and (8) we observe that the fractional change of resistance due to heating is proportional to

$$\gamma_0\rho_0\cdot\frac{n^2}{(r_1^n-r_0^n)^2}\cdot\frac{m}{r_1^m-r_0^m}\cdot\frac{r_1^p-r_0^p}{p} \quad . \quad . \quad . \quad (9)$$

and it is required to find the values of a, b, and c for which this expression is a minimum.

III. It may be seen that the error (9) is less as $\gamma_0\rho_0$ becomes less, therefore $\gamma_0\rho_0$ should be made as small as possible so that *when wires of two metals, as for example copper and German silver, are employed, the wire for which $\gamma\rho$ has the least value, that is the copper, should be used for the inner winding.* It is, however, when we consider the waste of electric energy in the coil, that the great objection to the use of German silver for the internal winding becomes still more striking. For the rate of production of heat in the coil is proportional to C^2R, which, from (6) and (5), equals

$$\frac{x_0^2 n^2 M^2}{K^2 l^2 (r_1{}^n - r_0{}^n)} \times \frac{2\pi\rho_0 l}{m x_0} (r_1{}^m - r_0{}^m).$$

Hence to produce the same magnetic effect M in a coil of given length l, the rate of production of heat is proportional to

$$\frac{n^2}{(r_1{}^n - r_0{}^n)^2} \times \frac{r_1{}^m - r_0{}^m}{m} \rho_0. \quad . \quad . \quad . \quad . \quad (10)$$

Consequently when a given angular deflection is produced, the rate of wasting electrical energy in heat will be thirteen times as great if German-silver wire be used as it will be if copper is used, no matter what be the gauge of wire employed, that is, whether the voltmeter be wound to measure a maximum potential-difference of 50 or of 500 volts.

Eliminating r from (3) and (4) it follows that

$$\left(\frac{\gamma\rho}{\gamma_0\rho_0}\right)^{\frac{1}{c}} = \left(\frac{\rho}{\rho_0}\right)^{\frac{1}{b}}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where b may have any arbitrary value. Hence if there is a regular change possible in the value of $\gamma\rho$ such as given in (4), we must have

$$c = Pb,$$

where P is some constant. Equation (11), therefore, becomes

$$\frac{\gamma\rho}{\gamma_0\rho_0} = \left(\frac{\rho}{\rho_0}\right)^P. \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

If, therefore, our wire in the inside of the coil is of copper and on the outside of German silver,

$$\gamma\rho = \frac{13}{9} \gamma_0\rho_0,$$

or

$$\rho = 13 \rho_0.$$

Hence from (11)

$$\frac{13}{9} = 13^P,$$

or

$$P = 0{\cdot}143,$$

and

$$c = 0{\cdot}143 \, b. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

It is certain that generally the relationship between γ and

ρ cannot be of the simple character here assumed; but inasmuch as our results are only applied in cases where the windings are either of German silver or of copper, or of the two together, and in these cases the expressions used are quite correct, there is no practical objection to the use of such a law. The law is very nearly the same as the assumption that a wire of any material, lying electrically between German silver and copper, is made up of wires of German silver and copper.

Since from (7),

$$p=2+b-4a+c,$$

it follows, using (13), that

$$p=2+1{\cdot}143b-4a, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and the values of m and n are given respectively in terms of a, b, and d in (5) and (6), and are

$$m=2+b-2a \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$n=d-a+1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

In our Solenoid Voltmeter, r_0 equals 1, r_1 equals 8, and d equals -1; and since the greatest value of ρ is $13\rho_0$, it follows that r^b cannot be greater than 13, but b is a constant, and the greatest value of r is 8, therefore b must be less than 2. From (14), since b is always small, we see, after a has reached a certain large value, that p, m, and n increase numerically as a increases, and are positive when a is negative, and *vice versa*; also that, finally, p equals $2m$ or $4n$.

Substituting the values for r_0 and r_1, the error (9) may be written

$$\frac{\gamma_0\rho_0\left(\frac{n}{8^n-1}\right)^2\left(\frac{m}{8^m-1}\right)}{\frac{p}{8^p-1}},$$

and it may be seen by inspection that each of the factors of which it is composed is always positive, whether m, n, and p be positive or negative. Therefore the error is always positive. For large values of m, n, and p, the error may be written

$$\frac{\left(\frac{n}{8^n-1}\right)\left(\frac{2n}{8^{2n}-1}\right)}{\frac{4n}{8^{4n}-1}},$$

which equals

$$\frac{\left(\frac{n}{8^n-1}\right)^2}{\frac{2}{8^{2n}+1}},$$

or

$$\frac{n^2({}^{2n}+1)}{8^{2n}+1-2\times 8^n}.$$

This expression is always greater than n^2 whether n be positive or negative, and is therefore very great since n is great. Consequently for large positive or negative values of m, n, and p, the error (9) becomes very great, and therefore it can have no maximum. The values of a and b, therefore, found from equating to nought its differential coefficients with respect to a and to b, will give a minimum value of this error. And the error will be a minimum when its logarithm is a minimum. Now taking its logarithm, putting r_0 equal to 1, and r_1 equal to 8, differentiating with regard to a and b respectively, and equating to zero, we arrive at the equations

$$\phi(n)-0{\cdot}857\,\phi(p)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\phi(m)-1{\cdot}143\phi(p)=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where

$$\phi(\alpha)=\frac{\log_e 8}{1-8^{-\alpha}}-\frac{1}{\alpha}. \quad . \quad . \quad . \quad (17)$$

To assist in the solution of these simultaneous equations we calculated the following Table :—

TABLE I.

a.	$\phi(a)$.
− 3	0·3293
− 2	0·4670
− 1	0·7029
0	1·0397
1	1·3764
2	1·6124
3	1·7502
4·5	1·8474
10	1·9794
100	2·0694

And in order to solve these equations we used the following artifice:—A curve was first plotted on squared paper with $\phi(a)$

as ordinate and a as abscissa, and by means of this curve for any value of $\phi(a)$ given we could at once find a approximately.

Table II. was then arrived at in the following way:—A value of p was chosen, and $\phi(p)$ written down. Then since $0·857\,\phi(p)$ is equal to $\phi(n)$ by (15), n was known from this by the curve for $\phi(a)$; m was next found in the same way from (16). Thus columns 1 and 4 in Table II. contain values of p and n which satisfy (15), and which were obtained in this way, while in columns 1 and 6 we have values of p and m which satisfy (16).

Table II.

p.	$\phi(p)$.	$0·857\,\phi(p)$, or $\phi(n)$.	n.	$1·143\,\phi(p)$, or $\phi(m)$.	m.
2	1·6124	1·381	1·03	1·842	4·35
1	1·3764	1·18	0·39	1·572	1·78
0	1·0397	0·8913	−0·425	1·189	0·425
−1	0·70295	0·6026	−1·370	0·8035	−0·69
−2	0·467	0·4002	−2·38	0·5337	−1·69

Now first using the pair of columns 1 and 4, we chose corresponding values of p and n, say 2 and 1·03; then, since from (14)

$$2 = 2 + 1·143b - 4a,$$

and

$$1·03 = d - a + 1,$$

we could calculate a pair of values for a and b which satisfy (14) and (15), since d was assumed to be known. Next taking another pair of values of p and n from Table II., another pair of values of a and b was calculated, and so on. Plotting these values of a and b as coordinates of points on squared paper we obtained the curve $s\,s\,s$, fig. 1 *, the coordinates of every point of which are the values of a and b that satisfy (15). In the same way we drew the curve $t\,t\,t$ for (16), and the coordinates of the point of intersection Z are the values of a and b which satisfy (15) and (16), and therefore make the error (9) a minimum.

Thus for example, taking $d = -1$, as seems to be the case in our solenoid instrument, we find that, with some approximation to accuracy,

$$a = 0·19 \text{ and } b = -0·82$$

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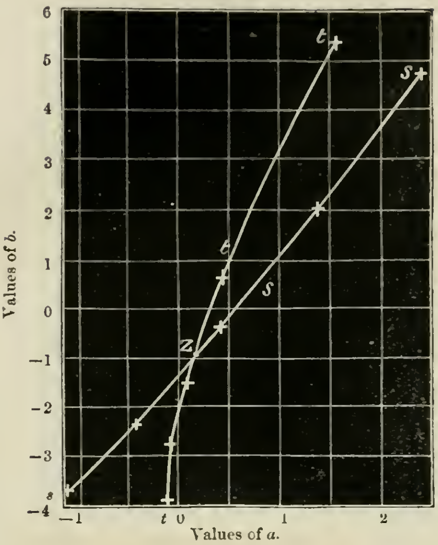
* This and the two succeeding figures are only about one twelfth of the size each way of the figures actually employed in the calculations.

Fig. 1.



for minimum error. But if we have used our material of least resistance for the inner winding, b cannot in practice be less than 0, for ρ cannot be less than ρ_0, and since r is never less than 1, ρ would be some fraction of ρ_0 if b were less than 0. Hence in practice we find that b must equal 0, that is, *a less heating-error is produced when all the wire is of copper than when we use German-silver windings on the outside of the coil.*

IV. Making b equal to nought as the least value of b attainable, we can now find the value of a to make the error a minimum. To do this we must put b equal to nought, take d equal to -1 in (9), differentiate with respect to a, and equate the result to 0.

Thus

$$\phi(m)+\phi(n)-2\phi(p)=0, \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where $\phi(a)$ has the signification given to it in (17).

Since $b=0$

and $d=-1,$

it follows from (14) that

$$\left.\begin{aligned} m&=2-2a \\ n&=-a \\ p&=2-4a, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

therefore, from (17)

$$\phi(2-2a)+\phi(-a)-2\phi(2-4a)=0.$$

This equation cannot be solved generally, but by giving various values to a we can find which of these values makes the expression on the left-hand side most nearly equal to nought, and to ascertain the value of the function for each of the values of a we can conveniently use the curve connecting $\phi(\alpha)$ and α previously employed.

For $a=0{\cdot}5$ we have

$$\begin{aligned}\phi(1)+\phi(-0{\cdot}5)-2\phi(0)&=1{\cdot}375+0{\cdot}865-2\times1{\cdot}04\\&=+0{\cdot}16\,;\end{aligned}$$

for $a=0{\cdot}4$ we have

$$\begin{aligned}\phi(1{\cdot}2)+\phi(-0{\cdot}4)-2\phi(0{\cdot}4)&=1{\cdot}43+0{\cdot}9-2\times1{\cdot}182\\&=-0{\cdot}034\,;\end{aligned}$$

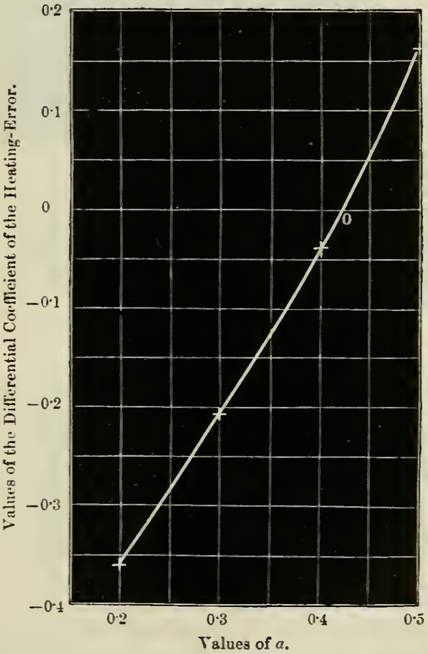
for $a=0{\cdot}3$ we have

$$\begin{aligned}\phi(1{\cdot}4)+\phi(-0{\cdot}3)-2\phi(0{\cdot}8)&=1{\cdot}48+0{\cdot}936-2\times1{\cdot}311\\&=-0{\cdot}206\,;\end{aligned}$$

for $a=0{\cdot}2$ we have

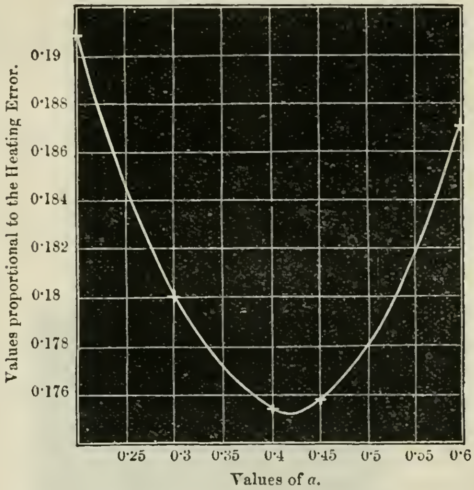
$$\begin{aligned}\phi(1{\cdot}6)+\phi(-0{\cdot}2)-2\phi(1{\cdot}2)&=1{\cdot}53+0{\cdot}97-2\times1{\cdot}43\\&=-0{\cdot}36.\end{aligned}$$

Fig. 2.



Plotting these points, we find (fig. 2) that the curve for the differential coefficient cuts the axis along which a is measured at a point 0, for which a has the value 0·42; or, in other words, a *equal to* 0·42 *makes the differential coefficient equal to nought, and hence is the value of* a *that makes the heating-error a minimum.* As a check on this we have drawn the curve for the values of the heating-error for different values of a (fig. 3), and from this also it is seen that the heating-error has a minimum when a equals 0·42. Hence it follows that the law of increase of the sectional area of the wire with the radius of the convolutions should in our Solenoid Voltmeter follow the law

Fig. 3.



$$x = x_0 r^{0\cdot42},$$

in order that the error due to heating may be a minimum.

Fig. 3 not only gives the value of a that makes the heating-error a minimum, but it shows by how much the heating-error is increased if a has a value greater or less than 0·42. For example, if a equals 0, that is to say if the voltmeter be all wound with wire of the same gauge, then, continuing the curve backwards, we find that the heating-error is increased by about one third.

V. One plan of diminishing the heating-error with voltmeters, and one that we have frequently employed, is to place in the same circuit with the instrument a coil wound with

German-silver wire, and having a resistance far greater than that of the voltmeter itself. By using wire of large gauge, wound on a bobbin of large volume, and with as efficient an arrangement for cooling as can be conveniently employed, the heating-error can be rendered extremely small. Such a bobbin, however, is both costly and bulky, and the employment of such an outside resistance-coil wastes energy, and can only be used with voltmeters in electric light and power installations where such a waste of energy is unimportant. The following investigation has therefore been made for the purpose of determining what must be the volume of this outside resistance-coil, and what must be its resistance relatively to that of the voltmeter-coil, so that the heating-error may not exceed any given value.

Let R be the resistance of the coil of copper wire wound on a voltmeter, let H be the rate of production of heat when the maximum deflection is obtained ; then, as already shown, H will be constant for a voltmeter of a given size wound according to a definite law, whether it be wound with fine wire for a 500-volt instrument or with thicker wire for a 50-volt one. Let C be the current passing round it when this maximum deflection is being produced ; then

$$C^2R = H, \text{ a constant.}$$

Let the increase of resistance produced by the passage of the current for some time be r; then $\frac{r}{R}$ is proportional to the product of γ, the coefficient of increase of the resistance of copper per degree of temperature, into H, since, as already explained, the voltmeter is so wound that the rate of production of heat is proportional to the increase of temperature. Hence

$$\frac{R}{r} = \text{a constant, A say.}$$

Now let there be a resistance-coil of German-silver wire of uniform cross section, of volume V in series with the instrument, and let us suppose that for any coils thus added the rise of temperature is proportional to the energy wasted per second per unit volume, that is to say proportional to the rate of production of heat per unit volume.

Let R_1 be the resistance of this added coil, then $\frac{C^2R_1}{V}$ is proportional to its rise of temperature ; hence, if r_1 be the increase of resistance and γ_1 the coefficient of increase of resistance of German silver per degree,

$$\frac{r_1}{R_1} \propto \gamma_1 \frac{C^2R_1}{V},$$

or

$$r_1 = B\frac{C^2R_1^2}{V} \text{ say,}$$

where B is a constant. Hence, if e is the error due to the proportional change of resistance,

$$e = \frac{r + r_1}{R + R_1},$$

$$= \frac{AR + \frac{BC^2R_2}{V}}{R + R_1}.$$

Let

$$\frac{R_1}{R} = y,$$

then

$$e = \frac{A + \frac{B}{V}{}^2 y}{1 + y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

To determine the value of the constants A and B we may proceed as follows :—Wind a voltmeter according to the law which is to be adopted with any or no resistance-coil outside; find the potential-differences P_1 and P_2 required to produce the maximum reading of the instrument,

1st, immediately on making connection;

2nd, after connection has been made for some time; then

$$e = \frac{P_2 - P_1}{P_1}.$$

Let e be experimentally determined in two cases,—one where there is no resistance-coil outside, and the other where there is such an auxiliary resistance-coil, obtaining values e_1 and e_2 respectively. Measure y, that is the ratio of R_1 to R, and also V. Then from the equations

$$e_1 = A,$$

$$e_2 = \frac{A + \frac{B}{V}y^2}{1 + y},$$

the values of the constants A and B can be determined; and when determined, the error arising with the employment of an outside resistance-coil of any resistance and of any volume can be calculated from (20).

It is obvious that as V becomes greater the error becomes less and less, but there is a practical inconvenience in largely adding to the weight of the instrument.

VI. *To determine the best resistance to give to the outside coil of given volume.*—When V is fixed, e is a maximum or minimum, when

$$\frac{de}{dy}=0.$$

Now

$$\frac{de}{dy}=\frac{\frac{B}{V}y^2+2\frac{B}{V}y-A}{(1+y)^2},$$

and

$$\frac{d^2e}{dy^2}=\frac{2\left(\frac{B}{V}+A\right)}{(1+y)^3},$$

y must be positive, therefore $(1+y)^3$ is positive, also A and B are both positive, therefore $\frac{d^2e}{dy^2}$ is positive, and therefore e is a minimum, when

$$\frac{de}{dy}=0,$$

that is, when

$$\frac{B}{V}y^2+2\frac{B}{V}y-A=0,$$

or

$$y=-1\pm\sqrt{1+\frac{AV}{B}}\;;$$

but y cannot be negative, therefore only the positive sign can be used, or

$$y=\sqrt{1+\frac{AV}{B}}-1 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

makes e a minimum.

Substituting this value of y in (20), we find that

$$e=2\frac{A+\frac{B}{V}-\sqrt{1+\frac{AV}{B}}}{\sqrt{1+\frac{AV}{B}}} \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

VII. *To determine the best volume, and the best resistance to give to the outside coil for a given permissible error.*—From the preceding it is easy to see that if the maximum allowable value of e is given, the minimum value of the volume that can be employed is given from (22), and for this value of the volume, the best value of y, that is the best ratio of the resistance of the outside coil to that of the magnetizing coil of the voltmeter, can be calculated from (21).

VIII. *To determine the sectional area to be given to the inner wire of a voltmeter in terms of the maximum potential difference so as to make the heating-error a minimum.*—By experiment ascertain the potential difference that is necessary to produce the maximum deflection with any voltmeter of the shape and size to be employed and wound according to the law

$$x = x_0 r^a,$$

where a has the value that makes the heating-error a minimum, and which value will depend on the shape and size of the instrument, and may be calculated for any special type of voltmeter in the same way as it has been calculated in what precedes for the Long-Range Magnifying Spring-instrument. Then if it is desired to wind another instrument, of the same volume and shape, so that it will have its maximum deflection given by P_2 volts, it follows, since the heating will, as already proved, be the same in the two instruments for their maximum deflections, that their resistances must be proportional to the squares of P_1 and P_2, and hence, from (5), since the same law of winding is followed, that the cross section of the innermost layer of wire in the two instruments must be inversely proportional to P_1 and P_2.

To have the same heating-error in the two cases, with outside resistance-coils of the same shape and size, it follows from (21) that it is necessary to use the same ratio between the resistance of the outside coil and the resistance of the magnetizing coil. To have a less or greater heating-error in the second than in the first case for the maximum deflection, it is only necessary to determine from (22) (the constants of which have been deduced by experiment with the first instrument) the greater or less volume V of the outside resistance-coil needed with the second instrument, and calculate the ratio y of the resistance of the outside coil to that of the magnetizing coil by (21).

IX. As to the second error, arising from the sensibility of the instrument being temporarily varied by external magnetic disturbance referred to in § I. This can be overcome in three distinct ways: by

1. Shielding the instrument by putting it in an iron case with very thick walls.
2. Using a very powerful controlling field.
3. Using a motion of *translation*, and *not of rotation*, for the body in the instrument that is deflected by the current.

The first method to be successful requires that the iron case should be heavy and cumbersome, and makes it unsuitable for portable instruments.

A very powerful controlling field necessitates a very powerful deflecting force, and so either makes the instrument unsensitive or necessitates a considerable expenditure of electric energy in the instrument. The third method, consisting in giving the deflected body a *motion of translation*, is the best, since, no matter how strong the disturbing magnetic field may be, provided it is uniform throughout the small space traversed by the deflected body on its motion, no increase nor diminution of the deflection will be caused by the outside magnetic field. For this reason we have adopted this third method in our Magnifying Spring-instruments, and experiment shows that the shielding produced in this way is even better than in our older form of instruments provided with a powerful permanent magnet.

X. As to the third error, arising from certain types of voltmeters altering in sensibility so that their constants vary from time to time. This error arises from two causes. In some voltmeters, such as those in which a controlling permanent magnet is employed, there is an error which gradually comes on from the demagnetization of this magnet, an error which is greatly increased by a mistaken careful regular employment of a keeper for the magnet when the instrument is not in use. This error can be avoided by dispensing with a permanent magnet, and using a spring or a weight, or an electromagnet which is magnetized by the current to be measured. A second time-error arises from the employment of iron in the neighbourhood, and has the effect of making the indications of the instrument depend not merely on the current passing at the time of measurement, but also on the currents that have lately passed through the instrument. This error is especially marked in those instruments in which the controlling force, or the force tending to bring the needle back to zero in opposition to the deflecting force, is produced by the attraction of an electromagnet containing a core of soft iron wire, and which it is *assumed* is magnetized to saturation by the current which it is our object to measure. With small currents, however, which produce deflections in the lower part of the scale, this iron core is not saturated, and differences in the values of the readings of as much as 30 to 40 per cent. are obtained, depending on whether it is an increasing or a decreasing current that is being measured with such an electromagnetic instrument.

XI. The fourth error, arising from the volt standards employed by various people differing several per cent. from one another, has been hitherto a very serious matter. The standards employed have usually been—

1. The E.M.F. of a Daniell's cell.
2. The E.M.F. of a Latimer Clark's cell.
3. A standard depending on the electrochemical equivalent of silver and the value of the legal ohm.
4. The indication of a voltmeter graduated by some well-known maker, but probably graduated in a way quite unknown to the user.

Standard 1 is vague unless the details of the method employed in setting up the Daniell's cell are more carefully specified than heretofore; for example, Carpart, in some recent tests of the E.M.F. of a Daniell's cell, made out of a U-tube, with a contraction in the lower part, found it to vary from 1·111 legal volts when the zinc-sulphate solution had 25 per cent. of $ZnSO_4$, to 1·142 legal volts when the solution had only 3 per cent. of $ZnSO_4$. His method of testing is based on the electrochemical equivalent of silver and the legal ohm, and as a proof of its accuracy he finds that the E.M.F. of a Latimer Clark's cell is 1·434 volts. If, however, we compare his results for a Daniell's cell with 1·072 volts as found by Sir W. Thomson when the zinc-sulphate solution had a specific gravity of 1·2, we see how Daniell's cells differ among one another*.

The E.M.F. of a Latimer Clark's cell has also some vagueness attached to it, unless the temperature-coefficient of variation of E.M.F. of the particular Latimer Clark's cell is known and taken account of. Generally the users of these cells are contented to say that the E.M.F. of a Latimer Clark's cell, as determined by Lord Rayleigh, is 1·435 true volts, or 1·438 legal volts, and they neglect the temperature variation altogether, which amounts to about 1 per cent. diminution per 12° C. elevation of temperature with certain Latimer Clark's cells.

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* Since the reading of this paper this subject has been very fully treated by Dr. Fleming, in a paper "On the Use of Daniell's Cell as a Standard of Electromotive Force," read before the Physical Society on June 27, 1885 [Phil. Mag. [5] vol. xx. p. 126 (August 1885)].

Standard No. 3 is the one that we have used for some time; and as we have obtained very satisfactory results with it, it may be well to describe our mode of using it a little in detail. First, by means of a large number of direct comparisons with a copper voltameter, we determine the most probable value in amperes of the indications in different parts of the scale of an ammeter *fixed permanently in position* by being screwed to the table. A current is now sent through this ammeter in series with a long thick copper wire having about 6 ohms resistance and wound in a large open coil. This coil has attached to its two ends the standard voltmeter, which is also fixed *permanently in position*. Simultaneous readings of the ammeter and voltmeter are now taken by two observers, when a signal is given and the bridge-piece of a mercury commutator is moved so as to cut off the current and connect the copper wire together with the voltmeter, which is joined with it in parallel, to a differential galvanometer. Then *time* measurements, for about ten minutes, are taken by a third observer of the parallel resistance of the thick copper wire and the attached voltmeter. Next a curve is drawn connecting the resistance of the cooling coil with the time, and on completing the curve backwards we ascertain with great accuracy, by interpolation, the resistance at the moment of stopping the current, that is at the moment of making the simultaneous observations on the ammeter and voltmeter. Our copper wire is sufficiently thick that for a current of some 15 amperes passing through it, corresponding with about 80 volts maintained at its ends, the time-curve of its resistance, obtained after stopping the main current, is nearly a straight line with hardly any inclination to the axis along which the time is measured; or, in other words, the change of resistance due to cooling while the measurements of resistance are being made is very small and easily allowed for. And this resistance, in legal ohms, multiplied by the current passing in amperes, gives of course the potential difference in legal volts.

In using the copper voltameter to calibrate the ammeter it is of course necessary, in order that a firmly adherent deposit should be obtained, that the area of the immersed surfaces of the anode and cathode opposed to one another should exceed the limit given by Dr. Hammerl, viz. one square decimetre per 7 amperes, or rather more than two square inches per ampere; and in our experiments we have taken care to use a larger area in proportion to the current. Our negative plates consisted of a number of separate sheets of very thin hard copper, so that the weight of the deposit could be accurately measured; the current was supplied by accumulators and increased or diminished by a carbon resistance worked with a screw. By watching the ammeter and slightly turning this screw one way or the other, the current could be kept very constant for a long time. The value of the electrochemical equivalent employed for copper was 0·3295 milligrammes per coulomb, which is deduced from the mean of the electrochemical equivalents of silver, 1·118 milligrammes per coulomb as given by Lord Rayleigh, and 1·1183 by F. and W. Kohlrausch, and by using 63·47, 107·56, 32·07, and 16 as the atomic weights of copper, silver, sulphur, and oxygen respectively. The solution of copper sulphate employed was a saturated one, the crystals of copper sulphate used in making it being chemically pure.

To avoid errors being introduced by oxidation of the copper that had just been deposited on the copper plates, they were, on being taken out of the sulphate of copper bath, on the stoppage of the current, immediately and quickly washed, first in water, secondly in alcohol, thirdly with ether poured over them, and then dried.

The currents that a given set of accumulators will send through a copper voltameter depends of course partly on the distance between the alternate positive and negative plates, and partly on the depths to which they are immersed in the saturated solution of copper sulphate. The proper arrangements of the plates to allow any particular current to pass cannot conveniently be determined with the plates that are going to be used for the experiment, as an unknown weight of copper would be deposited on them during the process of adjustment, and great delay would be introduced if the plates had to be dried and weighed after the adjustment and before making the final experiment. Hence after the proper plates to be used as the anodes had been very carefully cleaned and weighed, a spare set of exactly the same size and shape were put into the bath, and their distance, as well as the carbon resistance, adjusted until the desired current was passing; then the spare set was removed and the weighed set substituted for them, and the experiment carried out.

Having determined our volt-standard in the way above explained, we tested various voltmeters of different makers, and we found that whereas the indications of some of them agreed very well with our standard, the indications of others differed by several per cent.

XV. *On the Theory of Fractional Precipitation.*

By John J. Hood, *D.Sc.*[*]

THERE are at the present time several elements known belonging to the group of earths, analogous in some respects both to alumina and to lime, resembling each other so closely in their chemical properties that their separation seems to be one of the most tedious operations in mineral chemistry. So similar, indeed, are these elements in their chemical behaviour, that many, if not all, of the recent additions that have been made to the list of earths have passed through the hands of several eminent chemists without raising a suspicion that the material whose chemical properties they were examining was in reality a complex body. For instance, what was up till about the year 1877 termed erbia, an oxide found in gadolinite and a few other minerals, is now known to be a mixture of no less than five oxides—viz. scandia, ytterbia, holmia, thulia, and the true erbia.

The investigations that resulted in these discoveries may be considered as extensions of the work of Mosander, who in 1843 showed that the gadolinite earth, then termed yttria, was a mixture of three oxides—yttria and other two which he named terbia and erbia, separable from each other by fractional precipitation as oxalates.

A similar history belongs to the earths extracted from the mineral cerite; the latest discovery in this direction[†] being that the didymia from this mineral contains a considerable proportion of samaria, an earth first discovered in the mineral samarskite in 1878 by Delafontaine.

The methods that are employed for the separation of these earths from each other depend for success upon differences existing in the basic strengths of the several oxides; that is to say, if a mixture of salts, particularly the nitrates of two or more of these oxides be heated, there will be a tendency for the nitrates of some of the oxides, the less basic, to decompose first or in relatively greater quantity than the nitrates of the more basic oxides: or, if to a dilute solution of these salts a precipitant be added such as ammonic hydrate, less in amount than is requisite to precipitate all the salts, some of the hydrates or oxides will tend to accumulate more rapidly in the precipitates than others by many repetitions of the process. If differences do exist in the basic strengths of the materials,

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[*] Communicated by the Author.

[†] According to Welsbach, didymium is a mixture of two elements which he names neodymium and praseodymium (Journ. Chem. Soc. Nov. 1885).

then, by fractional decomposition of the nitrates by heat or by fractional precipitation, the tendency of one constituent to be decomposed or precipitated before another will be so much the greater as the difference in their basicities is greater, and their separation by either process consequently so much the easier.

Supposing, however, that two such oxides were of the same basic strength in relation to all acids and precipitants, and at all temperatures at which the experiments could be conducted, then it is evident that in such a case no separation could be effected, however many times the operations were repeated on the fractions obtained. If the ratios of the basic strengths vary with the temperature, which is probable, and with the nature of the precipitant, which may not be true, then it is quite possible that, in the separation of some of the rare earths by fractional precipitation, the temperature at which the experiments are made and the precipitant employed may be the very worst possible that could be selected.

From a theoretical point of view, the problems presented by fractional precipitation would seem to be of considerable importance, and the process offers a wide and doubtless a fertile field for experimental study. Viewed in a practical light, or as regards the application of the process to the separation of bodies differing in basic strength, the problem to be solved is: Given a mixture of two or more such substances, what is the best method of conducting the operations so that a given mass of material may yield a maximum of one or other of the pure oxides with the least amount of labour or the smallest number of precipitations? Evidently, for an answer to this question to be of value, the theoretical side of the problem must first be studied experimentally for the commoner elements to decide whether or no the ratios of the basic strengths of the materials vary with the temperature and in what manner, decreasing or increasing as the temperature is increased; whether these ratios vary with the nature of the precipitant or of the acid combined with the base, and whether retarding the precipitation by introducing extraneous bodies into the chemical system affects the ratio of the materials in the precipitate. In other words, under what conditions can the ratio of the less basic to the more basic material in the precipitate be made the greatest possible by adding a fraction of the total precipitant to a solution containing two salts?

In such a chemical change as is expressed by the equation $NiSO_4+Na_2CO_3=NiCO_3+Na_2SO_4$, if the chemical affinities operating among the constituents be considered, it is evident that, however simple the final result of the change may be these affinities or attractions constitute a very complex system of forces. There is a set of forces tending to change the system from the state represented by the left-hand member of the equation to the state represented by the right-hand one, and another set of forces tending to bring the system back to its initial state. If, instead of one, two or more precipitable salts be present, then the system of forces at work becomes much more complex; and to attempt to introduce all these attractions or affinities into formulæ relating to fractional precipitation would lead to complicated results; the equations would be as complex as those proposed by Guldberg and Waage in their theory of limited chemical actions. It is here assumed, however, that one of the products of the change of each particular constituent is practically insoluble; and that the inverse action does not take place, at least to any extent compared with that producing the precipitate.

If a number of solutions, each containing an equal mass of a single sulphate, as $NiSO_4$, $CoSO_4$, $MnSO_4$, &c., be considered, to which a common precipitant is added, the experimental conditions being the same in each case, the changes occurring in the several solutions will be brought about by forces analogous in kind, but the intensity of the action of the precipitant may differ in degree with the nature of the sulphate: this may be expressed by saying that each system exhibits a resistance to undergoing change, differing in degree according to the sulphate employed. This resistance is here looked upon as being exhibited by the sulphate, nitrate, or other salt that is submitted to the action of the precipitant, and the relative values of which may be determined by the simultaneous action of the precipitant on mixtures of two or more such salts. Representing the resistance of a particular salt to the action of a precipitant by the symbol ϵ, it becomes a measure of the stability of the salt, or of the intensity of the affinities holding the structure together, and is probably of a complex character, a function of the conditions to which the chemical system may be subjected. If a hydrate, such as $NaHO$, be the precipitant, ϵ measures the intensity of the attraction of the metallic base for the acid with which it may be united: the greater the value of ϵ, the greater the attraction between the base and acid.

The symbol ϵ might be defined as the coefficient of resistance to change for a particular chemical system, or as the basic power of a particular base with relation to a particular acid; but the phrase "coefficient of affinity," however appropriate it may seem, is objectionable, as there has been already sufficient confusion introduced into science by the use of this term; besides, as this value ϵ is interpreted above, it has the inverse meaning to that attached to coefficient of affinity by Guldberg and Waage in their tract *Sur les Affinités chimiques*. For convenience it will be termed the basic power, or strength of a particular base, a relative magnitude to be determined by the process of precipitation ; but it will remain for future experiments to give it a more definite meaning.

Suppose, then, that to a solution of sulphates or other salts of two metals a precipitant is added less in amount than requisite for complete precipitation ; the salt which offers the greater resistance to the action of the precipitant, and for which the magnitude ϵ is the greater, will suffer less change than the second salt in the solution. If the element time be introduced, the rates of change or of formation of the precipitates vary inversely as the basic strengths, for the greater the value of ϵ the slower the rate of precipitation.

No account is taken of the precipitation of so-called basic salts, but simply the total action of the precipitant on the salt-solution, whatever may be the nature of the material precipitated. The secondary actions that might possibly occur between the products of the change are also neglected ; such, for instance, as the action of the precipitate α obtained from the salt A reacting on B to precipitate β and re-form A; and, conversely, β acting on A to form α and change into B.

Let the masses of the two salts in the solution be A and B, to which a precipitant C is added, insufficient for complete precipitation. The rates of formation of the precipitates may be formulated on the usual assumption that they are proportional to the products of the active materials existing in the system at any time. The amounts of A and B that remain unchanged being $A-x$ and $B-y$, and since for the formation of x a quantity of the precipitant p has been utilized, and for y a quantity q, the amount of C that still remains capable of effecting further precipitation is $C-p-q$, the rates of change are

$$\frac{dx}{dt}=\frac{1}{\epsilon}(A-x)(C-p-q),$$

$$\frac{dy}{dt}=\frac{1}{\epsilon'}(B-y)(C-p-q),$$

where ϵ and ϵ' are the basic powers.

Since $p=\alpha x$ and $q=\beta y$, and the total mass of the precipitant necessary for complete precipitation $A\alpha+B\beta$, if the fraction C be $\frac{A\alpha+B\beta}{\lambda}$, these equations become

$$\frac{dx}{dt}=\frac{1}{\epsilon}(\mathrm{A}-x)\left[\left(\frac{\mathrm{A}}{\lambda}-x\right)\alpha+\left(\frac{\mathrm{B}}{\lambda}-y\right)\beta\right], \quad . \quad . \quad . \tag{1}$$

$$\frac{dy}{dt}=\frac{1}{\epsilon'}(\mathrm{B}-y)\left[\left(\frac{\mathrm{A}}{\lambda}-x\right)\alpha+\left(\frac{\mathrm{B}}{\lambda}-y\right)\beta\right], \quad . \quad . \quad . \tag{2}$$

by the integration of which the amounts of the precipitates x and y formed at any time could be determined; results, however, which would be of little practical value.

Comparing the rates of formation of the precipitates

$$\frac{dx}{dt}:\frac{dy}{dt}=\frac{1}{\epsilon}(\mathrm{A}-x):\frac{1}{\epsilon'}(\mathrm{B}-y), \quad . \quad . \quad . \quad . \tag{3}$$

or

$$(\mathrm{A}-x)^{\epsilon}=\mathrm{F}(\mathrm{B}-y)^{\epsilon'};$$

but as $\mathrm{A}^{\epsilon}=\mathrm{FB}^{\epsilon'}$, the equation becomes

$$\left(1-\frac{x}{\mathrm{A}}\right)^{\epsilon}=\left(1-\frac{y}{\mathrm{B}}\right)^{\epsilon'}, \quad . \quad . \quad . \quad . \quad . \quad . \tag{4}$$

or

$$\frac{\epsilon}{\epsilon'}=\frac{\log\left(1-\frac{y}{\mathrm{B}}\right)}{\log\left(1-\frac{x}{\mathrm{A}}\right)};$$

which gives the quantities of the precipitates formed, x, y (calculated in terms of the original salts A and B), in terms of the basic powers. Hence by a single experiment it is possible to calculate the ratio $\frac{\epsilon}{\epsilon'}$, A being the more basic material, and consequently $\epsilon>\epsilon'$.

If $\epsilon=n\epsilon'$, then the greater the value of n the greater will be the tendency of B to accumulate in the precipitate; and considering that fractional precipitation is the only method yet discovered for effecting the separation of several of the rare earths, for pairs of which the value of n evidently does not differ much from unity, the experimental study of the process, employing the commoner metals, with regard to temperature in particular, might indicate in which direction to work so as to increase n and render the operations less tedious. If n increases with the temperature, then fractional precipitation would be more effectual at high than at low temperatures, and *vice versâ*.

It is customary, in the separation of the rare earths, to employ the nitrates and ammonia as the precipitant, the solutions being made so dilute that no precipitate is perceptible for some minutes after mixing; indeed the precipitate may be delayed for a considerable time by using solutions sufficiently dilute. But it would seem from the above equations that the ratio of the materials in the precipitate is independent of the time taken to form, and whether the precipitant is added all at once, or in small successive quantities.

If the fraction of the total material in solution that is precipitated be $\frac{A+B}{\lambda}=x+y$, and the ratio of the two salts in solution be ν, and in the precipitate μ, or $A=\nu B$, and $x=\mu y$, then equation (4) may be written

$$\left(1-\frac{\mu(1+\nu)}{\nu\lambda(1+\mu)}\right)^{\epsilon}=\left(1-\frac{1+\nu}{\lambda(1+\mu)}\right)^{\epsilon'}; \quad . \quad . \quad . \quad (5)$$

from which it may be seen that the ratio of the less to the more basic material increases the smaller the fraction precipitated, and that the maximum value of this ratio will be $\frac{\epsilon}{\nu\epsilon'}$ for an infinitesimal precipitate ($\lambda=\infty$).

If the ratio $\frac{\epsilon}{\epsilon'}$ differ but little from unity, the separation of two such bodies by many repetitions of the process on each precipitate obtained would be very tedious; in the extreme case of $\epsilon=\epsilon'$, then $\mu=\nu$, or the ratio of the two materials in the precipitate will be the same as in the original solution, and no separation of the two constituents could be effected. Consequently the complex nature of a body might never be detected, at least by the application of such a process of separation; nor can the negative results obtained by Marignac* for some of the commoner elements be looked upon as deciding their homogeneous character.

The following experiments by Mills and Bickett† are of interest as showing the validity and application of the equation

$$\left(1-\frac{y}{B}\right)^{\epsilon'}=\left(1-\frac{x}{A}\right)^{\epsilon}.$$

In each experiment the volume of the solution was 100 cubic centimetres, the same quantity of precipitant (Na_2CO_3) being added to each.

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* *Ann. Ch. et Phys.* 1884.

† Phil. Mag. [5] vol. xiii.

Solution.		Precipitate.		Temp.	$\frac{\epsilon}{\epsilon'}$.
$NiSO_4$. B.	$MnSO_4$. A.	$NiSO_4$. y.	$MnSO_4$. x.		
grm.	grm.				
·1	·9	·0953	·5850	12°·9	2·91
·2	·8	·1852	·4616	13·6	3·03
·3	·7	·2799	·3766	12·5	3·50
·4	·6	·3588	·2976	13	3·31
·5	·5	·4305	·2450	13·6	2·93
·6	·4	·4788	·1536	12·8	3·30
·7	·3	·4991	·1089	17	2·76
·8	·2	·5584	·0722	17	2·68
·9	·1	·5841	·0363	15·2	2·32
Mean value of ratio $\frac{\epsilon}{\epsilon'}$ ... . = 2·97					

These experiments are not all made at the same temperature, and it is seen that generally $\frac{\epsilon}{\epsilon'}$ decreases with increase in the temperature.

Taking the mean value of $\frac{\epsilon}{\epsilon'}$ as being nearest the truth, it would appear that $MnSO_4$ resists the decomposing action of sodic carbonate with a force 2·97 times greater than does $NiSO_4$, when both salts are simultaneously subjected to the action of this reagent. If a solution had been employed containing these salts in the ratio $MnSO_4 : NiSO_4 = 2·97 : 1$, and an extremely small fraction precipitated, the ratio of the two in the precipitate would have been 1 : 1; or, if the solution had contained equal weights of the two sulphates, the small precipitate would have consisted of $MnSO_4 : NiSO_4 = 1 : 2·97$; the larger the precipitate in this latter case, the more nearly would this ratio equal unity. In the experiment in the foregoing table, in which equal masses (·5 grm.) were employed, the fraction precipitated being large, the $NiSO_4$ is a little less than twice the amount of $MnSO_4$ precipitated.

Another interesting series of experiments by Mills and Smith* relating to fractional precipitation, in which sulphates of nickel and cobalt were employed, sodic hydrate being the precipitant, are given in the following table. In applying these results to the formulæ, the total amount of cobalt precipitated is taken, it being for this purpose immaterial whether or no the precipitate consists of a basic salt.

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* Proc. Roy. Soc. vol. xxix.

Solution.		Precipitate.		Temp.	$\frac{\epsilon}{\epsilon'}$.
$NiSO_4$. A.	$CoSO_4$. B.	$NiSO_4$. x.	$CoSO_4$. y.		
grm.	grm.			°	
·1	·9	·1050	·8105	7–8	0
·2	·8	·1980	·6687	6–7	0
·3	·7	·2765	·6215	7–8	·86
·4	·6	·3510	·5140	7–8	·92
·5	·5	·4465	·4420	7–8	·96
·6	·4	·5295	·3340	7–7·5	·84
·7	·3	·5825	·2615	7–7·5	1·15
·8	·2	·7080	·1760	8–8·5	·98
·9	·1	·7865	·0900	7–7·5	1·11
Mean value of $\frac{\epsilon}{\epsilon'}$				=	·97

The value $\frac{\epsilon}{\epsilon'} = {\cdot}97$ indicates a very near equality possessed by $CoSO_4$ and $NiSO_4$ to be decomposed by sodic hydrate. A simple inspection of the experimental results shows this fact, for it is seen that the ratios of the materials in the precipitates are almost the same as the salts in the solutions. It is evident therefore that if fractional precipitation were to be employed for the separation of nickel and cobalt, the process would be found as tedious (at least as sulphates and with sodic hydrate) as that of the separation, say, of samaria from didymia.

This near equality in precipitability is an interesting result when it is remembered that the atomic weights of nickel and cobalt are almost equal; but, judging by other experiments on precipitation, it does not seem that the precipitability or basic power is related to the atomic weight. For instance, the atomic weights of the three elements Sm, Di, and La are 150, 142·3, and 138·5; yet the separation of samaria from didymia is a much more tedious operation than that of didymia from lanthana, the precipitability of the first two oxides or their basicities being more nearly equal than the second two, didymia and lanthana. Another illustration of this fact is shown by the six earths scandia, ytterbia, holmia, thulia, erbia, and yttria, whose atomic weights are (R_2O_3), Sc = 44·5, Yb = 173, Ho = 162 (?), Tm = 169·5 (?), Er = 166, and Y = 89·5; but their separation from each other is a very tedious operation, indicating only slight differences in basic strength, Sc and Yb being the least basic of the group, and Y the most basic.

Debus*, in his experiments on the fractional precipitation of

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* *Ann. Ch. Pharm.* vols. lxxxv., lxxxvi., lxxxvii.

mixtures of baryta and lime by carbonic acid, found that if the ratio of the two oxides in solution be α and in the precipitate β, then $\alpha=\kappa\beta$, and that within certain limits of α the value of κ was nearly constant. By equation (5) it is seen that if only a very small fraction of the material be precipitated, $\nu=\frac{\epsilon}{\epsilon'}\mu$, or $\alpha=\frac{\epsilon}{\epsilon'}\beta$; so that the values obtained by Debus for κ represent approximately the ratio $\frac{\epsilon}{\epsilon'}$ for this particular case.

Chizynski[*] employed solutions of $MgCl_2$ and $CaCl_2$, to which he added an insufficiency of phosphoric acid for complete precipitation, and to the clear acid solution ammonic hydrate, determining the amounts of CaO and MgO in the precipitates with variable quantities of $CaCl_2$ and $MgCl_2$. These experiments, however, do not seem to exhibit fractional precipitation in the true light; for before the addition of the ammonia the phosphoric acid has probably divided itself between the two bases in a determinate manner, and on neutralizing the acid solution the mixed phosphates are precipitated.

XVI. *On the Constitution of Acids.* *By* W. A. Dixon, *F.I.C., F.C.S., Instructor in Chemistry, Sydney Technical College, N. S. Wales*[†].

IN lecturing on Chemistry the question arose in my mind, Why do some acids form with the alkali metals alkaline hydrogen salts, whilst the similar salts of other acids are acid? And I wish to bring forward the answer to the question which seems to me probable.

We know that in organic compounds there are two cases in which hydrogen is readily replaceable by metals. The first is when the hydrogen is in combination with oxygen as hydroxyl, as in alcohols, phenols, &c., and that this hydrogen is more difficult to replace than in the second case, which is when the hydrogen is in combination with two oxygen atoms as oxyhydroxyl. The latter is the mode in which the readily replaceable hydrogen of all the organic acids exists. It seems to me that hydrogen in both these states of combination exists in inorganic acids, and that where both exist in the same acid the hydrogen of the oxyhydroxyl is invariably replaced first. It therefore happens that the principal acid function is in connection with oxyhydroxyl; and it is somewhat doubtful whether an acid which contains hydroxyl only is not more

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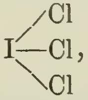
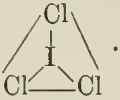
[*] *Ann. Ch. Pharm.* Suppl. vol. iv. 1866.

[†] Communicated by Prof. Mills, F.R.S.

nearly allied to alcohols and phenols than to the true acids. Hydrogen also enters directly into combination; but when it does so the compound generally exhibits acid properties of the feeblest description except when in combination with the extremely chlorous analogues, and when in combination in complex acids it is not replaceable by metals.

I give a few examples from the common acids to explain my meaning; and it will be observed that as a rule the lower, and what is generally to be regarded as the most stable, atomicity of the elements only is required. The exception to this is the halogen group, which must be regarded as entering into oxacid combination as triads. This is scarcely extraordinary, as we know that iodine forms a trichloride, and that therefore it at least must be a triad, or develops triadic functions by reason of its juxtaposition to chlorine. If iodine does so, why may not the other members of this closely allied group of halogens? It appears to me that the metals are more elemental in character, so to speak, and therefore less liable to atomic changes than the non-metals, and that most of the supposed variation in metallic atomicities would disappear if the halogens were triads in certain combinations. If iodine only of the group could assume triatomicity, there is no reason why the monatomic chlorine in iodine trichloride should not be replaceable by monatomic hydrogen; but there is little reason to expect such a substitution if by the combination of these elements triatomic functions were developed in both, so that the compound was not


, but

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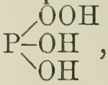
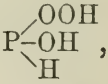
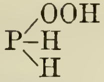
To come to examples, let us first take the phosphorous acids.

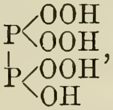
The orthoacid has probably the composition  $P\begin{cases}OOH\\OH\\OH\end{cases}$, because the acid itself has strong acid properties; but these are immediately lost or neutralized by the replacement of the hydrogen of the oxyhydroxyl group by sodium, whilst the replacement of the hydrogen of one hydroxyl group gives a salt having an alkaline reaction.

Phosphorous acid has probably the constitution  $P\begin{cases}OOH\\OH\\H\end{cases}$, and is therefore dibasic, the hydrogen atom being only replaceable by compound radicals resembling itself; but this acid does not form a true acid salt with the alkali metals.



Hypophosphorous acid is $\mathrm{P}{-}\begin{matrix}\diagup\mathrm{OOH}\\ \mathrm{H}\\ \diagdown\mathrm{H}\end{matrix}$, and is therefore monobasic.

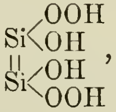
Pyrophosphoric acid is probably



$$\begin{array}{l}\mathrm{P}{<}\begin{matrix}\mathrm{OOH}\\ \mathrm{OOH}\end{matrix}\\ \,|\\ \mathrm{P}{<}\begin{matrix}\mathrm{OOH}\\ \mathrm{OH}\end{matrix}\end{array},$$

as the dipotassic and disodic salts are acid in reaction, whilst the dipotassic ammonium hydrogen salt is alkaline, showing the feeble acidity of the OH group; and a tripotassic or trisodic pyrophosphate should also be alkaline.

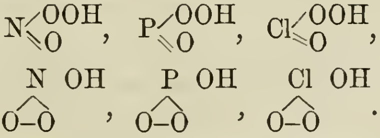
Orthosilicic acid is usually supposed to be tetrabasic, and could then have only four hydroxyl atoms and no oxyhydroxyl, and should therefore possess scarcely acid properties. The acid obtained by diffusion when perfectly free from chlorine has a very faint acid reaction; but as this solution evaporated *in vacuo* leaves a residue having the composition H_2SiO_3, the acid in solution may be



$$\begin{array}{l}\mathrm{Si}{<}\begin{matrix}\mathrm{OOH}\\ \mathrm{OH}\end{matrix}\\ \,\|\\ \mathrm{Si}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{OOH}\end{matrix}\end{array},$$

and hence give an acid reaction.

Of the sulphur acids we have sulphuric, $\mathrm{S}{<}\begin{matrix}\mathrm{OOH}\\ \mathrm{OOH}\end{matrix}$, and sulphurous, $\mathrm{S}{<}\begin{matrix}\mathrm{OOH}\\ \mathrm{OH}\end{matrix}$, the first forming acid and the second alkaline hydrogen salts with the alkaline metals. There is also hyposulphurous acid, $\mathrm{S}{<}\begin{matrix}\mathrm{OOH}\\ \mathrm{H}\end{matrix}$, which should be monobasic, and actually only forms one sodium salt. The substitution of sulphur for oxygen in sulphuric acid renders this sulphuric acid too unstable to form acid salts with the alkali metals. There are some monobasic acids, as nitric, metaphosphoric, and chloric, which may have the same or different constitutions. They may be

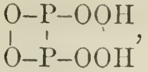


$$\mathrm{N}{<}\begin{matrix}\mathrm{OOH}\\ =\mathrm{O}\end{matrix},\quad \mathrm{P}{<}\begin{matrix}\mathrm{OOH}\\ =\mathrm{O}\end{matrix},\quad \mathrm{Cl}{<}\begin{matrix}\mathrm{OOH}\\ \equiv\mathrm{O}\end{matrix},$$

or

$$\begin{array}{c}\mathrm{N\ \ OH}\\ \wedge\\ \mathrm{O{-}O}\end{array},\quad \begin{array}{c}\mathrm{P\ \ OH}\\ \wedge\\ \mathrm{O{-}O}\end{array},\quad \begin{array}{c}\mathrm{Cl\ \ OH}\\ \wedge\\ \mathrm{O{-}O}\end{array}.$$

Chloric acid may have the latter constitution; but it seems most probable that nitric acid, from its strongly acid character, has the former, and also metaphosphoric from analogy and from its formation of dimetaphosphates,



$$\begin{array}{l}\mathrm{O{-}P{-}OOH}\\ \,|\quad\;|\\ \mathrm{O{-}P{-}OOH}\end{array},$$

the acid of which is unknown; and more complex compounds of similar type.

Of the lower oxacids of chlorine and nitrogen, chlorous and nitrous, $\mathrm{N}\!\left\langle{}^{\mathrm{OH}}_{\mathrm{O}}\right.$ and $\mathrm{Cl}\!\left\langle{}^{\mathrm{OH}}_{\mathrm{O}}\right.$, are feeble acids, though forming stable metallic compounds; whilst hyponitrous and hypochlorous may be $\mathrm{N}\!\left\langle{}^{\mathrm{H}}_{\mathrm{O}}\right.$ and $\mathrm{Cl}\!\left\langle{}^{\mathrm{H}}_{\mathrm{O}}\right.$, and so are scarcely acids at all. The latter may however contain univalent chlorine, and be Cl–OH.

XVII. *Evidence respecting the Reality of "Transfer-resistance" in Electrolytic Cells.* *By* G. Gore, *LL.D., F.R.S.**

In a paper published in the 'Proceedings of the Royal Society,' 1885, no. 236, vol. xxxviii. p. 209, I have stated that "a species of electric-resistance, distinct from that of polarization and ordinary conduction-resistance, varying greatly in amount in different cases, exists at the surfaces of mutual contact of metals and liquids in electrolytic and voltaic cells," and "this resistance varies largely in amount with different metals in the same solution, and with the same metal in different solutions."

As conduction-resistance is attended by evolution of heat, I took advantage of this fact to search for a difference of temperature produced by "transfer-resistance" at the surfaces of different metals in the same solution, and I now employ the same fact in a somewhat different way to search for difference of heat evolved at the surface of the same metal in different liquids. I use an air-thermometer instead of mercurial ones, and make an experiment like that of Peltier's, but employing a metal and electrolyte instead of two metals.

I took a thin platinum bottle, of a conical shape, of 10·0 cm. total height, 5·0 cm. in diameter at the bottom, and 1·25 cm. diameter at a height of 8·5 cm., at the bottom of the neck.

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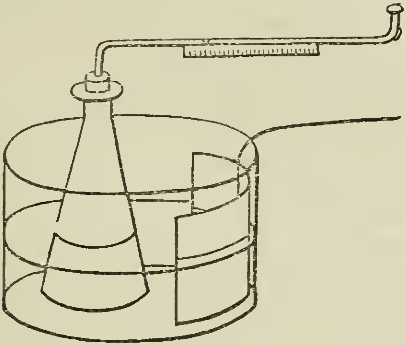
* Communicated by the Author: read before the Birmingham Philosophical Society, January 21st, 1886.

It had a slightly concave bottom, and was placed in a flat-bottomed glass basin 12·0 cm. in diameter. It was closed air-tight by a perforated indiarubber bung, having a narrow horizontal glass tube, open at both ends, fixed in it. The tube had an internal diameter of about 2·0 mm.; it was provided with a small divided scale, and contained a minute drop of water to act as an index of the expansion or contraction of the enclosed air (see sketch).



After ballasting the bottle by means of a heavy ring of glass encircling its neck, the electrolyte was poured into the glass basin up to a height of 3·0 cm. A sheet of platinum 8·0 cm. × 15·5 cm., with its largest dimension horizontal, was placed vertically in the liquid to act as an anode. Under these circumstances the amount of external surface of the platinum bottle in contact with the liquid, excluding that of the bottom, was about 40·0 square centimetres, whilst that of the front side of the sheet of metal was about 46·5 sq. cm. These several conditions, and the distance of the sheet from the bottle, were kept the same in each experiment.

In some preliminary trials, using a current from a battery of six pairs of zinc and platinum in dilute sulphuric acid, in single series, and a large anode of zinc instead of the platinum one,—on passing the current through a mixture of one volume of sulphuric acid and one hundred of water, into the bottle, whilst much hydrogen was evolved at the cathode, a small expansion of the air in the bottle at once occurred, and moved the index forward 1·0 mm. in about two or three seconds. The current was then stopped, and the index returned to its former position in about one minute. The piece of zinc was then replaced by a platinum wire which was brought into contact with the bottom of the bottle, and the circuit again closed. The current now circulating was about the same in strength as before, and none of it appeared to pass through the liquid; but notwithstanding no cooling influence by evolution of hydrogen now operated, there was no visible movement of the index or expansion of air in the bottle. This experiment of passing the current alternately through the liquid and through the bottle was repeated a number of times, and the same results respectively obtained. With nitric acid diluted in the same proportion, instead of the sulphuric acid, the effects were similar but a little more conspicuous, probably because the resistance was greater, and a portion of the hydrogen was oxidized.

As when the current passed through the liquid, certain amounts of heat must have been absorbed by the liberation of hydrogen, and by that substance assuming the gaseous state, each result ensuing at the surface of the bottle, and notwithstanding these cooling influences, the temperature of the bottle rose, an amount of heat more than sufficient to compensate for these losses must have been produced by the current. What was the source of this heat? Was it due to ordinary conduction-resistance in the mass of the electrodes or liquid, or to some action at the surface of the bottle? As the index did not suddenly advance when the current was passed through the bottle only, the heat was not due to ordinary conduction-resistance of that vessel; and whatever the amount of heat produced by such resistance was, it must have been very small in comparison with that which produced the expansion. As the expansion was sudden, it could not have been due to resistance of any kind at the anode. And as the temperature of the bottle rose suddenly and fell quickly, and the mass and specific heat of the liquid were each considerable, it could not have been produced by heat of conduction-resistance of the liquid. The sudden expansion was therefore probably due to some influence, other than that ot chemical change, acting at the surfaces of mutual contact of the liquid and bottle.

The influence of difference of liquid with currents of equal strength was also tried, the electrolytes consisting of (1st) a mixture of one volume of strong sulphuric acid and ten of water, and (2nd) of ordinary concentrated nitric acid for the purpose of preventing the evolution of free hydrogen. The current was from six Grove's cells in single series, and its strength in each case was $=\cdot454$ ampère; it was stopped in each instance after a few seconds (whilst the expansion was increasing, though at a diminished rate), in order to exclude as much as possible the influence of heat of conduction-resistance of the liquid. The anode of sheet platinum was used in each case.

With the dilute sulphuric acid the expansion was = 3·0 mm. in two seconds, and on then stopping the current the contraction was 1·0 mm. in three seconds. Hydrogen was freely evolved. Increasing the density of the current by raising the bottle partly out of the liquid, increased the rate of expansion and decreased that of contraction.

With the strong nitric acid the expansion was 1·0 mm. in three seconds, and on then stopping the current a contraction occurred of about ·2 mm. in three seconds. No gas was evolved at the cathode. Increasing the density of the current in the above manner had but little effect. By passing the same strength of current up through the flask, by means of a platinum wire in contact with the bottom of the bottle, an expansion of only ·5 mm. was produced in ten seconds.

The larger expansion with the dilute sulphuric acid than with the strong nitric acid, notwithstanding the cooling influence of the evolved and gaseous hydrogen in the former case, was probably due to greater resistance of some kind at the surface of the bottle in the former than in the latter liquid. If this conclusion is correct the heat produced by such resistance at the platinum cathode in dilute sulphuric acid was greater than that absorbed by the liberation and assumption of the gaseous state of the hydrogen in that liquid, and also greater than that evolved by such resistance in strong nitric acid. The small amount and slowness of expansion occurring when the current was passed up the flask, showed that the sudden expansion was not due to heat of conduction-resistance of that vessel.

In another experiment with dilute sulphuric acid one volume of strong acid to ten of water, and a current of ·336 ampère, the expansion was 3 mm. in two seconds; and on then stopping the current the contraction was 1·0 mm. in thirty seconds. And with nearly concentrated nitric acid, and a current of ·084 ampère, the expansion was 1·0 mm. in three seconds, and by then stopping the current, a trace of contraction in thirty seconds. Of course, in every one of the experiments, the amount of expansion shown by the index was less than the total, because the bottle itself expanded as well as the air in it.

If the sudden expansion in these cases was really due to some "resistance" at the surface of the bottle, it ought to vary directly with it. In order to test this point the amounts of such "resistance" at the surface of the bottle when used as a cathode were carefully measured whilst a current of ·454 ampère was passing. That in the dilute sulphuric acid (one to ten) equalled 3·41 ohms; whilst that in the strong nitric acid was ·17 ohm, or $\frac{1}{20}$ the former amount. The amount of "resistance," therefore, at the surface of the bottle in the two liquids varied directly as the heat evolved and expansion produced. As the liquids were not stirred, the "resistances" measured included that due to polarization and its counter electromotive force. As I had already in many cases found large differences of "resistance" at the surfaces of the same metal in different electrolytes, whilst the latter was being rapidly stirred in order to prevent polarization, I did not repeat these experiments under the additional condition of stirring.

Separate experiments were carefully made to measure any alterations of temperature occurring in the mass of the liquids during the passage of the current of ·454 ampère through them, under exactly the above conditions; the thermometer employed being capable of indicating one fiftieth of a Centigrade degree. With the dilute sulphuric acid (1 to 10), and with the strong nitric acid, no perceptible alteration of temperature took place, even by continuing the current during three minutes. This fact agrees with the circumstance observed, that in each of these liquids, on stopping the current, the bottle cooled quickly; but had its heat been derived from the mass of the liquid this would not have happened. The absence of change of temperature in the dilute sulphuric acid is consistent with the inference that the heat produced by the resistance of the liquid, and that produced by surface "resistance" at the anode and cathode, and imparted to the liquid, was exactly neutralized by that absorbed by the chemical changes at the electrodes. In strong nitric acid the circumstances were somewhat different, although the final result was similar. In that case both the amount of heat of conduction-resistance of the liquid, and that of "resistance" at the electrodes were comparatively small, and the portion of heat absorbed by chemical action was also small, and these two quantities neutralized each other.

The surface "resistances" were measured by means of a Wheatstone's slide-wire bridge, one terminal of a low-resistance galvanometer being connected with the slider, and the other connected first to the cathode and then to a platinum wire (idle electrode) close to the cathode, but not touching it, in the liquid; a balance being obtained in each case by moving the slider.

XVIII. *Some Thermodynamical Relations.*—PART III.

By WILLIAM RAMSAY, *Ph.D., and* SYDNEY YOUNG, *D.Sc.*[*]

IN the first of this series of papers (Phil. Mag. Dec. 1885) two relations between the vapour-pressures of different substances were described:—1. The product of the rate of increase of pressure per unit rise of temperature $\left(\frac{dp}{dt}\right)$ into the absolute temperature (t) is approximately the same for all bodies at the same pressure, but the differences are real, and are not due to errors of experiment or of calculation. 2. The rate of increase of this value $\frac{dp}{dt}\,.\,t$ with rise of pressure is very nearly the same for all bodies. This was shown in the tables by making the product $\frac{dp}{dt}\,.\,t$ for one substance equal to unity at each pressure, and reducing the values for other substances at the same pressure in the same ratio. It was pointed out that, at pressures between 150 or 200 millim. and 1500 or 2000 millim., the variations from constancy are very small, but that they are frequently greater at lower and at higher pressures; and it was suggested that these variations might possibly be due either to errors of experiment or of calculation.

In the second paper a relation was proved to exist between the absolute temperature of any two bodies corresponding to equal vapour-pressures, which may be expressed by the equation

$$R'=R+c\,(t'-t),$$

where R' is the ratio of the absolute temperatures of any two bodies at a given pressure, R the ratio at another given pressure, t' and t are the temperatures of one of the two bodies corresponding to those vapour-pressures, and c is a constant. The value of c may be determined graphically by making the temperatures (absolute or Centigrade) of one of the bodies (A) ordinates and the ratios of the absolute temperatures of the two bodies (A and B) at pressures corresponding to the temperatures of (A) abscissæ, when the points representing this relation fall in a straight line.

In the case of nearly related bodies such as chlorobenzene and bromobenzene, $c=0$ and $R'=R$ at all pressures, and in those cases the ratios of the products $\frac{dp}{dt}\,.\,t$ are also equal at

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[*] Communicated by the Physical Society: read December 12, 1885.

all pressures; and it appeared likely that if the variations from constancy of the reduced values of $\frac{dp}{dt} \cdot t$ for other substances were real, they would be related in some way to the variations from constancy of the ratios of the absolute temperature. This is indeed the case; for if we compare the values of $\frac{dp}{dt} \cdot t$ for any two substances, and make the temperatures of one of them ordinates, and the ratios of the products $\frac{dp}{dt} \cdot t$ abscissæ, we again find that the points representing the relation of the ratios of the product $\frac{dp}{dt} \cdot t$ at definite pressures to the temperatures of one of the bodies corresponding to those pressures, fall in a straight line. We therefore obtain a similar equation,

$$R' = R + c\,(t' - t),$$

R′ and R in this case representing the ratios of the products $\frac{dp}{dt} \cdot t$. The cause of the apparently greater deviation from constancy at low and at high pressures is simply this—that at low pressures a small change of pressure corresponds to a large change of temperature, while at high pressures the intervals of pressure taken are very great, and therefore the intervals of temperature are also great. This is clearly seen by referring to the table of absolute temperatures corresponding to the pressures taken. Taking water as an instance, we have the following numbers:—

P.	t absolute.	Interval of t.	P.	t absolute.	Interval of t.
millim.	°	°	millim.	°	°
10	284·3	27·0	600	366·5	4·2
50	311·3	13·4	700	370·7	3·75
100	324·7	8·4	800	374·45	3·35
150	333·1	6·5	900	377·8	3·05
200	339·6	9·3	1000	380·85	12·35
300	348·9	7·1	1500	393·2	9·3
400	356·0	5·7	2000	402·5	14·0
500	361·7	4·8	3000	416·5	19·35
600	366·5		5000	435·85	

The determinations of the products $\frac{dp}{dt} \cdot t$ are, however, necessarily less accurate than those of the temperatures, especially at low pressures, for the sources of error are more numerous and have greater influences on the results; yet the values calculated directly from the vapour-pressure curves generally agree very well with those recalculated from the equation

$$R' = R + c(t' - t),$$

as will be seen in the following table. With the exception of chlorobenzene and bromobenzene, the comparison is only made for those substances which have been investigated through a large range of pressure, for otherwise it is impossible to determine the value of c with sufficient certainty.

1. *Water and Carbon Bisulphide.* Ratios of the products $\frac{dp}{dt} . t$ for CS_2 to those of water at the same pressures taken as abscissæ, and the temperatures of water corresponding to those pressures taken as ordinates. $c = -0{\cdot}000399$.

Pressures.	Reduced ratios of $\frac{dp}{dt} . t$, calc. from curves.	Reduced ratios of $\frac{dp}{dt} . t$, recalc. from equation.	Products $\frac{dp}{dt} . t$ for CS_2, calc. from curves.	$\frac{dp}{dt} . t$ for CS_2, recalc. from values for water and recalc. ratios.	Δ per cent.
millim.					
50	·804	·8042	675·7	675·9	+0·03
100	·796	·7989	1280·0	1284·0	+0·31
150	·794	·7955	1839	1842	+0·16
200	·787	·7929	2373	2391	+0·75
300	·787	·7892	3430	3442	+0·35
400	·784	·7864	4436	4451	+0·34
500	·784	·7841	5417	5417	0·0
600	·782	·7822	6361	6364	+0·05
700	·780	·7805	7317	7320	+0·04
800	·783	·7790	8235	8197	−0·46
900	·785	·7777	9281	9196	−0·92
1000	·780	·7764	10102	10054	−0·48
1500	·781	·7715	14507	14325	−1·27
2000	·767	·7678	18460	18481	+0·11
3000	·750	·7622	26056	26476	+1·59
5000	·755	·7545	41128	41106	−0·05

There are only two cases in which the difference between the calculated and recalculated values amounts to 1 per cent., and these two cases occur close together and are in opposite directions. Generally the differences are much smaller than 1 per cent., while the differences between the ghest and lowest of the reduced values of $\frac{dp}{dt} . t$ (calculated or recalculated) exceeds 6 per cent.

2. *Bromo-benzene and Chloro-benzene.* The values for these substances appeared to be identical. They were therefore taken together and compared both with carbon bisulphide

and with water, to find whether the recalculated values would be the same in the two comparisons. This is shown by the table opposite to be the case.

3. *Carbon Tetrachloride and Water.* Values of $\frac{dp}{dt} . t$ for H_2O taken as unity at each pressure. Temperatures of water as ordinates. $C = -0·0006945$.

Pressures.	Reduced ratios of $\frac{dp}{dt} . t$.		$\frac{dp}{dt} . t$ for CCl_4.	
	Calculated.	Recalculated.	Calculated.	Recalculated.
millim.				
50	·859	·8455	722	710·6
100	·830	·8362	1333	1344
150	·827	·8304	1915	1922
200	·832	·8258	2510	2491
300	·811	·8194	3537	3573
400	·809	·8145	4580	4610
500	·823	·8105	5684	5599
600	·819	·8072	6669	6567
700	·794	·8042	7446	7543
800	·799	·8016	8403	8435
900	·789	·7993	9330	9452
1000	·785	·7972	10170	10323
1500	·779	·7886	14470	14642
2000	·780	·7822	18783	18828
3000	·765	·7724	26564	26830
5000	·759	·7590	41344	41351

4. *Ether and Water.* Values of $\frac{dp}{dt} . t$ for H_2O taken as unity at each pressure. Temperatures of water as ordinates. $c = -0·0003194$.

Pressures.	Reduced ratios of $\frac{dp}{dt} . t$.		$\frac{dp}{dt} . t$ for $(C_2H_5)_2O$.	
	Calculated.	Recalculated.	Calculated.	Recalculated.
millim.				
100	·811	·8305	1304	1335
150	·833	·8278	1928	1916
200	·839	·8257	2531	2490
300	·825	·8228	3598	3588
400	·840	·8205	4752	4644
500	·812	·8187	5612	5655
600	·826	·8171	6723	6648
700	·818	·8158	7673	7651
800	·811	.8146	8530	8571
900	·808	·8135	9559	9620
1000	·812	·8126	10513	10523
1500	·798	·8086	14819	15013
2000	·822	·8057	19787	19393
3000	·798	·8012	27730	27830
5000	·795	·7950	43314	43313

a. Values of $\frac{dp}{dt}.t$ for CS_2 taken as unity at each pressure. Temperatures of CS_2 as ordinates. $C=-0{\cdot}0007626$.

b. Values of $\frac{dp}{dt}.t$ for H_2O taken as unity. Temperatures of H_2O as ordinates. $C=-0{\cdot}0009850$.

Pressures.	$CS_2=1$.		$H_2O=1$.		$\frac{dp}{dt}.t$ for chloro-benzene. Calculated.	$\frac{dp}{dt}.t$ for bromo-benzene. Calculated.	Mean values of $\frac{dp}{dt}.t$ for chloro- and bromo-benzene.	$\frac{dp}{dt}.t$ for chloro- and bromo-benzene. Recalculated.	
	Mean of reduced ratios of $\frac{dp}{dt}.t$ for chloro- and bromo-benzene. Calculated.	Reduced ratios of $\frac{dp}{dt}.t$ for chloro- and bromo-benzene. Recalculated.	Mean of reduced ratios of $\frac{dp}{dt}.t$ for chloro- and bromo-benzene. Calculated.	Reduced ratios of $\frac{dp}{dt}.t$ for chloro- and bromo-benzene. Recalculated.				$CS_2=1$.	$H_2O=1$.
millim. 50	1·095	1·0974	0·880	0·8785	...	740	740	741·5	738·4
100	1·086	1·0870	0·8645	0·8653	1384	1395	1390	1391	1391
150	1·068	1·0803	0·848	0·8570	1982	1946	1964	1987	1984
200	1·071	1·0752	0·8425	0·8506	2558	2525	2542	2551	2565
300	1·068	1·0675	0·8405	0·8415	3670	3657	3664	3662	3670
400	1·0625	1·0618	0·833	0·8345	4724	4703	4714	4710	4723
500	1·057	1·0571	0·829	0·8289	5728	5724	5726	5726	5726
600	1·055	1·0531	0·8245	0·8241	6740	6678	6709	6699	6705
700	1·050	1·0496	0·8195	0·8200	7678	7688	7683	7680	7691
800	1·045	1·0465	0·818	0·8163	...	8602	8602	8618	8589

5. *Chloroform and Water.* Values of $\frac{dp}{dt}.t$ for water taken as unity at each pressure. Temperatures of water as ordinates. $c = -0{\cdot}0006701$.

Pressures.	Reduced ratios of $\frac{dp}{dt}.t$.		$\frac{dp}{dt}.t$ for CCl_3H.	
	Calculated.	Recalculated.	Calculated.	Recalculated.
millim.				
200	·854	·8545	2575	2577
300	·836	·8483	3646	3699
400	·843	·8436	4772	4775
500	·844	·8397	5829	5801
600	·842	·8365	6850	6806
700	·838	·8337	7862	7819
800	·838	·8311	8812	8745
900	·821	·8289	9709	9802
1000	·838	·8269	10846	10708
1500	·818	·8186	15191	15199
2000	·805	·8123	19364	19552
3000	·801	·8030	27813	27893
5000	·777	·7900	42320	43041

6. *Ethyl Bromide and Ethyl Chloride with Water.* Values of $\frac{dp}{dt}.t$ for water taken as unity at each pressure, and compared with mean values of $\frac{dp}{dt}.t$ for ethyl bromide and ethyl chloride. Temperatures of water as ordinates. $c = -0{\cdot}0006335$.

Pressures.	Mean of reduced ratios of $\frac{dp}{dt}.t$.		Mean values of $\frac{dp}{dt}.t$ for C_2H_5Br and C_2H_5Cl.	
	Calculated.	Recalculated.	Calculated.	Recalculated.
millim.				
50	·851	·8449	715	710·1
100	·849	·8364	1364	1344
150	·829	·8311	1919	1924
200	·823	·8271	2483	2495
300	·8085	·8211	3525	3581
400	·8045	·8166	4555	4622
500	·8085	·8130	5587	5616
600	·817	·8099	6647	6589
700	·8085	·8073	7580	7572
800	·8045	·8049	8463	8469
900	·7955	·8028	9407	9493
1000	·798	·8008	10330	10370
1500	·793	·7930	14721	14723
2000	·790	·7871	18994	18946
3000	·7835	·7783	27207	27035
5000	·7615	·7660	41504	41733

7. *Mercury and Water.* From determinations of vapour-pressures of mercury by Ramsay and Young *. If Regnault's values are correct, the equation $R' = R + c(t' - t)$ does not hold good. Values of $\frac{dp}{dt} . t$ for water taken as unity at each pressure. Temperatures of water as ordinates. $c = -0{\cdot}0004236$.

Pressures.	Reduced ratios of $\frac{dp}{dt} . t$.		$\frac{dp}{dt} . t$ for Mercury.	
	Calculated.	Recalculated.	Calculated.	Recalculated.
millim.				
10	·866	·8600	160	158·9
50	·850	·8486	714	713·2
100	·833	·8429	1339	1355
150	·843	·8393	1950	1943
200	·835	·8366	2519	2523
300	·834	·8326	3639	3631
400	·827	·8296	4682	4696
500	·827	·8272	5715	5714
600	·829	·8252	6741	6714
700	·824	·8234	7731	7723
800	·829	·8218	8717	8647
900	·814	·8204	9621	9701
1000	·818	·8191	10595	10607
1500	·811	·8139	15064	15112
2000	·816	·8099	19633	19494
3000	·804	·8040	27919	27928
5000	·800	·7958	43562	43356

8. *Mercury and Carbon Bisulphide.* Employing the values of $\frac{dp}{dt} . t$ for mercury and carbon bisulphide, both recalculated from their ratios with those of water, these values bear an almost constant ratio to each other at all pressures, or $c = 0$. The calculated ratios vary only between 1·0547 and 1·0552.

XIX. *Mechanical Integration of the Product of two Functions.*

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

IN connection with my paper (Phil. Mag. August 1885) on the mechanical integration of the product of two functions, Professor Nanson, of the Melbourne University, has sent me the following suggestion by which the necessity for the special piece of mechanism there described is obviated.

Let $\int_{\alpha_1}^{\alpha_2} \phi(\theta)\psi(\theta)d\theta$ be required; plot the two curves

$$r = \phi(\theta) + \psi(\theta), \quad r = \phi(\theta) - \psi(\theta);$$

---

* The data for these determinations are to be found in the 'Journal of the Chemical Society,' January 1886.

then the area of the figure enclosed by these two curves and the straight lines $\theta=\alpha_1$, $\theta=\alpha_2$ is

$$\frac{1}{2}\int_{\alpha_1}^{\alpha_2}\{\phi(\theta)+\psi(\theta)\}^2d\theta-\frac{1}{2}\int_{\alpha_1}^{\alpha_2}\{\phi(\theta)-\psi(\theta)\}^2d\theta$$
$$=2\int_{\alpha_1}^{\alpha_2}\phi(\theta)\psi(\theta)d\theta.$$

Hence all that is necessary for finding the value of the integral is to measure the above area by means of a planimeter. At first sight it might appear as if, in the practical application of the above method, to analyze the arbitrary curve traced by a piece of self-recording physical apparatus into its harmonic constituents, the construction of the curves $r=\phi(\theta)\pm\psi(\theta)$ with any accuracy would be very tedious; but if it is remembered that in all cases the curves actually traced are traced with Cartesian coordinates, it will be seen that to pass from the curves $y=\phi(x)$, $y=\psi(x)$ to the above sum and difference-curves is about as easy as to pass to the curves $r=\phi(\theta)$, $r=\psi(\theta)$.

Wind the two curves $y=\phi(x)$, $y=\psi(x)$ on a circular cylinder so that the axis of x is at right angles to the generating lines, and arrange two pointers for following the curves so that they are free to move parallel to the generating lines and therefore to the axis of y; attach them to the ends of a string which passes over two fixed pulleys at the level of the top of the cylinder and round a movable pulley, which, as the pointers move, the cylinder remaining at rest, describes a diameter of the top of the cylinder: to enable it to move both backwards and forwards it must be provided with a counterpoise or spring. If the length of the string is so adjusted that, when the pointers are on the axis of x, the movable pulley is at the centre of the top of the cylinder, then the distance r of the pulley from the centre will always be the mean of the distances $\phi(x)$ and $\psi(x)$ of the pointers from the axis of x. As the cylinder is caused to rotate round its axis and the pointers are kept on the two curves, a pencil attached to the movable pulley will trace on a sheet of paper on the top of the cylinder the curve $r=\frac{1}{2}\{\phi(a\theta)+\psi(a\theta)\}$, where a is the radius of the cylinder.

By drawing the reflection of the curve $\psi(x)$ with respect to the axis of x and using it with $\phi(x)$ in the above manner, the curve $r=\frac{1}{2}\{\phi(a\theta)-\psi(a\theta)\}$ can be obtained; or by replacing the fixed pulleys with an obvious arrangement of strings and axles and using the two original curves, the difference-curve can be traced. Then

$$\int_{x_1}^{x_2}\phi(x)\psi(x)dx=\int_{\alpha_1}^{\alpha_2}\phi(a\theta)\psi(a\theta)d(a\theta)=2a\times \text{ area}$$

between the two curves and the lines $\theta=\alpha_1$, $\theta=\alpha_2$.

I am, yours &c.,
Melbourne, December 11, 1885. WILLIAM SUTHERLAND.

XX. *The Differential Equation of a Conic.*
By THOMAS MUIR, *LL.D.*[*]

1. THE differential equation of a conic,

$$9\left(\frac{d^2y}{dx^2}\right)^2\frac{d^5y}{dx^5}-45\frac{d^2y}{dx^2}\frac{d^3y}{dx^3}\frac{d^4y}{dx^4}+40\left(\frac{d^3y}{dx^3}\right)^3=0,$$

which Boole attributes to Monge, and to which Sylvester in this week's 'Nature' (vol. xxxiii. p. 224) so fully directs attention, can be very readily obtained as follows.

2. Let the equation of the conic be

$$a_0+b_0x+b_1y+c_0x^2+c_1xy+c_2y^2=0;$$

and let us denote the successive differential coefficients of y with respect to x by $y_1, y_2, y_3, \ldots.$ Then taking the third, fourth, and fifth differential coefficients of both sides of the equation, we have

$$\left.\begin{array}{l}(2c_2y+c_1x+b_1)y_3+(2c_2y_1+c_1)3y_2 \qquad\qquad\quad =0,\\ (2c_2y+c_1x+b_1)y_4+(2c_2y_1+c_1)4y_3+2c_2\,.\,3y_2^2 \quad =0,\\ (2c_2y+c_1x+b_1)y_5+(2c_2y_1+c_1)5y_4+2c_2\,.\,10y_2y_3=0;\end{array}\right\}$$

whence at once, by elimination,

$$\begin{vmatrix} y_3 & 3y_2 & \\ y_4 & 4y_3 & 3y_2^2 \\ y_5 & 5y_4 & 10y_2y_3 \end{vmatrix}$$

or

$$y_2(40y_3^3-45y_2y_3y_4+9y_2^2y_5)=0,$$

as was required. (*Cf.* Jordan's *Cours d'Analyse*, i. p. 53.)

3. The method is perfectly general. To be seen at its best, however, it requires that for $y_2, y_3, y_4, \ldots$ we write $2!\alpha$, $3!\beta$, $4!\gamma, \ldots.$ Thus, if the equation of any cubic be

$$a_0+b_0x+b_1y+c_0x^2+c_1xy+c_2y^2+d_0x^3+d_1x^2y+d_2xy^2+d_3y^3=0,$$

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[*] Communicated by the Author.

we take the 4th, 5th, 6th, 7th, 8th, and 9th differential coefficients, and find

$$\begin{array}{llll}
M\gamma+N\beta+P\alpha+Q\alpha^2 & & & = \\
M\delta+N\gamma+P\beta+Q\,.\,2\alpha\beta & +R\alpha^2 & & = \\
M\epsilon+N\delta+P\gamma+Q(2\alpha\gamma+\beta^2) & +R\,.\,2\alpha\beta & +S\alpha^3 & = \\
M\zeta+N\epsilon+P\delta+Q(2\alpha\delta+2\beta\gamma) & +R(2\alpha\gamma+\beta^2) & +S\,.\,3\alpha^2\beta & = \\
M\eta+N\zeta+P\epsilon+Q(2\alpha\epsilon+2\beta\delta+\gamma^2) & +R(2\alpha\delta+2\beta\gamma) & +S(3\alpha^2\gamma+3\alpha\beta^2) & = \\
M\theta+N\eta+P\zeta+Q(2\alpha\zeta+2\beta\epsilon+2\gamma\delta) & +R(2a\epsilon+2\beta\delta+\gamma^2) & +S(3\alpha^2\delta+6\alpha\beta\gamma+\beta^3) & =
\end{array}$$

where

$$\begin{aligned}
M&=b_1+c_1x+2c_2y+d_1x^2+2d_2xy+3d_3y^2,\\
N&=c_1+2c_2y_1+2d_1x+2d_2xy_1+2d_2y+6d_3yy_1,\\
P&=d_1+2d_2y_1+3d_3y_1^2,\\
Q&=c_2+d_2x+3d_3y,\\
R&=d_2+3d_3y_1,\\
S&=d_3\,;
\end{aligned}$$

and where consequently, as it is most important to observe for the purpose of deducing any one equation from the preceding,

$$\frac{dM}{dx}=N, \qquad \frac{dN}{dx}=2P+2Qy_2=2P+4Q\alpha,$$

$$\frac{dP}{dx}=4R\alpha, \qquad \frac{dQ}{dx}=R, \qquad \frac{dR}{dx}=6S\alpha.$$

Eliminating M, N, P, Q, R, S, we have the required differential equation

$$\begin{vmatrix}
\gamma & \beta & \alpha & \alpha^2 & & \\
\delta & \gamma & \beta & 2\alpha\beta & \alpha^2 & \\
\epsilon & \delta & \gamma & 2\alpha\gamma+\beta^2 & 2\alpha\beta & \alpha^3 \\
\zeta & \epsilon & \delta & 2\alpha\delta+2\beta\gamma & 2\alpha\gamma+\beta^2 & 3\alpha^2\beta \\
\eta & \zeta & \epsilon & 2\alpha\epsilon+2\beta\delta+\gamma^2 & 2\alpha\delta+2\beta\gamma & 3\alpha^2\gamma+3\alpha\beta^2 \\
\theta & \eta & \zeta & 2\alpha\zeta+2\beta\epsilon+2\gamma\delta & 2\alpha\epsilon+2\beta\delta+\gamma^2 & 3\alpha^2\delta+6\alpha\beta\gamma+\beta^3
\end{vmatrix}=0.$$

4. The equation of the conic, written with like symbols, is

$$\begin{vmatrix}
\beta & \alpha & \\
\gamma & \beta & \alpha^2 \\
\delta & \gamma & 2\alpha\beta
\end{vmatrix}=0.$$

In both we note as part of the law of formation of the elements, that when one non-zero element of a column has been obtained, the next is got from it by the usual "rules of derivation" modified from those of Arbogast to suit the case where, as here, each differential coefficient is replaced by its appropriate submultiple. (*Vid.* De Morgan's 'Calculus,' p. 330.)

5. In the 'Proceedings of the Edinb. Math. Soc.' 1884–85, pp. 95–100, Professor Chrystal has a note on "A Method for obtaining the Differential Equation of an Algebraical Curve." In the case of the cubic he gets for the non-zero side of the equation a determinant of the 6th order which he says can be simplified further. I find that when this simplification is made, and $y_2, y_3, \ldots$ are expressed in terms of $\alpha, \beta, \ldots$, the result agrees perfectly with the above*.

Bishopton, Glasgow, January 9, 1886.

XXI. *Relations of Surface-resistance at Electrodes to various Electrical Phenomena.* By G. Gore, *LL.D., F.R.S.*[†]

In some experiments described in a paper on "Evidence respecting the Reality of 'Transfer-resistance' in Electrolytic Cells," read before the Birmingham Philosophical Society, January 21, 1886[‡], I found that when a current of voltaic electricity was passed from dilute nitric or sulphuric acid, or strong nitric acid, into the surface of a thin platinum bottle used as a cathode, the temperature of the bottle suddenly rose, notwithstanding that certain amounts of heat must have been absorbed by the copious liberation of hydrogen which occurred, and by that substance assuming the gaseous state, each at the surface of the bottle; and I further found that this rise of temperature was not due to heat produced by ordinary conduction-resistance of the bottle or of the liquid, nor to resistance of any kind at the anode, and that it was due to some influence other than that of chemical change, at the surfaces of mutual contact of the liquid and bottle; and further, that it varied in quantity directly as the amount of "resistance" to the passage of the current into the surface of the bottle. I also found similar thermal effects of "resistance" at the surface of the bottle, when the latter was used as an anode.

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[*] The differential equation of the cubic appears to have been first given by Mr. Samuel Roberts in the 'Educational Times.' The question and solution are reprinted in 'Math. from Educ. Times,' x. pp. 47, 48. The date of the first publication of the question, which unfortunately can in no case be got with certainty from the Reprint, should probably be 1868.—T. M. (January 18).

[†] Communicated by the Author: read before the Birmingham Philosophical Society, January 21st, 1886.

[‡] See p. 130 of the present Number.

In a previous investigation on "transfer-resistance" (Proc. Royal Soc. vol. xxxviii. p. 209) I also found "that a species of electric resistance distinct from that of polarization and of ordinary conduction-resistance, varying greatly in amount in different cases, exists at the surfaces of mutual contact of metals and liquids in electrolytic and voltaic cells. That this resistance varies largely in amount with different metals in the same solution, and with the same metal in different solutions," "and is usually small with easily corrodible metals which form readily soluble salts, and large with those which are not corroded;" and "that the same voltaic current was resisted in different degrees by every different metal when employed as an anode, and when used as a cathode;" "and that the resistance at the anode was usually smaller than that at the cathode;" and "that by rise of temperature 'transfer-resistance' was usually and considerably reduced." This "transfer-resistance" differs essentially from electric potential, because it is incapable of producing a current.

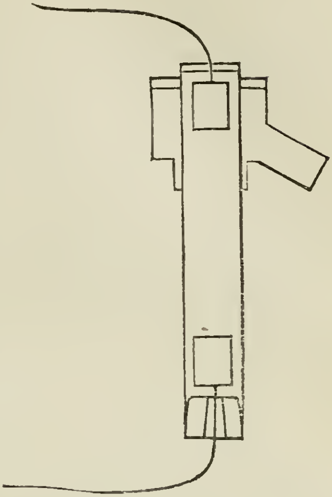
The present experiments were made for the purpose of examining some relations of this "surface-resistance" to various electrical phenomena. I call it "surface-resistance" in the present case, because, in consequence of omission of stirring, it includes other forms of resistance besides that of "transfer" at the surfaces of mutual contact of the metals and liquids employed.

First.—In cases of thermoelectric currents produced by heating the junction of a metal and electrolyte. We know that when heat is applied to one of the two ends of a piece of non-corrodible metal in contact with opposite parts of an electrolyte, an electric current is usually produced, and we infer from the principle of conservation of energy that when such a current occurs heat is absorbed and disappears at or near the heated junction, and is converted into and produces the current.

In order to determine whether the relative amounts of "surface-resistance" at the junctions of such a thermo-couple vary with temperature, and also whether the direction of current produced by such a couple is influenced by the relative total amounts of such "resistance" in the two directions in the circuit, I made the following experiments:—

The liquids employed were dilute sulphuric and nitric acids, each being composed of one volume of strong acid and ten volumes of water; and the electrodes were two perfectly similar sheets of platinum, each having a total immersed area of surface of about 24·0 sq. cm.

The thermoelectric apparatus consisted of a vertical glass



tube, open at its upper end, 19·0 cm. high, and 3·0 cm. internal diameter (see sketch). One of the platinum plates was suspended vertically in the upper end of the tube by means of a platinum wire; and the other, welded to a stout platinum wire, was supported vertically in the lower end by passing the wire through a cork fixed in a hole in a vulcanized indiarubber bung which closed the end of the tube. The two plates were 9·0 cm. apart. The glass tube was nearly filled with the acid liquid; its upper end was surrounded by a water-bath, the water in which was heated by applying a flame to a projecting arm of the bath. The bulb of a thermometer was immersed in the acid liquid near the upper plate; and the wires from the plates were attached to a dead-beat D'Arsonval galvanometer. The liquids were not stirred during the experiments.

With the lower plate at 14° C., and the upper one at 95° C., in the dilute nitric acid, a thermoelectric current of about ·00004 ampère was produced. At the same temperature, in the dilute sulphuric acid, the strength of current produced was about ·00001 ampère. The current flowed from the cold plate through the liquid to the hot one in each case. As platinum is a thermoelectro-positive substance, though in a feeble degree, in metallic couples, these results indicate that both these liquids were thermoelectro-positive, and much more strongly so than platinum.

The electromotive forces of these couples during a state of balanced current were measured by means of a modified form of Poggendorff's method; and the values found were as follows:—With the plates at 14° and 95° C. in the dilute nitric acid, ·418 volt; in the dilute sulphuric acid, ·282 volt; and in a mixture of one volume of hydrochloric acid and ten of water, ·208 volt.

The amounts of "surface-resistance" were also measured by using a rheostat as a slide-wire bridge; the same electrodes, with the same amounts of immersed surface, being employed as were used in the thermoelectric experiments.

The electrodes faced each other at about 5·0 cm. apart in the respective liquids in a glass cup, the one which was positive in the thermo-couple being used as the anode; and the strengths of current employed were the same as the thermoelectric ones, because I have found that an alteration of strength of current affects the amount of "transfer-resistance." One terminal of a Thomson's reflecting-galvanometer of 3040 ohms resistance was connected with the slider; and the other connected, first to the anode (or cathode), and then to a vertical platinum wire (or idle electrode) immersed in the liquid close to the anode (or cathode) but not touching it; a balance being obtained in each case by moving the slider.

In the dilute nitric acid, with a current of ·00004 ampère, the amounts of "surface-resistance" were:—

	At 14° C.	At 95° C.
At the anode . .	49266 ohms.	531 ohms.
At the cathode .	29784 ,,	494 ,,

By a rise of temperature, therefore, of one of the pieces of platinum of the thermoelectric couple 81 Centigrade degrees, the amount of "surface-resistance" of that piece was reduced, as a cathode or in the direction of the thermoelectric current, 98·34 per cent., and in the opposite direction, or as an anode, 98·92 per cent.; and the total "surface-resistance" in the circuit was also reduced 37·05 per cent. in the direction of that current, and 61·65 per cent. in the opposite one.

The results also show that the cold platinum offered 39·55 per cent., and the hot platinum 6·97 per cent., less amount of "surface-resistance" as a cathode than as an anode; also that the total amount of such "resistance" in the two directions in the circuit, when one of the junctions was heated to 94° C., was 64·14 per cent. greater in the direction of the thermoelectric current produced than in the opposite one.

In the dilute sulphuric acid, with a current of ·00001 ampère, the amounts of "surface-resistance" were:—

	At 14° C.	At 95° C.
At the anode . . .	63500 ohms.	3848 ohms.
At the cathode . .	18350 ,,	2152 ,,

By a rise of temperature, therefore, of one of the pieces of platinum of the thermoelectric couple 81 C. degrees, the amount of "surface-resistance" of that piece was reduced in the direction of the thermoelectric current, or as a cathode, 88·27 per cent., and in the opposite direction, or as an anode, 93·94 per cent.; and the total "surface-resistance" in the circuit was also reduced 19·79 per cent. in the direction of that current, and 72·88 per cent. in the opposite one.

The results also show that the cold platinum had 71·10 per cent. and the hot platinum 44·08 per cent. less amount of "surface-resistance" as a cathode than as an anode; also that the total amount of such "resistance" in the two directions in the circuit, when one of the junctions was heated to 94° C., was 195·75 per cent. greater in the direction of the thermoelectric current than in the opposite one.

The results obtained with these two liquids show that the amount of "surface-resistance" at each junction of such thermoelectric couples varies very greatly with temperature; and that the amount of such "resistance" to the passage of a current in either direction was more largely decreased by rise of temperature with the dilute nitric than with the sulphuric acid. I had previously found with thermoelectric couples composed of metals and electrolytes, "that by rise of temperature 'transfer-resistance' was usually and considerably reduced." (Proc. Roy. Soc., 1885, No. 236, p. 210.)

The direction of thermoelectric current produced in each of these two cases was the same as that indicated by the relative amounts of "surface-resistance" in opposite directions at the heated junction, but the reverse of that indicated by the relative total amounts of such "resistance" in opposite directions in the entire circuit.

As in each of the two couples, the total amount of "surface-resistance" in the circuit, when one of the junctions was heated, was very much greater in the direction of the thermoelectric current produced than in the opposite one, I conclude that the direction of that current was not chiefly determined by the alteration of such "resistance" by rise of temperature. The thermoelectric action and the "surface-resistance" therefore appear to be largely distinct phenomena; and as both liquid and metal in those couples were thermoelectro-positive substances, the direction of the current was probably caused chiefly by the thermoelectro-positive potential of the liquid increasing more rapidly than that of the metal by rise of temperature. We may also infer that the strength of the thermoelectric current in those couples was very largely increased by the great diminution of "surface-resistance."

In a paper on "Some Relations of Heat to Voltaic and Thermoelectric Action of Metals in Electrolytes" (Proc. Royal Soc. 1884, No. 233, pp. 251–290), I have shown by numerous experiments that "when metals in electrolytes were heated they were more frequently rendered electro-positive than negative, in the proportion of about 2·8 to 1·0; the proportion in strong solutions was about 3·27 to 1."

Second.—With regard to voltaic couples. As heat affects largely the amount of "surface-resistance," and the strength of current, in a thermoelectric couple composed of a metal and an electrolyte, we may infer that it would also, chiefly by altering that "resistance," affect the strength of current in a voltaic cell.

In order to experimentally examine this, the lower platinum plate in the thermoelectric apparatus, already described, was replaced by a rod of amalgamated zinc 8·0 mm. long and 2·0 mm. thick; the upper platinum plate being retained in its place. The tube was then filled with the cold mixture of one volume of sulphuric acid and ten of water.

With the entire apparatus and liquid at 14° C., the electromotive force (determined by the above-named method) was ·704 volt, and the strength of current without additional resistance in the circuit was ·022 ampère.

With the platinum plate and upper portion only of the liquid at 95° C., and the zinc electrode and liquid around it at 14° C., the electromotive force was ·763 volt, and the strength of current ·0705 ampère.

These results show that the electromotive force was increased about 8·38 per cent., and the strength of current 220 per cent., or to 3·2 times its original amount, by raising the temperature of the platinum negative plate 81 C. degrees. This increase of strength of current was about 24 per cent. greater than when the lower plate was composed of platinum. This great increase of current was, I consider, largely due to decrease of "surface-resistance" at the negative plate, and in some measure also to the increase of electromotive force attending increased thermoelectro-positive potential of the liquid; also to several other manifest but minor circumstances, such as diminished conduction-resistance of the liquid, &c.

Third.—With regard to the thermoelectric phenomena of metals. Some experiments were made to try and detect any special degree of resistance at the junctions of ordinary metallic thermoelectric couples, in the following manner:—

The first couple consisted of a smooth horizontal bar of bismuth, and one of antimony, soldered end to end; each bar being 2·0 cm. long, ·7 cm. wide, and ·5 cm. thick. Whilst a current of ·2 ampère was being passed from one end of the bar to the other, the ends of two thin copper wires, about 1·0 cm. apart, forming the terminals of a Thomson's reflecting-galvanometer of 3040 ohms resistance, were slid very slowly at right angles to and in a horizontal direction, from one end to the other, to and fro, along the upper surface of the couple; the direction of voltaic current being occasionally reversed. Under these conditions, a small portion of the current passed through the galvanometer. There was no sudden change in the deflection of the needles at any time when the wires crossed the junction of the two bars. A similar negative result occurred when a thermo-couple formed of iron and German-silver wires 1·5 mm. diameter was employed; and also when a pair composed of platinum wire and mercury was used.

Had there existed a difference of resistance equal to ·001 ohm at the junction in either case, it would probably have been detected. I conclude, therefore, that if "surface-resistance" of any kind exists at the junctions of metallic thermoelectric couples, it must be exceedingly small in amount, and that it does not sensibly affect the direction or strength of the currents produced by them.

Some attempts were made to ascertain whether the amount of "transfer-resistance" at an electrode formed of a loop of platinum wire was affected by passing a separate current of electricity through it simply as a conductor, but the results were not satisfactory.

Several of the results of experiments described in this paper agree with the conclusion that differences of "transfer-resistance" are incapable of producing a current, and are essentially unlike differences of electric potential; also, that heat decreases "transfer-resistance" whilst increasing contact-potential in metal-electrolyte thermoelectric couples.

XXII. *On the Numerics of the Elements.*—Part II.

By Edmund J. Mills, *D.Sc., F.R.S.*[*]

> *πεπερᾶσθαί τε τὸ πᾶν καὶ ἕνα εἶναι κόσμον· γεννᾶσθαί τε αὐτὸν ἐκ πυρὸς καὶ πάλιν ἐκπυροῦσθαι κατά τινας περιόδους ἐναλλὰξ τὸν σύμπαντα αἰῶνα· τοῦτο δὲ γίνεσθαι καθ' εἱμαρμένην.*—Diog. Laert. ix. 8.

Contents.—Introduction.—New Data and Verifications.—Genesis of the Elements.—Scale of Celestial Temperature.—Variable Stars.—Classification of the Elements.—Polymers.—Periodicity.—Evenness.—Frequency.—Table of the Elements.

In Part I.[†] I have shown that the Numerics of the Elements, so far as they have been accurately determined, may all be expressed by the equation

$$y=pn-n\left(\frac{n}{n+1}\right),$$

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[*] Communicated by the Author.

[†] For Part I. see Phil. Mag. [5] vol. xviii. p. 393 (1884).

where $n=15$, p is the periodic or group number (*i. e.* 1, 2, 3, &c., as the case may be), and x is an ordinal integer. A fair example of the accuracy of the theory occurs in Group II., for which the equation is

$$y=2\times15-15(\tfrac{15}{16})^x,$$

$$=30\quad-15(\cdot9375)^x.$$

Element.	x.	y.	y calculated.
O . . .	1	15·96	15·94
F . . .	5	18·98	19·14
Na . .	12	23·00	23·09
Mg . .	15	24·28	24·30
Al . . .	25	27·01	27·01
Si . . .	32	28·20	28·10

On examining the above numbers, it will be seen that the agreement between calculation and experiment is very striking. The first, third, fourth, and fifth numerics are certainly known to the first place of decimals; and here the coincidence is closest: the second and sixth are not known so accurately; and here the coincidence is less close. Similar comments might be made on nearly all the sixteen groups.

As the differences between consecutive values of y diminish with the increase of x, the verification of the theory is necessarily dependent in the main upon low values of x. In about 46 cases the value of x is 20 or less, and the corresponding values of y (having been well determined) agree well with theory; but beyond the limit of $x=20$, there are at least 15 cases of good determinations which also exhibit a very satisfactory agreement.

The difference y_1-y_2 in any group is equal to ·88 ;

$$y_{10}-y_{11}=\cdot49;\ y_{20}-y_{21}=\cdot26.$$

All these differences are greater than are found in accurate determinations of numeric. Even the difference $y_{42}-y_{43}=\cdot06$ is perfectly accessible to refined experiment. When, then, the theory agrees very closely with a long range of experimental numbers which might apparently have had any other values whatever, it may be regarded as having a reasonable foundation.

The following corrections, partly based on new data, enable me to adduce additional evidence of the general correctness of the theory.

Lanthanum.—Cleve's result (confirming Brauner's) becomes La=137·58, if we take the calculated numerics O=15·94, S=31·82. The third member of Group X. has the numeric 137·64.

Cerium.—Brauner has most exhaustively confirmed Robinson's long series of results. We may therefore take mean experimental Ce as finally settled at 139·89. Hence Ce is the sixth member of Group X., its calculated numeric being 139·82.

Didymium.—According to Cleve, didymium free from samarium has the numeric 141·70 (recalculated as for La). It is accordingly the ninth member of Group X., for which $y=141·61$.

[The above three numerics constitute an exact triad as regards their order in this group, the values of x being 3, 6, 9 respectively.]

Samarium.—Cleve's new result is (recalculated as previously) Sm=149·36. This agrees exactly with $x=49$ in Group X.

Erbium.—The balance of evidence is, on the whole, favourable to Er=165, nearly. This is the value of y when $x=0$ in Group XII.

Ytterbium.—The most trustworthy results, on recalculation, make Yb=172·22. The tenth member of Group XII. has the numeric 172·13.

Tantalum.—Marignac's best number is undoubtedly the one which depends on the ratio $2K_2SO_4 : Ta_2O_5$, because the method of calculation necessarily diminishes the effect of experimental errors. Putting K=38·92, and otherwise recalculating as before, Ta=181·84. The agreement with y_2 (in Group XIII.) =181·82 is still closer than indicated in Part I.

Thorinum.—Nilsson's experiments (1883) are perhaps more valuable than those of his predecessors. His mean numeric (also recalculated) is Th=230·47. The seventh member of Group XVI. has the numeric 230·45.

Uranium.—In Part I., U=239·70, on the basis of Peligot's results. If the calculated values of C and O be taken, U=239·64, corresponding to the fifty-ninth numeric (239·67) in Group XVI. A glance at the Table (*infrà*) shows that position to be quite anomalous, and that the numeric has been much over-estimated.

Scandium, Yttrium, and *Platinum* have been examined afresh. The numerics assigned to them in Part I. are confirmed.

[*Note.*—I have observed that the earlier values of numerics are apt to be too high.]

GENESIS OF THE ELEMENTS.

The equations in Part I. were obtained empirically by trial amongst the numerics. The sixteen groups to which they correspond represent the well-known phenomenon of periodicity, which probably accompanies all kinds of seriated chemical change. But the nature of the operator x in the expression

$$y=pn-n\left(\frac{n}{n+1}\right)^x$$

was not at that time discussed. I now propose to interpret the equations, and therefore to account for the genesis of the elements, on simple suppositions derived from the existing phenomena of experimental chemistry.

All investigators who have discussed the formation of stellar or elementary matter agree that at one time it was in an intensely heated condition; and that it has arrived at its present state by a process of cooling. The process of cooling may be assumed to have been practically a free process, (1) because it could not have been affected by elements not yet existing, and (2) because space may be regarded as infinite and vacuous as regards nebular matter.

Chemical substances in the process of cooling naturally acquire an increase of density; and if the increase of density be measured as a function of time or temperature, we not unfrequently observe that there are critical points, corresponding to the formation of new and well-defined substances. Thus, by cooling or loss of heat, common phosphorus becomes red phosphorus, the substance I furnishes I_2, S_2 yields S_6, and NO_2, N_2O_4; styrol is transformed into metastyrol, aldehyde into paraldehyde, cyanates into cyanurates, turpentine into metaterebenthene; &c., &c. At the critical points heat is evolved in marked abundance, and the bodies then formed are termed "polymers;" the changes themselves admit, as a rule, of reversal. If it were possible for us to cool down chemical substances through a vast range of temperature, there would, doubtless, be a much greater number of critical points, or points of multiple proportion, discovered than are at present experimentally known to us.

The process, then, of cooling the primitive matter may be regarded, from a chemical point of view, as resulting in the formation of a succession of polymers $(1, 2, 3, \ . \ . \ .)n$, n being the primitive density. But on account of the evolution of heat when a polymer is formed, there will ensue, as a physical consequence, the inversion of more or less of the cooling, and therefore of the polymerization.

The law of free cooling is known to us by the researches of Dulong and Petit.* Its simplest expression is

$$\nu = ma^t,$$

where ν is the number of Centigrade degrees lost per minute, t is the temperature, m is a constant of condition, and $a=1{\cdot}0075$ is a constant † uniformly the same for all matter. The law of heating will of course be the inverse of this, and take the form

$$\nu = m\left(\frac{2}{1{\cdot}0075}\right)^t = m({\cdot}99256)^t.$$

Inasmuch, however, as we are now dealing with temperature on some celestial scale, a modification will be required in the numerical value of the universal geometrical factor. This factor and m should be deducible from experiment. On the whole, if the numerics of the elements depend on polymerization, more or less inverted by heat necessarily developed at the critical points, they must correspond to the equation

$$y = (1, 2, 3, \quad . \quad . \quad .)n - ma^t.$$

The induction given in Part I. (where x is written for t) shows that this is actually and very exactly the case. The values of n and m are the same (15); and there is a universal factor $a = {\cdot}9375$ for all elements within the common system. This system may be typically represented as

$$y = (1, 2, 3, \quad . \quad . \quad .)n - n\left(\frac{n}{n+1}\right)^t,$$

an equation which not improbably includes other systems of elementary bodies.

Scale of Celestial Temperature.—The universal constant a of Dulong and Petit has an average value of 1·16143 for 20° C., or $\sqrt[20]{1{\cdot}16143} = 1{\cdot}0075$ for 1° C. Now the reciprocal of ·9375 is $1{\cdot}0\dot{6}$; which, when raised to the power 2·3173, is equal to 1·16143. Twenty Centigrade degrees, therefore, correspond to 2·3173 degrees on the celestial scale, one degree of which is, consequently, equal to 8°·6307 C. The equation $y = -15({\cdot}9375)^t$ represents a rate of heating when the conditions are supposed to be constant in the unit of time.

Variable Stars.—When the process of polymerization above

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* *Ann. Ch. Phys.* vii. 252 (1817).

† Dulong and Petit give 1·0077. The above value is calculated from all their determinations.

referred to takes place on a sufficiently large scale, there will not only be cooling down attended by periodic evolution of heat, but, if the heat be sufficiently intense, light will be emitted, and the site of these operations will vary periodically in brightness. Hence the star will have what is called a "variable" character; and a star of this kind may be regarded as in the process of forming its elements. It is probable that all stars are, or have been, "variable" stars.

CLASSIFICATION OF THE ELEMENTS.

An element may be defined as one of a list of comparatively simple substances whose numerics are of the form

$$y = (1, 2, 3 \dots) 15 - 15 (\cdot 9375)^t.$$

The position of any numeric in a classification will depend upon the periodic, polymeric, or group number $p = 1, 2, 3 \dots$, and upon t. I have calculated these positions for all known numerics, and give them in the accompanying Table.

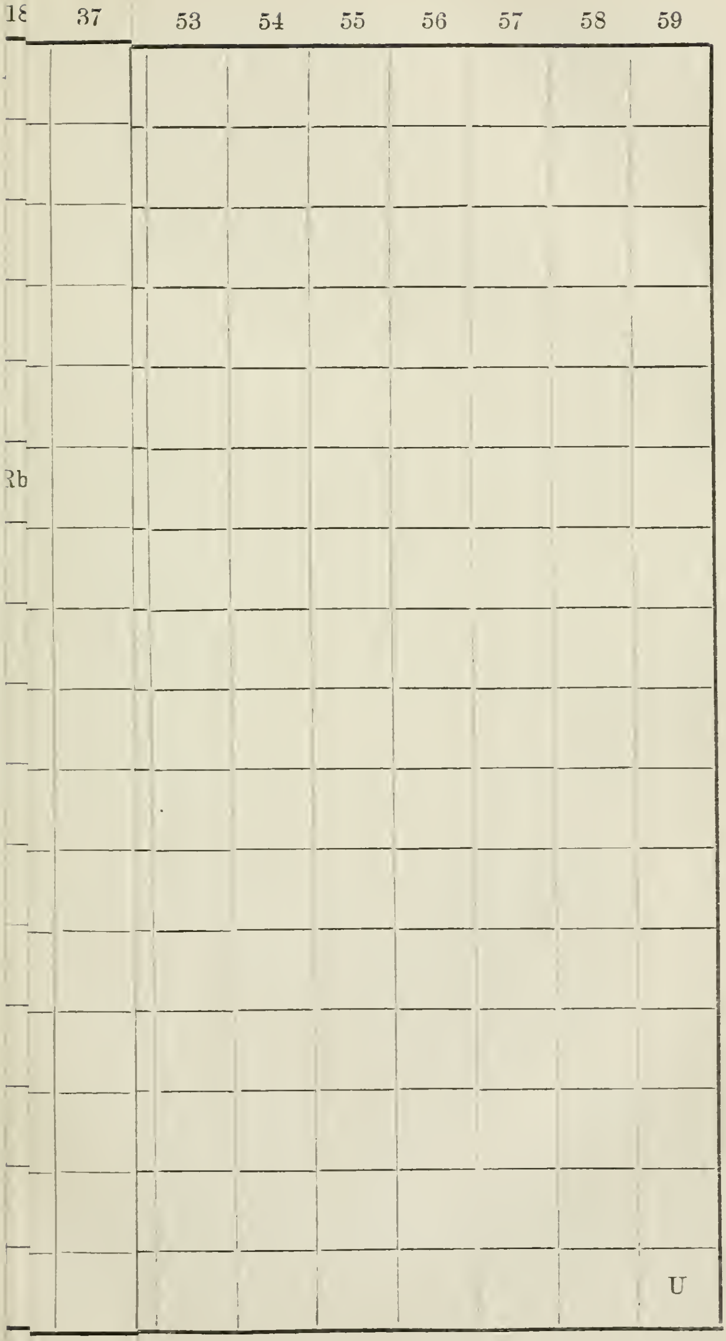
The classification of the elements according to the genetic method of the Table leads to some results of considerable interest:—

1. *Polymers.*—The only known polymers of the primitive matter are As, Sb, probably Er, and perhaps Os. I have placed these under $t=0$ in a later, rather than under $t=\infty$ in an earlier group, because they appear to me to belong naturally to the places assigned to them. Their respective numerics are 74·92, 119·96, and 165; all obviously multiples of 15. Zr, Ru, Sm, and Pt closely approach the positions of other polymers.

2. *Periodicity.*—The polymers whose numerics are multiples of 15 are the first or prime indications of periodicity. Other periodicity must be sought within the groups, as a function of t; or from group to group, as a function of p; or as a function of p and t conjointly.

Of periodicity within the group there is a beautiful instance in Groups II. and IV.; the numerics of O, F, Na, Mg in the former group being exactly imitated, five divisions further to the right in the latter, by Ti, Cr, Mn, Fe. [It is difficult to resist the impression that Ni=57·84 ($t=30$), and that it corresponds to Al in the same imitation; we can also see that, when Si or Co is exactly known, Co or Si will be fairly within our reach.]

A similar example occurs in Groups I., II., III., VI., where the respective values of $t=10$, 12, 14, 18 correspond to the analogous elements Li, Na, K, and Rb. Again, F, Na, Mg


18
37
53
54
55
56
57
58
59
Rb
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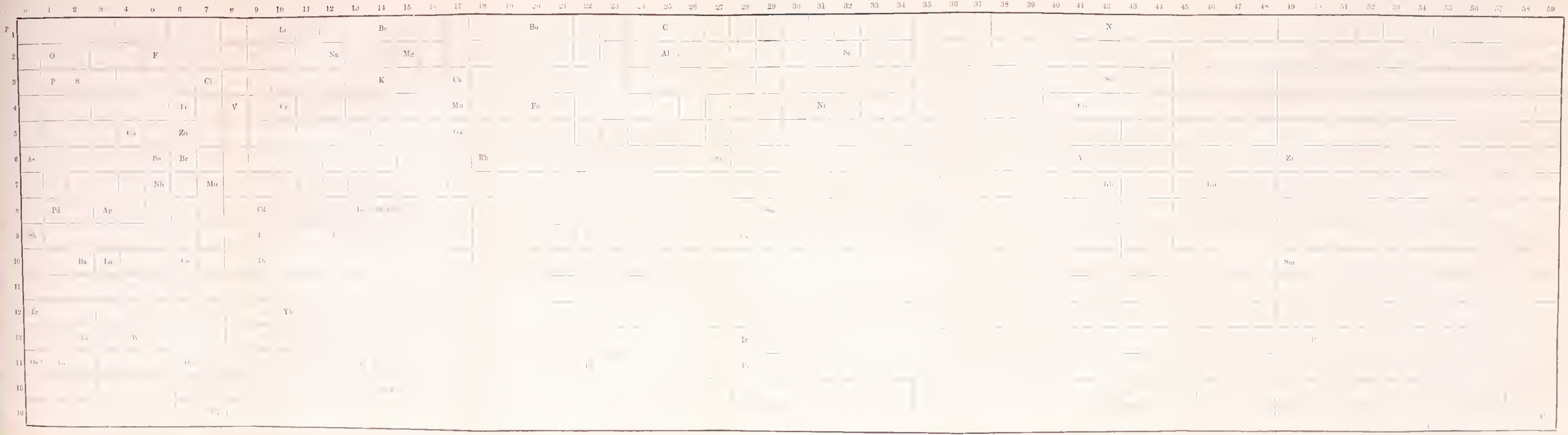
CLASSIFICATION OF THE ELEMENTS
(GENETIC METHOD.)

$y = 15p - 15(\cdot 9375)^t$.



in II. are equidistantly imitated by Cl, K, Ca, analogous elements in Group III.

Of periodicity with regard to p only, we have the interesting set of instances :—

$p =$	3	6	9
	Cl	Br	I
	K	Rb	Cs
	S	Se	Te

Of diagonal periodicity ($p+t=$const.) several instances may be observed by a glance at the table. Other periodic relations may he worked out, or suggested, with the help of this table.

Evenness.—The physical relations of seriated carbon compounds are differently expressed according to evenness ; *i. e.* according as the coefficient of C in their formula is even or odd. I have thought it worth while to examine the numerics of the elements with respect to the evenness of p and t. As regards the evenness of p, 42 numerics occur in evenly numbered groups, and only 26 in the odd groups ; here the evenness is significant. As regards the evenness of t, there are 32 odd and 32 even occurrences, exclusive of 3 zero values ; here nothing depends upon evenness.

Frequency.—In addition to the remarks in the last paragraph it may be observed that 45 numerics have their positions in the first eight groups, the remaining 23 occurring in the last eight groups. Thus it is about two to one that a numeric will occur in an early and in an even group.

It follows from the equations given in this memoir, that the number of the elements may be infinite. The genetic method of classification is the only one hitherto adduced that includes this possibility, and comprises, without exception, all known elements. But the number of experimental methods is not infinite ; and the history of past discovery has convinced me that few, if any, elements are now likely to be discovered, unless by a new method or by a new combination of existing methods.

According to the Herakleitic seer, the All surceased and the world is One ; it was born from fire and will again be burned up—period after period, in alternate phases, through all duration ; and this takes place in terms of a rigorous law. The fundamental view of this memoir has an antiquity of at least two thousand three hundred years.

Glasgow, Jan. 13, 1886.

XXIII. *Notices respecting New Books.*

Theoretische Optik: gegründet auf das Bessel-Sellmeiersche Princip. Von DR. E. KETTELER, *Professor an der Universität in Bonn.* Large 8vo. (Pp. 652.) Viewig und Sohn: Braunschweig.

PROFESSOR KETTELER has done a useful service in thus issuing in a collected form the results of his numerous and important optical papers which have appeared from time to time in Wiedemann's *Annalen*, and in enabling the reader to grasp, as a whole, the theory which he has put forward. The book treats of the propagation of light in isotropic and crystalline media, of dispersion and absorption, and of the conditions which are satisfied at the surface of two separate media. The theory is based on the mutual reaction between the æther and the particles of the transparent medium through which the light is being propagated.

Various suggestions as to the form of this reaction have been made by Sellmeier, Helmholtz, Lommel, and Voigt, and the equations of motion to which they lead may be summed up in the forms

$$\left.\begin{aligned} m\frac{d^2\xi}{dt^2} &= \mathrm{X}+\mathrm{F}(\xi,\xi'), \\ m'\frac{d^2\xi'}{dt^2} &= \mathrm{X}'-\mathrm{F}(\xi,\xi'), \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where m and m' are the densities of the æther and matter, ξ, ξ' their displacements, X and X′ the forces on the æther and matter, so far as they do not depend on the mutual action between the two, while $\mathrm{F}(\xi, \xi')$ expresses this action. The main difference in their theories arises from variations in the form assigned to the function F. Ketteler holds that it is impossible, with our present knowledge, to determine with certainty the form of F, and endeavours to eliminate it from the equations. This he does by considering the system of æther and matter as a whole, and equating the increase of kinetic energy of an element of volume to the work done on the element by the action of the æther and matter external to it.

This leads him to the equation

$$m\frac{d^2\xi}{dt^2}-\Sigma m'\frac{d^2\xi'}{dt^2}\mathrm{C}=e\nabla^2\xi+\Sigma \mathrm{B}m'\left(\mathfrak{k}\xi'+\mathfrak{g}'\frac{d'\xi'}{dt}\right), \ldots\ldots \quad (2)$$

C being a constant, and the symbol Σ being supposed to include all the different kinds of matter elements possible. This expresses what is called by Ketteler Sellmeier's principle.

But a second equation is required to solve the problem, and in some of his earlier papers the author endeavoured to extract this out of the energy equation. In the book before us he realizes the impossibility of this endeavour, and (p. 88) "combines with the above a second, expressing the special form of action of the matter-particles which *can be no other than** the renowned fundamental equation of Bessel's theory of the pendulum"!!

This equation is

$$C\frac{d^2\xi}{dt^2}+\frac{d^2\xi'}{dt^2}=-\left(\mathfrak{k}\xi'+\mathfrak{g}'\frac{d\xi'}{dt}\right). \qquad (3)$$

These two equations form the basis of this new theory of Optics; and it is difficult to see that it obtains from them any firmer support than the other theories which have been put forward do from the special form of reaction assumed in each of them. In fact, as Ketteler has shown himself, the theory is, except in one point which seems hardly essential, identical in its results with that which follows from supposing that

$$F(\xi,\xi')=\beta^2\frac{d^2}{dt^2}(\xi-\xi).$$

Helmholtz puts

$$F(\xi,\xi')=\beta^2(\xi-\xi'),$$

and Lommel

$$F(\xi,\xi')=\beta^2\frac{d}{dt}(\xi-\xi').$$

The equations are integrated (on pages 98 and following) and lead to a formula connecting the refractive index and the period which has been verified by careful experiments by Ketteler, and is undoubtedly an exceedingly close approximation to the truth.

Ketteler's own equations (VII) (p. 98), with his interpretation of the constants, seem to contradict the third law of motion completely, though a slight alteration in the meaning of the constants will remove this fatal difficulty.

The foundations of the theory of double refraction appear to be even less secure. The quantity denoted by B in equation (2) is supposed to be a function of the direction—for a transparent medium $\mathfrak{g}'$ vanishes. The displacements are shown not to be in the wave-front, and while in the term $\nabla^2\xi$ the whole displacement is introduced, in the other terms, it is only the component of the displacement resolved in the wave-front with which we have to deal. It is *assumed* that æther and matter-particles vibrate in parallel directions, and from this it follows that C is a constant independent of the direction. The complete equations are given on p. 309.

The surface conditions developed by Ketteler are not those which hold between two elastic solids. His fundamental principles are given correctly on p. 130, but in applying (1), "the principle of continuity," he neglects the resolved part of the displacement normal to the interface, and hence avoids the difficulty of dealing with the pressural wave of Green's theory, which he considers (p. 275) has played "eine ominöse Rolle" in theoretical optics.

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* The italics are ours

He also attempts to show that his third principle, "the conservation of energy," implies the continuity of the molecular rotations across the interface; but in his proof of this (p. 148) he omits, in calculating the stresses, the terms involving the dilatation. Now though this vanishes, its coefficient in the expression for the stress is infinite, and the product of the two, as Green showed, must be retained.

A chapter at the end of the theoretical part is devoted to the Electromagnetic theory of Light, and there is some confusion between the periodic changes in the æther which constitute light, and those to which electric and magnetic displacement are due. According to Maxwell's theory, the electric displacement is normal to the plane of polarization, the magnetic displacement is in that plane, and both are in the wave-front; but Maxwell nowhere states that the displacement which constitutes light coincides with the electric or magnetic displacement, and either view is open to his supporters.

XXIV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 78.]

December 16, 1885.—W. Carruthers, Esq., Vice-President, in the Chair.

THE following communications were read:—

1. "Old Sea-beaches at Teignmouth, Devon." By G. Wareing Ormerod, Esq., M.A., F.G.S.

The author stated that while old records show that no important changes have taken place in the level of the Teignmouth district during the historical period, the excavations made in recent drainage-operations in the present year showed the existence of at least two series of beaches. The oldest sea-beach, which is a few feet above the present sea-level, was partly washed away and then covered up by later deposits exhibiting evidence, in a number of delicate bivalve shells in an unbroken condition, of having been deposited in a calm sea.

2. "On the Gabbros, Dolerites, and Basalts of Tertiary Age in Scotland and Ireland." By Prof. John W. Judd, F.R.S., Sec. G.S.

In previous papers, published in 1874 and 1876, it has been demonstrated by the author that there exist in Scotland and in Hungary igneous rock-masses presenting the most perfectly crystalline characters and belonging to the Tertiary period. It was further shown that such highly crystalline, plutonic rocks are seen passing insensibly into volcanic rocks of the same chemical composition—gabbros into basalts, diorites and quartz-diorites into andesites, and quartz-andesites and granites into rhyolites—the lavas in turn graduating into the perfectly vitreous types known as tachylytes and obsidians.

The present paper deals with the basic rocks of Western Scotland

and Northern Ireland, which are shown to exhibit the most marked analogies with rocks of the same age in the Faroe Isles and Iceland; these facts lend strong support to the doctrine of the existence of petrographical provinces. The Tertiary age of the Scotch and Irish rocks is placed beyond dispute by the fact that they overlie unconformably the youngest members of the Cretaceous system, and are interbedded with stratified deposits of Lower Tertiary age.

With regard to the nomenclature of these rocks, the identification of the more crystalline forms with the gabbros, which was made by Zirkel and Von Lasaulx, is supported; while the use of the term "dolerite" as a convenient one for the connecting links between the gabbros and basalts is advocated.

Of the original minerals contained in these rocks, plagioclase felspar (ranging in composition from anorthite to labradorite), augite, olivine, and magnetite are regarded as the essential ones: while enstatite, biotite, chromite, picotite, and titanoferrite are among the most frequently occurring accessories. It is shown, however, that these original minerals may belong to different periods of consolidation. The Secondary minerals are very numerous, including quartz, epidote, zoisite, hornblende, serpentine, and zeolites, with many other crystallized and uncrystallized substances. There are remarkable variations in the relative *proportions* of the original minerals in different examples of the rock; and by the complete disappearance of one or other of the constituents, the gabbros are sometimes found passing into picrites, eucrites, or troctolites.

In their microscopic structure these rocks present many interesting features. From the highly crystalline gabbros there are two lines of descent to the vitreous tachylytes: one through the *ophitic* dolerites and basalts, and the magma-basalts with skeleton-crystals; and the other through the *granulitic* dolerites and basalts, and the magma-basalts with granular microliths. The former are shown to result from the cooling down of molten masses which were in a state of perfect internal equilibrium; while the latter were formed when the mass was subject to movement and internal strain.

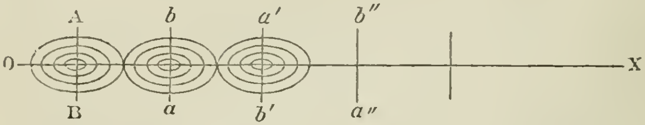
It is shown that in the most deeply seated of these rocks (gabbros) the whole of the iron-oxides combine with silica; but, as we approach the surface, the quantity of these oxides separating as magnetite increases, until it attains its maximum in the tachylytes. In all the varieties the order of separation of the different minerals is shown not to depend solely on chemical causes, but to be influenced by the conditions under which the rocks have cooled down.

Although these rocks are not highly altered ones, yet they afford admirable opportunities of studying the incipient changes in their constituent minerals. The nature of these changes is discussed, and they are referred to the following causes:—(1) the corrosive action of the surrounding magma on the crystals; (2) the changes produced by solvents acting under pressure in the deep-seated masses (these have been already described under the name of "schillerization"); (3) the action of heated water and gas escaping at the surface; (4) the action of atmospheric agents on the rocks when exposed by denudation; and (5) the changes induced by pressure during the great movements to which rock-masses are subjected.

XXV. *Intelligence and Miscellaneous Articles.*

A SIMPLE WAY OF EXPLAINING CLERK MAXWELL'S ELECTROMAGNETIC THEORY OF LIGHT. BY MISS J. M. CHAMBERS, B.SC.*

THE following is how I have supposed the "series of oppositely directed magnetizations and electromotive forces" of C. Maxwell's theory to arise. I do not in the smallest degree pretend to comprehend his mathematics, and it is only from his verbal explanation that I have formed the following conception of what his meaning is.



Suppose we have a straight linear conductor A B in which from some cause or another a quantity of electricity is continually bobbing up and down. We know that the lines of magnetic force, arising from these alternate up and down currents, will be circles having the linear conductor for axis. Suppose we have a row of these conductors parallel to one another.

When the magnetic force-lines cut the next conductor *ba*, an electromotive force of opposite sign to that in A B will be engendered, in accordance with Lenz's law, and a current will ensue which will in its turn be surrounded by magnetic force-lines. When the current in A B is reversed, the induced one in *a b* will be so too.

The action of *a b* on *a′ b′* will be the same as that of A B on *a b*; and the same effects will be propagated along the whole line of molecules. We have here the electromotive forces and the magnetic forces acting in directions perpendicular both to one another and to the direction of propagation, O X, as the theory requires. Of course this explanation would be for a plane-polarized ray.

It seems to me that this explanation presents to the non-mathematical mind, in a tangible form and in accordance with well-known electrical phenomena, what may be the manner of production of the "series of oppositely directed magnetizations and electromotive forces."

It is not necessary that the conductors should be linear; we may suppose them globular and touching one another, without inter-

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* Communicated by the Author.

fering with the idea of the action above explained. We may in fact suppose them merely portions of the æther.

Perhaps it may be objected that my conductors are not circuits; but a current which keeps passing backwards and forwards from a condenser acts in precisely the same manner as a true current (see art. 776 Maxwell &c.), and why not also without the condenser?

Note.—Perhaps this idea is nothing new, and has occurred to others as well as to me. I have been told, however, that C. Maxwell himself would never precisely define the action by which he supposed light and electromagnetic induction propagated.

ON A NEW APPARATUS FOR MEASURING ELECTRIC CURRENTS.

BY M. DE LALANDE.

The apparatus for measuring electrical currents based on the use of magnetic needles or of permanent magnets are known to be largely influenced by the variations in the terrestrial magnetism, as well as by variations in the magnetic conditions of the magnets themselves. The data furnished by instruments of this kind which are provided with a fixed graduation in amperes or volts, can only be guaranteed when their standard is verified at close intervals. This is a serious inconvenience, especially for industrial application, for which these instruments have the great advantage of giving direct and continuous indications.

The amperemeters and voltmeters which I have the honour to exhibit to the Academy have no permanent magnets in their construction, and therefore are free from the source of errors just mentioned. They depend on the actions exerted by a solenoid on a bundle of soft iron wires movable in the interior, and kept by an antagonistic force. They belong to the type of M. Becquerel's electromagnetic balance, and like this instrument enable us, so to speak, to *weigh* the electrical action of currents.

The apparatus, which might be called an electrical areometer, consists of a bundle of soft iron wires placed inside a metal areometer which is immersed in a glass cylinder full of water, and round which is coiled the wire through which passes the current to be measured. The original position of the areometer (regulated by the level of the liquid, which is kept constant) is always the same; it will be seen that it will take a position of equilibrium by sinking to a certain depth, which varies with the strength of different currents which traverse the bobbin, but which is constant for the same strength. The top of the stem of the areometer is flat, and forms the index, which runs along a vertical scale graduated experimentally. An important peculiarity is the guiding of the stem of the areometer, which passes through a metal eye in *the interior of the liquid.* This arrangement suppresses friction against the sides of the cylinder and does not alter the sensitiveness of the instrument.

By varying the dimensions of the bobbin, and those of the bundle of soft iron wires or of the stem of the areometer, we can for a given strength obtain as great a displacement as desirable. In the models constructed by M. J. Carpentier, who has studied all the details with the greatest care, a displacement of about 10 centim. corresponds to a strength of 10 to 25 amperes according to the apparatus, or to a difference of potential of 100 volts.

The coils of the amperemeters consist of one or two layers of very thick wires; they need only have a resistance of 0·01 to 0·02 of an ohm, and thus the apparatus may without inconvenience be introduced into ordinary electric circuits. The coil of the voltmeter is of fine wire, and offers a resistance of about 1700 ohms.

The curves which represent the displacement of the areometer as a function of the intensity or of the electromotive force of the currents show a bend, in the vicinity of which they do not differ much from a straight line; the variables have been determined in such a manner as to more particularly utilize this portion of the curve*.

The apparatus is aperiodic; it is not sensibly influenced by variations of temperature; its indications are not altered by the vicinity of masses of metal, or of even very powerful magnets; its sensitiveness is very great. These various advantages will, we are sure, enable it to perform real services.—*Comptes Rendus*, Oct. 19, 1885.

ON A NEW SECONDARY ELEMENT. BY M. KALISCHER.

The element consists of iron and lead in a concentrated solution of lead nitrate. The iron acting as anode becomes passive, and when the currents are not too strong it becomes coated with coherent thick layers of black peroxide of lead, which protect the iron from contact with the liquid and from decomposition. The change is complete when there is a strong disengagement of gas at the anode, and the solution gives only a slight precipitate with sulphuric acid. In order to prevent a growth of the lead from the kathode to the anode, amalgamated lead in contact with mercury is used. In discharging, the peroxide becomes brown, and ultimately changes into monoxide, to become again changed into peroxide of dark black colour. The electromotive force rises to 2 or even 2·5 volts, and when the current is open it sinks to 1·8 volt. When the elements have been discharged for some time, in which the electromotive force has sunk to about 1·7 volt, it rises gradually on opening to 1·76 volt, as in the lead accumulators, and the resistance decreases.

From its solubility in nitric acid the lead kathode must be occasionally replaced. Carbon can be used instead of iron.—*Beiblätter der Physik*, No. 7, 1885.

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* The apparatus might be modified in several ways according to the object proposed. I may mention especially the arrangement in which the solenoid and the areometer are brought to a constant relative position. This is easily effected by loading the areometer, or by displacing the coil. In this case the law of the action is simpler, and the graduation of the apparatus is reduced to knowing a single coefficient instead of determining a curve.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

MARCH 1886.

XXVI. *On the Theory of Explosions. By* RICHARD THRELFALL, *B.A., Assistant Demonstrator of Physics in the Cavendish Laboratory, Cambridge*[*].

IN his papers on the action of Detonators, Sir Frederick Abel described some curious experiments, which he strove to account for by a hypothesis of "synchronous vibrations." This hypothesis has been treated at considerable length by Berthelot in his work *Sur la Force des Matières Explosives*; and although much light, both experimental and theoretical, has been thrown on the matter by Vieille and Berthelot, the explanations offered by the latter do not seem altogether satisfactory. I have therefore been led to imagine that perhaps something of interest might be gathered from a study of the behaviour of the products of explosion, especially as regards the manner in which they escape from the centre at which the explosion takes place.

Much might possibly be learned from a measurement of the velocity of transmission of a shock to points at small distances from the centre of explosion. This would be merely a question of apparatus. Lord Rayleigh has suggested to me the use of a sensitive flame and revolving mirror, which would at all events give some idea of the sort of disturbance experienced. But the best method of all seems to me to begin by examining cases where the results of explosion can be seen; and for this purpose I carried out the following series of experiments during last autumn.

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[*] Communicated by the Author.

A tank, measuring a yard each way, was constructed and filled with windows of strong plate glass about a foot square in each of two of its adjacent sides. This tank was filled with water. It was at first intended to introduce small charges of fulminate of mercury contained in glass bulbs of $\frac{1}{2}$ inch in diameter, and capable of being fired electrically. The bulbs were to be surrounded by water coloured by some dye-stuff, and the distribution of this after the explosion was to be observed. However, this was soon found to be unnecessary, for the débris of explosion afforded sufficient guide. One observer (Mr. William Walker) was generally stationed at one of the windows; I fired the charge by means of a contact-key in connection with a small coil, and looked in from the top, or side, as seemed most desirable. We soon found that the general effects were pretty regular in some ways, and irregular in others. When a small glass globe one half-inch in diameter had been filled with pure fulminate of mercury shaken well down, but not pressed, the ends of a pair of insulated wires twisted together were passed in and pushed down to measurement till the points were as nearly as possible about the middle of the globe. A little melted paraffin was run round the neck of the bulb to make it water-tight, and the whole was lowered by means of the wires to a constant depth of about 18 inches. At first we were astonished to find that the débris of explosion had the appearance of being shot down to the bottom; not in a jet, but with exactly the rolling motion that smoke has in coming out of a chimney,—as if, in fact, there was vortex motion of some sort. I was anxious to try instantaneous illumination, but found I had not the apparatus to produce a bright enough spark. I shall hope, however, to be enabled to do this at some future time. Noticing the constancy of the downward action of the explosion, it occurred to me that it was produced by the want of symmetry introduced by the neck and wires of the cartridge. In order to test this I turned the next bulb on its side, and then the débris seemed to move with its peculiar rolling motion away from the neck. In fact, the appearance presented to the unaided eye was that of a more or less definite column of rolling white smoke shot out with great velocity, and coming to rest very rapidly when about five inches from the centre, as if acted on by an irresistible force. I also made some experiments by exploding a charge in the centre of a Florence oil-flask filled with red dye and immersed in the water. The dye was shot out with the débris, and the flash appeared to be suddenly stopped some two or three inches outside where the flask would have been if it had not disappeared. There were so many sources of misinterpretation to be feared in this method that I did not continue it, but noted the peculiar rolling, and the dead-beat motion, of the dye as it was shot out.

Unfortunately, just as I had reached the conclusion of these observations, one of the windows gave way, and I decided to board them both up, and take some observations with an impact gauge or gauges, which I had meanwhile constructed. Each gauge consisted of a short hollow cylinder of brass, about 3 inches in diameter and an inch deep. One end was made of stout brass, and the other had a sheet of india-rubber stretched tambourine-fashion over it. A brass tube, $\frac{1}{2}$ inch in diameter and 18 inches long, was fastened into the cylinder in such a way that when the plane of the india-rubber was vertical, the tube was also vertical. Into this brass tube there projected and was cemented a tube of glass projecting upwards about a meter, and having an internal diameter of about $\frac{1}{16}$ in. Two such gauges were made, and carefully fastened into, and backed by, wooden supports, on which were carried the graduated scales by whose aid any rise or fall of liquid in the glass tube could be measured. These supports were then firmly fastened to the two adjacent sides of the tank. The centres of the india-rubber faces were as nearly as possible in the same horizontal plane, and about 18 inches below water-level when the tank was full. The gauges themselves were filled with water (coloured with rosaniline) to such a point that the coloured liquid stood about an inch above water-level when the tank was full. Precautions were of course taken to prevent any air being entrapped in the gauges. The explosions were caused entirely by fulminate of mercury enclosed in glass bulbs of about $\frac{1}{4}$ inch in diameter, and blown as carefully as I was able. The covered wires projected their bare ends pretty accurately to the middle of the bulbs, and these latter were rendered water-tight by passing round the joints a little melted paraffin.

A wooden rod laid across the top of the tank had an iron rod projecting from it vertically downwards to a depth of about 16 inches. The wires carrying the charge were tied to this rod, and allowed to project beyond its end sufficiently far to place the bulb in the horizontal plane of the centre of the two gauges.

By means of marks on the sides of the tank and of the wooden rod, the latter could easily be adjusted so as to place the bulb at a point equidistant from the two gauges. This distance was varied in different experiments by shifting the gauges and the wooden bar supporting the charge. The gauges were always equidistant from the explosion centre.

A key placed in a convenient position enabled me to fire the charge whenever I desired, without distracting my attention from the reading of one of the gauges. The other gauge was read by Mr. Walker, who soon learned the way of it and became an accurate observer. The results were at first surprising. It will be noticed that extreme precautions were taken to make the distribution of effect about the vertical axis through the point of ignition as symmetrical as possible. In spite of these precautions I found that the gauges by no means kept pace with each other. First one would give a large reading, and then the other. The average reading was about 3 inches of coloured water. I finally traced this out to the almost unavoidable unevenness in the glass of the bulbs. A new set of bulbs were therefore blown of thinner glass, and carefully examined as to uniformity before being used. The readings now became more consistent, though not so much so as I should like to have seen them. While considering how to make certain of a more perfect symmetry, I discovered a peculiar action which finally caused me to abandon this form of gauge entirely, as I could not be sure about its theory. I had imagined that the energy of explosion would be transmitted by the almost unstrained layer of thin india-rubber without appreciable loss to the interior of the gauge, and that the result of the impact would be a rise of the liquid in the tube, much as if the gauge had been struck on its face by a hammer. Now the tambourine-shaped end of the gauge and about 6 inches of the connecting-tube projected freely into the water below the wooden support, so that the distance from the back of the gauge to the side of the tank was about 4 inches.

After several shots had been fired, I noticed that both the tubes of the gauges were bent *towards* the centre of the explosion, not away from it. A wedge placed behind the tambourine and between it and the side of the tank, and pressed tight in, increased this effect. How it came about, I was at a loss to discover ; but the result was that I decided I knew too little about the motion of the water to trust to the proper deformation of the india-rubber. The rapidity with which the coloured liquid rose and fell was also a drawback. The gauges were troublesome to set besides, so that I finally determined to make two new ones. In these I adopted a pendulum method. The two ends of a bit of brass tube, one inch in diameter and four inches long, were closed by caps. Through the centre of these caps I bored holes three eighths of an inch in diameter and immediately opposite one another. The tube was fastened horizontally to a wooden support, and a brass rod moved piston-wise through the holes in the ends; the rod was about six inches long. Inside the tube was coiled a spiral spring of hard-brass wire; one end of the spring rested against the inner surface of one of the caps, and the other was pinned to the brass rod. The result was, that the rod was always held by the spring in one position. One end of the rod was furnished with a brass disk about three inches in diameter, the other end abutted on the bob of a lever pendulum so suspended as always to press slightly on it. The pendulum was supported by a small shaft passing through it and through holes in two brass brackets. The distance from the bob (which weighed about six ounces) to the fulcrum was one inch, and the pendulum was extended upwards about 20 inches by a pointer of sheet zinc; the end of this pointer moved over a paper scale. When properly supported in the tank the gauges occupied much the same position as the ones previously employed. The flat disks of the gauges were placed so as to face towards the centre of explosion. These gauges seemed to leave little to be desired either as to convenience of reading or otherwise, and, both being exactly alike, gave tolerably consistent readings.

By firing some dozen charges, arranged as symmetrically as possible, I managed to find out that the indications of the gauges were proportional, in about the ratio of 1·3 to 1. I did not require to be very accurate, because all I was looking for was to find whether the streams of débris formerly observed through the window were also streams of explosive effect.

To decide this I made the explosion cartridges purposely unsymmetrical, either by having the glass too thick on one side, or by turning up the ends of the covered wires so that they entered the bulb horizontally and facing one of the gauges. The effects now became more puzzling, but on the whole there can be no question that the gauge towards which the bulb was turned suffered most. In fact the direction taken by the streams of explosive energy appeared to coincide with the directions of projection of débris, and with the direction foretold from the initial conditions.

The experiments were repeated at various distances and in various manners with more or less compressed charges, and with variations in the position of the firing-point. The pendulum readings were on the whole certainly proportional to the direction of explosion as foretold from the initial conditions. Of course, in some few cases, there were unexpected actions on the gauges; but this was hardly avoidable, since I had seen by the previous experiments how small a change in initial conditions could lead to great variations in the result. The position of the firing-point was the least satisfactory part of the experiments; and it seems probable that when the gauges did not go as they were expected to go, the change of effect was to be traced to imperfect centering of the firing-point; about 10 per cent. of experiments would decline to travel on the paths laid out for them.

Some considerable difficulty was experienced in making the tank water-tight. The continual shock of explosion stended to produce leaks, and for some time this was very tiresome. Mr. Walker, however, recollected that the introduction of a little horse-manure into the tank was a method sometimes employed for stopping leaks, and on trying it we found it succeeded in absolutely stopping each leak as it was caused within a very few minutes; the fine particles having about the same density as water remain suspended for a long time and get carried into the holes as soon as a leak appears.

These experiments leave very little doubt in my own mind that the direction in which the maximum explosive effect is transmitted will, in a great measure, depend on the initial arrangement of surrounding obstacles; at all events, when the explosion is caused by fulminate of mercury and small charges are used.

The shock of an explosion must be transmitted in one or more of three different ways:—

I. By actual bodily motion of the products of explosion through the surrounding medium, either alone or becoming gradually more and more mixed up with the medium itself, which is thereby also set in motion.

II. By an undulatory motion set up in the medium.

III. By a vortex-ring motion.

In the explosion of gunpowder, and other slow explosives, the energy is doubtless transmitted chiefly by I. and II.

The distance to which a considerable quantity of the energy may be conveyed by means of waves of comparatively great amplitude is in some cases remarkably great. This is evidenced by the effects produced by the explosion of powder magazines. In the case of the fulminates of mercury and silver, gun-cotton and nitro-glycerine, that is explosives of the class examined under water, the effect falls off very rapidly with the distance, and in water, at all events, is of a directed character.

This would point to the third mode of transmission being in these cases of some importance; and if we consider the way in which the products of explosion escape, we shall find that the conditions for the production of vortex motion do in fact exist. Let there be a sphere of fulminate of mercury fired from its geometrical centre. Then by Vieille's experiments (*Comptes Rendus*, 1882 and 1883) on the time of explosion, it seems likely that the outer portions of fulminate will be decomposed before they are removed to any appreciable distance from their original positions. We shall therefore have a sudden expansion in all directions, caused by the increase in volume of the explosive substance during the explosion. There seems no reason under perfectly symmetrical conditions why the expansion should not go on as it began, until the cooling of the sphere of hot gases becomes so marked as to prevent further expansion.

If the conditions, however, are not such as to allow of symmetrical expansion—as always occurs in practice—then we shall have the bounding surface of the explosion-gases more curved in some places than in others—that is, the strain will be greater at some parts than at others, and in fact may become so great at points of great curvature as to lead to what I venture to call a state of "break-down." In other words, the compressed gases will in this case escape, not by gradual expansion but by jets, from points whose position is fixed by the conditions of explosion. In these jets we should have the necessary and sufficient conditions for the establishment of vortex motion. If vortex motion were set up, then it seems likely that much greater effects might be transmitted in some directions than in others, though at considerable distances the effects would tend to become uniform in all directions. This view of the actions of explosions will, I think, enable us to explain several difficulties which I mentioned as occurring in the interpretation of Abel's experiments. These experiments are fully described by Abel in various papers in the 'Philosophical Transactions,' and in the *Annales de Chimie et de Physique*, vol. 165. They have been discussed at some length by M. Berthelot in his work on Explosives, and though much light has been thrown on many points, I venture to think that the complete elucidation of others is still to be sought. Among these I would place the three following:—

The want of correspondence between the explosive actions, as measured by the effect produced on copper plates, and the effects produced in causing other explosions. The apparent capriciousness of explosions of the more violent kinds; and the production of explosions by influence.

With respect to the explosion of gunpowder, M. Berthelot has nothing new to add to the generally received theory that it differs in nothing from ordinary combustion, except that it is more rapid.

The theory of detonation, however, is more fully treated, and is summed up by M. Berthelot somewhat as follows:—The kinetic energy of the shock of the explosion (by the detonator) is transformed into heat at the point struck; the temperature of this point is thus raised to the temperature of explosion; a new shock is produced which raises the temperature of the neighbouring portions to the same degree; they then explode and the action is thus propagated with an ever-increasing velocity.

Many experiments tend to show the justness of this view. To begin with, Abel found that almost any variety of effect could be obtained by burning explosives under diminished pressure. For the lower the pressure the more easily do the products of decomposition escape, and carry with them the energy due to their liberation. By this means the temperature of explosion is constantly kept down, and the chemical character of the products modified in such a way that they correspond to the temperature. In other words, the compounds liberated are as a rule more complex than those which would be set free at a higher temperature, and therefore the energy run down is less.

Again, it will come to the same thing, so far as the propagation of an explosion is concerned, whether the products of decomposition are facilitated in their escape by conducting the experiment in a partial vacuum, or whether the decomposition is itself so slow that the products are enabled to escape without marked hindrance under ordinary pressure. Now the resistance of the air to the escape of the products of combustion will depend on the rate at which they are liberated. And the shock given to neighbouring portions of the explosive will be proportional to the pressure of the explosion gases at these points; and, therefore, ultimately to the resistance of the air, and hence to some function of the velocity of decomposition. But, in order to convert an explosion by combustion into an explosion by detonation, what is required is, that the temperature of any point shall be raised sufficiently to determine its complete, as distinguished from its incomplete, decomposition. The raising of the temperature of any point, however, will depend on the violence of the shock to which it is subjected; and this, as before stated, will be proportional to some function of the velocity of the decomposition producing it If the necessary temperature is anywhere attained, we shall have detonation thereafter; if not, an explosion by combustion will result. It appears, therefore, that in order to produce a detonation, we require the initial velocity of decomposition to rise above a certain minimum value; that there is in fact a "critical velocity" of initial decomposition determining the kind of reaction which ultimately takes place. If the temperature of the whole mass be previously raised, then the "critical" velocity will become less. Berthelot considers that a specific change takes place in the stability of an explosive as its temperature is raised. This is doubtless true; but if a minimum temperature of any part be the necessary and sufficient condition for the production of a detonation, then the ease with which it can be obtained, when the mass starts with a high temperature, will *cœteris paribus* be greater than if the original temperature is low. If, therefore, we find that nitro-glycerine is more liable to detonation the higher its initial temperature, we shall not be required to make any assumption as to "increased sensitiveness," since we see that the minimum temperature will be more easily reached, and that therefore the "critical" velocity of initial decomposition may be smaller. In other words, supposing we try to detonate nitro-glycerine by an explosive which just fails at ordinary temperatures, we should expect its chances of success to increase as the temperature rises; and this does in fact occur.

The sensitiveness of an explosive to detonation will also, as Berthelot points out, depend on its state of mechanical aggregation. The critical velocity required to produce detonation will *cœteris paribus* depend on the nature and value of the elastic constants of the explosive as well as of the medium in which it is to be exploded. We should, in fact, expect a change in the critical velocity of detonation if we exchanged the viscous resistance of liquid nitro-glycerine for the elastic resistance of the same substance when frozen. Again, it seems possible, as a result of this theory, that less powerful detonation might be required to explode a given substance in water than in air; I am not, however, aware of any experiments on this point. And so in other cases, though the critical velocity of detonation must necessarily be a very complex function, and difficult to predict, I see no reason on that account to minimise its importance. On the other hand, it seems to me to be in complete harmony with Abel's experiments, and substantially embodies the view set forth by Dixon in his paper "On Conditions of Chemical Change in Gases," Phil. Trans. 1884. As far as I know, there is not a single experiment which offers any evidence against it. What is required by the theory for the formation of a detonation is that a small part of the mass should be raised above a given temperature, and not that a large portion should be raised to a temperature below it.

This leads at once to the consideration of the second point, viz. the action of detonators. The apparently anomalous effects discovered by Abel may be summed up by taking the most extreme case. Gun-cotton could be detonated by a charge of fulminate of mercury, whereas ten times as much nitro-glycerine was required to cause a similar sample of gun-cotton to detonate. By firing the detonating charges on copper plates, Abel naturally observed that the destruction produced by the nitro-glycerine was much the greater, and hence concluded that some other factor, besides the "explosive violence," must come into play. This is undoubtedly true, but the mistake arises in looking at the experiments from one point of view alone, viz. that of the copper plate. There will be no effect produced on the plate at all till the resistance of the air becomes greater than that of the plate; and this will never be the case, however great the volume of gas liberated, unless the time of explosion is sufficiently short. The resistance of the air varies at least as the square of the velocity of attack; and therefore this will be the conditioning factor of the destructive effect producible by explosions in free air. For a given increment of volume occurring in an explosion till the time of explosion diminishes to a certain value depending on the strength of the plate, no effect will be observed; directly this limit is passed, the destructive effects will depend, in the usual manner, on the quantity of energy liberated. There is in fact a critical velocity of explosion, below which the plate will not be attacked. But in a detonation the case is different. We do not require any great destructive effects, we only require that the time should be so short that a portion, no matter how small, of the substance to be detonated shall be raised to the appropriate temperature. If the detonator has a time of explosion too great, then, although the air may be the stronger obstacle and the explosive be destroyed, no detonation will be produced. This is precisely what happened in Abel's experiments, where the gun-cotton was blown to pieces by the nitro-glycerine. The instantaneous rise of pressure is not so great for nitro-glycerine as for fulminate of mercury, though the energy run down is much greater. This point has been satisfactorily proved by Vieille in his experiments with the crusher-gauge. Moreover the density of mercury fulminate is three times that of nitro-glycerine, which allows a given mass to be on the whole much nearer its work if it consist of fulminate of mercury than if it consists of nitro-glycerine.

We ought not therefore to be surprised that the detonation of gun-cotton is easily accomplished by fulminate of mercury, and hardly accomplished at all by nitro-glycerine. If there is any surprise, it would seem more fitting that it should be exhibited at the detonation which large charges of nitro-glycerine seem able to effect.

This fact would tend to show merely that nitro-glycerine has a velocity very near the critical point for gun-cotton, so much so, that when large charges are employed the acceleration in the explosion of the nitro-glycerine is sufficient to pass the limit. We know from Dixon's work on gases that at first the explosion gains in velocity till the steady velocity of detonation is obtained; and there seems no reason against, but, on the other hand, every probability in favour of, the same thing taking place in nitro-glycerine.

Above and beyond this the difference in the mode of application of the two detonators must be taken into account. In Abel's experiment the fulminate was enclosed in a tube of copper or tin plate, while the nitro-glycerine was merely applied in a capsule whose diameter was large compared with its depth. The upper end of the fulminate tube was probably closed by the electric firing apparatus; and this, as was shown by the experiments in water, already described, together with the fact that the fulminate was fired at the top, would give it an enormous advantage. For there is considerable probability that in explosions of high velocity in air, the final mode of "break-down" of the gas liberated is very dependent on the initial conditions, just as I found it to be in water. The nitro-glycerine was deprived by Abel of these advantages; and for these and the reasons above mentioned, though it was able to blow blocks of compressed gun-cotton into powder, and even to cause some of this powder to penetrate the hard wood of the support, it failed to cause detonation.

The other apparently anomalous facts observed by Abel require further treatment, and most of all those explosions by influence which seem, at first sight, only explicable by some theory such as that of synchronous vibrations suggested by Abel himself.

On the Hypothesis of Synchronous Vibrations.

The difference in the behaviour of nitro-glycerine and fulminate of mercury regarded as detonators, led Abel to suggest that there might be some synchronism between the vibrations caused in air or ether by the latter explosive, and the natural period of vibration of a gun-cotton molecule. At all events, the supposition is made that fulminate of mercury when exploded can produce vibrations which are not produced by explosions of nitro-glycerine; and that the superior detonating power of fulminate of mercury may be due to the presence of these vibrations. The first set of experiments bearing on this point have been already discussed, with the result that the hypothesis is perhaps unnecessary. There are, however, a great number of other experiments, some of which cannot be so easily explained. In one case an explosion was induced, in a charge of fulminate of silver placed at the end of a tube, by the explosion of a similar charge at the other end. This effect was not interfered with by placing diaphragms across the tube; but the state of the internal surface of the tube seemed to exercise considerable influence. Experiments were also made on the action of fulminate of mercury on gun-cotton through tubes (Proc. Roy. Soc. 1874, vol. xxii. p. 160). The great influence exerted on the detonating power by the smoothness or roughness of the walls of the tube seems a strong argument against the supposed synchronism having much to do with the effect in these cases. On the other hand, it is just what we should expect if there was a bodily motion of air down the tube, or even if, as in the case where diaphragms were inserted, the motion was transmitted from layer to layer without any great amount of displacement in each individual particle. It seems possible that some of the vortex motion caused by the "break-down" might be transmitted through the tube, and that the diaphragms merely served to change the portions of air of which the rings were actually composed. I admit that this is not very satisfactory; but if the roughening of the internal surface of the tubes actually exerted the effect attributed to it, we are, I think, justified in supposing that the explosions were not caused by the transmission of vibrations through the material of the pipe itself. Again, vibrations, to be of any effect in producing chemical change, must be comparable, as to period, with the molecular vibrations. If such vibrations are transmitted through ether, it is difficult to see where the influence of chalking the inside of the tubes can come in, and if through air, their wave-length would be too small (as will be shown) to be likely to be much influenced by particles of the size of chalk-dust.

The similar experiments of Campion and Pellet (*Comptes Rendus*, lxxv.) are sufficiently explained by their statement that they used iodide of nitrogen. Unless any one likes to suppose that the period of a fiddle-string may be comparable with the period of an iodide of nitrogen molecule, the further experiments of Campion and Pellet cannot be held to have much bearing on the subject. One can only wonder that they found a string that would vibrate slowly enough not to fire their iodide. As to their experiments with mirrors, blackened or otherwise, the results obtained might be anticipated on almost any theory except that of "synchronous vibration." For the vibrations supposed on this theory to be most active, would be precisely those absorbable by lampblack. This point has been investigated by Berthelot, in volume i. of the Treatise, in a manner which leaves little doubt that he misunderstood Abel's theory. In order to show the importance of vibrations in producing chemical change, Berthelot experimented on various chemicals by swinging them on tuning-forks. No effect was produced, nor indeed was it to be expected, unless the reagents were of such a nature that they required intense shaking to keep them mixed. Berthelot also experimented on ozone at much higher frequencies of vibration by causing a tube filled with the gas, mixed with oxygen, to be set into violent longitudinal vibration. No change in the ordinary rate of decomposition of ozone was observed. This is very interesting, but does not, as far as I can see, touch Abel's theory. In order to disprove the theory, Berthelot ought to have made his tube vibrate till it got luminous, and observed the effect on the ozone all the way up.

There are many well-established cases of torpedoes exploding one another by influence, and the same thing occurs in firing dynamite shots in mines. The former alone possess any interest for our present purpose. If the effects due to fulminate of mercury when fired under water are in any way similar to those which may be supposed to take place on the detonation of large charges of gun-cotton, then, by the experiments described above, it would be likely that quite extraordinary effects might be propagated in some cases. There ought, however, to be a capriciousness in the observed action of torpedoes on one another; but whether this has been observed or not, I am unfortunately unable to state. However, I will assume that it has not, and that here we have a case where the effect is largely due to "synchronous vibration." We will therefore consider the ways in which vibrations of sufficiently small period could be transmitted. I assume that no vibrations can have any influence unless they are of such a period as to be comparable with the natural period of vibration of the molecules of the substance to be xploded.

Let a body be gradually heated and its temperature measured as soon as light comes from it having the same refrangibility as the line A in the solar spectrum. Let the temperature be, say, of the order of 1500° Centigrade. Then the molecules of the body will be vibrating in some way comparable with the period of the A line; that is, about 4×10^{14} times per second.

Suppose gun-cotton could be heated red-hot without decomposition, then its molecular period would be of this order. We are quite unable to say how the period varies with the temperature in solid bodies at low temperatures. But the spectroscope shows that it does not change much at high temperatures.

The only possible way of obtaining an idea would be to extend the spectroscopic investigation even further than it has been done by Abney; either photographically, or by means of a thermopile. We will assume, however, that as the bodies cool, their molecular vibrations, if altering at all as to period, tend to become slower, as well as of smaller amplitude. Let us consider the limiting condition of propagation of waves of longitudinal displacement. There seems no reason for supposing that the velocity of propagation would fall off till we come to waves of wave-length comparable with molecular distances; for instance, with the mean free path. Now by experiments on diffusion it seems that the mean free path in oxygen is of the order of $5{\cdot}6\times10^{-6}$ centimetres; in sugar solution it is 10^{-5} of this, or $5{\cdot}6\times10^{-11}$ centimetres; while in solids it is probably much less. The size of a molecule, however, seems to be of the order $5{\cdot}8\times10^{-8}$ centim., so this will give our superior limit in liquids and solids.

Suppose that the smallest possible wave-length is the diameter of a molecule, and that the velocity of propagation is the same as that of sound, down to this limit. Then if V be the velocity of propagation, or the number of vibrations per second, and λ the wave-length in water, we have

$$n=\frac{V}{\lambda}=\frac{1{\cdot}4\times10^{5}}{5{\cdot}8\times10^{-8}}=2{\cdot}4\times10^{12}.$$

But it is unlikely that we could get a wave-length anything like so small as this; so let us take as our limiting value the wave-length equal to a thousand molecular diameters. This gives us for the limiting frequency

$$n=2{\cdot}4\times10^{9}.$$

Comparing this with the n for the A line, which is 4×10^{14}, we see that it is about a million times too slow to produce any effect on molecules vibrating so as to emit red light. But bodies at the ordinary temperature might possibly vibrate slowly enough to be influenced directly, though this is unlikely. I must confess to being rather surprised that the numbers are as comparable as they seem to be. If we perform the same operation for gases, putting $\lambda=1000$ mean free paths, we get for oxygen $n=5\times10^6$. Here the discrepancy is a thousand times as great; so that if longitudinal vibrations are to be considered as likely to produce any effect, they will certainly be considerably more likely to do so if transmitted through solids or liquids than through gases.

We have still, however, got the ether to fall back on, and there we are safe, for there is no reason why vibration of the right period should not be transmitted through it.

The experiments with tubes, however, seem to point exclusively to the air as the medium through which vibrations are to be transmitted, and that may, I fancy, be fairly regarded as unlikely. If the theory of synchronous vibration can be disproved at all by experiment, then Abel has, at all events, made the most telling experiment against it; there may of course be other experiments with which I am unacquainted, though not for want of endeavour on my part to discover them; and these may point in the opposite direction. Still, in the light of what has been published on the subject, there is little doubt that our natural hesitation to accept a theory of vibrations is justified by a consideration of the facts. On the other hand, if we allow that vortex motion may exist, it will account for some of the effects observed in the neighbourhood of violent explosions. The most important effect to be accounted for is the capriciousness of explosions. Instances are so numerous that it is hardly worth while to dwell on them in detail; I happen, however, to have an account of the famous explosion at Bremer Haven from an eye-witness, and was especially struck by the way in which the bystanders seemed actually selected for injury, and that not always from flying débris. Such effects as these are difficult to account for, on any theory of uniform propagation of wave-motion. Again, any of the observed phenomena of propagation of explosion are as well explained by vortex propagation as by wave-motion. There is no reason why the two states of propagation should not exist together, varying in their relative importance according as the explosion is of long or short duration. In ordinary cases of detonation I imagine the shocks are given chiefly by the explosion-gases before any considerable break-down has taken place. In conclusion, I wish to say that, though I have given prominence to the vortex-ring method of propagation, I do not intend to offer it as necessarily the most important of the phenomena in all cases, but only to point out that in some circumstances, chiefly those which have been inadequately explained, a consideration of its possible influence helps us to understand the facts.

XXVII. *Notes on the Calibration and Standardizing of Mercurial Thermometers.* By Spencer Umfreville Pickering, M.A., *Professor of Chemistry at Bedford College**.

HAVING had occasion to calibrate a considerable number of delicate mercurial thermometers, a short notice of the general results, in their bearing on the accuracy attainable in calibration, may not be without interest to those who may have occasion to study this question.

Although several slightly more accurate methods of calibration exist, Gay-Lussac's *step-by-step* method will no doubt be the one generally employed, owing to its simplicity and the comparative shortness of the calculations involved by it. It is the method which is recommended in a Report made to the British Association (1882) by a Committee, consisting of Professors Balfour Stewart, Rücker, and Thorpe, appointed for the purpose of investigating the several methods existing. This method, which is the one which the author has invariably adopted, will alone be referred to in the present communication.

The instruments calibrated were all made by Casella, and were etched with arbitrary scales, each division in the first six instruments mentioned being 1·2 millim., and in the remaining two, 1 millim. The other details respecting their construction are as follows:—

Instrument.	Range.	Weight of mercury in bulb.	Length of scale.
	° C.	grams.	centim.
55080	10 – 25	13·6	47
55081	10 – 25	13·5	47
55083	1 – 16	14·3	46
55084	0 – 27	14·3	45
56117	−5–102	......	52
56916	5 – 21	15·4	50
62839	x–(x+3·3)	36·2	57
63616	x–(x+3·8)	30·5	60

The average length of the scales, being thus about 51 centim., is somewhat greater than that of the instrument studied by the above-mentioned Committee, the length of which was 49 centim.

On these thermometers twenty-seven calibrations were performed, sixteen with the aid of the calibrating instrument devised by F. D. Brown (Phil. Mag. [5] xiv. p. 59), and the remaining eleven with a lens only. In every case Gay-

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* Communicated by the Author.

Lussac's method was used purely as a *step-by-step* method, and not as a *principal-point* one (see the Report referred to above).

The following table contains the maximum difference observed at any point when a pair of calibration-curves are compared :—

Instrument.	With lens.	With Brown's instr.	Variation of the two mean curves.
	millim.	millim.	millim.
55080	......	A and B=0·18	......
55081	A and B=0·24	A and B=0·096	0·126
	A and C=0·40		
	A and D=0·29		
	B and C=0·35		
	B and D=0·18		
	C and D=0·21		
55083	A and B=0·18	A and B=0·19	0·114
	A and C=0·27		
	B and C=0·12		
55084	......	A and B=0·17	......
56117	A and B=0·19	A and B=0·096	0·156
56916	A and B=0·40	A and B=0·19	0·108
	A and C=0·23		
	A and D=0·20		
	B and C=0·44		
	B and D=0·51		
	C and D=0·42		
62839	......	A and B=0·09	......
63616	......	A and B=0·11	......
	0·29	0·14	0·126

It will be seen that when a lens only is employed the average maximum divergence is 0·29 millim.*; while the substitution of Brown's instrument for the lens reduces the error to one half of this amount, 0·14 millim. This average maximum difference corresponds very nearly indeed to that observed by the Committee in the two Gay-Lussac's curves which they obtained, the quantity there being 0·157 millim.†

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* Omitting calibration B of thermometer 56916, this average is reduced to 0·252 millim.

† This number is taken from the curves given in the Report (plate i. fig. 1), and is somewhat higher than that given in the text (p. 16), where it is stated that the "two curves nowhere differ by more than 0·12 millim., except at the point 135° ;" whereas it would appear, from a study of the curves themselves, that there is a difference of 0·145 millim. at and near 123°, the difference at 135° amounting to 0·157 millim., as given above. I have taken this maximum difference, inasmuch as the differences quoted in the above table were measured in the same manner.

It would seem, therefore, that this must represent very nearly the limits of accuracy of which the method is capable—a limit which gives, for the maximum probable error of any point in the mean curve deduced from two such calibrations, a quantity corresponding to about 0·08 millim. of the mercurial column. It would, however, seem difficult to reduce this error much further by increasing the number of calibrations performed; for the numbers given in the third column of the table show that the mean curve deduced from those obtained with a lens still differs from the mean deduced from those with Brown's instrument by as much as 0·126 millim.

A possible error of 0·08 millim. represents in the first three and the fifth thermometers 0°·0029 C., while in the last two it represents only 0°·0005 C.

In their Report the Committee recommend a means of separating for calibration-purposes a thread of mercury of any required length, consisting in applying a very small flame to the point at which the separation of the column is desired. I find, however, that it is most undesirable to apply such heat to a portion of the divided scale itself. Some alteration in the bore and in the nature of the glass appears to be effected at the point heated; in five or six cases it was found that the thread of mercury when travelling in one direction would not pass the point which had been thus heated, whereas when travelling in the opposite direction it rushed past it at an ungovernable rate. In one case a very noticeable alteration in the size of the bore was observed to have occurred at the heated part. One of Mr. Casella's assistants, a man on whose powers of observation I can rely, assures me that he can at once tell the point at which a fine thermometer-tube has been heated in this manner, by means of the peculiar jerky motion of the mercurial column when passing it. All the tubes to which the present remarks apply were very flat and fine in the bore, probably much more so than in the instrument examined by the Committee, and this no doubt accounts for their not having observed any injurious effects produced by heating. Separation of a thread by means of the so-called *vacuum bubble* is not possible in these very fine tubes, so the flame method must be adopted, taking care, however, that it be applied to a point either above or below the graduated portion of the stem. Another, but less convenient, method consists in passing some of the mercury into the top chamber of the instrument, and distilling a certain quantity of it back into the tube.

Great difficulty is sometimes experienced in passing a short thread of mercury past certain points in a very fine tube, even where no sudden alteration in the bore sufficient to affect the calibration-curve can be detected. It will often, though not always, be found that the obstacle may be passed by wrapping round the tube a rag soaked in ether which is evaporating rapidly. This same method of cooling is of great service in helping the mercury to become detached from the bulb, when it is required to run it into the upper chamber of the instrument.

The thermometers here mentioned were intended for calorimetric purposes, and therefore an accurate knowledge of the exact temperatures which they registered was not of so much importance as a knowledge of the value of any given interval on them, and that they should all be strictly concordant among themselves. Instead, therefore, of being standardized by a direct comparison with the natural standard 56117, they were all compared with 55084, which embraced the ranges of all of them, and which had previously been standardized by means of the natural standard itself. Inasmuch as the scale of 55084 was three and a half times as open as that of the natural standard, a proportionate gain in concordance of the instruments compared with it was in this manner obtained.

The comparison was effected by suspending the two instruments in a large bath of water which had been brought to the required temperature, the surrounding atmosphere being likewise heated as nearly as possible (within 0°·2 C.) to this same temperature. After thorough agitation of the water, the upper ends of the thermometers were tapped, and the height of the columns in each read by means of a lens ; immediately afterwards they were read again, reversing the order in which they were taken. After tapping them again, they were again read twice over as before : the water was then stirred, and a second series of four readings of each instrument obtained in the same way. The operation was repeated a second time; and thus the readings at the points of comparison consisted in reality of twelve separate readings of each instrument. The points of comparison were the highest and lowest available ones in the thermometer being standardized. During every comparison the temperature of the bath was falling appreciably, though very slightly.

In the case of the two most delicate instruments, 62839 and 63616, three and two such comparisons were made respectively, using different portions of the standard 55084 for each, *i. e.* at different temperatures; this being effected by removing by heat some of the mercury in the thermometers to be standardized into the upper chamber. In the three comparisons of 62839, the lowest point in the scale was thus made to register about 7°·7, 12°·5, and 17°·7 C. respectively; and in the two comparisons of 63616, 5°·5 and 17°·3 C. These repeated standardizations give the means of ascertaining the experimental error involved in the process.

The results obtained were as follows :—

With 62839,

		deg.		deg.	
A.	An interval of	53·2811*	= an interval of	4·5362	of 55084,
B.	„ „	51·9524	= „ „	4·4260	„ „
C.	„ „	53·7366	= „ „	4·5819	„ „

From which was deduced, that the average value of 1 degree (*i. e.* 10 millim.) of 62839 is

A. . . . 0° 0601967 C.
B. . . . 0°·0602480 C.
C. . . . 0°·0603066 C.

With 63616,

		deg.		deg.	
A.	An interval of	55·1059	= an interval of	5·0039	of 55084,
B.	„ „	53·1093	= „ „	4·8184	„ „

From which, 1 degree of this thermometer represents

A. . . . 0°·0641605 C.
B. . . . 0°·0641059 C.

Now the extreme difference in these numbers in the case of the first instrument is 0°·0001099 C., while the average difference between any pair of observations is 0°·0000733 C.; in the case of the second instrument this difference is somewhat less, namely 0°·0000546 C. This latter number I take to represent more nearly the error which would be likely to be obtained with any ordinary thermometer; for, owing to the large size of the bulb of No. 62839, the readings were subject to a source of error which was not thoroughly understood and guarded against at the time when the comparisons were made.

This difference of 0°·0000546 C. in the results would be caused by a total error in the readings of 55084 of 0·0043 deg., or in those of 63616 of 0·056 deg., or by an error in those of both thermometers of 0·004 deg. each. As any such pair of comparisons involves four readings of each instrument, it follows that any temperature can be read with an error of 0·001 deg., or 0·01 millim. (remembering that each such reading is really the mean of twelve observations).

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* One of these arbitrary degrees, with thermometers 62839 and 63616 measures 10 millim., with 55084 12 millim. All the numbers given here are fully corrected.

With delicate thermometers, such as those described, this quantity is negligible (amounting to 0°·00006 C.*) ; it is of importance in the standard instrument only. The natural standard No. 56117 is nearly as long as such a thermometer can be made with due regard to convenience ; and the distance between the freezing- and boiling-points of water on it being 480 millim., this error of 0·01 millim.† at each point of comparison represents 0°·002 C. The value of the total scale of any very delicate thermometer can thus be determined in a single comparison with an error of ±0°·004 C. If the thermometer is not very much more delicate than the standard itself, the error in reading it will become appreciable, and the probable error in the determination of the value of the distance between its extreme points will be $\left(\cdot 004+\frac{\cdot 004}{x}\right)^\circ$ C., where x represents the ratio between the ranges of the standard and the instrument compared with it.

XXVIII. *On the Flow of Gases.*

By Professor Osborne Reynolds, *LL.D., F.R.S.*‡

1. AMONGST the results of Mr. Wilde's experiments on the flow of gas, one, to which attention is particularly called, is that when gas is flowing from a discharging vessel through an orifice into a receiving vessel, the rate at which the pressure falls in the discharging vessel is independent of the pressure in the receiving vessel until this becomes greater than about five tenths the pressure in the discharging vessel. This fact is shown in tables iv. and v. in Mr. Wilde's paper : thus, the fall of pressure from 135 lbs. (9 atmospheres) in the discharging vessel is 5 lbs. in 7·5 seconds for pressures in the receiving vessel, ranging from one half-pound to nearly 5 or 6 atmospheres.

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* With the majority of the instruments mentioned in the previous tables this 0·001 deg., or 0·01 millim., would correspond to 0°·0004 C. These differences include all errors due to imperfections in the calibration-corrections applied.

† I shall show elsewhere that the average error of reading, as deduced from a large number of calorimetric determinations, is ±0·011 millim. It will also be shown that the error at any point due to imperfections in calibration and standardization amount to ±0·014 millim.; but this had been deduced from simultaneous observations on two different instruments, and by far the greater portion of this error I believe to be due to an imperfection, hitherto uninvestigated, which renders concordance between two such instruments throughout their scales impossible, unless, perhaps, the height of the column of mercury is the same in each.

‡ Communicated by the Author, having been read before the Manchester Literary and Philosophical Society, November 17, 1885.

With smaller pressures in the discharging vessel the times occupied by the pressure in falling a proportional distance are nearly the same until the pressure in the receiving vessel reaches about the same relative height.

What the exact relation between the two pressures is when the change in rate of flow occurs is not determined in these experiments. For as the change comes on slowly, it is at first too small to be appreciable in such short intervals as 7·5 and 8 seconds. But an examination of Mr. Wilde's table vi. shows that it lies between ·5 and ·53.

This very remarkable fact, to which Mr. Wilde has recalled attention, excited considerable interest fifteen or twenty years ago. Graham does not appear to have noticed it, although on reference to Graham's experiments it appears that these also show it in the most conclusive manner (see table iv., Phil. Trans. 1846, vol. iv. pp. 573–632; also Reprint, p. 106). These experiments also show that the change comes on when the ratio of the pressures is between ·483 and ·531.

R. D. Napier appears to have been the first to make the discovery*. He found, by his own experiments on steam, that the change came on when the ratio of pressures fell to ·5 (see *Encyc. Brit.* vol. xii. p. 481). Zeuner, Fliegner, and Hirn have also investigated the subject.

At the time when Graham wrote, a theory of gaseous motion did not exist. But after the discovery of the mechanical equivalent of heat and thermodynamics, a theory became possible, and was given with apparent mathematical completeness in 1856. This theory appeared to agree well with experiments until the particular fact under discussion was discovered. This fact, however, directly controverts the theory. For on applying the equations giving the rate of flow through an orifice to such experiments as Mr. Wilde's, it appears that there is a marked disagreement between the calculated and experimental results. The calculated results are even more remarkable than the experimental; for while the experiments only show that diminishing the pressure in the receiving vessel below a certain limit does not increase the flow, the equations show that by such diminution of pressure the flow is actually reduced and eventually stopped altogether.

In one important respect, however, the equations agree

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* The account of R. D. Napier's experiments is contained in letters in the 'Engineer,' 1867, vol. xxiii. January 4 and 25. They were made with steam generated in the boiler of a small screw-steamer and discharged into an iron bucket, the results being calculated from the heat imparted to a constant volume of water in the bucket in which the steam was condensed.

with the experiments. This is in the limit at which diminution of pressure in the receiving vessel ceases to increase the flow, which limit by the equations is reached when the pressure in the receiving vessel is ·527 of the pressure in the discharging vessel.

The equations referred to are based on the laws of thermodynamics, or the laws of Boyle, Charles, and that of the mechanical equivalence of heat. They were investigated by Thomson and Joule (see Proc. Roy. Soc., May 1856), and by Prof. Julius Weisbach (see *Civilingenieur*, 1856); they were given by Rankine (articles 637, 637A, Applied Mechanics), and have since been adopted in all works on the theory of motion of fluids.

Although discussed by the various writers, the theory appears to have stood the discussion without having revealed the cause of its failure; indeed, Hirn, in a late work, has described the theory as mathematically satisfactory.

Having passed such an ordeal, it was certain that if there were a fault, it would not be on the surface. But that by diminishing the pressure on the receiving side of the orifice the flow should be reduced and eventually stopped, is a conclusion too contrary to common sense to be allowed to pass when once it is realized; even without the direct experimental evidence in contradiction, and in consequence of Mr. Wilde's experiments, the author was lead to reexamine the theory.

2. On examining the eqnations, it appears that they contain one assumption which is not part of the laws of thermodynamics or of the general theory of fluid motion. And although commonly made and found to agree with experiments in applying the laws of hydrodynamics, it has no foundation as generally true. To avoid this assumption, it is necessary to perform for gases integrations of the fundamental equations of fluid motion which have already been accomplished for liquids. These integrations being effected, it appears that the assumption above referred to has been the cause of the discrepancy between the theoretical and experimental results, which are brought into complete agreement, both as regards the law of discharge and the actual quantity discharged. The integrations also show certain facts of general interest as regards the motion of gases.

When gas flows from a reservoir sufficiently large, and initially (before flow commences) at the same pressure and temperature, then, gas being a nonconductor of heat when the flow is steady, a first integration of the equation of motion shows that the energy of equal elementary weights of the gas is constant. This energy is made up of two parts, the energy of motion and the intrinsic energy. As the gas acquires energy of motion, it loses intrinsic energy to exactly the same extent. Hence we have an equation between the energy of motion, *i. e.* the velocity of the gas, and its intrinsic energy. The laws of thermodynamics afford relations between the pressure, temperature, density, and intrinsic energy of the gas at any point. Substituting in the equation of energy, we obtain equations between the velocity and either pressure, temperature, or density of the gas.

The equation thus obtained between the velocity and pressure is that given by Thomson and Joule; this equation holds at all points in the vessel or the effluent stream. If, then, the pressure at the orifice is known, as well as the pressure well within the vessel where the gas has no energy of motion, we have the velocity of gas at the orifice; and obtaining the density at the orifice from the thermodynamic relation between density and pressure, we have the weight discharged per second by multiplying the product of velocity with density by the effective area of the orifice. This is Thomson and Joule's equation for the flow through an orifice. And so far the logic is perfect, and there are no assumptions but those involved in the general theories of thermodynamics and of fluid motion.

But in order to apply this equation, it is necessary to know the pressure at the orifice; and here comes the assumption that has been tacitly made: *that the pressure at the orifice is the pressure in the receiving vessel at a distance from the orifice.*

3. The origin of this assumption is that it holds, when a denser liquid like water flows into a light fluid like air, and approximately when water flows into water.

Taking no account of friction, the equations of hydrodynamics show that this is the only condition under which the ideal liquid can flow steadily from a drowned orifice. But they have not been hitherto integrated so far as to show whether or not this would be the case with an elastic fluid.

In the case of an elastic fluid, the difficulty of integration is enhanced. But on examination it appears that there is an important circumstance connected with the steady motion of gases which does not exist in the case of liquid. This circumstance, which may be inferred from integrations already effected, determines the pressure at the orifice irrespective of the pressure in the receiving vessel when this is below a certain point.

4. To understand this circumstance, it is necessary to consider a steady narrow stream of fluid in which the pressure falls and the velocity increases continuously in one direction.

Since the stream is steady, equal weights of the fluid must pass each section in the same time; or, if u be the velocity, ρ the density, and A the area of the stream, the joint product $u\rho A$ is constant all along the stream, so that

$$A = \frac{W}{g\rho u},$$

where $\frac{W}{g}$ is the mass of fluid which passes any section per second.

In the case of a liquid ρ is constant, so that the area of the section of the stream is inversely proportional to the velocity, and therefore the stream will continuously contract in section in the direction in which the velocity increases and the pressure falls, as in fig. 1, also fig. 2 A.

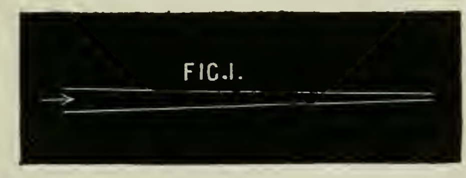

FIG. I.

In the case of a gas, however, ρ diminishes as the velocity increases and the pressure falls; so that the area of the section will not be inversely proportional to u, but to $u \times \rho$, and will contract or increase according to whether u increases faster or slower than ρ diminishes.

As already described, the value of ρu may be expressed in terms of the pressure. Making this substitution, it appears that ρu increases from zero as p diminishes from a definite value p_1 until $p = {\cdot}527 p_1$; after this ρu diminishes to zero as p diminishes to zero. A varies inversely as ρu, and therefore diminishes from infinity as p diminishes from p_1 till $p = {\cdot}527 p_1$; then A has a minimum value and increases to infinity as p diminishes to zero, as in fig. 2.

FIG. 2.

The equations contain the definite law of this variation, which, for a particular fall of pressure, is shown in fig. 2 A.

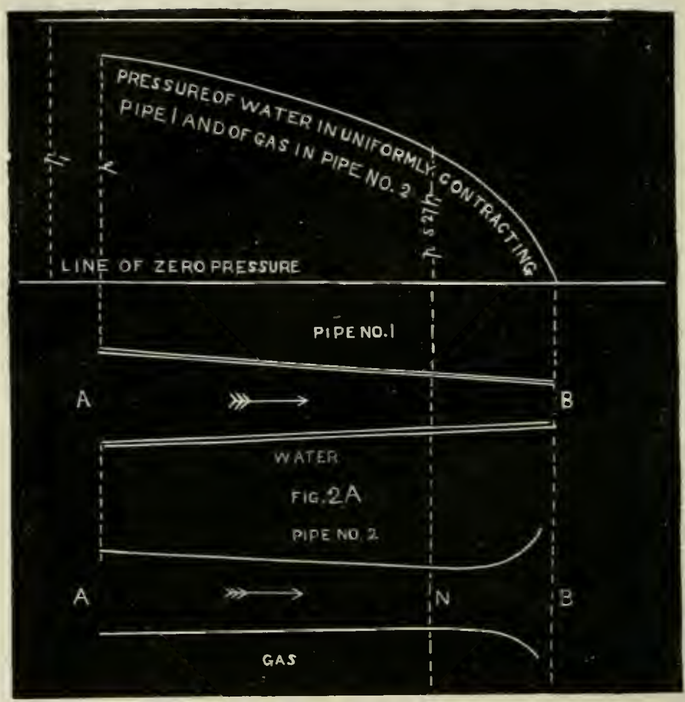

FIG. 2A

For the present argument it is sufficient to notice that A has a minimum value when $p = \cdot527p_1$; since this fact determines the pressure at the orifice when the pressure in the receiving vessel is less than $\cdot527p_1$, that being the pressure in the discharging vessel.

5. If, instead of an orifice in a thin plate, the fluid escaped through a pipe which gradually contracted to a nozle, then

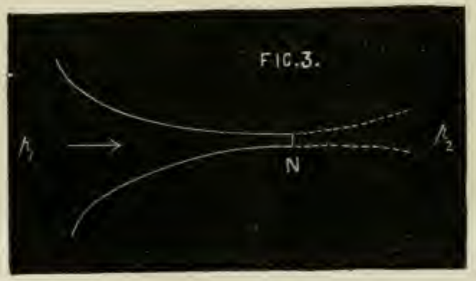

FIG. 3.

it would follow at once, from what has been already said, that when p_2 was less than $\cdot527p_1$, the narrowest portion of the stream would be at N, for since the stream converges to N the pressure above N can be nowhere less than $\cdot527p_1$; and since emerging into the smaller surrounding pressure p_2 the stream would expand laterally, N would be the minimum breadth of the stream, and hence the pressure at N would be $\cdot527p_1$. In a broad view we may in the same way look on an orifice in the wall of a vessel as the neck of a stream. But if we begin to look into the argument, it is not so clear, on account of the curvature of the paths in which some of the particles approach the orifice.

Since the motion with which the fluid approaches the orifice is steady, the whole stream, which is bounded all round by the wall, may be considered to consist of a number of elementary streams, each conveying the same quantity of fluid. Each of these elementary streams is bounded by the neighbouring streams, but as the boundaries do not change their position they may be considered as fixed.

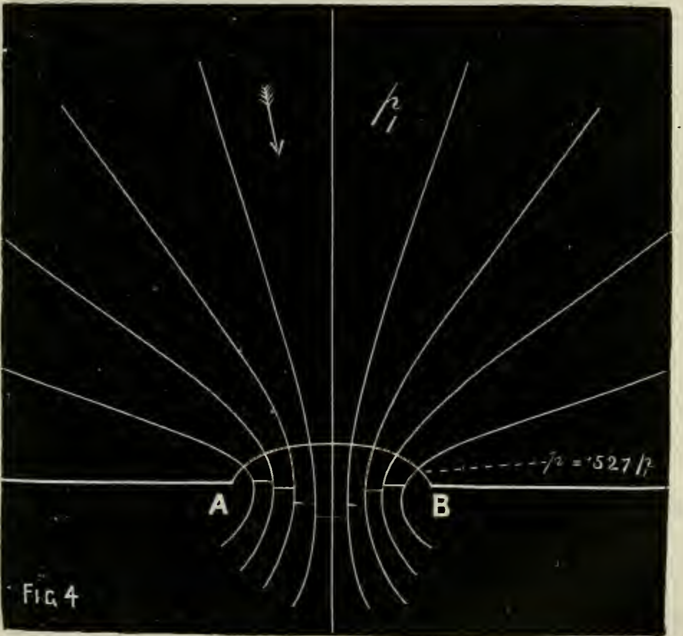

FIG 4

The figure (4) shows approximately the arrangement of such stream. But for the mathematical difficulty of integrating the equations of motion, the exact form of these streams might be drawn. We should then be able to determine exactly the necks of each of these streams. Without complete integration, however, the process may be carried far enough to show that the lines bounding the streams are continuous curves which have for asymptotes on the discharging-vessel side lines radiating from the middle of the orifice at equal angles, and, further, that these lines all curve round the nearest edge of the orifice, and that the curvature of the streams diminishes as the distance of the stream from the edge increases.

These conclusions would be definitely deducible from the theory of fluid motion could the integrations be effected, but they are also obvious from the figure and easily verified experimentally by drawing smoky air through a small orifice.

From the foregoing conclusions it follows, that if a curve be drawn from A to B, cutting all the streams at right angles, the streams will all be converging at the points where this line cuts them, hence the necks of the streams will be on the outflow side of this curve. The exact position of these necks is difficult to determine, but they must be nearly as shown in the figure by cross lines. The sum of the areas of these necks must be less than the area of the orifice, since, where they are not in the straight line A B, the breadth occupied on this line is greater than that of the neck. The sum of the areas of the necks may be taken as the effective area of the orifice; and, since all the streams have the same velocity at the neck, the ratio which this aggregate area bears to the area of the orifice may be put equal to K, a coefficient of contraction.

If the pressure in the vessel on the outflow side of the orifice is less than $\cdot 527 p_1$, this is the lowest pressure possible at the necks, as has already been pointed out, and on emerging the streams will expand again, as shown in the figure, the pressure falling and the velocity increasing, until the pressure in the streams is equal to p_2, when in all probability the motion will become unsteady.

If p_2 is greater than $\cdot 527 p_1$, the only possible form of motion requires the pressure in the necks to be p_2, at which point the streams become parallel until they are broken up by eddying into the surrounding fluid (fig. 5).

6. There is another way of looking at the problem, which is the first that presented itself to the author.

Suppose a parallel stream flowing along a straight tube with a velocity u, and take a for the velocity with which sound would travel in the same gas at rest, the velocity with which a wave of sound or any disturbance would move along the tube in an opposite direction to the gas would be $a-u$.

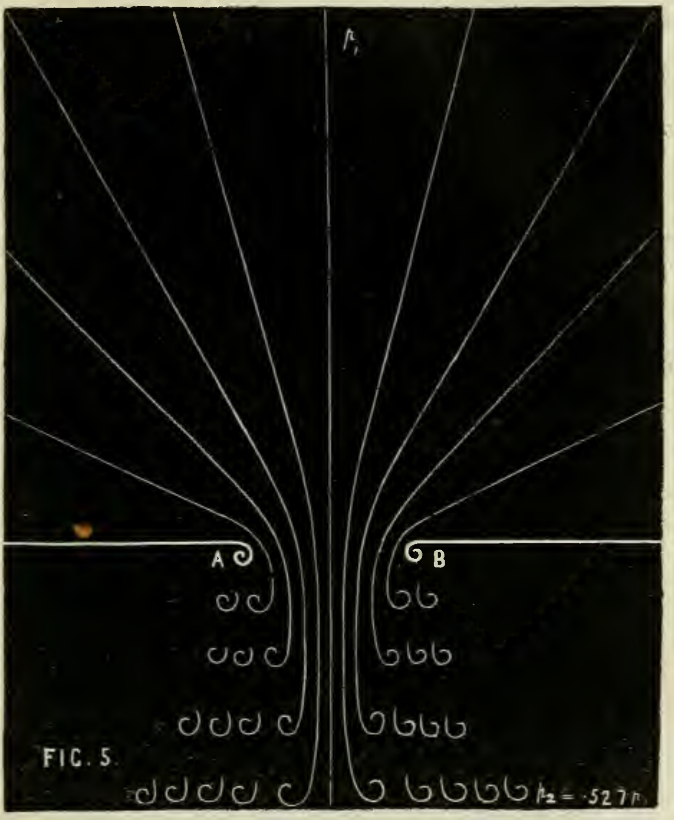

FIG. 5

If then $a=u$, no disturbance could flow back along the tube against the motion of the gas ; so that, however much the pressure might be suddenly diminished at any point in the tube, it would not affect the pressure at points on the side from which the fluid is flowing. Thus, suppose the gas to be steam and this to be suddenly condensed at one point of the tube, the fall of pressure would move back against the motion, increasing the motion till $u=a$, but not further ; just as in the Bunsen's burner the flame cannot flow back into the tube so long as the velocity of the explosive mixture is greater than the velocity at which the flame travels in the mixture.

According to this view, the limit of flow through an orifice should be the velocity of sound in gas in the condition as regards pressure, density, and temperature of that in the orifice; and this is precisely what it is found to be on examining the equations.

7. The following is the definite expression of the foregoing argument.

The adiabetic laws for gas are: p being pressure, ρ density, τ absolute temperature, and γ the ratio of specific heat,

$$\frac{\tau}{\tau_0}=\left(\frac{p}{p_0}\right)^{\frac{\gamma-1}{\gamma}}=\left(\frac{\rho}{\rho_0}\right)^{\gamma-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The equation of motion, u being the velocity and x the direction of motion, is

$$\rho u\frac{du}{dx}=-\frac{dp}{dx},$$

or

$$\frac{u^2}{2}=-\int_0^p\frac{dp}{\rho}+\mathrm{C}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Substituting from equations (1),

$$\int_0^p\frac{dp}{\rho}=\frac{\gamma}{\gamma-1}\frac{p_0}{\rho_0}\frac{\tau}{\tau_0};$$

$$\therefore\ u=\sqrt{\frac{2g\gamma}{\gamma-1}\frac{p_0}{\rho_0}\frac{\tau_1}{\tau_0}\left\{1-\left(\frac{p}{p_1}\right)^{\frac{\gamma-1}{\gamma}}\right\}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\rho=\frac{\rho_0\tau_0p_1}{p_0\tau_1}\left(\frac{p}{p_1}\right)^{\tau_0}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\therefore\ \frac{w}{g}=\mathrm{A}p_1\sqrt{\frac{2\gamma g\rho_0\tau_0}{(\gamma-1)p_0\tau_1}}\sqrt{\left\{1-\left(\frac{p}{p_1}\right)^{\frac{\gamma-1}{\gamma}}\right\}}\left(\frac{p}{p_1}\right)^{\frac{1}{\gamma}}. \quad . \quad (5)$$

Hence along a steady stream, since W is constant, equation (5) gives a relation that must hold between A and p.

Differentiating A with respect to p and making $\frac{d\mathrm{A}}{dp}$ zero, it appears

$$2p_1^{\frac{\gamma-1}{\gamma}}=(\gamma+1)p^{\frac{\gamma-1}{\gamma}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

or

$$\frac{p}{p_1}=\left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For air $\gamma=1{\cdot}408$.

$$\therefore\ \frac{p}{p_1}={\cdot}527. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It thus appears that as long as p falls, the section continuously diminishes to a minimum value when $p = \cdot 527 p_1$, and then increases again. Substituting this value of p in equation (3),

$$u = \sqrt{\frac{2\gamma g p_0 \tau_1}{(\gamma+1)\rho_0 \tau_0}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$= \sqrt{\frac{2\gamma g p_0}{(\gamma+1)\rho_0}\left(\frac{p_1}{p_0}\right)^{\frac{\gamma-1}{2\gamma}}}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$= \sqrt{\frac{2\gamma g p_0}{(\gamma+1)\rho}\left(\frac{p}{p_0}\right)^{\frac{\gamma-1}{2\gamma}}\left(\frac{p_1}{p}\right)^{\frac{\gamma-1}{2\gamma}}}. \quad . \quad . \quad . \quad (11)$$

Hence by equation (6),

$$u = \sqrt{\frac{\gamma g p_0 \tau}{\gamma_0 \tau_0}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which is the velocity of sound in the gas at the absolute temperature τ.

It thus appears that the velocity of gas at the point of minimum area of a stream along which the pressure falls continuously is equal to the velocity of sound in the gas at that point.

8. From the equation of flow (5) it appears that for every value of A other than its minimum value, there are two possible values of the pressure which satisfy the equation, one being greater and the other less than

$$\cdot 527 p_1.$$

It therefore appears that in a channel having two equal minima values of section A and C, as in fig. 6, the flow from A to B may take place in either of two ways when the velocity is such that the pressure at A and B is $\cdot 527 p_1$, *i. e.* the pressure may either be a maximum or a minimum at C. In this respect gas differs entirely from a liquid, with which the pressure can only be a maximum at C.

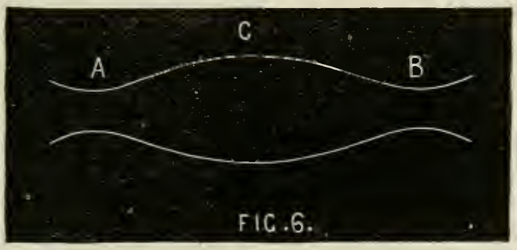

FIG. 6.

9. For air through an orifice, since $\gamma=1{\cdot}408$, when the pressure in the receiving vessel is less than $\cdot 527p_1$, the numerical value of U_n, the velocity in the neck of the orifice, is

$$U_n=997 \text{ (feet per sec.)} \sqrt{\frac{\tau_1}{\tau_0}}\,; \quad . \quad . \quad . \quad (13)$$

and if the temperature is 57° F., as in Mr. Wilde's experiments,

$$U_n=1022. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Reducing this in the ratio of the density at the neck to the density in the discharging vessel,

$$\left.\begin{aligned}\rho_n&=(\cdot 527)^{\frac{1}{\gamma}}\\ \rho_1&=\cdot 6345\end{aligned}\right\} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

We have the reduced velocity

$$U_n\frac{\rho_n}{\rho_1}=650 \text{ (feet per sec.)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Therefore the discharge will be given in cubic inches per second, KO being the effective area of the orifice, by

$$\left.\begin{aligned}\rho_1 Q&=12U_n\rho_n KO\\ &=12\times 650KO\end{aligned}\right\} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Or, since the actual area in square inches

$$O=\cdot 000314 \text{ sq. inches,}$$

$$Q=2{\cdot}44K \text{ (cubic inches per sec.)}. \quad . \quad . \quad . \quad (18)$$

10. In order to compare the experimental discharges with those calculated, it is necessary to know, besides the size of an orifice and the pressure and temperature of the discharging vessel, the coefficient of contraction or the effective area of the orifice. To obtain this from the equations requires that the terms depending on viscosity should be introduced, which renders the integration so far impossible. The only plan is to obtain this coefficient by comparing the theoretical results with the experimental. Such comparisons have been made by Prof. Weisbach for air; and in the case of short cylindrical orifices such as that used by Mr. Wilde (a cylindrical hole through a plate having a radius equal to the thickness of the plate), the value of K, the coefficient of contraction, given by Weisbach ('The Steam Engine,' p. 324, Rankine) is from ·73 to ·833. Whether these are the real coefficients of contraction may, however, well be doubted, as it is extremely difficult to determine the experimental quantities

of gas discharged owing to the great effect of slight variations of temperature on the relations between changes of pressure and changes of temperature, such changes of temperature being almost necessarily incidental on changes of pressure.

11. In Mr. Wilde's experiments the pressure was allowed to fall in the discharging vessel during the discharges; this would cause a corresponding fall of temperature, which would again cause heat to flow from the metal vessel into the gas within.

It is difficult therefore to say what the change of temperature was except in the extreme cases. With the experiments on the highest pressure, however, the times 7·5 seconds, and the greatest possible falls of temperature 5°·5, were so small that the communication of heat from the walls of the receiver would have been very slight; and hence we might expect that the discharges, calculated on the assumption of no communication of heat, would agree with the theoretical discharges multiplied by the real coefficient of contraction. This would be shown by an agreement in the successive coefficients obtained from the experiments with the higher pressures. On the other hand, with the lowest pressures the times were so considerable, 170 seconds, and the greatest possible falls of temperature (assuming no conduction, 94°) so great, that the communication of heat would have been very great and, considering the comparatively small mass to be heated (only one thirteenth of what it is in the highest experiments), might maintain the temperature approximately constant after falling some considerable amount below the initial temperature. In these last experiments, therefore, it would be expected that the discharge might be estimated as taking place at nearly constant temperature.

The intermediate experiments would give intermediate results.

According to this view, for the high pressures, since

$$\frac{\rho}{\rho_1}=\left(\frac{p}{p_1}\right)=\left(\frac{p}{p_1}\right)^{\cdot 71}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and

$$\frac{d\rho}{\rho_1}=\cdot 71\frac{dp}{p_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

or putting V for the volume 573 cub. in. of the discharging vessel,

$$\frac{\mathrm{Q}}{\mathrm{V}}t=\cdot 71\frac{dp}{p_1}t, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where t is the time. Or, since $tdp=5$ lbs.,

$$K=\frac{\cdot 835}{p_1 t} \quad \quad (22)$$

Substituting the value of $p_1 t$ in the first six experiments, we have :—

p.		K.		V_n Velocity at orifice.		$V_n \frac{\rho_n}{\rho}$.
135	...	·825	...	1022	...	650
130	...	·826	...	"	...	"
125	...	·835	...	"	...	"
120	...	·820	...	"	...	"
115	...	·810	...	"	...	"
110	...	·790	...	"	...	"

For the first three of these experiments K is nearly constant, showing that the conduction of heat could have but slight if any effect, but the effect is decidedly apparent in the next three.

Proceeding now to the other extreme, and assuming that the temperature, after undergoing some diminution, remains constant, we have

$$\frac{dp}{p_1}=\frac{Q}{V};$$

or, integrating,

$$\log_e \frac{p_1}{p_2}=\frac{Q}{V}t,$$

$$\log p_1-\log p_2=\frac{Q}{V}\log e;$$

from which, taking the last three experiments in Table 2,

p.		K.		V_n.		$V_n \frac{\rho_n}{\rho_1}$.
4	...	·95	...	1022	...	650
3	...	·98	...	"	...	"
2	...	·89	...	"	...	"

In these it appears that the values of K are approximating to the value ·825 ; but the great differences show that the temperature effect is far from having become steady, and are quite sufficient to explain the discrepancies in the actual values of K. There is thus no reason to doubt but that ·825 is about the real value of the coefficient of contraction for the orifice, and that the experimental results are quantitatively in accordance with the theory.

Pipe No. 1.—WATER (see fig. 2A, page 190).

$$V_B=\sqrt{2g\frac{P_1}{D}}$$

Pipe No. 2.—GAS.

$$V_B=\sqrt{\frac{\gamma}{\gamma-1}}\times\sqrt{2g\frac{P_0}{D_0}}\times\sqrt{\frac{T_1+461}{32+461}},$$

$$V_W=\sqrt{\frac{\gamma-1}{\gamma-1}}V_B.$$

AIR.

$$V_B=2\cdot413\text{ (feet per second)}\sqrt{\frac{T_1+461}{31+461}},$$

$$V_W=\ \ 997\text{ (feet per second)}\sqrt{\frac{T_1+461}{32+461}}.$$

XXIX. *On the Effect of Temperature on the Viscosity of Air and Carbon Dioxide.* *By* SILAS W. HOLMAN, *Associate Professor of Physics in the Massachusetts Institute of Technology*[*].

[Plates I. & II.]

THE investigation described in the present paper is a continuation of the work done on the same subject by the author in 1876[†]. The experimental portion of the work consists of about 250 independent measurements of the viscosity of air and 140 of carbon dioxide (carbonic acid), besides somewhat extended incidental researches on thermometry. The temperature-ranges for air were from 0° to 124° C.; for carbonic acid, from 0° to 225° C. The plan adopted at the outset was to make some study of the method and of the best form of apparatus; then to proceed to the study of several gases which have been already well investigated, either in regard to their viscosity or other properties, making measurements of the viscosity at temperature-intervals of about 20° from low to high temperatures. But the laborious nature of the observations, and the large amount of time demanded by the observations and their reduction, have rendered the fulfilment

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[*] Communicated by the Author, being a slight abridgment of a paper read before the American Academy of Arts and Sciences, May 13, 1885.

[†] "On the Effect of Temperature on the Viscosity of Air," Proc. Amer. Acad. Arts and Sci. xii. (1876) p. 41; Phil. Mag. iii. p. 81 (1877); Wied. *Beibl.* i. p. 222.

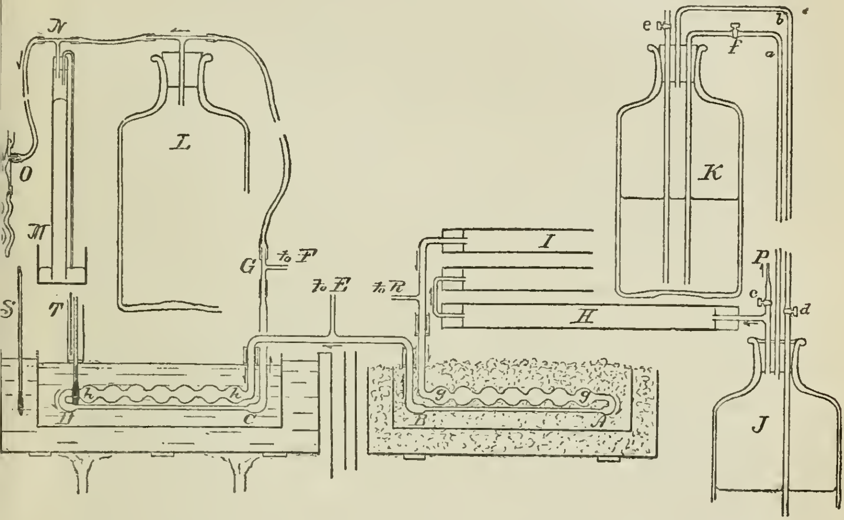
of the plan impossible for one whose available time has been fully occupied with laboratory instruction. It will be seen that the last of the observations given were made in April 1880. Since that date it has been wholly inconsistent with the author's duties and health to continue the work; and the incomplete results are now presented in the hope that, despite their limited range, they may be a contribution of some permanent value to the subject treated.

The expenses of the investigation have been mainly defrayed by an appropriation granted by the American Academy of Arts and Sciences from the Rumford Fund for researches on Light and Heat.

The objects of the investigation were concisely stated in the paper of 1876. The extension of the work was looked to for the development of data, which not only should furnish another experimental check on the deductions of the kinetic theory of gases, but should provide material of sufficient precision (approximating to that with which the coefficient of expansion of gases is known) to serve as a part of that experimental basis on which the complete theory of gases, and indeed of molecular physics in general, must eventually rest. The critical review of the method, given at p. 204, is intended to furnish the material for the formation of a judgment as to how far this object has been fulfilled in the case of the gases investigated.

APPARATUS.

The apparatus used is shown in the schematic section given by the accompanying diagram. It is in principle the same as that used in the former measurements. The dried gas is transpired successively through two glass capillaries of about 30 centim. in length, from a space containing the gas at a measured pressure to another space from which the gas is continuously exhausted as fast as it enters, and which is thus maintained at a constant and measured pressure. The pressure of the gas in the intermediate space is also measured. The capillaries are maintained at known or measured constant temperatures, *A B* being usually packed in finely pounded ice, and *D C* being in a jacketed double oil-bath, of which the temperature is maintained nearly constant by regulating the flame of the gas-burners, and is measured by the thermometer with its bulb at *D*, the entrance to the capillary. Both inner and outer oil-baths are continuously stirred by an agitator moved to and fro through the troughs by a water motor with connections, not shown in the sketch. This arrangement maintained temperatures as high as 225° constant, within about 0°·5 in most measurements, and so nearly uniform throughout the trough that no perceptible difference could be found at various points along the capillary. A thermometer at S in the outer bath served to adjust the lamps so that their heating should be such as to maintain a nearly constant temperature. Automatic thermo-regulators were tried, but were found in general to be quite as much of a disadvantage as benefit, and were abandoned.



The details of the apparatus will be described, beginning at the point where the gas enters. When air was used, the laboratory air was drawn in through caustic potash to remove the carbonic acid, and through concentrated sulphuric acid, fused chloride of calcium, and anhydrous phosphoric acid in the tubes H and I. When carbonic acid was used, the gas was formed by the action of hydrochloric acid on marble, purified by washing in water, dried, and freed from hydrochloric acid by passing through tubes of pumice coated with anhydrous copper sulphate. The gas was then drawn through P into J by withdrawing the concentrated sulphuric acid from J into K, as about to be described, and was there held for use. When a measurement was in progress, the gas in J, being slowly and uniformly displaced by the sulphuric acid returning from K, passed into and through H and I, arranged as already described. The glass bottles J and K held each about 10 litres, and one was filled with concentrated sulphuric acid. *K* was placed about a metre above *J*. The two were connected by two glass tubes, *a* and *b*, each containing a stopcock, and had other tubes arranged as shown in the sketch. To withdraw the sulphuric acid from *J* into *K*, and to replace this by the CO_2, it was simply necessary to connect *P* to the gas-holder or generator, to close *e* and *f*, to open *c*, to exhaust the air from *K* by an aspirator, and, opening the cock in *b*, to allow the H_2SO_4 to be transferred to any desired extent. This being accomplished, *d* and *c* were closed and the generator disconnected. When a measurement is in progress, the CO_2 passing at a uniform rate from *J* through *H* must be replaced by sulphuric acid from *K* through *a*. This flow is regulated by a tangent-screw motion on the cock *f*, until the liquid drops or runs into *J* at such a rate as to displace not only the necessary amount of CO_2, but slightly more than this, the excess escaping slowly through *c* and a fine orifice at *P*. This arrangement maintains an almost constant pressure in *J*; and as the pressure is thus always outward, there can be no inward leakage of air either during the measurements or at other times. The gas, after passing, always with this slight excess of pressure within, through *H*, *I*, enters the glass bulbs *g g*; and the pressure p_1 at entrance is measured by the barometric height at the time plus the pressure indicated by the gauge at *R*, read by the cathetometer. The bulbs *gg* were spherical enlargements of about three centimetres in diameter of a glass tube of about half a centimetre in diameter. The contents of these bulbs would be transpired by the capillaries once in about fifteen minutes. The tube *g g* and the capillary were connected into one piece at *A* by melting them together, and a similar solid connection was made at *B* to an exit-tube. The tubes *C D* and *h h* were similar in all respects to *A B* and *g g*, the capillaries being of very nearly the same length, and cut from the same piece of tubing, which was one of those used in the experiments of 1876. The tube connecting *B* to *h h* was of about 3 millim. internal diameter and 50 centim. length, and at its middle point contained a branch, which extended, with one joint of the kind described, to the gauge *E*, which in connection with the barometer served to measure p_2. The gas at exit from *C* passed about 50 centim. of 3 millim. tubing to the point *G*, where a side branch led to the gauge *F*, which gave the pressure p_3. Passing by *G*, the gas moved forward past *N* to the aspirator *O** and then escaped. The

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* Richard's jet-aspirator was used. See Amer. Jour. Sci. [3] viii. p. 200; Chem. News, xxxiv. p. 141; Trans. Amer. Mining Eng. vi. p. 492 (1879).

bottle *L*, of about 10 litres capacity, sometimes two bottles each of that volume, connected between *G* and *N*, served to reduce the rate of pressure-fluctuations arising from irregularities in the aspiration. At *N* was connected the pressure-regulator, which I will describe in detail, as it is, so far as I know, wholly new, and is available for many purposes.

The aspirator under a given head of water can exhaust at a definite rate, maintaining a certain exhaustion ; if the head be increased or lessened, the rate of exhaustion will be increased or diminished, and thus if the leakage into the exhausted space, as through the capillaries in this case, be sensibly constant, the pressure in the exhausted space must diminish or increase. It is often impracticable, as it was for me, to maintain a constant head of water, and some means is therefore necessary to overcome this irregular action. The arrangement used was that shown in the sketch. A large glass tube, *M*, open at both ends, stands upright in an open mercury-trough of considerably larger dimensions. Into its top is inserted a rubber stopper with two borings, through one of which passes one arm of a T-joint, whose other two arms are connected respectively with the aspirator and the vessel to be exhausted. Through the other boring passes a tube of 1 to 2 millim. diameter bent twice at right angles, and dipping into the mercury in the trough. Suppose that the vessel to be exhausted is close (the apparatus covers cases ranging from this to a leakage of about half the rate of exhaustion of which the pump is capable), and the aspirator set in operation. As the exhaustion proceeds, the mercury rises equally in both large and small tubes until the mercury in the trough drops below the point of the latter ; whereupon, as soon as the excess of external pressure is sufficiently great to overcome the friction of the mercury, the column in the fine tube rises rapidly and flows over into the upper part of the large tube and upon the mercury surface in it. This overflow is of course immediately followed by an inrush of air through the open point, and a consequent sudden lowering of the mercury in the large tube with a corresponding rise of level in the trough, which closes, or partly closes, *D*. This first sudden action is followed by several of lessening violence, and a steady condition is soon reached, in which there is a continuous inflow of air and small drops of mercury at the point, the proportion between the two depending upon the relation between the sizes of the tubes, the capacity of the aspirator, and the supply of gas from the vessel to be exhausted. If a fluctuation occurs in either the rate of the aspiration or the supply of gas to be exhausted, a greater or less proportion of air will be taken in, with a corresponding but very small change of the pressure within the apparatus. For the successful working of the apparatus, a proper proportioning of parts to the work to be done is of course necessary, and this is mainly to be accomplished by varying the size of the point to which the fine tube is drawn out. The sensitiveness of the apparatus may be increased by using a U-tube, instead of a vertical straight tube with cistern, and allowing the fine tube to extend into the open arm of this tube. A stricture at some point of the U-tube reduces the too sudden fluctuations. Various other modifications will readily suggest themselves to persons using the apparatus. The regulator is of course of service in other ways than merely rendering uniform the action of the aspirator. It is possible to maintain with it a constant exhaustion of any desired amount up to the full exhaustion which the aspirator can produce when working under the smallest head of water likely to occur; and in the form of a U-tube, with various lengths of tube DE, to be inserted at A and raised or lowered, it affords a very convenient means of varying the exhaustion at will.

CRITIQUE OF THE METHOD.

The quantity deduced as the result of each experiment of the present investigation is a ratio between the coefficients of viscosity of a gas at two different measured temperatures. As I have already shown*, this ratio is expressible by the following equation,

$$y=\frac{\eta_t}{\eta_0}=\frac{\mathrm{R}_2^4\lambda_1}{\mathrm{R}_1^4\lambda_2}\cdot\frac{p_2^2-p_3^2}{p_1^2-p_2^2}\cdot\frac{1+3\mathrm{A}t}{1+\alpha t}:$$

where

η_t = coefficient of viscosity of the gas at $t°$ C.;
η_0 = ,, ,, ,, ,, 0° C.;
R_2 = radius, and λ_2 = length, of second capillary at $t°$;
R_1 = radius, and λ_1 = length, of first capillary at 0°;
p_1 = pressure of gas at entrance to first capillary;
p_2 = ,, ,, exit from first capillary, which is the same as that at entrance to second;
p_3 = pressure at exit from second capillary;
t = temperature of second capillary;
0° = ,, ,, first ,,
A = coefficient of linear expansion of the glass;
α = mean coefficient of expansion of the gas between 0° and $t°$, and under the pressure p_2.

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* Phil. Mag. iii. p. 81 (1877).

Since the variation to be studied in the present investigation is one of quite small amount, and is determined as the result of a somewhat complex measurement, any systematic error of even quite small magnitude might mask the quantity sought. It is essential therefore to show how far such errors of sensible magnitude have been avoided or eliminated. A discussion * of the various possible sources of error, of their influence on the final result, and of the probable magnitude of the error in the measurements as actually performed, indicates that it is quite unlikely that known sources could have introduced accumulated errors into that result exceeding 0·5 per cent. even at the highest temperatures, and the means from which the equations are deduced are probably less than that amount in error.

The cathetometer and barometer used were carefully corrected for instrumental errors, and the temperatures are properly corrected and reduced to the air-thermometer by tables of errors† determined by a comparison with the air-thermometer. For the latter purpose the comparator and air-thermometer employed by Prof. H. A. Rowland for the same purpose in his investigation of the Mechanical Equivalent of Heat was used between the limits of 0° and 100° C. The results of the comparison are given in full in his memoir on that subject‡. The comparisons above 100° were made by me in his laboratory in another comparator designed by Prof. Rowland, and described in full in my paper just referred to.

The advantages of the method arise from its simplicity and directness. The only measurements of precision required are the temperature of the second capillary, and of the lengths of several mercury columns. No measurements of volume are involved. The two capillaries through which identically the same mass of gas is successively transpired, are as nearly as possible alike, and under the same conditions except as to temperature. The gas is transpired through each under nearly the same pressure-difference, and at a pressure not far from one atmosphere. The flow of the gas is perfectly uniform, except for slight accidental fluctuations, throughout the whole of a measurement or set of measurements, tending thus to the elimination of a class of errors possible in such methods as that of oscillating plates, or of transpiration when the driving-pressure falls from a given initial to a less final amount. The disturbing effect of eddies, or other special

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* Holman, Proc. Amer. Acad. Arts and Sci. xxi. pp. 25–44 (1885).

† Holman, Proc. Amer. Acad. Arts and Sci. xxi. pp. 40, 41 (1885).

‡ Rowland, ibid. xv. 117 (June 1879).

action, at the entrance to or exit from the tube, would be in part eliminated in this method, since the measurements give the ratios of the resistance in two tubes under constant and nearly identical conditions. No complete discussion of these effects has been yet given, and their experimental elimination certainly seems more easy than their mathematical treatment. It seems quite possible that they are still sensible sources of deviation from the assumed law of transpiration ; but as the magnitude of the disturbance is small, and cannot be widely different in the two tubes used in this apparatus, and since the determination of the constants of the tubes dependent on their diameters, lengths, &c. are experimentally made by the same process and under conditions identical with those of the subsequent work, the resulting error must be small. It should be noted also, that the debated question as to the slip of the gas over the inner surface of the glass tube has an influence in my results only to the extent by which this slip is affected by the temperature.

The freedom of the method from constant error is indicated by the close accordance of the results on dry air as obtained by the first, fourth, and fifth series. The first series was made with an apparatus * totally different from that afterwards used in all details of disposition of parts and of instruments used, except that the tube No. I. of that series was the same that was afterwards cut into three pieces, of which two nearly equal ones served as the capillaries in the fourth and fifth series. Observations with other tubes in the preliminary measurements, however, checked satisfactorily with these. The instruments and arrangements for measuring the pressures in the fourth series were wholly different from those used in the fifth series. The results at 100° for the three series are given in the following Table, in which the two last values are taken from the equation deduced for the respective series :—

Series.	$\frac{\eta_{100}}{\eta_0}$.	*d*.
I.	1·270	−0·0017
IV.	1·2672	−0·0045
V.	1·2717	0

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* See Phil. Mag. for February 1877, p. 84.

PROCEDURE IN MEASUREMENTS.

The first operation is thoroughly to dry the apparatus and fill it with pure dry gas. This was accomplished by repeated exhaustion and refilling of all necessary parts of the tubing, gauges, &c., none but thoroughly dry gas being admitted. This operation was repeated on each separate day of measurement, so that any error from slight leakage or diffusion of either air or moisture should be avoided. On the first introduction of the dry air or carbonic acid, the further precaution was taken to run the apparatus under quite high exhaustion for many hours consecutively; and in all cases, on each day of measurement, the apparatus was run for an hour or more before any readings were taken.

The procedure in measurement was as follows:—The aspirator was set in operation, *J* being full of the gas. The generator and purifiers were connected at *P*, and the cock *c* opened, *f* remaining closed, so that the supply of gas came from the generator; the temperature of *D C* was regulated, the stirrer being in continuous operation; the ice-bath was placed round *A B*, the regulator at *N* adjusted, and the transpiration allowed to proceed until the gauges *E* and *F* were nearly stationary. Then *c* was closed, and *f* opened and adjusted so that the reading of *R* slowly increased, whereupon *c* was again opened for the slow escape of the gas and the maintenance of a constant initial pressure p_1. The transpiration was allowed to proceed until *E*, *F*, and *R* were sufficiently near stationary, when readings of the mercury columns by the cathetometer and of the thermometers were taken systematically. After a complete set of readings had been thus obtained, the apparatus was thoroughly inspected and a second set made; and so on until the number was deemed sufficient, whereupon the temperature of *D C* was changed or the pressure modified as desired. The results thus obtained furnished, on reduction, the values of p_1, p_2, p_3, and t for the computation of the ratio of the coefficient of viscosity at the higher temperature to that at 0° C.; the further requirements being the constants $\frac{R_2{}^4\lambda_1}{R_1{}^4\lambda_2}=K$ for the tubes, R_1 and λ_1, R_2 and λ_2 being the radius and length respectively of the tubes *A B* and *C D*, as shown at page 209. This value of K was found from measurements similar in all respects to those just described, except that the tubes *A B* and *C D* were both surrounded with ice at the same time.

The apparatus was also arranged to place *D C* in steam. When left at night for subsequent use, an outward pressure was created in all parts of the apparatus.

EXPERIMENTAL RESULTS.

The results will be here given as they were for convenience classified during the progress of the work, viz. with dry air in five series, with carbonic acid in two series. The method of reduction of the results is given at page 204, and in my first paper.

Air.

First Series.—This consists of the twenty-one measurements made in 1876, as given at page 49 of the article referred to *, and gives as a mean result of the ten measurements of $\frac{\eta_1}{\eta_2}$, as shown in Table I. below, the value $y=\frac{\eta_1}{\eta_2}=1{\cdot}234$, with an average deviation † of 0·044, or about 4 per cent. A glance at the page referred to will show, however, that of these ten measurements but six were at the temperatures of 0° and 100° respectively. These six, as shown in Table II., give the mean

$$y=\frac{\eta_{100}}{\eta_0}=1{\cdot}270\pm a.d.\ 0{\cdot}005\ ;$$

and this mean I shall use in comparing this series with the later ones, omitting those results obtained at temperatures between 0° and 100°, because the want of certainty in the temperature-measurements would render the labour of the necessary computations fruitless.

TABLE I.

No.	$\frac{\eta_1}{\eta_2}$.	$d.$
2 ...	1·083	−·151
7 ...	1·212	−·022
8 ...	1·206	−·028
9 ...	1·215	−·019
11 ...	1·272	+·038
12 ...	1·267	+·033
13 ...	1·271	+·037
14 ...	1·273	+·039
18 ...	1·277	+·043
21 ...	1·259	+·025
	1·234	0·044

TABLE II.

No.	$\frac{\eta_1}{\eta_2}$.	$d.$
11 ...	1·272	+·002
12 ...	1·267	−·003
13 ...	1·271	+·001
14 ...	1·273	+·003
18 ...	1·277	+·007
21 ...	1·259	−·011
	1·270	0·005

Second Series. April 1878.—In making a study of the best forms of apparatus, a careful trial was given to capillaries in

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* Phil. Mag. iii. p. 85 (1877).

† Let $a_1, a_2, a_3, \dots a_n$ be a series of measurements of the same quantity, and let m be their arithmetical mean; then $a_1-m=d_1$, $a_2-m=d_2$, $a_3-m=d_3$, &c. will be the deviation of these measurements from their mean, and $\frac{d_1+d_2+d_3+\dots+d_n}{n}$ will be the average deviation if, in the summation of the numerator, the values of d_1, d_2, &c. be taken arithmetically, without regard to algebraic sign.

the form of a helix, as these facilitate the maintenance of constant and uniform temperatures of the bath, and render the use of longer and larger tubes possible. The coils were successfully made by winding the tubing, as it was drawn from the tube of the glass-worker, upon a wooden drum. The second series was made with a pair of such coils, and consisted of only eight measurements. The results in the measurements of K were so wholly discordant that they were at once rejected.

Third Series.—A second pair of smaller coils was mounted in a manner similar to that just described, and with the same general results, showing the coils to be utterly useless; probably, as was to be anticipated, because of changing curvature of the coils owing to expansion or change of position. Several straight capillaries were also studied, varying in size and in the form of tube employed for heating the gas. These experiments covered the whole 126 measurements of this series, and resulted in the selection of the form and size given in the general description of the apparatus at page 200. No systematic study was made, however, of the effects of the proportions of the tube on the law of the transpiration, though the apparatus seems well adapted for that purpose.

Fourth Series. October, November, and December 1878.—The capillaries used in this series were those described in the general account of the apparatus at page 200, viz. straight tubes of about 30 centim. in length and 0·0110 centim. in diameter, and were cut from tube No. I. of the apparatus of 1876. The mercury columns were read to 0·1 millim. by the reading-telescope from steel millimetre-scales placed behind the gauges. Corrections were applied to these scales, but the precision of reading was much less than in the fifth series; the temperature-measurements were also somewhat less precise; and the whole series should have much less weight, owing to the conditions under which it was taken, than the fifth series on air, or the second series on carbonic acid. The results obtained are given in the original paper.

The results from No. 49 onwards are of much greater precision than those preceding, chiefly from the use of greater pressures, which increased the precision of measurement. Measurements 49 to 99, when combined by the method of least squares, give for constants in the empirical equation

$$\frac{\eta_t}{\eta_0}=\frac{\eta_2}{\eta_1}=1+\mathrm{A}t+\mathrm{B}t^2$$

the values, between the limits $t=0°$ and $t=100°$,

$$\mathrm{A}=0·002821, \text{ and } \mathrm{B}=-0·00000149.$$

These values, however, I have regarded as entitled to so much less weight than those of the fifth series for air, that they are given here merely as a satisfactory and important check upon the further results of that series. The equation deduced from this latter series I regard as best representing my measurements on dry air. It will be noticed, on comparing the two series, that the greatest deviation of the two series is at 100°, where it amounts to less than 0·4 per cent.

Measurements 1 and 2 were taken during preliminary trials of the apparatus. In 3 to 8 the first capillary was in boiling water, the second in ice, this reversal of the usual sequence of temperature being made in order to test the apparatus. The mean of these five measurements (the sixth having been rejected when made as having been taken before the static condition of the process was reached) gives

$$y = \frac{\eta_{100}}{\eta_0} = 1{\cdot}267 \pm a.d.\ 0{\cdot}002.$$

The above equation gives for $t = 99^\circ{\cdot}94$,

$$\frac{\eta_t}{\eta_0} = 1{\cdot}2666\,;$$

and the direct observation made, as were all those from which the equation is derived, with the first capillary at 0°, gives as the mean at $99^\circ{\cdot}66$,

$$\frac{\eta_t}{\eta_0} = 1{\cdot}2666.$$

The close agreement of these numbers seems to indicate a freedom from constant error of any considerable magnitude in the value of K, and in the expansion-correction to this value.

Fifth Series. April 1880.—This series was taken with the apparatus as described at page 200, immediately after the completion of the second series with carbonic acid. The measurements were made under as favourable conditions as any of this paper, and are of greater weight than all of the others upon air. The full data for the computation of these results are given in Table III. in such form that a recomputation, in so far as relates to those portions subject to possible modification of such amount as to materially change the result, may at any time be made. The value of K used was the same as that used for the second series of carbonic acid.

These measurements may be divided, according to temperatures, into six groups, and are very concordant, except that the sixth group shows a deviation of about 0·6 per cent. from the value which the other five groups would indicate at that temperature. There appears to be in this group some considerable constant error, due probably to a mistake in the reading of the thermometer, which was a different one from that used in the preceding groups. The deviation is so large

TABLE III.—Air. Fifth Series.

No.	p_1-p_2.	p_1+p_2.	p_2-p_3.	p_2+p_3.	α.	t_2.	$\frac{\eta_2}{\eta_1}$.	Computed $\frac{\eta_2}{\eta_1}$.	d.
1.	92·31	1418·23	113·29	1212·63	·0036693	13°·70	1·0374		
2.	92·26	1417·90	113·37	1212·27	....	13·93	1·0378		
3.	92·15	1417·71	113·35	1212·21	....	14·21	1·0378		
					Means=	13·947	1·0377	1·0383	−·0006
4.	83·93	1423·93	122·09	1217·91	·0036694	42·60	1·1180		
5.	83·86	1423·50	122·13	1217·51	....	43·04	1·1178		
6.	83·81	1423·35	122·27	1217·27	....	43·30	1·1187		
7.	83·98	1422·78	122·41	1216·39	....	43·17	1·1178		
8.	83·98	1422·44	122·25	1216·21	....	42·76	1·1179		
					Means=	42·974	1·1180	1·1176	+·0004
9.									
10.	77·39	1425·25	128·88	1218·98	·0036694	67·74	1·1861		
11.	77·34	1425·16	128·76	1219·06	....	67·74	1·1859		
12.	77·34	1425·08	128·83	1218·91	....	67·94	1·1831		
					Means=	67·81	1·1850	1·1850	·0000
13.	72·44	1429·96	133·48	1224·04	·0036695	88·67	1·2381		
14.	72·29	1430·11	133·59	1224·23	....	88·64	1·2419		
15.	72·20	1430·14	133·49	224·45	....	88·85	1·2419		
16.	72·20	1429·96	133·59	1224·17	....	88·92	1·2424		
					Means=	88·77	1·2411	1·2415	−·0004
17.	70·20	1441·48	136·41	1234·87	·0036696	99·69	1·2684		
18.	70·28	1441·22	136·35	1234·59	....	99·02	1·2686		
19.	70·23	1440·51	136·58	1233·70	....	98·93	1·2716		
20.	70·05	1440·43	136·11	1234·27	....	99·41	1·2695		
21.	70·05	1440·19	136·14	1234·00	....	99·03	1·2710		
22.	70·10	1440·10	136·16	1233·84	....	99·18	1·2695		
					Means=	99·21	1·2698	1·2696	+·0002
23.	64·94	1446·20	141·17	1240·09	·0036697	124·61	1·3321		
24.	64·86	1446·46	141·21	1240·39	....	124·36	1·3350		
25.	65·12	1446·42	140·95	1240·35	....	124·17	1·3279		
26.	64·98	1446·72	141·02	1240·70	....	124·22	1·3314		
27.	65·12	1446·94	140·96	1240·86	....	124·69	1·3264		
					Means=	124·41	1·3306	1·3368	−·0062

that I have thought it best to reject the sixth group wholly in the computation of the empirical equation for this series on air. I fully recognize that this rejection may be considered somewhat arbitrary, and also that the retention of the sixth group would make the accordance between the fourth and fifth series greater than now; but I am so fully satisfied that there is some mistake in the rejected group that I unhesitatingly lay it aside. I thus obtain, by the method of least squares, for measurements 1 to 22 on dry air, fifth series,

$$\frac{\eta_t}{\eta_0}=1+0·002751t-0·00000034t^2,$$

between the temperature-limits of 0° and 100° C. The last column of the table, headed d, gives the deviations of the observed means from the values of $\frac{\eta_t}{\eta_0}$, computed for the same temperatures t_2 by the preceding equation and given in the ninth column. The average deviation of the means from the equation is thus only 0·0003, or about 0·03 per cent., for the first five means, the deviation of the sixth mean being ten times the next greatest deviation. The average deviation of the individual observations from their respective means, disregarding the correction corresponding to the slight differences of the observed temperatures for the mean, is 0·0012, or about 0·1 per cent.

Carbonic Acid, CO_2.

First Series.—Twenty-one measurements were made in January 1879, after the close of the fourth series on air, and with the same apparatus, with the addition of the necessary apparatus for holding the gas. The precision of the results was less than in the fourth series for air, chiefly because of the somewhat greater complication of the apparatus for the supply of the gas. The results are of little value, but are given as a check on the second series. The pressures were about the same as in No. 49 to 98 of the fourth series on air. The temperature t_1 of the first capillary was always 0° C. The following Table IV. gives the mean results. The coefficient of expansion used was 0·003699, a value taken from Regnault's work by interpolation for the actual pressure p_2, under which the expansion occurs.

The column headed n gives the number of measurements going to make up the corresponding means.

Table IV.—CO_2. First Series.

n.	t_2.	$\frac{\eta_2}{\eta_1}$.	Computed $\frac{\eta_2}{\eta_1}$.
8	29·61	1·103	1·108
5	48·56	1·178	1·175
8	100·09	1·324	1·351

Second Series.—One hundred and twenty measurements were made from January to April 1880, with the complete apparatus as described at pages 200 and 209. The thermometers used were Casella 32378, Baudin 7335 up to 180°, and Baudin 7789 above 200°. The first twenty measurements were preliminary, being made with various tubes and forms of apparatus before satisfactory forms were obtained. The remainder are given in the following table. In all cases $t_1=0°$.

TABLE V.—CO_2. Second Series.

No.	p_1.	p_2.	p_3.	K.	Mean K.
1.	784·08	720·53	653·77	1·0422	1·0440
2.	786·69	720·17	653·99	1·0918	
3.	787·48	721·58	654·10	1·0737	
4.	785·44	722·30	654·54	1·0204	
5.	790·61	724·59	654·84	1·0397	
6.	758·59	700·78	640·07	1·0364	
7.	758·17	700·30	639·71	1·0638	
8.	757·60	699·82	639·23	1·0380	
9.	757·15	699·27	838·57	1·0381	
10.	773·74	707·56	637·41	1·0390	
11.	774·14	707·50	636·92	1·0169	
12.	780·55	718·34	652·49	1·0330	
13.	780·74	718·12	652·18	1·0387	
14.	748·64	699·58	649·47	1·0510	1·0375
15.	748·45	699·99	649·37	1·0276	
16.	748·27	699·72	649·27	1·0330	
17.	748·52	699·55	648·81	1·0365	
18.	748·37	699·34	648·75	1·0408	
19.	748·19	699·33	648·68	1·0359	
20.	771·58	614·35	409·82	1·0402	1·0395
21.	771·62	614·36	409·70	1·0376	
22.	771·66	614·35	409·57	1·0399	
23.	771·67	614·28	409·22	1·0394	
24.	772·11	614·50	409·16	1·0397	
25.	772·38	614·57	408·98	1·0401	
26.	770·73	611·24	400·91	1·0353	1·0380
27.	770·55	610·67	400·83	1·0404	
28.	770·37	610·55	400·81	1·0404	
29.	771·92	701·15	625·09	1·0335	
30.	771·71	700·74	624·68	1·0366	
31.	771·50	700·54	624·90	1·0419	
32.	767·36	705·39	640·08	1·0386	
33.	767·46	705·46	640·22	1·0394	
34.	766·90	705·13	639·89	1·0362	
35.	766·80	705·01	639·71	1·0357	
36.	767·34	712·33	655·13	1·0406	
37.	767·29	712·39	655·18	1·0383	
38.	766·95	712·12	654·91	1·0370	

Table V.—CO_2. Second Series (*continued*).

No.	p_1.	p_2.	p_3.	100 a.	t_2.	$\frac{\eta_2}{\eta_1}$.	Mean t_2.	Mean $\frac{\eta_2}{\eta_1}$.	Computed $\frac{\eta_2}{\eta_1}$.
39.	746·72	693·79	630·67	0·37047	17°·62	1·0688			
40.	746·53	693·62	630·49		17·87	1·0684			
41.	746·18	693·31	630·10		18·09	1·0696			
42.	745·93	692·94	629·77		18·29	1·0658			
43.	745·64	692·71	629·47		18·62	1·0669	18°·10	1·0679	1·0666
44.	745·41	696·50	628·79	0·37053	41·15	1·1468			
45.	745·64	696·68	629·03		41·28	1·1472			
46.	745·97	697·01	629·24		40·86	1·1481			
47.	746·41	697·32	629·70		40·86	1·1426			
48.	746·73	697·75	630·22		40·87	1·1438			
49.	747·45	698·54	630·98		40·87	1·1461	40·98	1·1458	1·1485
50.	769·40	723·90	653·79	0·37071	59·02	1·2125			
51.	769·56	724·17	653·75		59·30	1·2197			
52.	769·49	724·18	654·04		59·54	1·2164			
53.	769·47	724·20	654·31		59·50	1·2163			
54.	769·25	723·90	654·43		58·93	1·2064			
55.	769·23	723·89	654·25		58·72	1·2102			
56.	769·26	724·01	654·68		58·96	1·2068	59·14	1·2126	1·2119
57.	774·14	732·22	659·65	0·37077	79·56	1·2847			
58.	774·07	732·31	659·96		79·58	1·2860			
59.	773·93	732·35	660·33		79·72	1·2857			
60.	773·66	732·17	660·48		79·73	1·2829	79·65	1·2848	1·2820
61.	773·71	735·84	662·96	0·37081	99·67	1·3550			
62.	773·62	735·83	663·22		100·17	1·3514			
63.	773·50	735·77	663·52		100·24	1·3468			
64.	773·78	736·13	663·86		100·60	1·3490	100·17	1·3506	1·3508
65.	780·77	745·42	670·80	0·37087	119·11	1·4147			
66.	780·70	745·31	670·68		119·20	1·4129			
67.	780·32	745·04	670·69		119·27	1·4120			
68.	779·81	744·65	670·56		119·37	1·4119			
69.	779·58	744·58	670·24		119·55	1·4223	119·30	1·4148	1·4139
70.	770·66	738·34	663·10	0·37083	141·53	1·4774			
71.	770·52	738·18	662·91		141·89	1·4757			
72.	770·55	738·38	663·11		141·90	1·4836			
73.	770·43	738·52	663·31		141·87	1·4948			
74.	770·18	738·28	663·31		141·92	1·4919			
75.	769·77	737·82	663·10		142·25	1·4824	141·893	1·4843	1·4875
76.	766·48	734·44	652·66	0·37078	158·40	1·5492			
77.	766·22	734·26	652·58		158·83	1·5498			
78.	766·06	734·26	653·19		159·44	1·5446			
79.	765·38	733·54	652·85		159·05	1·5415			
80.	763·89	732·12	652·69		157·87	1·5218			
81.	763·60	731·91	652·61		157·56	1·5244			
82.	763·28	731·63	652·46		157·62	1·5341			
83.	763·05	731·56	652·45		157·50	1·5310	158·283	1·5371	1·5400

Table V. (*continued*).

No.	p_1.	p_2.	p_3.	100 α.	t_2.	$\frac{\eta_2}{\eta_1}$.	Mean t_2.	Mean $\frac{\eta_2}{\eta_1}$.	Computed $\frac{\eta_2}{\eta_1}$.
84.	773·83	745·39	666·15	0·37088	181°·49	1·6141			
85.	773·96	745·70	666·23		180·99	1·6309			
86.	773·97	745·67	666·23		180·96	1·6280			
87.	774·14	745·64	666·21		181·70	1·6136			
88.	774·01	745·49	666·38		181·45	1·6072			
							181°·32	1·6188	1·6135
89.	774·41	747·71	660·30	0·37090	223·9	1·7284			
90.	774·32	747·94	661·30		225·0	1·7312			
91.	773·99	747·87	660·78		223·4	1·7631			
92.	774·33	748·38	661·66		223·7	1·7669			
							224·0	1·7474	1·7488
93.	771·47	722·92	666·03	0·37071	16·20	1·0668			
94.	770·89	722·21	665·19		16·62	1·0646			
95.	769·33	677·80	561·76	0·37036	17·18	1·0602			
96.	769·14	677·75	561·63		17·30	1·0621			
97.	768·79	677·40	561·21		17·47	1·0620			
98.	768·73	677·38	561·12		17·62	1·0625			
							17·07	1·0630	1·0628

Measurements 39 to 98 furnish data for computing the constants in an empirical equation for carbonic acid ; and the equation thus deduced is

$$\frac{\eta_t}{\eta_0} = 1 + 0{\cdot}003725\,t - 0{\cdot}00000264\,t^2 + 0{\cdot}00000000417\,t^3,$$

between the limits of 0° and 224° C.

The term containing t^3 is necessary on account of the rapid curvature of the line representing the observations. The last column of Table V. shows the value of $\frac{\eta_2}{\eta_1} = \frac{\eta_t}{\eta_0}$ deduced from this equation for the temperature means of the second column, showing as close an agreement with the observed means of $\frac{\eta_2}{\eta_1}$ as could be expected, except at 100°, where the deviation amounts to about 2 per cent. The first series is, however, of much less weight than the second series. The last column of Table V. shows the values of $\frac{\eta_2}{\eta_1}$ computed to correspond with the means of the preceding column. The average deviation of the observed means from those computed from the above equation is thus 0·0020, or about 0·15 per cent. The average deviation of the individual results from their corresponding means, taken as in the fifth series for air, is 0·0052, or about 0·4 per cent.

Effect of Pressure.

In Series IV. for air, the total driving pressure used, p_1-p_3, was varied within considerable ranges, to test whether the value obtained of $\eta_2:\eta_1$, or of K, was thereby affected except through errors of observation. In 3, 4, and 5, $p_1-p_3=248$ mm., and $\eta_2:\eta_1=1·267$; in 7 and 8, under the same conditions otherwise, $p_1-p_3=376$ mm., and $\eta_2:\eta_1=1·266$, showing no effect due to increase of the pressure by one half. Measurements 9 to 13, made with p_1-p_3 ranging from 258 to 485 mm., give values of K with an average deviation of about 0·2 per cent. Measurements 21 to 48 give values of $\eta_2:\eta_1$ about one per cent. lower than those obtained in the remainder of the series, made with greater values of p_1-p_3, but the precision of these measurements is much less than of the later ones. The value of K found from 50 to 54 and 60 to 66, with $p_1-p_3=530$ mm. about, is within 0·5 per cent. of that found in 9 to 12, under $p_1-p_3=258$ mm., and agrees precisely with 12, under $p_1-p_3=361$ mm. And, finally, the mean of 97 and 98 differs from 99 by less than 0·25 per cent., though the pressures p_1-p_3 are respectively 540 and 250 mm.

In the second series for carbonic acid, the effect of pressure was somewhat tested in measurements 26 to 38, where p_1-p_3 varied from 370 to 111 mm. without producing any traceable effect in K. This is the best test made, owing to the greater precision of the measurements. Also in measurements 93 to 98 of the same series, the pressure was changed from 105 to 207 without materially affecting the results.

In the first series for air, the average value of p_1-p_3 was about 740 mm., and the mean value of $\eta_2:\eta_1$ at $t_2=100°$ is 1·270, while that of the fourth series, under $p_1-p_3=$ from 248 to 540, is about 1·267, and that of the fifth series, under $p_1-p_3=225$ mm., is 1·272, thus showing no effect traceable to the difference of the driving pressures used.

Deduction from Results.

The results of my measurements seem to show conclusively, that the variation of the viscosity with the temperature of the gas, in the case at least of dry carbonic acid and of dry air freed from carbonic acid, which may be taken as typical gases, is not proportionate either to the square root or to any numerical power of the absolute temperature reckoned from $-274°$ C. They point thus to the inference that all hypotheses yet advanced to account for the variation of the viscosity of gases, and hence also for the viscosity itself, are incomplete for this phenomenon, in the same general way as are the analogous hypotheses regarding the compressibility of gases and other phenomena. The hypothetical deductions fail to accord completely with the results of quantitative measurements.

DISCUSSION OF RESULTS OF ALL RESEARCHES ON AIR AND CO_2.

The experimental results which I have given in the foregoing tables, and the deduced equations, show that, unless some considerable and regular source of error affects them, the viscosity of both dry air (freed from CO_2) and carbonic acid increases with the rise of temperature according to a rate which varies with the temperature and is smaller as the temperature is higher. The ratio $\eta_t : \eta_0$ is therefore not proportional to the first power (Maxwell) of the absolute temperature ; it is not expressible by a linear equation of the first degree, *e. g.* $\eta_t = \eta_0 (1 + bt)$, where t = temperature C. and b = a constant ; nor is it given by the equation $\eta_t = \eta_0 (1 + at)^n$, or its equivalent $\eta_t \div \eta_0 = c\tau^n$, where τ = absolute temperature. The last three equations are the only ones thus far used by observers in discussing their results, although the work of E. Wiedemann and A. von Obermayer shows a decided departure from these expressions. The insufficiency of the latter equations may be shown by discussing the observational data by the logarithmic method which I used in my former paper. Nor could the equation $\eta_t = \eta_0 (1 + at)^n$ be more than an empirical equation at best, unless possibly when a were expressed as a function of t and the pressure, a condition which I have not thought worth consideration at present. For the expression of my own results, I have employed merely the empirical equation with increasing powers of t, as I have found no theoretical hypothesis which led to results corresponding to the observed relation of η and t.

The deviation of both air and carbonic acid from the equation $\eta_t = \eta_0 (1 + bt)$ is so small, and the difficulties of precise measurement so considerable, that these deviations may often be masked by accidental errors of measurement, and by "constant errors," arising from imperfect drying or purification of the gas, from differences between the thermometer indications and the actual temperature of the gas, from faulty proportioning of apparatus, and from other sources. This discussion of my own method in these regards I give at page 205 ; that of others, I cannot advantageously attempt. But I will proceed to a review of the results obtained by all others who have worked in this field ; and shall show that for air and carbonic acid no results are found giving a value of b (rate of change of $\eta_t : \eta_0$ with rise of temperature) increasing with the temperature; that some results can give only a constant value to b, owing either to the want of sufficient precision, or to the insufficient number of temperature intervals employed; that some results show a marked diminution, as do my own, of b; and that many of these last, when carefully discussed, afford material for getting at a numerical measure of the change in b which is in substantial accordance with my own results. These facts indicate, either that all measurements show conclusively that b does diminish with rise of temperature, or that the method of transpiration through capillary tubes upon which these demonstrations rest (for the measurements with oscillating plates are of insufficient precision for determination of this change) is faulty in either its experimental application or its mathematical theory. In the consideration of this last proposition the statements which I have made at page 205 should be reviewed.

In the discussion of the results of former observers, I have adopted the graphical method as best adapted to the purpose; but as the point to be considered is one in which changes in the fourth and sometimes the fifth place of significant figures must be exhibited, a special device must be resorted to. I have therefore assumed for carbonic acid an equation $\eta_t=\eta_0\left(1+\frac{t}{300}\right)$, and for air $\eta_t=\eta_0\left(1+\frac{t}{400}\right)$, as convenient equations to which to refer the results on these gases respectively. I have computed for two or many temperatures (usually those of observation) values of $\eta_t : \eta_0$ from these equations, and subtracting these from the experimental data for the same temperature (or from ratios $\eta_t : \eta_0$ deduced by myself from the data), I have obtained differences or residuals, which I have used as ordinates in the lines shown in the plots on Plates I. and II. These lines or "residual curves"* easily show the fourth place of decimals in the ratio $\eta_t : \eta_0$, and develop as a curvature the change of the rate b. As the residual curves are plotted, convexity upwards shows a diminution of b with rise of t, concavity upwards would show an increase of b, and no curvature of course indicates a constant value of b. Above and below the 50°, 100°, and 200° points of my own results will be seen a vertical row of points marked $1^0/_0$, $2^0/_0$, $-1^0/_0$, etc., which indicate differences in $\eta_t : \eta_0$ of 1, 2, &c., per cent. from my results, and afford a convenient means of comparing the relative con-

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* See Pickering, Physical Manipulation, i. p. 12; Journ. Franklin Inst. lxi. p. 272.

Mintern Bros. imp.

cordance between the results of various observers. It should be borne in mind, however, that some of the lines are plotted from means, some from single observations, and others from equations deduced either by the observers or by myself. The individual points, therefore, must not be used without qualification as a measure of the precision of the results obtained by any single observer.

Carbonic Acid, CO_2.

The curve OA on Plate I. is from the equation deduced at page 215 for my own results. There can be no question as to the decided curvature shown being far beyond the limits of variable experimental error. My computations have also shown that the third power of the temperature in the linear equation was necessary. The experimental means are marked along the curve.

The curve D O B is from an equation of the same form

$$\eta = \eta_0 (1 + \mathrm{A}t + \mathrm{B}t^2),$$

in which A and B are computed from the results of A. von Obermayer * with capillary "I." The term $\mathrm{C}t^3$ was omitted because of the smaller number of points and their somewhat less precision. That the line represents approximately the data will be seen from noting the distribution about it of the observed points. The curvature is here also undoubted, although Obermayer merely remarks that "it follows from these experiments with some probability that the increase in coefficient of friction with rising temperature is less at higher than at lower temperatures." A comparison of this curve with mine shows that Obermayer's results and my own are in substantial agreement as to the rate of change in b, the curvature of the two lines being very nearly the same. Indeed, if my results be thrown into the same equation, using only the first and second powers of t, the value of B becomes 0·00000136, while that from Obermayer's data is B= 0·00000137. The value of A from my results is, however, considerably larger than from Obermayer's, so that his value of $\eta_t : \eta_0$ at 100° is about 0·7 per cent. below mine, and at 200° about 1 per cent. below. The line O C is from the equation

$$\eta_t = \eta_0 (1 + 0{\cdot}003585t - 0{\cdot}00000105t^2),$$

deduced by me from Obermayer's experiments at the three indicated temperatures with the capillary "D." This is in still closer agreement with mine in numerical values of $\eta : \eta_0$, but has slightly less curvature (B=0·00000105). The value

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* A. von Obermayer, *Wien. Ber.* lxxiii. p. 468 (1876).

for A in my results is 0·003637, with the same terms in the equation. When methods as different in detail as those of Obermayer and myself are in so close agreement as these appear to be when thus discussed, the chances of large constant errors other than those inherent in the use of transpiration methods seem to be much reduced.

On the line J H are three points showing the results obtained by Eilhard Wiedemann. The line is drawn from the equation

$$\eta_t = \eta_0\,(1 + 0{\cdot}003727t - 0{\cdot}00000320\,t^2),$$

which I have deduced from these three points. The curvature is much greater than for either of the other lines, the value of B being more than twice as great as in the lines O A and O B, and three times as great as in O C. A reference to my discussion of the results for air will show that Wiedemann's results there exhibit similar relative characteristics. Up to 100° for CO_2 the results differ numerically by less than 0·7 per cent. from those of Obermayer and myself, but at 200° the difference is nearly 3 per cent.

The results by Puluj, as shown by the line O F, obtained by oscillating plates, are smaller than all others, a difference which characterizes his results for air. The range of temperature used is too limited to render the results available in the present consideration.

Conclusion.—In the absence of any really satisfactory means of assigning proper weights to the results of Obermayer, Wiedemann, and myself, it seems best to allow the results to stand in the form above given, without an attempt to deduce a mean.

Air.

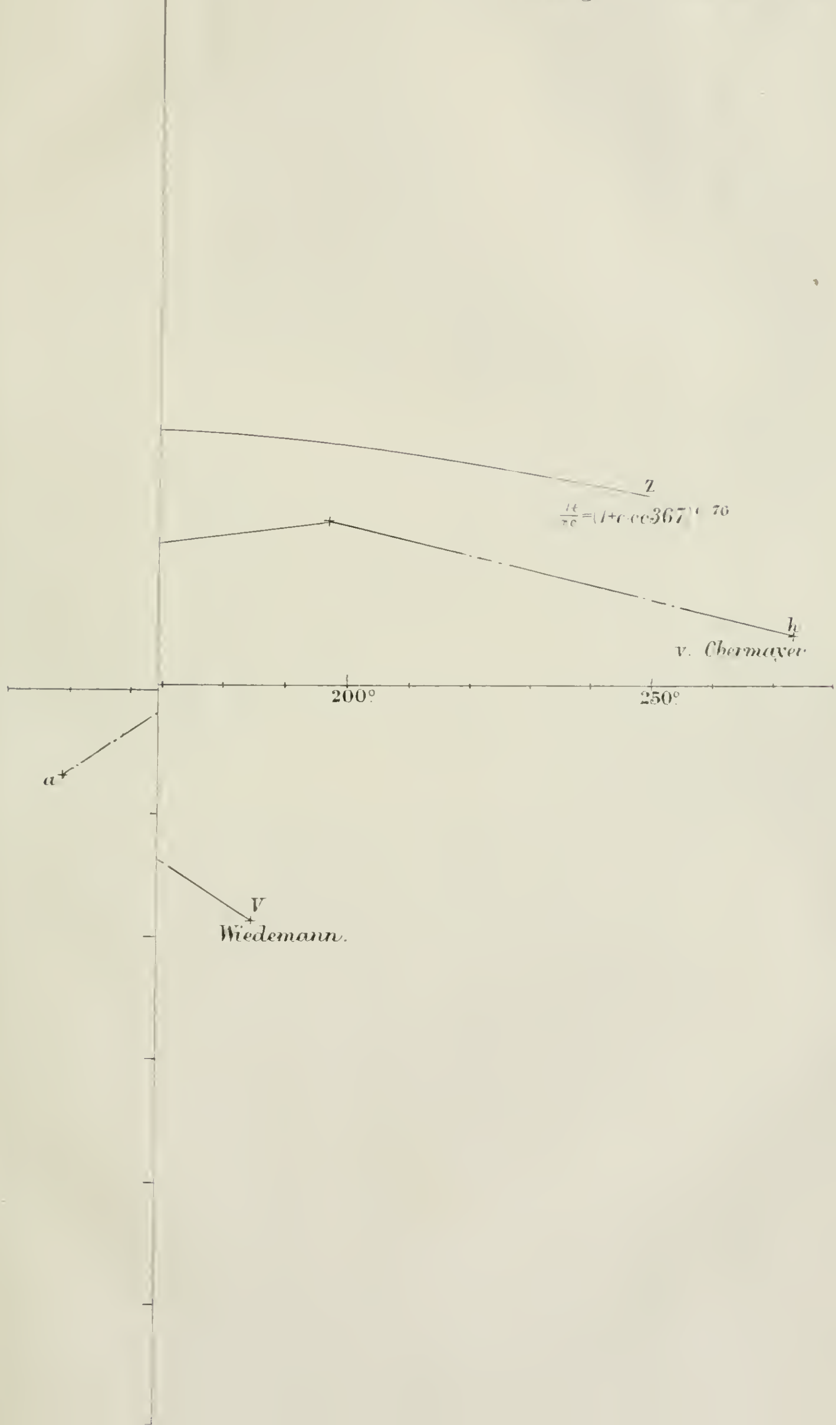
In Plate II. are shown the residual curves for all available observations on air. The line I J, representing Maxwell's results, doubtless owes its steepness to some large constant error, for which several explanations have been offered. The lines for O. E. Meyer's results from capillary transpiration are

AB from Eqn. $\eta = 0{\cdot}000171\,(1 + 0{\cdot}0024\,t)$, Range $\overset{\circ}{20}$ to $\overset{\circ}{99}$;
CD „ $\eta = 0{\cdot}000170\,(1 + 0{\cdot}0028\,t)$, „ 21 to 100;
EF „ $\eta = 0{\cdot}000174\,(1 + 0{\cdot}0030\,t)$, „ 21 to 100;

and from oscillating plates the line is G H from the mean of the equations,

$$\eta = 0{\cdot}000186\,(1 + 0{\cdot}0030\,t),$$

and $\eta = 0{\cdot}000189\,(1 + 0{\cdot}0025\,t)$, range 19° to 82°,


Z
$\frac{\eta_t}{\eta_0}=(1+t\cdot 00367)^{\cdot 76}$
h
v. Obermayer
200°
250°
a
V
Wiedemann.

Mascart
F Meyer
D Meyer
H Meyer
Y Holman
Warburg
Obermayer
Obermayer
Puluj
W
Z
367
50°
100°
150°
200°
B Meyer
Puluj
Puluj
P Puluj (points marked
Wiedemann
0.1
0.2
0.3
0.4
0.5
0.6
R
Puluj (points marked

given for different methods of computing one series of data. It is perhaps worthy of remark, that the mean of Meyer's results at 100° agrees with the results of my fifth series within 0·2 per cent. Meyer's observations were made chiefly at two temperatures, and thus, as well as on account of the magnitude of the errors of observation, are incapable of indicating the small deviation of $\eta_t : \eta_0$ from the equation of the first power of t.

The observations of Puluj are shown by the lines K L, M N, O P, Q R, and S T, of which all but S T are from transpiration experiments, this being by oscillating plates. From the data which I have used in plotting the lines, Puluj deduces the first power equations :—

KL, $\eta = 0·000179\,(1+0·0024\,t)$, Range $1\overset{\circ}{3}·0$ to $2\overset{\circ}{7}·0$.
MN, $\eta = 0·000179\,(1+0·0023\,t)$, „ 13·6 to 76·7.
OP, $\eta = 0·000181\,(1+0·0022\,t)$, „ 1·1 to 77·4.
QR, $\eta = 0·000180\,(1+0·0021\,t)$, „ 1·5 to 92·7.
ST, $\eta = \text{constant}\,(0·03855+0·00010213\,t)$ „ $-3·0$ to 25·0.

From the plots on Plate II., and from others which I have made, it appears to me that the data shown in K L cannot be represented by a straight line, nor are they to be relied upon for giving the rate of change of $\eta_t : \eta_0$ at all, the curvature of the line K L, which approximately represents the data, being undoubtedly the result of uncorrected constant error. The points of the line M N show an upward convexity of slight amount ; those of the line O P are so irregularly distributed as to conceal any slight systematic deviation from the straight line. The points of Q R are also very irregularly distributed, but are unquestionably more nearly represented by the line Q R, which I have drawn approximately through them, than by the straight line SR_1, which corresponds to the equation given by Puluj, or by any other straight line. The line Q R should certainly be convex upwards.

The numerous experiments of Obermayer give almost unquestionable evidence that even for air the coefficient of viscosity increases at a less rapid rate at higher than at lower temperatures. The line *a* S *b c* represents the mean of results by capillaries "11," "26," and "D." (I was obliged to omit "I" from consideration, owing to an apparent error. *Wien. Ber.* lxxiii. p. 440.) The separate results are fairly accordant. This line agrees quite closely with my fifth series, SY. The results obtained with a brass capillary are indicated by the line *d e*, which is a continuation also of S *b*, since the brass capillary agreed substantially with the others at *b*. The curvature of this line, as well as of *a* S *b c*, is decidedly convex upward, much more so than S Y. Obermayer's further series with capillary "D" is of much value. It is represented in the line *g h*, and the three marked points indicate the points yielded by the experiments. This line is also decidedly convex upward, and its curvature seems to be beyond the range of variable errors of measurement. I have connected the individual points with each other by a broken line, because, owing to the small number of points, almost any form of curve could be drawn through them, and to select any one equation would be wholly arbitrary. This remark applies also to the line U V, representing Wiedemann's results. This line is still more convex upward than either of the preceding. The line W X, representing Warburg's results with oscillating plates, is in substantial accord with the results by Obermayer, Wiedemann, and myself, as well as with the mean of Meyer's results; but as it is derived from observations including but one temperature interval, it cannot serve to determine any beyond the first power variation in the coefficient.

To show the relation of the several lines to one from an equation of the exponential form which has been so generally adopted, I have drawn the line Z from the equation

$$\frac{\eta_t}{\eta_0}=(1+0\cdot003670)^{0\cdot76}.$$

The fifth series of my own results is shown in the line S Y, the experimental means being denoted by crosses. The deviation of S Y from a straight line is very slight, and I am confident that this is a close approximation to the true result, and that the greater curvature of the lines from my own earlier results and those of other observers is due in part to impurities in the air, either in the form of carbonic acid or of vapour of water. I regard those of my measurements on air which precede the fifth series merely as checks upon the accuracy of the process, and as possessing small weight as compared with that series, for reasons assigned in the Critique of the Method. The same is true of all but the last series with carbonic acid.

Rogers Laboratory of Physics,
Mass. Institute of Technology,
Boston, Mass., May 1885.

XXX. *Examination of* Dr. Croll's *Hypotheses on Geological Climates. By* Dr. A. Woeikof *.

THE hypotheses of Dr. Croll have attracted such general attention during the last ten years, especially in Great Britain, but also in the United States and other countries, that a review of them by a meteorologist is, I think, desirable. This work is just now particularly opportune, because Dr. Croll has recently published a new book on these matters† in which he further explains and extends his views, and replies to his critics, whilst in the preface he mentions that he wishes to devote the coming years to work in a wholly different direction. Thus we have now before us a system as complete as it is likely to be made by the author.

I do not propose to review the whole work of Dr. Croll in glacial geology and cosmology, but only to consider some points which are within my line of study.

In answer to Prof. Newcomb, Dr. Croll considers the mean temperature of land and ocean‡, and arrives at the startling conclusion that "the ocean must stand at a higher *mean* temperature than the land." Now, once the *mean* and not *surface* temperature is mentioned, the meaning of the author is, it seems, clear; but the result is entirely opposed to what we know. Not only have the oceans which receive cold under-currents from polar seas a much lower mean temperature§ than the land, but even seas which receive no such cold water, and are known as exceedingly warm, as the Mediterranean and Red Seas, have a temperature considerably lower than the land.

It might perhaps be remarked, that Dr. Croll's startling statement is a simple "*lapsus pennæ*," and that he does not consider the mean temperature of the whole volume of ocean water, but *the mean annual temperature of the surface*; yet, especially from p. 33, it is seen that this is not so. Dr. Croll considers the difficulty of the sea "getting quit of its heat as rapidly as the land;" and in this passage, as in the former, he seems entirely to have forgotten the mobility of the particles of water, which is so exceedingly important and so essentially affects the thermal relations of water by the convection-currents which it causes. (A few pages before he mentions the

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* Communicated by the Author.

† 'Climate and Cosmology,' Edinburgh, 1885.

‡ P. 26 and following.

§ I understand the mean temperature as that of the whole column of water from top to bottom.

mobility of the particles, but only as causing the removal of heat from the tropics by ocean-currents.) Dr. Croll seems to think that the high temperature of the surface of the ocean is caused by the difficulty with which water gets rid of its heat by radiation, as if, here as in the case of land, loss of heat by radiation caused a low temperature of the surface.

Now this is evidently not the case, and the convection-currents originating as soon as the surface temperature sinks below that of the stratum immediately under it, bring the latter to the surface, and thus maintain constantly a higher temperature of the surface than of the other strata, although they are rather conducive to a loss of heat by the whole mass, as the colder water sinks to the bottom, where it is out of the reach of the radiant heat of the sun, and receives heat only by the slow process of conduction*.

Dr. Croll does not see that, instead of "the difficulty of the water to get rid of its heat," he really considers the cause of the high temperature of the surface of the ocean; and here misses the most efficient cause.

The next point I have to notice is this: "The quantity of heat lost by expansion must therefore be trifling in comparison of that lost by radiation; and although the heat lost by expansion is fully restored by compression, yet the air would reach the earth nearly entirely deprived of the heat with which it left the equator. All that it could possibly give back would be the heat of compression; and that would hardly be sufficient to raise the air at −50° F. to the freezing-point."†

As before this, Dr. Croll considers the temperature of the upper atmosphere, even under the equator, to be 80° F. *below freezing-point*; and as this is reached, according to him, at such a height that the air, returning towards the surface of the sea, would be warmed to the freezing-point, it is clear that, in his opinion, the atmosphere is in a state of *unstable equilibrium, because otherwise the temperature at which the upper strata arrive at sea-level could not be lower than the existing temperature of the lower strata*; but in Dr. Croll's opinion it is 48° lower, as the mean temperature of the equator is about 80° F., and the air of the higher regions, in sinking to sea-level, would bring with it a temperature of 32° F. Now if this was really the case, if there existed an unstable equilibrium, why do not convection-currents of great magnitude arise in our atmosphere and bring a temperature of 32° to the sea-level at the

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* I consider here the case of a body of water having constantly a higher temperature than that of the maximum density. The oceans are certainly in that state.

† Pp. 25 and 26.

equator? The reason why such convection-currents do not arise is, that the normal state of the air is a stable equilibrium, even a very stable one, so that if, by any cause, the higher strata be forced down, they would acquire, by compression, a much higher temperature than the lower have.

An unstable equilibrium, a few cases excepted[*], exists only in the lower strata up to a few thousand feet, and this only in the day-time, when the surface of the ground is much heated by the sun. It disappears about sunset, or even somewhat earlier. It does not occur in winter in high or even in higher middle latitudes (say, from 50° onward). All this has been established by so many observations in mountain-countries and in balloons that it can scarcely be doubted.

In any case, if Dr. Croll doubts such well-known facts, *i. e.* if he doubts that between the lower strata of air and those some tens of thousands of feet high there exists a stable equilibrium, the *onus probandi* rests with him. In fact, a temperature of −50° F. must occur at such a considerable height above sea-level, that the air, if forced down, would arrive warmer, and not colder, than the air existing at sea-level.

Besides, I maintain that the radiation of particles of air is but a very trifling cause of loss of heat by our globe, and that by far the principal causes of it are the radiation of the surface of the ground (or snow) and that of the surface of the water. If the lowering of temperature of the surface of land and of the air be considered, the loss of heat by radiation of the surface of the ground (and snow) is by far the most important.

I can much better agree with Dr. Croll in what he remarks about the conservative character of snow once formed, though, as will be seen further on, I do not agree as to the importance of winter in aphelion during high excentricity. Besides, I think Dr. Croll does not well understand the cause of the fogs, which have been so often noticed in high latitudes in summer. He thinks the fogs are caused directly by the melting of the snow, and, interposing a screen between the sun and snow, are effectual in lessening the amount melted.

The melting of the snow by the sun has not the power to cause fogs by itself. On extensive continental regions of Europe, Asia, and America snow lies in winter, and is melted from March to June, yet fogs are of exceedingly rare occurrence during that time, and they are more frequent at night, *i. e.* are rather instrumental in preventing the loss of heat by radiation than the heating influence of the sun's rays. In

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[*] For example, in thunder-storms, hail-storms, &c.

the same regions fogs are frequent in autumn during anticyclones. The cause of these fogs is the same as that of the London fogs, *i. e.* the temperature of the river- or lake-water is much higher than that of the air, and thus the vapour is soon condensed. Neither are fogs common in summer over mountain-snow and glaciers, notwithstanding the great amount of melting. But fogs are experienced on the sea in the vicinity of melting ice, because here we have two masses of air, of unequal temperature, both nearly saturated, and their meeting must produce saturation, *i. e.* fogs. Thus it is easy to see that fogs are not necessary consequences of the melting of snow and ice *per se*; but some other conditions are necessary for them; and Dr. Croll has no right to say about a glaciated country at some distance from the sea, "Fogs prevent, to a great degree, the melting of the snow and ice."

Mr. A. R. Wallace * has mentioned that in Northern Siberia the powerful sun of June cannot melt the snow until the warm southerly winds bring warm air. In so far as the beginning of melting depends on this, I am quite of the same opinion; but Dr. Croll is wrong when he too much extends the influence of these southerly winds, and believes them to prevail in summer on the north coast of Siberia. On the contrary, cold winds from the sea prevail in summer and certainly chill the air, while southerly winds prevail in winter. Thus Dr. Croll's hypothesis, "Matters would be still worse if these southerly winds, instead of ceasing, were simply to change from June and July to December and January; for then, instead of producing a melting effect, they would greatly add to the snowfall,"† is realized as far as the winds are concerned; but the snowfall of winter is exceedingly light, because the southerly winds come from the colder interior of the continent; and, besides, they are descending winds, and in descending become relatively dry. We know these facts from the observations of Wrangell and Anjou at Nijnekolymsk and Ustjansk; and they were confirmed by the recent observations of the Russian polar station of Sagastyr at the mouth of the Lena ‡.

Dr. Croll returns over and over again to the importance of knowing the temperature of space, as well in 'Climate and Time' as in his new book; and in the latter he is rather in favour of a lower value for it than that of Herschel and Pouillet, which he admitted in 'Climate and Time.' He thinks this knowledge of the utmost importance for the determina-

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* 'Island Life,' p. 135.

† P. 88.

‡ Iswestia of the Russ. Geogr. Soc. 1885, no. 4.

tion of the temperatures which obtained during high excentricity and winter in aphelion ; and repeatedly he admits that the temperature of a place, other things being equal, is proportional to the heat received from the sun. To make us quite sure of his meaning, he has a table in 'Climate and Time,' p. 320, where he gives the value of excentricity for different periods, and the midwinter temperature of Great Britain for periods of great excentricity and winter in aphelion. So, for example, it was, according to him, −6°·3 F. 850,000 years ago, when the excentricity was 0·0747; 1°·3 F. 210,000 years ago, excentricity 0·0575, &c. The temperatures of Great Britain are evidently given only as an illustration ; and there is no doubt that a similar decrease of temperature was experienced, according to him, even in the midst of the Atlantic Ocean. Admitting even the present mean winter temperatures there to be 6° F. higher than in Great Britain at the same latitude, we should then have, at the highest excentricity, with winter in aphelion −0°·3 F. and 4°·7 F. 210,000 years ago ; *i. e.* temperatures which were possible only if the ocean was covered with solid ice—which is an impossibility with anything like the present geographical conditions ; and Dr. Croll repeatedly admits that they have not changed since the glacial epochs.

It is exceedingly strange that Dr. Croll has not tried how his method works when applied to the existing mean temperatures of different latitudes. The mean temperatures at intervals of 10° have been calculated by different scientists. I use the calculation of Ferrel as the most recent. The mean temperature of January may be regarded as the result of the position of the earth towards the sun at the winter solstice. Thus, if we compare the mean January temperature of 50° and 60° N., we have

50° N., 21·3, 60° N., 1·7.

The quantity of solar heat received at the winter solstice at the 60th parallel N. is but 0·35 of that at the 50th parallel N. Thus, if the temperature of the former was less in proportion to the quantity of solar heat received, it should be = −147°·9 F. It is easy to see how large the discrepancy is.

Dr. Croll ascribes the relatively small decrease of temperature with latitude to the influence of ocean-currents, which abstract warm water from the tropics and bring it to high latitudes. But on the 60° N. there is considerably more land than on the 50° N., and air over the land under 60° N. is colder than over the sea.

But to be quite sure of getting beyond the influence of ocean-currents, I will take the mean January temperature in the strictly continental climate of Eastern Siberia under 120° E. According to Ferrel's tables:—

Under 50° N., we have 0° F.
„ 60° N. „ −30° F.

If the January temperature decreased from 50° to 60° N., according to the hypothesis of Dr. Croll, it should be under 60° N. = −155°·3.

But to be quite sure of taking the most favourable case for the hypothesis of Dr. Croll, I take the highest January temperature under 50° N. in Ferrel's tables, *i. e.* that at 20° W. = 44° F., and the coldest January temperature under 60° N., *i. e.* that at 120° to 130° E. = −30° F. Yet, in proportion to the quantity of heat received, the mean temperature of January at 60° N. should be = −140° F.

The following Table gives the results of the three cases considered:—

	Mean temperature 50° N.	Mean temperature 60° N.		
		On the hypothesis of Dr. Croll.	Actual.	Difference.
Mean January temperature of all meridians.	21°·3	−147°·9	1°·7	149°·6
Mean January temperature in 120° E. (East Siberia)	0	−155·3	−30	125·3
Mean January temperature of warmest meridian under 50° N. and coldest meridian under 60° N.	44	−140	−30	110

If the discrepancies are so great in taking even the means of a whole parallel, or strictly continental climates, and even in the last example, how much must Dr. Croll's calculations for Great Britain be wrong. In so oceanic a climate an equal difference in the amount of sun-heat will certainly cause a smaller fall of temperature.

I give another example, which shows how little the method of Dr. Croll is applicable even to the mean annual temperatures. In Chapter IX. of 'Climate and Cosmology' he states that the difference of temperatures between the equator and the north pole ought to be at least 200° F. if they were in proportion to the heat received from the sun, and the temperature of space (−239° F.) was taken as the initial one; but actually the difference is but 80° F. This small difference, he thinks, is caused by the ocean-currents, which bring an immense quantity of heat from low to high latitudes. That ocean-currents have a great influence on the temperature of our earth I do not deny, but it is not so great as Dr. Croll believes.

To prove this, I will take two places in as different latitudes as possible, and both uninfluenced by the ocean-currents. The first is Iquitos, on the Amazons, 3½° S., and about 300 feet above the sea-level. The mean yearly temperature is 76°·4. The reduction to sea-level would make it about 77°·8, and the reduction to the temperature of the equator would give 78°·3. Now Iquitos is more than 1000 miles from the Atlantic; and though nearer to the Pacific, is separated from it by the chain of the Andes. It must be admitted, then, that this place gives us a good idea of the temperatures near the equator, uninfluenced by the heat-abstracting influences of ocean-currents.

The other place which I choose for comparison is Verkhojansk in N.E. Siberia, under 67° N., and having the coldest winter known on our globe (January, −56° F.). I think it will be readily admitted that this place is out of the influence of ocean-currents, bringing heat from low latitudes, and in most favourable circumstances for radiation of heat. The mean yearly temperature of this place is 1°·9 F.; the reduction to sea-level may bring it to about 2°·3 F.*

Thus we have, out of the influence of ocean-currents, the following mean yearly temperatures at sea-level:—

	° F.
Equator	78·3
67° N. lat.	2·3
Difference	76·0

Reasoning on the premises of Dr. Croll, we ought to expect a difference of 172° F. between the equator and 67° N. The actual difference is less than half that amount (scarcely over ⅖); yet heat is certainly not abstracted from the vicinity of the equator in the interior of South America by ocean-currents, nor are the continental regions of N.E. Siberia warmed by ocean-currents.

The Rev. O. Fisher † has already proved that if Dr. Croll's reasoning was right, the mean temperature of the equator should be higher in January than in July by 21° F., on account of the greater nearness of the earth to the sun in the

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[*] The actual height is not known, but in any case small.

[†] Nature, vol. xx. p. 577.

former month, while it is known that at most places on the equator the warmest and coldest months do not differ even by 3° F., and nowhere so much as by 5° F.

Dr. Croll has answered the Rev. O. Fisher *, and this answer is a curious illustration of the difficulties in which he has involved himself. The question as to why the annual range on the equator is so small is a very simple one. The quantity of heat received from the sun varies but in the ratio of 100 : 115 ; and besides, the observations on which our knowledge of the temperature of the equator depends were mostly made on the sea-coast—two good reasons indeed for a small annual range. Under the 50° N., the quantities received on the days of the winter and summer solstices are in the ratio of 100 : 562 ; and yet in some places in England the yearly range is not above 20° F., and nowhere above 27° F. It is thus the small annual range in many regions of the middle and high latitudes which much more needs explanation. Dr. Croll, in his reply, expresses the opinion that the northern hemisphere is the dominant one; and as the whole earth has a higher temperature in July than in January, so by the operation of this cause the normal excess of the temperature of the equator in January is weakened and even abolished. I replied to this, that the temperature on the equator was almost entirely influenced by cold winds from cold ocean-currents in some regions (the west coasts of Africa and America and the adjoining parts of the Pacific and Atlantic), and in these the equator was considerably colder in July than in January, for example at the island of St. Thomé, W. Africa, by 2°·7. These cold winds come from the south, while winds from the north seldom reach the equator, and can never have a depressing influence on the temperature. In most places the temperatures on the equator were influenced by the rainy season; so that when it was at its height in January, this month was cooler than July. This is the case even in Batavia, 7° S.; while when January is a dry month and July rainy, the former is warmer not only on the equator, but even to some degrees north of it (so, for example, it is warmer by 7°·2 at Lado, Upper Nile, 5° N., and by 3°·4 at Freetown, Sierra Leone, 8½° N.)†.

All this is, I think, conclusive enough, and proves that *Dr. Croll's system of estimating temperatures breaks down when tested seriously.* Small errors would be quite natural in a

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* Nature, vol. xxi. p. 129. Reprinted in 'Climate and Cosmology,' chap. iv., omitting some passages relating to the Rev. O. Fisher.

† Nature, vol. xxi. p. 249; reprinted also in the 'American Journal of Science,' 1880.

question of that kind; but I have shown that the *errors are enormous*, amounting to 100° F. and more, *i. e. they are greater than the difference of annual temperature between the equator and the north pole.*

There is certainly a mistake somewhere, or, rather, the whole method is a failure. How can we judge of the change of temperature resulting from this or that distance from the sun, even if we knew accurately the temperature of space*, when we do not know the diathermancy of the atmosphere under different conditions? We know only that it is exceedingly different according to the different quantities of carbonic acid and aqueous vapour contained in it, and in a far higher degree according to the absence or presence, in different quantities, of suspended liquid and solid particles (clouds, dust, smoke, &c.). Thus, when we do not know how far the loss of heat is impeded, even an accurate knowledge of the temperature of space would be of small use in this matter.

I will illustrate this by a homely example. Take a room where the fire is extinguished and the hearth or stove cold in the evening, and try to guess at the temperature the room will have in the morning. If we followed the method of Dr. Croll, we should inquire only about the outside temperature, and not about the thickness of the walls, the windows, &c. I think that, taking the average construction of Russian, English, and Italian houses, if the inside temperature was in all three cases 65° in the evening, and the outside temperature −20° in Russia, 32° in England, and 45° in Italy, the morning temperatures in the room would not be very different, and probably even higher in the Russian room owing to its thick walls, double windows, &c.

It is also interesting to note that a calculation by the method of Dr. Croll of the mean January temperature under 60° N. as given above, gives lower figures than the extreme minimum anywhere observed by reliable thermometers; this latter is about −90°·4 F. (−68° C.). Neither in the coldest part of N.E. Siberia nor in the highest latitudes of Greenland and Grinnell-land have lower temperatures been noted; and yet in Floeberg Beach the sun is absent from the horizon more than four months. The lower we make the temperature of space, the more conspicuous is the tenacity with which the surface of the earth and the lower stratum of air retain a relatively high temperature.

Dr. Croll says, in 'Climate and Time,' p. 43, "The stoppage of all currents would raise the temperature of the equator

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* I just see that Prof. Langley has determined the temperature of space; but the actual figures and all details are still wanting.

55°, *i. e.* give it a mean temperature of 135°." Now such a temperature is not only above anything known on the globe as the mean temperature even of a single month, but the absolute maximum known by exact observations does not exceed 131° F. (55° C.).

Though Dr. Croll repeatedly, and quite rightly, points out the far greater influence of ocean-currents as compared with air-currents in modifying the temperature of the globe, he quite unexpectedly expresses an opinion as to the power of air-currents in cooling the temperature of the ground and air at the equator, which ought not to remain unchallenged. "No knowledge whatever as to the intensity of the sun's heat can be obtained from observations on the temperature of the air at the equator. The comparatively cold air flowing in from temperate regions has not time to be fully heated by the sun's rays before it rises in an ascending current, and returns to the temperate regions from whence it came. More than this, these trades prevent us from being able to determine with accuracy the intensity of the sun's heat from the temperature of the ground; for the surface of the ground in equatorial regions is kept at a much lower temperature by the air blowing over it than is due to the intensity of the sun's heat"*.

Certainly no physicist or meteorologist ever thought of a determination of the sun's heat by observations on the temperature of the air or the ground at the equator or elsewhere. But Dr. Croll evidently thinks that this would be possible at the equator were it not for the influence of cool winds from temperate regions!

Let us first see how far facts corroborate this opinion. According to Ferrel's tables, the mean annual temperature of 10° N. is 81° F., of the equator 80°·1 F.; thus the equator cannot be cooled by winds from the northern hemisphere, as the lowest latitudes of the latter are warmer than the equator. The cool winds must come from the south. Yet the mean annual temperature of 10° S. is 78°·7, *i. e.* only 1°·4 lower than the equator. Even in July, the winter of the southern hemisphere, the difference amounts to but 3·8, *i.e.* in the annual mean to 0°·14 F. for a degree of latitude, in July to 0°·38 for the same.

The greater part of the equatorial region consists of ocean and islands, where, at least south of the equator, *the trade-winds* prevail. They *are not strong winds*, a few ocean regions excepted, they have a very easterly direction, and blowing

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* 'Climate and Cosmology,' chap. iv., and 'Nature,' vol. xxi. p. 129.

over very large extents of sea, *they bring to the equatorial regions the temperature which prevails over tropical seas.* There can be no question of an influence of aerial currents from the middle latitudes on the temperature of the equator, and the latitudes 10° N. to 5° S. at least. Two examples show how the thermal influence of stronger winds than the trades nearly disappears as soon as they have blown over an extent of about 1000 miles of sea. The coldest region of the tropics in winter is Southern China; near Canton frosts are not rare in winter; the N.E. monsoon blows as a strong steady wind towards the coast of Cochin China; and yet at Saïgon, but 12½° south of the tropic, the mean temperature of January is not below the normal of the parallel. We have:—

	Mean temperature of January.
Canton, 23° N.	54·8
Hong Kong (Victoria), 22° N . .	59·5
Saïgon, 11° N.	77·5

Thus, between Hong Kong and Saïgon the difference per degree of latitude is 1°·8 F., while the mean difference in January between 10° and 20° N. is 0·77 F. per degree of latitude. Thus we see, that when a cold wind from the middle latitudes reaches the borders of the tropical zone, it is soon warmed on passing over the broad expanse of the seas, and already north of 10° N. the cooling influence is not felt. The exceedingly small difference of temperature in the zone between 10° N. and 10° S. is a proof that the cooling influence of winds from middle latitudes is not felt there.

Another cold wind reaches the tropical zone—the famous *Northers* of the Gulf of Mexico. This is not a steady wind like the N.E. monsoon of China, but a cold wind blowing at times with the utmost violence. At the mouth of the Rio Grande (26° N.) frosts happen every winter, and even temperatures of 23° have been observed during Northers; the latter are frequent and dangerous at Vera Cruz (19° N.); but the temperature does not sink below 51°, and not below 59° on the exposed, relatively very cold plateau of Tarifa, on the isthmus of Tehuantepec. Owing to their extreme violence, the Northers keep for a longer distance a much lower temperature than other winds of the tropical zone. Notwithstanding the Northers, the mean January temperature of Vera Cruz (71°·7) is not below the mean for the latitude.

On the extensive wooded plains of the Upper Amazons weak winds and calms prevail for a great part of the year, and the S.E. winds of the drier months have so little the power of cooling the air, that at Iquitos the absolute minimum during a year was 66°·8 F. It is clear that in continental regions also, cold winds from the middle latitudes do not reach the equatorial zone.

It may be fairly asked, Where and how did Dr. Croll get his opinion about the cooling influence of winds from middle latitudes on the temperature of the equatorial regions? Would it not have been better to inquire about some of the best-known facts of climatology, before speculating "à perte de vue," and bluntly stating that the mean temperature of the equator would be 55° above what it is now, if it was not for the heat-abstracting action of ocean-currents? Why, on the Upper Amazons there is no such heat-abstraction; aerial currents can certainly not have a cooling influence of even a degree F.; and yet the mean temperature, reduced to sea-level, is not anything like 135° F., but below 80°. Besides the immense influence of the diathermancy of the atmosphere and its enormous variations in time and place, another exceedingly important consideration has been overlooked by Dr. Croll, viz. the very great difference of continent and ocean in the matter of temperatures, the fact that an equal loss of heat, expressed in calories, will have a very different influence on temperatures, both on account of the great caloric capacity of water and of the mobility of its particles. I must add that the latter condition is too often lost sight of, not only by Dr. Croll, but by many other scientists, in their speculations on the influence of a solid or liquid substratum on the distribution of terrestrial temperatures.

Besides, we have the formation of ice on the waters, which also has a great influence on the temperatures.

Thus it is easy to see, that the question how great will be the temperature of the air at a given place, say in midwinter, when the distance of the sun is greater or less than at present, cannot be answered, even approximatively, especially in the exceedingly crude way in which it is put by Dr. Croll, *i. e.*, without distinguishing high and low latitudes, continent and ocean, &c. One thing is certain, that such a change will certainly have a greater influence on the temperatures in the interior of continents than on the oceans and their borders. The caloric capacity of water is so great, and the mobility of its particles so effectual in resisting a diminution of the surface-temperature (by the convection-currents it causes), that I doubt very much if, during a great excentricity and winter in aphelion, the surface-temperature of the oceans can be lower in winter than now. The difference in the quantity of sun-heat is too small and too fleeting to give an appreciable difference in winter, and, as in the year there is no difference in the quantity of heat received by the waters, I think there will be no difference in the temperature of the waters, and thus no influence of great excentricity and winter in aphelion on the ocean temperatures, and also no greater snowfall than now. As to the continents, I admit that, though we are *unable to calculate the rate of decrease* of temperature of the winter months under these conditions, there is no doubt that *it will be appreciable, and be the greater the less a given place is under the influence of the seas.*

But what has this to do with glaciation? Even now, the temperatures in the interior of large continents are low enough in midwinter to allow of the snow remaining on the ground for some weeks, not only under 45° N., but under 40° N. And yet we have no glaciers on the North-American continent, which reaches to 71° N., or on the Asiatic, which reaches to 78° N., except in high mountain-regions, because the snowfall of winter is so small that it is melted in summer. Even the mountains of N.E. Siberia have no glaciers.

The greater part of the snow which lies on the ground in N.E. Siberia falls in autumn, when the air contains vapour of water enough to allow of a great precipitation; the snowfall of winter contributes very little. Now what would a further lowering of the temperature of winter produce? A further diminution of the quantity of the falling snow. It would then even sooner be melted in the warmer summer months.

The cold of winter in the interior of large continents of high latitudes, especially that of Asia, has very important indirect results: the high pressure and the resulting cold and dry winds of winter, especially towards the S. and E. of the region of high pressure. These winds, the cold dry winter monsoon winds of Eastern Asia, are unfavourable to snowfall, so that in the interior of Transbaikalia, for example, with mean winter temperatures of −13° F. and below, there is generally too little snow for sleighing; and if the quantity of snow falling near the mouth of the Amoor is larger, it falls almost entirely in October and November, *i. e.* at the beginning of the cold season, and in the few days with east winds, which bring warmer and moister air from the seas, not yet frozen in these months.

A lower winter temperature and an earlier beginning of the cold in the interior of Asia would increase the pressure towards the north and the interior of the continent, and thus give a greater impetus, strength, and duration to the dry N.W. winds, and so be even less favourable to snowfall and an accumulation of snow.

In summer the winds in Eastern Asia are S.E., and bring clouds and rain far inland. Owing to the high temperature of the continent and of the surrounding seas, rain and not snow falls even at great heights, for example, up to 15,000 feet in the mountains of Kansu in Western China (37° N.). Thus the heavy rains of summer are not favourable to an accumulation of snow, but, on the contrary, assist in melting the small quantity which may remain on the ground.

During a high excentricity and winter in aphelion the temperature must be higher in summer, and this would cause a lower pressure on the plateaux in the interior of Asia. This would increase the difference of pressure between the ocean and the interior of the continent, and give a greater impetus to the moist winds and bring larger quantities of rain, at least where the air is ascending. Such conditions would then favour the melting of snow to a greater height than now. At present, in Northern Thibet for example, permanent snow is found at 17,000 feet; then it would disappear perhaps even to 20,000 feet.

The climatic conditions of Asia show us, so to speak, the normal reactions between continent and ocean. Everywhere there is a tendency towards a higher pressure in the interior of continents in winter and on the oceans in summer, and to winds from the first in winter, from the second in summer; that is, there are what Coffin calls *monsoon influences.* A colder winter in the interior of the continents, with an unchanged temperature on the oceans, would certainly strengthen the winter winds from the interior, and thus bring more cold dry weather than is experienced now, and reduce the precipitation in winter. Such conditions are certainly not favourable to a greater accumulation of snow than prevails now. The Ural Mountains have, as well as those of Norway, prevailing W. winds and a much colder winter; but, on account of the smaller snowfall, no permanent snow and no glaciers, while the W. side of the Scandinavian mountains has enormous glaciers. If a high excentricity with winter in aphelion can have a considerable influence on climates, it would give to Western Europe colder winters with a greater proportion of dry east winds, and warmer summers, both conditions unfavourable to glaciation.

It has long seemed to me that those who have expressed an opinion on the favourable influence of winter in aphelion on glaciation, from Adhémar to Dr. Croll and his followers, have been influenced by the present difference of the northern and southern hemispheres. The glaciation is far more prevalent in the latter, and this has been ascribed to winter in aphelion on the well-known principle "post hoc, ergo propter hoc," as it gave a ready explanation of the former glacial periods of the northern hemisphere. I am quite sure that Dr. Croll was also influenced by the present differences of the two hemispheres.

Dr. Croll has long been an advocate of the wind theory of ocean-currents and has proved that, at present, a considerable quantity of warm water is brought by these currents from the southern to the northern hemisphere and serves to warm the latter. In these two questions he has rendered good service to science. The transport of warm water from the southern to the northern hemisphere is a fact; but what is the cause? Dr. Croll believes the cause to be, at least indirectly, winter in aphelion, which brings, especially during high excentricity, but to a certain degree even now, a host of other indirect results, by which the given hemisphere is cooled, its trade-winds are strengthened, and bring the more warm water into the other hemisphere, the higher the excentricity. I have shown above that the cause assigned by Dr. Croll is inadequate to produce any considerable lowering of temperature on the ocean in winter, and that even the small difference perhaps possible must be regained in summer. Thus winter in aphelion cannot cause the change in the velocity of the trade-winds and their more southerly extension when winter in aphelion exists in the northern hemisphere, and the reverse during winter in aphelion in the southern hemisphere. Why, then, are the trades of the southern hemisphere blowing into the northern at present, and also the conditions more favourable to glaciation in the southern than in the northern hemisphere? There are certainly good reasons for that.

1. The extent and depth of the oceans of the southern hemisphere. This gives a greater steadiness and force to the winds of that hemisphere; and the difference is even more marked in the westerly winds of middle latitudes than in the trades, but is certainly well seen in the latter. Now land acts in two ways on the trade-winds: it weakens them first by the increase of friction. But this is not all: the trades, few ocean-regions excepted, are not strong winds; they are important on account of their extent and steadiness. The gradient which causes them is small. Now in such cases land, even if it is not a continent but only a cluster of small islands, has a great influence on trade-winds in causing local gradients, which may have even an opposite direction to the general gradients, thus causing different and sometimes opposing winds. The land- and sea-breezes and the monsoons are cases in point. Even where the disturbances of the normal ocean gradients is not large enough to cause monsoons, we see generally the

trades oftener interrupted in summer, when they are weaker, and when local thunderstorms and rains are more frequent on land. For the two reasons given, the trades of the southern hemisphere must be more extensive and stronger than those of the northern.

2. The relatively small extent of sea in middle latitudes of the northern hemisphere in comparison with the southern, must tend to warm the seas of the former, even if the quantity of warm water from the tropical seas reaching them be equal. Thus, generally in middle latitudes, the evaporation goes on at a higher temperature from the seas of the northern than of the southern hemisphere. Now, this has a very great influence on the resulting precipitation; when the evaporation goes on at or near 32°, there is much more probability that the resulting precipitation will be snow and not rain even on lowlands; the higher the temperature at which the evaporation takes place, the greater must be the height at which snow can fall, on account of cooling by expansion.

3. Not all cold seas are favourable to glaciation. If they are surrounded by land on which the winters have a temperature much below 32°, they will be covered with ice, and thus evaporation will be checked just at the time when it is the most favourable to snowfall; the ice of the sea will be covered with snow; the temperature of the air over it may be very low, but the snowfall will not be great; and thus the conditions not favourable to glaciation. Such is the condition of many seas of the northern hemisphere, as the Arctic Ocean north of Siberia, the Kara Sea, the bays and inlets north of the North-American continent, the sea of Okhotsk, &c., which are covered with ice for many months. These conditions are favourable to a long and cold winter, but not to a large snowfall and the resulting glaciation. The observations made at many points of the coasts of Siberia and the North-American archipelago have shown that the snowfall is exceedingly light. The seas of the higher southern latitudes are deep and not surrounded by land, and thus by far not so ice-bound, both on account of the absence of very low temperatures favourable to the formation of ice, and of the rupture of the ice, when formed, by winds and currents. Such seas as these are favourable to snowfall and glaciation on land, as even in midwinter there is a great extent of water which evaporates freely. The only parts of the northern hemisphere where glaciation is considerable outside of high mountains, is the region from Greenland to Francis-Joseph Land; but here we have rather cold seas, which are yet not entirely ice-bound even in winter. These seas are more favourable

to snowfall and glaciation than those around Great Britain, because they are colder, and than those of the North-American archipelago, the Kara Sea, and the Arctic Ocean about Siberia, because they are less ice-bound in the cold season.

4. The intense glaciation of the highest southern latitudes gives an enormous quantity of icebergs floating northwards, *i. e.* to the seas of lower latitudes. As the surface of the southern seas to about 62° S. is below 32° F., even in midsummer, the icebergs cannot melt till they reach that latitude, and their immense size enables them to reach sometimes even the 35th parallel S. They certainly cool the waters, and thus produce conditions favourable to glaciation even in lower middle latitudes. This, besides, is a further direct cause of lower temperatures, and an indirect cause of stronger and more extensive trade-winds, which reach to beyond the equator and bring much warm water to the northern hemisphere. The geographical position is also favourable to this, especially the situation of Cape S. Roque and its vicinity.

It is easy to see from all this, that there is no necessity to seek far for the reason of the difference of the northern and southern hemispheres as to glaciation, without calling in aid the winter in perihelion of the former and the winter in aphelion of the latter; much simpler causes explain the result. The operation of these causes is exceedingly well illustrated in the glaciation of a part of the higher latitudes of the northern latitudes, while to the east and west there is none, with lower mean annual temperatures.

I take another example from the southern hemisphere. Its general geographical conditions are favourable to glaciation, but by no means everywhere equally. Thus the higher latitudes of the eastern part of South America have as little snow, even in winter, as the warmest parts of the European continent under the same latitudes; while a degree or two to the south, South Georgia is deeply glaciated. As to South America, I must disagree also with Mr. A. R. Wallace * as to the condition of this continent being a proof of the influence of winter in aphelion on glaciation. Besides what is stated above as to the conditions of the eastern part of the continent, I may mention the absence of snow and glaciers from the highlands of the Atacama Desert (above 10,000 feet high), and those between the coast and Lake Titicaca (about 14,000 feet). Only in the west of the continent, and south of 35° S., does glaciation prevail. But where, in the northern hemisphere, have we so enormous an extent of sea westwards, with

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* 'Island Life,' p. 142 and foll.

such regular brisk west winds, bringing an immense quantity of vapour, which is condensed as snow? The amount of precipitation on the west coast and the western slope of the mountains of South America, south of 40° S., is scarcely equalled anywhere in the tropics, and, besides, the greatest part falls in the cold season. The same may be said of the west coast of the southern island of New Zealand, where also high mountains rise, and to the west is an immense stretch of ocean, uninterrupted to the E. coast of South America. The snowfall is enormous, and glaciers reach down to 700 ft. above sea-level; and yet the mean temperature at sea-level is higher than in other meridians of the southern hemisphere, and the greater part of the northern also.

In the two examples given above, evaporation takes place from seas of relatively high surface temperature, about 50° F. or more, and in such cases permanent snow can exist but at a height of some thousand feet, because air rising to such a height is cooled by expansion, and its vapour precipitated in the form of snow. Mr. A. R. Wallace * has very well shown the importance of high land for glaciation; though, to my mind, he has gone too far in not admitting the possibility of glaciation on low lands.

I must conclude. An English geologist of note † has called Dr. Croll's hypotheses brilliant and fascinating. So they certainly are. The originality of the conception, the fertility of resource of the author, his indomitable will, are sympathetic in the highest degree. With a melancholy feeling I must state that, interesting and important as are some parts of the system of Dr. Croll, the main points of it are opposed to the most certain teachings of meteorology, and cannot be accepted. Besides the purely geological and cosmological part of his work, which I do not consider here, and the tables of excentricity, what can be accepted? The wind theory of the upper oceanic currents, the notion of the great climatological effects of these currents (though by no means in the exaggerated extent given to them by Dr. Croll), and some of his considerations on the conservative effects of snow and ice. *The main points on which rests, so to speak, the whole fabric in its explanation of glaciation and geological climates generally —the influence of winter in aphelion and perihelion during high excentricity and the calculation of temperatures in proportion to the sun-heat received—are, unfortunately, not acceptable.*

Geologists will have to look for other causes to explain the more or less frequent glacial and interglacial periods, which their studies lead them to admit.

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* 'Island Life.'

† Mr. Searles V. Wood, jun.

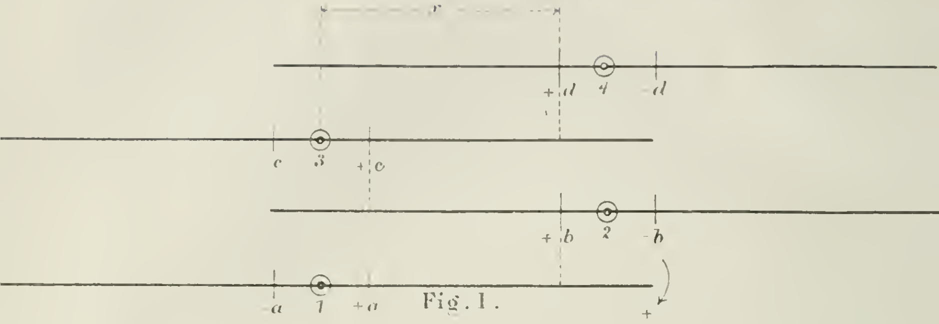

Fig. 1.

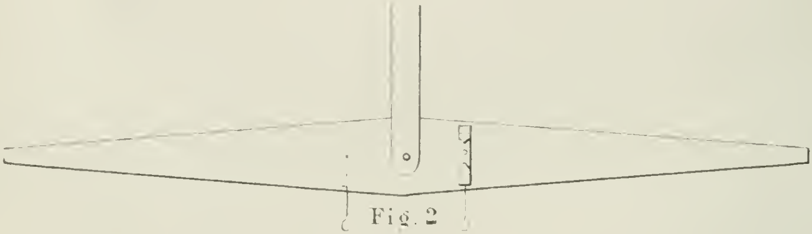

Fig. 2

Fig. 5.

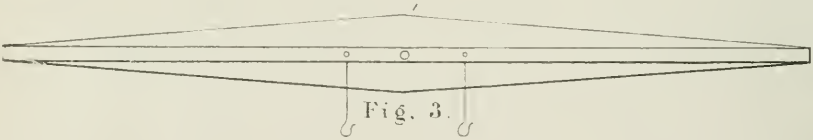

Fig. 3.

Fig. 6.

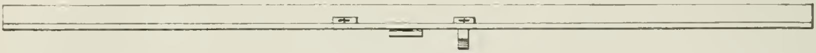

Fig. 4.

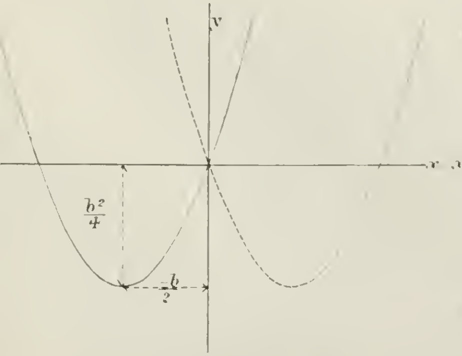

Fig. 7.

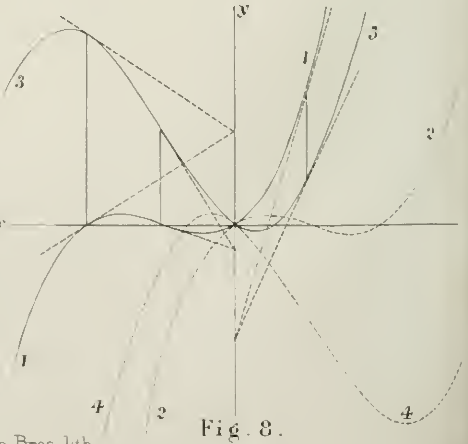

Fig. 8.

XXXI. *On a Machine for Solving Equations.*
By C. V. Boys*.

[Plate III.]

At a late meeting of the Physical Society Mr. C.H. Hinton showed some apparatus that he had made to explain the nature of equations. One of the instruments for representing the case of a simple equation was manageable enough; but the second, which dealt with the quadratic, could hardly be employed to solve a quadratic, as the root was not capable of continuous variation. It could, therefore, only after considerable trouble in trials and errors had been taken, find those real roots which consisted of whole numbers between the limits of the machine, say + and -10.

At the time that Mr. Hinton was trying to devise a quadratic machine (with the object not so much of solving quadratic equations, as of assisting boys to understand the method employed, now about ten years ago), he showed me what he had done; and it then occurred to me that continuous variation might be employed in a machine so that fractional roots could be found, and that the degree need not be limited to a quadratic, but that a cubic or one of any power of the form $a+bx+cx^2+dx^3+\&c.=0$ could be solved. I then half completed the machine I have now the honour of exhibiting before the Physical Society, but laid it on one side till the present time.

I find that Mr. A. B. Kempe has invented and described† a machine with the same object. He replaces the expression x by $\cos\theta$, and then by a known process changes the equation in which the terms are powers of cosines of θ into one in which the terms are cosines of multiples of θ. The equation is then in a state to be dealt with by his machine. A series of levers jointed on one another, the first hinging on the intersection of a pair of rectangular axes, have their lengths variable, so that each one in order can be set so as to be equal to the coefficient of the corresponding term; moreover, by mechanism each one makes with the last the same angle that the first makes with the axis of x. Thus, on rotating the first, the end of the last describes a curved line cutting at one or more points the axis of y; every angle θ of the first which causes this intersection is noted, and the value being inserted in the original equation gives at once one of the real roots.

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* Communicated by the Physical Society: read December 12, 1885.

† 'Messenger of Mathematics,' 1873, vol. ii. p. 51.

I am not aware of any other machines for solving equations of a high order, except Mr. Cunynghame's, which will be described this afternoon. Machines for solving simultaneous equations also exist.

Like Mr. Hinton, I made use of the equality of moments by arranging a series of levers to operate upon one another. Thus, let the levers be called successively 1, 2, 3, 4, &c.; then 1 is on a stationary axis; it has at unit distance from its axis and on either side of it pivots, from each of which hangs a pan or hook labelled $-a$ and $+a$. If, then, a weight of a units is put upon either of these pans, the moment of the force upon the beam will be $-$or $+a$ units.

Let a second beam 2 be connected with 1 by a sliding joint which is permanently at unit distance from the axis of 2; let the joint also carry a scale-pan, and let there be another scale-pan at unit distance on the other side. These are labelled $+b$ and $-b$. A weight of b units hung on either of these pans will produce a turning moment on b of $+$or$-b$ units, and a turning moment on a of $+$ or $-bx$ units, where $x+1$ units is the distance between the axes of 1 and 2. Such a pair of beams of course will solve a simple equation whether the root be positive, negative, whole, or fractional; for as the second beam is made to traverse, it must pass some position where $a \pm bx = 0$, and on the two sides of this position the moments on 1 will be opposite in sign. Therefore by shifting the beam till the arm changes position, the root can be exhibited by a pointer on a scale.

Similarly, if a third beam be mounted opposite 1 with a fixed axis, and if it be provided with pans as before, labelled $-c$ and $+c$, and if this be connected with 2, as 2 is with 1, then on pushing 2 along between these two beams a weight of c units on one of the c pans will exert on 2 a moment of $\mp cx$, and on 1 of $\mp cx^2$ units. If, then, a quadratic equation of the form $a+bx+cx^2=0$ has to be solved, weights of a, b, and c units are placed on the proper pans and the beam 2 slid along until the beam 1 shifts its position. The two places at which this occurs are the two real roots of the quadratic. When the quadratic has no real roots, the machine can be still employed to find the impossible roots, as will be explained later.

A fourth beam placed opposite to 2 and connected with 3, as 2 is with 1, will in the same way make the machine capable of finding the real roots of a cubic equation, and so by adding more beams to the stationary and movable sets, an equation of any degree can in theory be solved. Of course, as the number of joints increases, the friction and elasticity of the working parts increase enormously, and so with the best work possible there is a practical limit beyond which it is hardly possible to go.

The only difficulty lay in the design of the beams, which would allow the connections between them to be capable of continuous variations at all parts of their length. The joint must be able to slide freely past the axis and past the coefficient pans. All the beams are of the same construction except that alternate ones have the connecting joint on opposite sides of the centre, as shown by the diagram fig. 1. Fig 2 is a front view of a beam with its supporting-rod and coefficient hooks complete; fig. 3 a back view, and fig. 4 a plan of the same. Fig. 5 is a transverse section through the middle, and fig. 6 an end view of a beam and connecting joint but without supporting bar. It will be seen that there runs along the back of each beam a web which may be embraced at any part by a pair of fingers fixed to the front of the next beam behind it, *i. e.* by the beam which is next higher in order of number.

It is evident that this construction allows the connecting joint of each beam to slide past the centre of the next lower one.

The supporting bars hang from a series of longitudinal beams lying in a cradle, the alternate ones being joined together. These then can be shifted relatively past one another, and one set can carry an index reading on a scale on the other set, so placed as to read zero when the distance of the centres of consecutive beams is one unit.

To show how to apply the machine to find the impossible roots of a quadratic, it will be necessary to consider the quadratic equation $y=a+bx+cx^2$ as representing a parabola. In this parabola a has nothing to do with the shape of the curve. Variation in a only shifts it or makes it slide up and down the axis of y. It may therefore be struck out for the present. Then the parabola passes of necessity through the intersection of the axis of x and y. If the sign of b is changed, the new parabola will be a reflection of the old about the axis of y. Fig. 7 thus represents the double equation $x^2 \pm bx = y$.

The distances of the vertices of these parabolas from the axis of y are $\mp\frac{b}{2}$, and the values of y at the vertices are each $-\frac{b^2}{4}$. Now let a line parallel to the axis of x slide down the axis of y, and let its distance above the axis of x be a in a series of equations $a+bx+(c)x^2=y$ (the c may be omitted), then those values of x at which this line cuts the parabola will be roots of the equations. As it slides down, that is as

a increases algebraically, it approaches the vertex, and the two roots become more nearly equal until at the vertex they join, and there are two equal roots; here of course $b^2=4a$. If the sliding line is below this position, it misses the parabola, and there are no real roots.

Now going back to the case of real roots, it is clear that they are equally greater and less than $\mp\frac{b}{2}$, which is the distance of the vertex of the parabola from the axis of y, and the excess or defect is the half width of the parabola at the place of cutting. Now this half width is by the nature of the parabola equal to the square root of the distance along the axis from the vertex to the sliding line. If, then, the sliding line misses the parabola, the half width of the curve at the position of the line being equal to the square root of its distance above the vertex, will, as this distance is now negative, be impossible, or the curve at this region does not exist; nevertheless the imaginary half width is still the square root of the distance of the sliding line *above* the vertex. Geometry is incapable of representing this impossibility; but it is curious that the machine can be made to indicate its existence and measure its amount. Since the ordinates of the parabola represent the moments on the first beam for every value of x, it is clear that a minimum of moment will be produced in the case of impossible roots. If, then, the machine fails to find two real roots (which of course must be within its limits), the first beam must be constrained by a spring instead of being free. The deflection will then indicate moments, and therefore the position of the minimum may be observed. The reading on the scale of the instrument is then the real part of the root, and the square root of the moment, which may be found by applying weights, the impossible part.

In the case of a cubic equation there must be one real root, and there may be three; if only one exists this may be found and divided out, when the resulting impossible quadratic can be solved by the machine. If all these roots are real, they can of course be found directly.

In a biquadratic, or one of a higher order, the possible roots may be found. If there remain more than two impossible roots, the machine is incapable of finding them.

While attempting to find properties of such equations that might be made use of in the construction of a machine, I found a curious relationship between two pairs of curves which might be turned to account in a curve-tracing machine. They are probably well known, but if so it may be worth while to mention them, as they have an interest in connection with this paper.

If the signs of all the terms of an equation $bx+cx^2+dx^3$ + &c. $=y$ be changed, the curve of course is in no way changed. If the signs of the even powers be changed, the curve is obviously turned round about the origin through two right angles; but if the sign of the term containing x alone be reversed, the shape of the curve is entirely altered, yet the relation between the new and the old curve is very simple.

Firstly, they cross at the origin, making there equal angles on either side of the axis of y. Secondly, whatever value of x be taken the tangents of the two curves for that value will cross one another and the axis of y in the same point. This must be so, for the distance of this point from the origin $=y-x\frac{dy}{dx}$, and in this expression no part of the term involving x remains. Fig. 8 shows the series of curves for the particular series of equations

$$y=x^3+3x^2+2x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$y=x^3-3x^2+2x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$y=x^3+3x^2-2x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$
$$y=x^3-3x^2-2x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and shows the intersection of three pairs of tangents in y.

I should say, in conclusion, that I have brought this machine before the notice of the Physical Society not as a thing which is likely to be of any practical use, but because it has a certain interest, more especially in connection with another machine invented by my friend Mr. Cunynghame, which is really practically valuable, and which he will show this afternoon. (See p. 260.)

XXXII. *Note on some Organic Substances of High Refractive Power.* *By* H. G. Madan, *M.A.*[*]

In the course of some correspondence respecting M. Bertrand's polarizing-prisms, one of which I had the honour of showing to the Society last summer, I was informed that the cement used was naphthyl-phenyl-ketone dibromide. It was evident, from the theory of the prism, that this substance must have a refractive index at least as high as that of calc-spar for the ordinary ray, viz. 1·658; and as so highly refractive a cement seemed likely to be of great value for

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[*] Communicated by the Physical Society: read January 23, 1886.

many purposes, I thought it worth while to prepare some of the ketone and examine its properties. I now exhibit a specimen of it.

I prepared it by the general method devised by Grucarevic and Merz (*Berichte der deutschen chemischen Gesellschaft*, vi. pp. 60 & 1238) for obtaining double ketones; viz. by heating together benzoyl chloride and naphthalene, and placing in the mixture a strip of zinc. The product was fractionally distilled, to free it from the excess of naphthalene, and was finally obtained as a thick yellow oil, boiling at a point so nearly that of mercury that a mercury-thermometer could not be used to determine it. In properties it seems a very stable, neutral, harmless substance like Canada balsam; but unfortunately it does not appear capable of hardening like balsam, and hence it is not by itself adapted for a cement. It is insoluble in water, but dissolves readily in alcohol and benzol.

Its refractive index was determined in the usual way, a hollow prism (of refracting angle of 59° 48′) being filled with it, and the angle of minimum deviation for yellow sodium-light observed with a refractometer; from which data the usual formula gave as its refractive index, 1·666. This is even higher than that of carbon disulphide (1·63), and very nearly the same as that of calcspar given above.

I compared its dispersive power with that of a prism of very dense glass (refractive index 1·73) having a refracting angle of 60°, with the following results:—

Fraunhofer's line.	Ketone. $\mu=$	Glass. $\mu=$	Carbon disulphide. $\mu=$
B . . .	1·654	1·725	1·617
E . . .	1·678	1·744	1·643

From this it is easily seen that the coefficient of dispersion of the ketone is $1\frac{1}{4}$ times that of the glass, and almost exactly the same as that of carbon disulphide.

I have made the compound of the ketone with bromine, referred to by M. Bertrand, but I hesitate to recommend it as a cement, at any rate for anything made of calcspar; as it seems liable (like many similar bromides) to decompose with formation of hydrobromic acid, which of course acts upon the spar.

The ketone itself has a refractive index quite sufficiently high, if only some means can be found of hardening it.

I cannot, however, yet vouch for its permanency. It was made in August last, and remained for several months without change; but it has lately shown a tendency to pass from the colloidal to a crystalline condition, especially during the cold weather, although I had previously exposed it to a temperature of −20° without causing any alteration beyond an increase of viscosity.

I would also ask permission to show the Society a specimen of another highly refractive substance, viz., metacinnamene. It is a polymeric form of cinnamene, obtained by the action of light or heat upon the latter substance.

Cinnamene is a colourless liquid, obtained by distillation from the resin storax. Its refractive index I found to be 1·54 for the D line, nearly the same as that of Canada balsam. When this liquid is exposed to light for a few weeks, or heated to 190° in a sealed tube for half an hour, it becomes a glass-like solid, contracting greatly during the change.

In order to determine its refractive index, it was heated until it became viscous and placed in a hollow prism. The angle of minimum deviation for yellow sodium-light was found to be 39° 44′ 35″; whence its refractive index is calculated to be 1·593. This is much higher than that of any other resin, so far as I can make out; and metacinnamene would make a very valuable cement, since it is readily softened by heat and becomes remarkably hard and tough on cooling, but it does not show any great adhesiveness for glass. I hope to get good results by mixing it with other things, such as the ketone above described.

Another highly refractive organic substance is monobromonaphthalene, of which I exhibit a specimen.

It is a nearly colourless liquid, more stable than similar compounds containing bromine usually are, and boiling at the high temperature of 285° C. Its refractive index for the D line is 1·662; very nearly equal to that of naphthyl-phenyl-ketone. I am rather surprised that it has not come into use as a substitute for carbon disulphide for filling prisms, as it is much less volatile and inflammable than the latter substance, while it has an even higher refractive and dispersive power.

The great desideratum at present is, a substance which has all the excellent qualities of Canada balsam—colourless, neutral, permanent in the air, becoming fluid when moderately heated, but hard and tough when cold, and with a refractive index of *at least* 1·66.

Such a substance would not only be of great use in the construction of polarizing and other prisms, but it would also be invaluable as a medium for mounting microscopic objects; since details of structure are brought out much more clearly when the object is immersed in a medium which differs greatly from it in refractivity. Phosphorus, arsenic sulphide, and mercury-potassium iodide have been used for this purpose, but they are all open to grave objections. None of them are permanent in the air; some are dangerously inflammable; while most of them act on delicate organic structures, although available for such things as siliceous Diatomaceæ.

The most hopeful direction in which to look is undoubtedly towards some of those complex organic compounds which are now being built up by many workers in England and Germany.

XXXIII. *Note on the Determination of the Volume of Mercury in a Thermometer.* *By* A. W. CLAYDEN, *M.A., F.G.S., Bath College*[*].

IN Professor Clark's paper on the Heat-capacity of a Thermometer[†], he shows that it may be calculated approximately if the specific gravity of the instrument, and that of the glass of which it is made, be known. The first step in his method is to determine the volume of the contained mercury, which he points out may be ascertained by the following formula,

$$V_1 = \frac{V(S-S_2)}{S_1-S_2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which V_1 = the volume of mercury,
S_1 = its specific gravity,
V = the volume of the instrument,
S = its specific gravity,
S_2 = the specific gravity of the glass.

Now this expression will only be correct if the bulb and tube of the thermometer be completely filled with mercury, as they will be at a temperature (t°) slightly above the highest reading of the scale. At all lower temperatures V will be too large and S too small; an error being introduced, as Professor Clark points out, by the empty space of unknown capacity which occupies the unfilled portion of the tube.

At this higher temperature (t), V_1 becomes $V_1(1+\beta t)$, β being the absolute coefficient of expansion of mercury. Similarly V becomes $V(1+\alpha t)$, α being the coefficient of cubical expansion of the glass.

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[*] Communicated by the Physical Society: read January 23, 1886.

[†] Proc. Physical Soc. vol. vii. p. 113. [Phil. Mag. vol. xx. p. 48.]

Also

S becomes $\frac{S}{1+\alpha t}$; S_1 becomes $\frac{S_1}{1+\beta t}$; and S_2 becomes $\frac{S}{1+\alpha t}$.

If, now, these results be substituted for those in formula (1), the expression obtained will be theoretically correct, as the empty space vanishes at t°.

Thus

$$V_1(1+\beta t)=\frac{V(1+\alpha t)\left(\frac{S}{1+\alpha t}-\frac{S_2}{1+\alpha t}\right)}{\frac{S_1}{1+\beta t}-\frac{S_2}{1+\alpha t}},$$

which, by simplification, becomes

$$V_1=\frac{V(S-S_2)}{S_1-\frac{S_2(1+\beta t)}{1+\alpha t}}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It will be seen that (2) gives rather a larger result than (1), because β is greater than α. This, however, is what must be expected if reference is made to (1). There V is too large and S is too small, so that the product VS remains unaltered; because $S=\frac{W}{V}$ if V is the volume in cubic centimetres, whence $VS=W$; but the product VS_2 becomes greater as V increases. Hence (1) gives too *small* a value for V_1, a result which is compensated for in (2).

XXXIV. *On "Resistance" at the Surfaces of Electrodes in Electrolytic Cells.* *By* G. Gore, *LL.D., F.R.S.*[*]

In a former paper on "Evidence respecting the Reality of Transfer-resistance in Electrolytic Cells" (Proc. Birm. Phil. Soc. 1886, and Phil. Mag. February 1886, vol. xxi.), I have shown that the passage of an electric current into or out of an electrode of sheet platinum by means of dilute nitric or sulphuric acid, sets free at the surface of contact of the metal and electrolyte an amount of heat which cannot apparently be accounted for by any other cause than that of an obstacle of some kind to the passage of the current at those surfaces.

And in another paper, "On the Relations of Surface-resistance at Electrodes to various Electrical Phenomena" (ibid.),

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[*] Communicated by the Author, having been read before the Birmingham Philosophical Society, February 11, 1886.

I have further shown by experiments that, with a thermoelectric couple composed of a hot and cold sheet of platinum in dilute nitric or dilute sulphuric acid, "in each of these two couples the total amount of 'surface-resistance' in the circuit, when one of the junctions was heated, was very much greater in the direction of the current produced than in the opposite one;" and I inferred that the direction of current was not due to those differences of resistance. And I further stated that several of the results of experiments described in that paper "agree with the conclusion that differences of transfer-resistance are incapable of producing a current, and are essentially unlike differences of electric potential;" also "that heat decreases such resistance whilst increasing contact-potential in various metal-electrolyte thermoelectric couples."

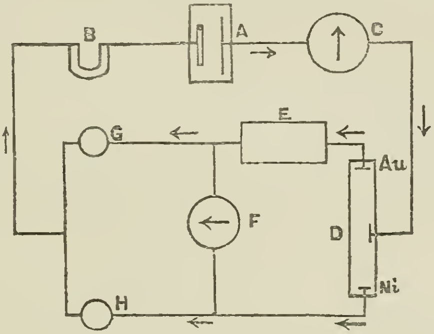
Lest it should still be supposed that the phenomena to which I have ventured to apply the term "transfer-resistance" are not really of the nature of "resistance," but are effects due to polarization, some kind of counter electromotive force, or other form of opposing difference of electric potential, I have further examined, by means of the following experiments, the question whether the phenomenon I have found can exist independently of such difference.

A single conclusive adverse fact is sufficient to upset the most fixed theory: if the phenomena termed "transfer-resistance" are really due to some form of opposing difference of electric potential, they ought to disappear wherever such difference is absent.

I have tested this point in the following manner:—By the aid of some tables of "Chemico-electric relations of Metals in Solutions of Salts of Potassium" (Proc. Roy. Soc. 1877, No. 200), and in another on "Some Relations of Heat" &c. (ibid. 1884, No. 233), I selected cases in which two different metals in an electrolyte produced no voltaic current, and examined those combinations of metals and liquid for any differences of "surface-resistance."

I nearly filled a glass trough, 10·0 centim. long, 2·5 centim. wide, and 3·0 centim. deep, with a solution consisting of about 3 grammes of potassic cyanide (of 92·1 per cent.) and 100 cubic centim. of water. In this solution was immersed, near the opposite ends of the trough, at 8·0 centim. apart, a sheet of nickel and one of pure gold, each being 1·0 × 1·0 centim., not varnished on the back, and connected with a graded, dead-beat, Despretz d'Arsonval galvanometer (see 'Nature,' vol. xxxi. p. 86), having a resistance of about 150 ohms, and I altered the strength of the liquid until all signs of difference of potential ceased. (The sensitiveness of the galvanometer was very largely increased by substituting for the suspending and connecting wires of silver above and below the movable coil, fibres of silk, and making the connections with the coil by means of spirals 3·0 millim. diameter, of platinum wire of about ·064 millim. thickness, enclosing the fibres. The instrument was then much more sensitive than an ordinary astatic galvanometer of 100 ohms resistance.)

To test for any difference of "surface-resistance" at the two metals, an electrode of nickel 2·0 × 1·0 centim. was placed in the electrolyte at exactly mid distance between the end plates, and the following arrangement employed:—



A. Battery of six pairs of zinc and platinum in dilute sulphuric acid. B. Regulator of current (see Proc. Birm. Phil. Soc. vol. iv. p. 422; the 'Electrician,' 1885, vol. xv. p. 196). C. D'Arsonval galvanometer. D. Electrolytic trough. E. Box of resistance-coils = 2000 ohms. F. Astatic galvanometer, resistance = 2 ohms. G, H. Two resistance-coils of 5 ohms each.

The cyanide solution was at 9° C., and the total strength of current employed was = ·00058 ampere, or ·00029 to each end plate. The middle electrode was of nickel. The total current was passed in either direction according to whether the two metals were used as anodes or as cathodes, the bridge galvanometer F being brought to zero by varying the resistance in E.

When the two end plates were used as anodes, 43 ohms required to be added on the side of the gold plate to restore the balance; and when they were employed as cathodes, 280 ohms had to be added on that side to restore it. The amounts, therefore, of total "surface-resistance" at the gold and nickel plates were in each case very unequal, that of the nickel one being the largest.

As the liquid was not stirred, the "surface-resistance" at each of the two plates included not only what I have termed "transfer resistance," but also any opposing influence due to polarization developed by the current. As, however, the reverse current, produced by first connecting the gold and nickel plates with the battery for a time equalling that of duration of the experiment, and then instantly switching them to a galvanometer, was less than one hundredth the strength of half the total current employed in ascertaining the inequality of "resistance," the opposing effect due to polarization must have been exceedingly small, and was equal at the two plates. I have already shown in a large variety and number of cases, described in an extensive research communicated to the Royal Society, March 2, 1885, that the "resistance" still exists, and varies greatly in amount in different cases, when polarization is nearly or entirely prevented by employing and rapidly stirring a suitable electrolyte. It may also be remarked that the amount of "resistance" is not directly proportional to that of polarization; for whilst the opposing force of the latter increases with increased strength of current, "transfer-resistance" decreases.

A second solution, composed of 7·0 grammes of potassic chloride, ·05 gramme of potassic cyanide (of 92·1 per cent.), and 80 cubic centim. of water at 8° C., was tested with plates of gold and iron in a similar manner. The plates were each 1·0 × 1·0 centim., about 9·0 centim. asunder, and not varnished on their backs; the gold was very faintly positive, and this disappeared on stirring the liquid. The total strength of current employed was ·0014 ampere, or ·0007 to each plate. The middle plate was of iron. With the two metals as anodes, the iron offered 1230 ohms less, and as cathodes 26·0 ohms less, "resistance" than the gold.

And with plates of nickel and copper 1·0 × 1·0 centim., 9·0 centim. apart, and varnished on their backs, in a third solution, composed of 1·89 gramme of potassic bromide dissolved in 100 cubic centim. of water at 8° C., the potentials were equal. The strength of current employed was ·00058 ampere, or ·00029 to each metal. The middle plate was of copper. With the two metals as anodes the nickel offered 650 ohms greater, and as cathodes 210 ohms less, than the copper.

We know that the contact of two pieces of the same metal with an electrolyte of uniform temperature produces no difference of potential. I therefore took two electrodes of sheet platinum, varnished on their backs, one being 1·0 × 1·0 centim., and the other 2·0 × 5·0 centim. and 8·0 centim. apart, in the solution of potassic bromide at 8° C.; no current was produced. I measured their amounts of "surface-resistance" in the same manner, by means of a middle plate of platinum and a total current of ·00058 ampere. As anodes, the "resistance" of the large one was 140 ohms less; and, as cathodes, 23 ohms less than that of the small one.

And in another similar experiment with plates of copper, one being 1·0 × 1·0 centim. and the other 2·0 × 5·0 centim., 8·0 centim. apart, and varnished on their backs, with a middle plate of copper, in a solution composed of 1·0 gramme of glacial phosphoric acid and 10·0 cubic centim. of water at 8° C. As anodes the "resistance" at the surface of the large one was 50 ohms less, and as cathodes 249 ohms less, than that at the small one.

In the first three of these combinations difference of "surface-resistance" was obtained by employing plates of different kinds of metal, and in the last two by using plates of the same of different sizes. I have already stated (Proc. Roy. Soc. 1885, No. 236, p. 209), "that this resistance varies largely in amount with different metals in the same solution;" also, that "the usual effect of diminishing the density of current alone, by enlarging one electrode only, was to diminish the resistance at that electrode."

The results of each of these ten experiments show that the influence which opposes the current at the surfaces of metallic electrodes in electrolytes, exists independently of counter electromotive force, polarization, and all other forms of electric potential, and is therefore a distinct phenomenon, and cannot be due to those causes.

The magnitudes of "surface-resistance" at each plate of different metal in the first three liquids were also separately measured by means of an ordinary method with a condenser. The two end plates were immersed, 4·0 centim. apart, in the liquid in a glass beaker; the battery, regulator, D'Arsonval galvanometer, a coil of 200 ohms resistance, and a closed connecting-key being in the circuit. A condenser of ·33 microfarad capacity was then connected, through a Thomson's reflecting galvanometer of 3040 ohms resistance and a key, with the electrolyte close to one of the plates by means of a wire of the same metal as one of the electrodes, and with the wire circuit near that electrode, and the deflection noted. After discharging the condenser, a second deflection was obtained in a similar manner by means of the potentials on each side of the other plate; and a third by means of those at the two ends of the coil; and the "resistances" calculated from the results.

With the gold and nickel plates in the solution of potassic cyanide at 8° C., and a strength of current $= \cdot 00029$ ampere, the "resistances" were :—

	As Anode.	As Cathode.
Gold . . .	114 ohms.	1044 ohms.
Nickel . . .	143 ,,	801 ,,

With the gold and iron in the mixture of potassic chloride and cyanide at 8° C., and a strength of current $= \cdot 0007$ ampere, the "resistances" were :—

	As Anode.	As Cathode.
Gold . . .	1136 ohms.	768 ohms.
Iron . . .	56 ,,	360 ,,

And with nickel and copper in the solution of potassic bromide at 8° C., and a current of ·00029 ampere, the "resistances" were :—

	As Anode.	As Cathode.
Nickel . . .	639 ohms.	1565 ohms.
Copper . . .	130 ,,	1565 ,,

The results obtained by this method agree substantially with those obtained by the previous one ; there are, however, some considerable discrepancies in the amounts. It need hardly be remarked that in such experiments it is very difficult to obtain perfectly concordant quantitative results by two such different methods, and that it would not be reasonable to expect them. The results uniformly confirm the conclusion that "surface-resistance" may exist independently of all difference of electric potential.

Equality of voltaic potential, attended by more or less difference of "surface-resistance," may be obtained by a variety of arrangements ; and a large number of additional instances might be selected in which the potentials are equal whilst the "resistances" are unequal. The ones chosen were preferred because they were convenient and comparatively manageable. Cases of equality of "resistance" accompanying difference of potential might probably also be found.

Is the phenomenon I have detected really of the nature of ordinary electric conduction-resistance? If it is, its characters will agree with the most essential ones of that influence. It agrees in several important points with ordinary conduction-resistance : first, it is not able to produce a current ; second, it is usually small with those liquids in which ordinary resistance is small ; and, third, it is considerably reduced in liquids by rise of temperature (see "Relations of Surface-resistance at Electrodes," Phil. Mag. vol. xxi., Feb. 1886). It differs, however, from conduction-resistance in the less important circumstance that it varies in amount with the strength and density of the current; with a given electrolyte it is also usually much larger in amount than the ordinary conduction-resistance of a short section of that liquid: this appears consistent with the difference of conditions.

From these various fundamental truths respecting it, "transfer-resistance" is a retarding influence essentially similar to ordinary conduction-resistance, but modified, increased in amount, and rendered more complex by taking place at the surfaces of mutual contact of two heterogeneous bodies instead of in the mass of a homogeneous substance; but whether it ought to be designated by some other term than the one I have found it convenient to employ is a question not yet settled. It is my intention, if I am not prevented, to further investigate the subject.

As the magnitude of this "resistance" to that of the mass resistance in a given electrolytic or voltaic cell is usually large, especially with non-corroded metals, it performs an important part in the action of voltaic batteries and electrolytic cells. One important practical application of the fact that "transfer-resistance" is usually diminished by enlarging the electrodes, has been made in the electro-metallurgical purification of copper on the large scale, where a great saving has been effected by arranging the depositing-vats in "multiple series." I have also shown (Phil. Mag. vol. xxi. 1886, p. 150) that in consequence of diminution of "transfer-resistance" by rise of temperature, with a voltaic element composed of zinc and platinum in dilute suphuric acid, "the electromotive force was increased about 8·38 per cent., and the strength of current 220 per cent., or to 3·2 times its original amount, by raising the temperature of the platinum negative plate 81 C. degrees."

XXXV. *Note on the Paper on some Thermodynamical Relations by* Prof. W. Ramsay *and* Dr. S. Young. *By* Professors W. E. Ayrton, *F.R.S., and* John Perry, *F.R.S.*[*]

WE have written this note partly for the purpose of drawing attention to the fact that, although scientific work of many kinds is being much more thoroughly done now than ever before in the history of the world, mainly because the workers are specialists, yet a great deal of valuable work is rendered comparatively useless because the specialist is now

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[*] Communicated by the Physical Society: read January 23, 1886.

too perfect a specialist, and so obtains no help from other departments of physics than that in which he himself is working.

We have ourselves, for example, wasted much time in useless observation of what seemed to be capricious behaviour of voltaic cells, a result to be expected when electricians who are not practical chemists conduct chemical investigations. Again, the specialist in pure mathematics might often do much more valuable work if he had practised the application of his mathematics to natural phenomena, for he would learn of new directions in which to conduct his special investigations. We have been told by certain authorities in Chemistry that a few chemists with a good working knowledge of mathematics possess at the present time facilities for rapidly improving our knowledge of chemical science.

Drs. Ramsay and Young must forgive us for making their recent papers the text of a discourse of this kind. We might have selected papers by other authors which show more clearly the truth of what we say; but the work done by these two gentlemen is of such a valuable kind, their scientific positions are so well established, that we can venture to take this liberty without feeling that we do any harm in making an illustration.

These gentlemen read a paper at the last meeting of the Physical Society, in which they gave the gist of two papers, one of which had been published in the December number of the Philosophical Magazine, and the other has since been published in the January number. Members of the Society will find the first of these in the number of the 'Proceedings' of our Society which reached them yesterday. Referring to the papers in the Philosophical Magazine and to the published abstract of the paper read before the Physical Society, we have for saturated vapours:—

I. Ramsay's first law:

$\frac{L}{s_1 - s_2}$ is constant for all substances at the same pressure; L being latent heat, and s_2 and s_1 the specific volumes of the liquid and saturated vapour.

II. Ramsay's second law:

$\frac{L}{s_1 - s_2}$ at pressure p_1 bears a constant ratio to $\frac{L}{s_1 - s_2}$ at pressure p_2 for all substances.

III. Young's law:

$t\frac{dp}{dt}$ is constant for all substances at any given pressure; t being the absolute temperature, and p the pressure of a saturated vapour.

Their paper, published in the December number of the Philosophical Magazine and in our 'Proceedings,' is devoted to the illustration of these three laws, and it is the record of an extraordinarily large amount of calculation.

IV. Ramsay and Young's law:

$\frac{d}{dp}\left(t\frac{dp}{dt}\right)$ is nearly constant for all stable substances at the same pressure.

One of us pointed out in the discussion on the paper, that to measure $\frac{dp}{dt}$ by drawing a tangent to a plotted curve was usually an inexact method; and that much greater accuracy would have been obtained by the authors if they had, for each substance, found the values of the constants α, β, and γ in Rankine's well-known formula

$$\log p=\alpha-\frac{\beta}{t}-\frac{\gamma}{t^2}+\&c.; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and that probably the best way of making a comparison between two substances and observing changes due to dissociation would be by remarking that, for the substances examined by Regnault,

$$\alpha-\frac{\beta}{t}-\frac{\gamma}{t^2}+\&c.=a-\frac{b}{\theta}-\frac{c}{\theta^2}+\&c., \quad . \quad . \quad . \quad (2)$$

if t and θ are the absolute temperatures of two saturated vapours at the same pressure. It is unlikely that any person will discover an improvement on Rankine's formula just given. It cannot merely be looked upon as an empirical formula being based on Rankine's molecular theory. The exactness with which Rankine has reproduced Regnault's numbers, using only three constants, is exceedingly remarkable. Rankine in his paper refers to the formula

$$\log p=\alpha-\frac{\beta}{t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which is the same formula but with two constants only, and is inexact for calculations of pressure.

To show that Messrs. Ramsay and Young might have employed a less laborious method of testing, we may first point out that it would have reduced the labour by something like 75 per cent. to have recognized the fact that I., II., III., and IV. are all identical. If any one of them is true, they must all be true. Thus III., when stated mathematically, is simply

$$t\frac{dp}{dt}=\phi(p), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$\phi(p)$ being the same function of the pressure for all substances. Differentiating (4) with regard to p, we obtain at once law IV. If it had sooner been observed that

$$\frac{L}{s_1-s_2}=\frac{t}{J}\frac{dp}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

is simply a statement of the Second law of Thermodynamics, the authors would probably have examined the truth of the law in the shape III. only; since the specific volumes of vapours are so difficult to test experimentally, that Rankine, to obtain the density of steam, calculated s_1-s_2 by dividing the latent heat L by $\frac{t}{J}\frac{dp}{dt}$ rather than depend on direct measurement. Again, since the first law is $\frac{L}{s_1-s_2}=\phi(p)$, if we insert L_1 and L_2, p_1 and p_2, s and σ, we see that law II. is identical with I., and therefore I., II., III., and IV. are merely different methods of stating the same law, and to test one is to test them all.

Now we are sorry to say that we should not have attempted to test any of these forms of the law. The form which may be tested with most accuracy is III., or, as it may be stated mathematically, as in (4)

$$t\frac{dp}{dt}=\phi(p),$$

or

$$\frac{dp}{\phi(p)}=\frac{dt}{t},$$

or

$$t=a\psi(p), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where t is the absolute temperature corresponding to the pressure p of a saturated vapour; a is a number which depends on the nature of the substance, and the function $\psi(p)$ is the same for all substances. Hence to test laws I., II., III., and IV. it is simply necessary to see whether (6) is true, as (6) is identical with them. Now if (6) is true, it follows that the ratio of the temperatures of two vapours to one another at any pressure is the same as at any other pressure, or

$$\theta=kt. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In fact, then, we can test laws I., II., III., and IV. by simply testing (7); and, as we find from Regnault's or Rankine's formula (1) or (2) that (7) is untrue, there is nothing further to be said about the four laws in question.

We draw attention to the fact that Dalton's law, which was the earliest law concerning saturated vapours, and of whose inaccuracy the text-books always warn us, is a much more correct law than the four identical laws which we have been considering. For, to state Dalton's law mathematically,

$$\frac{dp}{dt}=\phi(p). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

That is, the rate of change of pressure with temperature is constant at a given pressure for all saturated vapours. Integrating (8), we obtain Dalton's law in the shapes

$$t+a=\psi(p), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\theta=t+b. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

That is, there is a constant difference between the temperatures of two saturated vapours at the same pressure. Now this law has been known to be incorrect for a long time; but if, assuming this law to be correct, we calculate the temperatures of saturation corresponding to various pressures of, say, bisulphide of carbon from those of water, we shall find our errors to be much smaller than those obtained when we use any of the above-mentioned four laws.

Of the law connecting θ and t, which has been published in the January number of the Philosophical Magazine, it is easy to see that the two forms in which it has been stated by the authors are inconsistent with one another. Such inconsistency is not of much importance in the statement of empirical laws; but we think that one of the forms is preferable to the other on account of its symmetry, as it may be put in the form :—The reciprocals of the absolute temperatures of two saturated vapours at corresponding pressures are linear functions of one another, or

$$\frac{m}{t}+\frac{n}{\theta}=1.$$

Or, again, it may be put into the shape

$$\phi(p)=\alpha-\frac{\beta}{t}=a-\frac{b}{\theta},$$

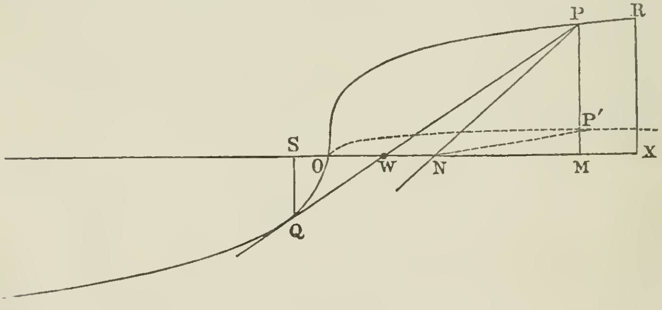
which may be compared with (3).

In conclusion, it will be observed that in calculating the temperature of a saturated vapour, a small-looking error may represent an error which looks much larger in the pressure. In comparing the errors of calculation from other empirical formulæ with those due to Rankine's formula, it is well to remember that Rankine calculated pressure, and that his errors, which for that reason might have been expected to appear large, were very small, thus showing the great accuracy of his formula.

XXXVI. *On a Mechanical Method of Solving Quadratic and Cubic Equations, whether the Roots be real or impossible. By* Henry Cunynghame, *Barrister-at-Law**.

THE method which I have the honour to bring before this Meeting depends upon the use of a parabola of the form represented by the equation $x^n = y$. And it is capable of effecting solutions of all equations of the form $x^n + mx = C$.

Let us first examine the case of a cubic equation. By Cardan's rule reduce the equation to the form $x^3 + Ax + B = 0$. In fig. 1 let P O Q be a cubical parabola, such that the ordinate at any point represents the cube root of the abscissa along the axis of X, measured negatively towards the right. That is to say, let $OM = (PM)^3$. From P draw any line such that the angle $PNM = \cot^{-1} A$, and let $ON = B$. Then it is clear that



$$OM + MN + ON = 0\ ;$$

that is,

$$(PM)^3 + PM \cot PNM + ON = 0\ ;$$

or, putting $PM = x$, $\cot PNM = A$ and $ON = B$, we have

$$x^3 + Ax + B = 0.$$

And this, therefore, shows that if from a point N, such that $ON = B$, we draw a line NP inclined at such an angle with

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* Communicated by the Physical Society: read December 12, 1885.

OX that tan PNM$=$A, then the value PM will represent a root of the equation $x^3+Ax+B=0$. Of course, if PN produced cuts the other branch of the cubical parabola, there will be two other real roots. If it does not, those other roots will be impossible.

In making a machine practically, it is well for convenience to draw on a paper a cubical parabola, say 2 feet wide, and make 1000 divisions on OX each way. Then make $XR=\sqrt[3]{1000}=10$. But as this would make the parabola too thin, let us multiply its ordinates by 10, and then take a cotangent protractor scale with the cotangents also multiplied by 10. So that the parabola drawn, as well as the tangent scale in any position, is an orthographic projection of the real one. Such a machine will find real roots true to two places of decimals.

To find the impossible roots. First find the real root, say P; draw P Q to touch the other branch of the parabola in Q. It may then be easily shown (though I am not aware that it has been before pointed out) that

$$SQ=\frac{PM}{2};$$

and that therefore

$$OS=SQ^3=\frac{PM^3}{8}.$$

And, further,

$$\frac{SW}{MW}=\frac{SQ}{PM}=\frac{1}{2},$$

and

$$SW+MW=SO+OM=\frac{PM^3}{8}+PM^3=\tfrac{9}{8}PM^3;$$

whence

$$3SW=\tfrac{9}{8}PM^3;$$

and

$$SW=\tfrac{3}{8}PM^3,$$

and

$$MW=\tfrac{6}{8}PM^3.$$

Now if α be the real root of the equation, so that $PM=\alpha$; then, by dividing $(x-\alpha)$ into $x^3+Ax+B=0$, we can easily show that the other two imaginary (or real) roots are given by the expressions

$$-\frac{\alpha}{2}\pm\sqrt{-\tfrac{3}{4}\alpha^2+A},$$

B being $=\alpha^3+A\alpha$. But we have already shown that

$$\tfrac{3}{4}\alpha^3=\tfrac{6}{8}PM^3=MW,$$

and we know that $A=\frac{MN}{MP}$; wherefore

$$\sqrt{A-\tfrac{3}{4}\alpha^2}=\sqrt{\frac{MN}{MP}-\tfrac{3}{4}\,\frac{MW}{MP}}=\sqrt{\frac{WN}{MP}};$$

which gives us this curious result—that if PM be the real root of the equation, the other two roots are

$$-\frac{PM}{2}\pm\sqrt{\text{ratio of WM : PM}}.$$

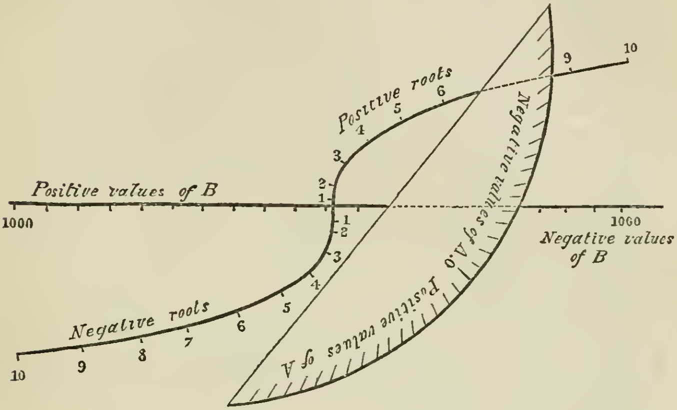
If W lies to the left of N, then WN is negative and the roots are impossible. If it lies to the right of N then the roots are real; and of course the ratio WN to PM is easy to find with the tangent scale; for it is the difference of the cotangents of the angles PNM and PWN, and may be read off at once by sliding the cotangent scale so as to have its centre at W and its edge parallel to NP; or, in fact, in any convenient manner.

It remains only to add, that a geometrical relation can always be found for the impossible parts of the roots of all equations given by the form $x^n+mx=C$. Thus, in a parabola the impossible part would be represented by the horizontal distance of the line PN, measured along the axis of X from the tangent to the curve drawn *parallel* to PN, and would thus be the square root of a line, not of a ratio.

The same instrument may be used to take square roots of any numbers, so as to find the square root of the ratio above mentioned, by holding the cotangent protractor so that its centre is at O, and the division on its scale corresponding to the square of which the root is required is on the axis of X. Then we shall have $\frac{OM}{PM}=\cot\alpha=$ division on the scale. But $OM=PM^3$; $\therefore$ division on the scale shows $\frac{PM^3}{PM}$, that is to say PM^2, whence PM gives the square root required. The values of PM should be written off in divisions and decimals along the branches OP and OQ, one being negative, the other positive; and the sides of the protractor, and also the axes OX, OX′, should be marked with their proper signs.

It will be observed throughout that I have treated lines and areas and ratios of lines as representing numerical values. Hence the equations above given have numerical values for x; and to make all the terms of the equations of the same order, constants would have to be introduced, which I have left out because they are unnecessary.

The following is a sketch of the machine represented in the act of solving the equation $x^3-20x-200=0$.



(One of these instruments is to be seen at the loan collection, South Kensington, where it will remain permanently.)

AM 21 [Mar. 1886]

XXXVII. *On the Seat of the Electromotive Forces in Voltaic and Thermoelectric Piles. Reply to* Professors Ayrton *and* Perry. *By* Dr. Oliver Lodge[*].

I AM glad that Professors Ayrton and Perry have reprinted their criticism of my paper to the Society of Telegraph Engineers at length in the Philosophical Magazine—with a few emendations and additions doubtless, but with no substantial alterations; for though I replied to the greater part of it at the time, as reported in the 'Journal' of the Society[†], there are one or two points which have been now brought more prominently and distinctly forward, notably a more precise statement of their thermoelectric views, first appended by Prof. Perry as a footnote, by Prof. Ayrton as a description of experiments with hot and cold mercury, to their respective communications in the Journal of the Society for last year. The difference between our modes of regarding electrical phenomena are so fundamental, and the smaller points at issue so numerous, that it would be easy to carry on the controversy by harassing each other in all manner of places

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[*] Communicated by the Author.

[†] April 1885.

at once, and to fight over the domain, not only of electricity, but of hydraulics and mechanics as well. Hitherto this has been our policy, but the result is that we stubbornly maintain our respective positions and neither side obtains any striking advantage. Moreover this kind of skirmishing at the present stage would consume a good deal both of time and space, and it is doubtful whether much of it would be profitable.

I propose therefore to change my tactics, and, fixing upon some one well-marked and crucial position, try to show under what conditions it can be held by either side, and what consequences would result from its abandonment by the other.

Such a position is afforded by the thermoelectric views deliberately and specifically expressed in their last communication in the January Philosophical Magazine. For our opinions on one part of this subject are quite definite and yet quite contradictory*.

I hold that local heat-production in a metallic circuit is a precise measure of local E.M.F. Professors Ayrton and Perry hold that the two things are unconnected, or at least quite otherwise connected.

The question then is, Does a seat of E.M.F. necessitate a source of reversible heat at the same spot? or, conversely, Does a local E.M.F. exist wherever reversible heat appears? and are the E.M.F. and the reversible heat directly proportional to one another?

In discussing this question we both have, and I especially (as more needing it) have, the great advantage of Dr. Hopkinson's communication on the subject, published in the Philosophical Magazine for October 1885, in which he judicially reviews the arguments used by both sides; and though he does not pronounce sentence one way or another, it is easy, I think, to see in which direction he himself inclines. To my unbounded astonishment, however, Professors Ayrton and Perry, in an appendix to their January paper, claim Dr. Hopkinson as a champion of their cause!

It would be both futile and ridiculous to argue about the views of a third person; but I may be allowed to say that, in the first three quarters of Dr. Hopkinson's paper, the only portion germane to the present subject, there is nothing with which I do not cordially and unhesitatingly agree; and if Messrs. Ayrton and Perry agree with it too it is not surprising, for, as I say, he judicially and fairly sets forth the

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* I may quote Prof. Ayrton in support of this (Journal of the Society of Telegraph Engineers, 1885):—"Dr. Lodge's reasoning is based on a totally wrong conception of the Peltier effect, which I am astonished to find exists in the mind of a man," &c.

arguments on either side without definitely committing himself to either view; but I must protest against their assumption that his equations support theirs. "But," say they, "his equations are the same as ours." So far as the mere shape of the formulæ is concerned, they are; but their tacit understanding, implied in the very symbols they use, as to the physical meaning of the expressions, is quite different, and involves a gratuitous assumption with which I entirely disagree. On this outpost, therefore, it is necessary that I join issue before proceeding to attack the position already specified.

I will first, for convenience, rehearse the general theory of thermoelectricity as laid down by Dr. Hopkinson, because nothing more concise and comprehensive than this portion of his paper has yet been written on the subject. With the statements so made I expect complete agreement. I shall then try to show that the particular interpretation Ayrton and Perry put upon these equations is certainly unnecessary and probably false. I cannot indeed *prove* it to be false; I can only show that it is unnecessary, and that to grant it requires an improbable hypothesis concerning electricity. This has been shown already, but perhaps too briefly and judicially, by Dr. Hopkinson.

The statement of the general theory may run thus:—

1. By experiment the total E.M.F. in a closed circuit of any one metal is zero, however temperature be distributed. Hence E.M.F. in a metallic circuit depends on a thing like a potential, or $d\mathrm{E}$ is a perfect differential of a function of the temperature; whence, in a simple thermoelectric circuit of two metals A and B, with junctions at $t_1°$ and $t_2°$,

$$\mathrm{E}=f(t_2)-f(t_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

2. The measure of E.M.F. in any complete circuit is the work done per unit electricity conveyed round it,

$$\mathrm{E}=\frac{\mathrm{W}}{\mathrm{Q}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let $\Pi(t)$ stand for the reversible heat generated per unit electricity at an AB junction whose temperature is t. Let $\Theta_{\mathrm{A}}(t)dt$ represent the reversible heat generated per unit electricity transmitted in the metal A from the temperature t to the temperature $t+dt$; and let $\Theta_{\mathrm{B}}(t)dt$ represent the same thing for the other metal. Then, by direct application of the first and second laws of thermodynamics and by differentiation, Hopkinson gets, in a few lines which can hardly be abbreviated or improved,

$$\Pi(t)=tf'(t), \quad . \quad . \quad . \quad . \quad (3)$$

$$\Theta_A(t)-\Theta_B(t)=tf''(t). \quad . \quad . \quad . \quad . \quad (4)$$

If, now, Θ is to be regarded as simple proportion, in accordance with the results of Professor Tait, f'' is a constant depending on the two metals only;
so

$$f''(t)=c,$$

$$f'(t)=b+ct,$$

and

$$f(t)=a+bt+\tfrac{1}{2}ct^2,$$

t meaning absolute temperature throughout.

So far everything is unassailable, except by one who may believe in some irreversible degradation of heat by conduction or otherwise as necessarily accompanying the process, and so deny the applicability of the second law altogether. Certainly Ayrton and Perry are not thinking of doing this: they accept the equations as they stand, and claim that their own are identical with them.

But now comes in the gratuitous assumption which causes them to misunderstand the true physical meaning of these equations, and which leads them into what seems to me error.

I speak from my own point of view: I do wish to show that their position is untenable, but I have no wish to dogmatize. I use language which may serve to bring out the differences between us plainly; and while I am sure neither Prof. Ayrton nor Prof. Perry, so I hope no one else, will misconstrue what I say in any offensive or disrespectful sense. From my standpoint their theory looks erroneous, and it is allowable to say so. They will no doubt return the compliment.

They beg the whole question by their interpretation of $f(t)$. All that is certain about $f(t)$ is that it is a potential function characteristic of the two metals in contact. Ayrton and Perry assume, without, so far as I can see, the slightest warrant for their assumption, that $f(t)$ is the "contact-difference of potentials" which has been measured electrostatically as the Volta-effect.

Once grant this, and things begin to go their way: thermoelectric force is a mere variation of Volta-effect with temperature; Peltier generation of heat is proportional to the rate at which Volta-effect changes per degree; the E.M.F. of a cell is due to differences of Volta-effects at the several junctions, just as the E.M.F. of a thermopile is due to their variations with temperature: and in general the Volta-effect, as observed inductively, is monarch of all it surveys, including the whole of electrochemistry and thermoelectricity under its sway. If Ayrton and Perry believe all this, or rather *since* they believe all this, their energy in experimenting on it, and the importance they have attached to questions of priority in connection with it, are no longer surprising.

It will be understood, then, that my first contention is that the function $f(t)$, characteristic of a thermoelectric circuit, *has no relation whatever* to the Volta-effect. The function $f(t)$ is something connected with the properties of the metals themselves: the Volta-effect is caused by an action between each metal and the medium surrounding it. The one is physical, the other is chemical. This, of course, is as yet an open question; but any way it is plain that, before one can legitimately assert a connection between such apparently distinct things, he should be prepared with full and satisfactory proof. I am not aware that Profs. Ayrton and Perry have attempted any proof; it would seem rather that they have been deceived by a jingle of names, as thus :—$f(t)$ is a potential function characteristic of two metals, the Volta-effect is a difference of electrical potential in the air near two metals, *hence* $f(t)$ and the Volta-effect are identical. If they have any stronger basis for their assumption than this singular syllogism I shall be glad to hear it. Till then I must regard it as a baseless conjecture; and I believe that with as much right they might say that $f(t)$ meant the specific gravity, or elasticity, or thermal conductivity of the two metals, as assert that it means their Volta-effect, at the specified temperature.

Nevertheless, although the Volta-effect is some hundred or thousand times greater than any concerned in thermoelectricity*, though it has no relation with bismuth and antimony or the thermoelectric order of metals, though it is plainly related to the affinities of metals for the oxygen in which they are immersed, being demonstrably connected with their chemical properties and calculable very approximately from them; notwithstanding all this, Profs. Ayrton and Perry, and those who think with them, believe that a thermoelectric current is propelled solely by the difference of two forces at the junctions, and that these forces are the same as those which Volta and Kohlrausch and Ayrton and Perry have observed and measured electrostatically in the air near metals in contact.

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* Profs. Ayrton and Perry will reply that the constant a is independent of thermoelectricity and may have any value they like, however great. So it may as a matter of mathematics; but what proof is there that the value they like is its correct value? The burden of proof assuredly rests with them.

As a matter of historical fact, this is exactly the basis on which Avenarius, in 1863, discovered the law of E.M.F. in a thermoelectric circuit. He knew Volta-effects very well: he surmised that they might vary with temperature, say as a quadratic function,

$$V_{AB} = a + bt + ct^2 ;$$

he considered it obvious, as every one did before Thomson (and as Ayrton and Perry do still), that the E.M.F. of a thermoelectric circuit depends on the junctions alone; and he made the natural jump of *supposing* that

$$\begin{aligned} E &= V_1 - V_2 \\ &= b(t_1 - t_2) + c(t_1^2 - t_2^2). \end{aligned}$$

This expression he verified by experiment so far as the variable part is concerned; and *in form* it stands correct at the present day.

What, then, is wrong with this theory? According to Ayrton and Perry, nothing! not even the neglecting of the then unknown Thomson effect, for its introduction will merely modify the value of the constant c, leaving all the equations unaltered.

According to my view, the only thing wrong is the supposition that the V involved in E has anything whatever to do with the totally distinct phenomenon observed by Volta: though this is enough to put all the constants quite wrong.

According to Prof. Tait, from whatever point of view he regards the error (I think he regards it mainly as a neglect of Thomson-effects), the falsity of the theory is so serious as to deprive Avenarius of every claim to credit, even to the credit of guessing at a formula and experimentally verifying it within certain limits of accuracy. Or perhaps Prof. Tait means that the credit of such an achievement as that is so small as to be negligible. I am unable to agree with this opinion; but I certainly have thought that the confounding of thermoelectric E with a temperature-variation of Volta-effect was an error so serious, however natural, as to diminish very considerably the brilliancy of his happy, though unsubstantially founded, guess.

But now that in the year 1886 Professors Ayrton and Perry, learned in the doctrines of Sir William Thomson, support and contend for this identical view, I beg to modify this opinion, and to withdraw everything that I have said adverse to Professor Avenarius's remarkable paper, written at Kiew in 1863. For, since the matter is at present one of controversy, its truth or untruth must be regarded as still *sub judice*, and not to be lightly commented upon. At the same time I remember that whenever direct experimental evidence in favour of this view has been sought for, as it has been industriously by Edlund and by Sundell, it wholly and admittedly fails to support it. So much for the outpost, now for the main attack.

Besides the above assumption, Ayrton and Perry hold tenaciously to another dogma. They believe (I feel sure they will acquiesce in this) that reversible heat-localities and seats of E.M.F. are quite disconnected; that Peltier-effects are no sign of a local difference of potential; conversely, that electricity may rise or fall in potential without disappearance or generation of heat or other form of energy; and in general that energy may disappear from, or be created at, any point of a circuit without any work being done on the spot.

Well, then, if I dissent from all this, what is it that I want to say instead? I only wish to generalize the above definition (2) so as to make it applicable, not only to the whole circuit, but also to every portion of it. I would remake the statement (2) so as to include all its old meaning and something more: and say,

2′. The measure of E.M.F. at any point of a circuit is the work done per unit electricity conveyed past that point.

$$dE = \frac{dW}{Q}. \quad \ldots\ldots\ldots \quad (2')$$

Surely a harmless modification; but once grant it, along with the baselessness of Ayrton and Perry's first assumption, and everything goes my way. Reversible heat-localities and seats of E.M.F. are identical in metallic circuits: reversible energy-localities and seats of E.M.F. are identical everywhere. Energy cannot appear or disappear at any point without equivalent work being done on the spot. Thermoelectric forces and Volta-effects are utterly distinct, having no connection with each other. Peltier-heat also is quite unconnected with Volta's effect, though wholly bound up with thermoelectricity. The E.M.F. of a cell is due to, and located along with, the reversible chemical and thermal actions from which it is admitted to be calculable, and whence its energy is derived; and the Volta-effect sinks into the comparative obscurity and insignificance of a disturbance in the electric condition of metals by reason of their chemical affinity with the particular atmosphere which happens to surround them.

My view of a thermoelectric current, then, is simply this:—An E.M.F. necessarily exists at every place where reversible heat phenomena, whether of Peltier or of Thomson, are occurring; its magnitude being measurable by the quantity of heat generated or destroyed per unit current. And the whole E.M.F. of a circuit is simply the algebraic sum of all such E.M.F.'s at every point of the circuit.

If we must put it into symbols, there is a slope of potential, $dE=\Theta(t)dt$, at any point of either metal (considering J as unity, *i. e.* that heat is measured in mechanical units); and at a junction, where a *finite* amount of heat, $C\,.\,\Pi(t)$, is produced, a finite E.M.F. exists,

$$\Delta E=\Pi(t).$$

The whole E.M.F. of a simple circuit is made up of four portions, one portion at each junction, and the rest in each metal wherever there is a temperature-slope,

$$E=(\Delta E)_1+\int_B dE-(\Delta E)_2-\int_A dE$$

$$=\Pi(t_1)-\Pi(t_2)+\int_{t_1}^{2}\{\Theta^{A}(t)-\Theta_{B}(t)\}\,dt.$$

And the second law of thermodynamics $\left\{\text{cycle}\int\frac{dE}{t}=0\right\}$, combined with this, gives us further the simple relation among these quantities already established,

$$\frac{\Pi}{t}=\frac{dE}{dt},$$

$$\frac{\Theta_A-\Theta_B}{t}=\frac{d^2E}{dt^2}.$$

And, as before, if the last expression is to be constant,

$$E=b(t_1-t_2)+\tfrac{1}{2}c(t_1^2-t_2^2)^*.$$

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* Perhaps the shortest way of putting the whole thing *ab initio* is as follows:—Regard the difference of the Thomson functions in the two metals as a single function; *i. e.* write for $\Theta_A(t)-\Theta_B(t)$ simply Θ. Then the second law of thermodynamics (in its differential form) gives us

$$\frac{\Pi}{t}=f'(t),\ \ldots\ \text{(i)},\qquad \frac{\Theta}{t}=\phi'(t);\ \ldots\ \text{(ii)}$$

where f and ϕ are unknown functions satisfying the condition

$$f'(t_1)-f'(t_2)+\phi(t_2)-\phi(t_1)=0,$$

or

$$f''=\phi'.\ \ldots\ldots\ldots\ldots\ \text{(iii)}$$

Further, by the first law of thermodynamics and the energy definition of E.M.F.,

$$E=\Pi_1-\Pi_2+\int_{t_1}^{t_2}\Theta\,dt,$$

Everything being so simple and straightforward from this point of view, we have next to ask, What fault can be found with it, and why is it not readily admitted?

The crux is the proposition 2′. It is granted that E.M.F. is work per unit electricity *for the whole circuit, i. e.* proposition 2; but it is not admitted that the same thing is true for every point of a circuit.

Well, then, supposing this legitimately questioned, there must be something to put in place of it. What is this something? Dr. Hopkinson answers the question completely and satisfactorily. I want to know if Professors Ayrton and Perry accept his answer.

The "something" is this. Electricity is supposed to have a specific heat like any ordinary fluid, and this specific heat is supposed to vary with temperature and with the substance in which it happens to be flowing, to the extent even of being positive in some metals, negative in others; and the variations in this hypothetical specific heat, since nothing is otherwise known about it, can be relied on to perform whatever office is required. Electricity can let heat drop, or pick it up again, at spots where its specific heat is supposed to change, and this without introducing any rigid work-and-energy considerations, nothing but a free and airy "specific-heat" hypothesis.

Dr. Hopkinson denies that there is anything "confusing" in this mode of regarding the matter; and Ayrton and Perry very naturally object to their view being considered "absurd." I should be sorry to bandy adjectives of any but a complimentary nature; and considering the high authority of many who have found themselves for various reasons able to maintain much the same position as Ayrton and Perry, it would be wholly unseemly to do so. But I must confess that were I unacquainted with the fact that such views are held by

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or

$$\frac{dE}{dt} = \Pi' - \Theta$$

$$= f' + tf'' - t\phi';$$

whence it follows that

$$f'(t) = \frac{dE}{dt}. \quad \ldots\ldots\ldots\ldots \quad \text{(iv)}$$

And all the relations are established.

They may be exhibited in one line, along with the approximate formula of experiment, thus:—

$$\frac{dE}{dt} = \frac{\Pi}{t} = \int \frac{\Theta}{t}\,dt = f'(t) = (k_a - k_b)(t_0 - t), \quad \ldots\ldots \quad \text{(v)}$$

persons of eminence. and were it only a question with myself as to which mode of expressing the fact was most consistent with ordinary common sense and with one's natural physical instinct, I should not hesitate to stigmatize myself as almost ludicrously wrong-headed were I to accept the arbitrary and hypothetical specific-heat-of-electricity hypothesis, and decline the simple proposition that E.M.F. and unit-current energy were proportional to one another, not only in an entire circuit, as is by all sides admitted, but also in every portion of such a circuit.

I believe that the idea of attributing to Electricity a real physical specific heat has arisen (wherever it has arisen) solely from the natural, allowable, but almost playful, analogy by which Sir W. Thomson chose to popularize his brilliant discovery of the E.M.F. existing between a hot and a cold piece of the same metal; or, what is the same thing, of the E.M.F. existing in any metal along which heat is flowing, *i. e.* which is subject to a slope of temperature.

He did not express it by saying there is an E.M.F. in iron, $\Theta(t)dt$, which tends to propel electricity from hot parts toward cold parts, and whose existence is proved, and amount measured, by the generation of heat which appears in the middle of a bar when a current is sent from its cold to its hot end: he perceived that if electricity were a real fluid with an actual capacity for heat, it would in flowing from cold to hot "carry cold with it," and so cool the middle of the bar; and he expressed the sense of the phenomenon he had discovered by saying that electricity in iron behaved as if it were a fluid with a negative capacity for heat, of value $\Theta(t)$. But I feel sure that at the time he had no notion that electricity in iron really was such a fluid, or that it had such capacity for heat. Soon afterwards he was able to prove that in copper electricity behaved like a fluid with a positive capacity for heat, "carrying heat with it" as it flowed from hot to cold, and *vice versâ*.

This term, "the specific heat of electricity in a metal," to express the function $\Theta_A(t)$ or $\Theta_B(t)$, was thus at first introduced "without theory, but by an obvious analogy;" and I surmise that any idea of an actual physical truth underlying the phrase, or the notion that electricity in different substances really had a thermal capacity specific to that substance, would have been scouted by the illustrious author of the phrase as an illiterate pressing of an analogy.

But the term survived; was adopted by Prof. Tait; we find the numerical value of the specific heat of electricity in various metals quoted and investigated in every memoir and research on thermoelectricity; and I am constantly using it myself.

Such phrases, however, unless they are closely related to a real physical entity, are dangerous ; and one has, it seems to me, a good example of this danger in the present instance. Observe, I am not questioning for a moment the existence of the analogy nor its convenience in expressing many of the facts ; I question the truth of the physical meaning which may, and has, come to be supposed to underlie the form of expression.

If there is any real reason for believing electricity to actually possess a specific heat, then all I here say falls to the ground; but if the idea is based solely upon the ordinary facts of thermoelectricity, then I say that it is a misleading idea founded upon a picturesque analogy which has too prominently intruded itself into science.

Once grant that electricity in a metal has a real specific heat which varies with temperature and with the nature of the metal, and the Peltier and Thomson effects are at once accounted for, without our being able to draw from them the slightest information about seat of E.M.F or anything else. For wherever specific heat falls in value, there heat must be dropped, so to speak, by the current; wherever it rises in value, there heat must be absorbed.

And, conversely, whenever it is desired to get rid of an awkward and undesirable energy which *ought* to produce some effect but does not, as, for instance, at the place of solution of zinc in any ordinary battery-cell, it can be done without trouble by this convenient hypothesis. Those who feel bound by mere work-and-energy considerations, knowing that where zinc combines with sulphuric acid, a considerable amount of energy is set free, which does not appear as heat on the spot, but does appear as the energy of an electric current, these simple folk are constrained to believe that it expends itself in propelling the current, *i. e.* that the zinc-acid junction is the main seat of E.M.F. in the cell. Not so those who have possessed themselves of the elastic specific-heat view—these can otherwise regard the transaction. They may say,

" True, energy is liberated by the solution of zinc ; and true, it does not appear as heat; but the reason is not that it is expending itself in doing work, but because the specific heat of electricity, as it flows from zinc to acid, rises so greatly in amount [no proof has been given of this gratuitous statement], that all the heat that would otherwise be there generated is taken up and absorbed by the flowing electricity. The place which really does the work of propelling the current is not the zinc-acid junction at all ; it is the zinc-copper junction. At this spot arises all the energy of the electric current."

" But," says a plain man, " surely that energy must come from somewhere : either the zinc and copper must combine, or the junction must cool itself vigorously,—something must disappear at the junction if it is to keep on propelling the current." "Not so, my unlearned friend," rejoins the philosopher armed with the elastic hypothesis; "you forget that it is possible for the specific heat of electricity suddenly to diminish as it flows from copper to zinc; I have no evidence that it does; in fact experiment proves that it does not; but I assert that it must, and in so diminishing it sets free an amount of heat exactly sufficient to maintain the junction at its usual temperature, notwithstanding its energetic propulsion of the current." "That is very strange," muses the other; "for where metals touch acid, activity is manifest; and if you change the solution in any way, say by dropping a little bichromate of potash into it, the E.M.F. at once changes; whereas nothing can seem more passive than the place where the metals touch each other, no chemical action nor any change of temperature goes on there; you may warm it, or cool it, or hammer it, or put it into all manner of different media, and you cannot change the E.M.F. of the cell an appreciable bit. I cannot see how it is possible that the metallic junction should be propelling the current."

"No, you wouldn't. You seem to expect some excitement and disappearance of energy wherever work is being done. You seem to expect a kind of Peltier-effect at a junction if it is doing work and propelling the current. You labour under the delusion that wherever energy is transformed from one shape to another, the transformation takes place by means of work being done. I am astonished to find such delusions in the mind of a person so generally sane as yourself."

This is the view of Ayrton and Perry. If it is not, I challenge them to state it better, and to refute the article of Dr. Hopkinson rather than claim it as on their side.

Let me restate their assumptions; every one of them gratuitous it seems to me, and unsupported by experiment.

a. The characteristic function $f(t)$ of a simple thermoelectric circuit is an expression for the Volta-effect between the metals of that circuit. [Mere assumption.]

b. The Volta-effect of two metals varies with the temperature. [Even this has never been safely proved so as to certainly eliminate all effects due to tarnishing.]

c. The total E.M.F. of a thermoelectric circuit is equal to the difference between the Volta-effects of its two metals at the temperatures of the hot and the cold junction respectively. [Baseless assumption. Disproved as far as was possible for it to be disproved by the experiments Ayrton and Perry made to support it. See their paper in January, and Prof. Ayrton's remarks at Soc. Tel. Eng. Disproved also by experiments of Edlund.]

d. The specific heat of Electricity, *i. e.* $\Theta(t)$, falls greatly as it flows from copper to zinc and rises a nearly equal amount as it flows from zinc to acid. [It really rises from about 240 to 600 on passing from copper to zinc; what it does on entering acid no one yet knows.]

e. The rate of variation of Volta-effect with temperature is a measure of the Peltier-effect at a junction. [Pure assumption.]

f. Heat is generated or destroyed at certain places in a circuit, because Electricity changes its capacity for heat there; or because some other hypothetical change goes on sufficient to account for the observed effect without having to fall back upon the too simple and obvious *vera causa* of an opposition or a helping E.M.F. located at these places. [Overpressing of a mere analogy.]

Only a little wilder is the following:—

g. Reversible energy-actions, *e. g.* chemical combination or disunion, may go on in a circuit when a current passes, without producing heat or any other form of energy on the spot, and without either propelling or retarding the current; because the energy which one would expect to appear there is taken up and disposed of by some change in the properties of Electricity as it passes that place, such as a change in its specific heat: and yet the total E.M.F. of the circuit shall be somehow numerically equal to the energy so available.

[This last statement reads almost like nonsense. It has nevertheless been virtually maintained by many contact philosophers, though I understand from their last communication that Ayrton and Perry have now given it up. It appears that they concede the seat of E.M.F. as regards chemical actions and the voltaic circuit, but retain their old persuasion in respect to thermal actions and the thermoelectric circuit.]

To be quite clear let me just recapitulate these statements, modifying them so as to be correct from my point of view.

a. The characteristic function $f(t)$ of a simple thermoelectric circuit represents *itself*, and no other physical phenomenon that has as yet been specially observed. At the same time I admit that the constant term in this function is unknown, and undeterminable by thermoelectric experiments; it thus affords a fine field for speculation, of which contact-theorists have availed themselves. If one knew the value of this constant a there would be no room for discussion, it would all be matter of fact.

b, e. The Volta-effect of two metals certainly varies with temperature if the heat tends to oxidize one metal more than another, or in any other way to interpose a barrier between metal and active medium; but the fact has no thermoelectric interest whatever.

c. The total E.M.F. of a thermoelectric circuit is the sum of the forces in the different parts of that circuit, viz. at the junction and in the metals, and has nothing on earth to do with Volta's, or Crookes's, or Hall's, or anybody else's "effect" except Peltier's and Thomson's.

d, e. The Peltier-effect at a junction is a measure and consequence of the E.M.F. located there.

f, g. Heat (or more generally energy) is generated or destroyed at places where the current does work or has work done upon it, *i. e.* whenever it is opposed or assisted by an E.M.F., and nowhere else.

In conclusion, a word of explanation. In the effort to be clear, and to bring opposing views into sharp collision and contrast, I fear I have been dogmatic, and sometimes perhaps in appearance arrogant. I beg to assure all who may do me the honour to read this lucubration that it is only an appearance. I doubt not but that much can be said on the other side, but I have also no doubt that whatever *can* be said *will* be said; and it is essentially because of the energy and ability of my opponents that I am forced to strike out vigorously.

Professors Ayrton and Perry very naturally endeavour to crush me with the weight of the name of Sir William Thomson, and were I to listen to an argument *ad verecundiam* I should indeed hold my peace. But in science one need not be silenced by authority, and I may well be pardoned for stating strongly the views which commend themselves to me. Sir William himself would be the first—as a matter of fact has been the first—to wish it. If Sir William Thomson really agrees in the main with the doctrines expounded by Ayrton and Perry, as I have some reason to believe he does, it is no part of my business to explain the phenomenon: if it were, I might tentatively suggest that perhaps he has not very recently, or very carefully, considered the subject. Nor can I say that I should wish him to trouble himself to do so. Let him reserve his tremendous powers and energies for higher and more momentous problems, such as the nature of Matter, of Elasticity, and of Light. The seat of E.M.F. in a pile, whether it be voltaic or thermal, is comparatively a small affair, and can if necessary be settled without his active participation in the controversy.

University College, Liverpool,
February 13, 1886.

XXXVIII. *Notices respecting New Books.*

Outlines of Organic Chemistry. *By* H. Forster Morley, *M.A., D.Sc., etc.* London: Churchill. 1886. Pp. xx and 490; cr. 8vo.

THE large number of manuals of Chemistry that have appeared in recent years may be accepted as a gratifying sign of an extended and awakened interest in the acquisition of experimental knowledge. But the very nature of the case precludes the infusion of much originality into the labours of authorship; and the process of preparing a book of this kind closely resembles the operation of pouring a liquid from one vessel to another. Under such circumstances the task of the reviewer, if undertaken at all, is reduced to chronicling, not an advance, but a kind of lateral transition. It is seldom we meet with a writer so enthusiastic and so frankly desirous of taking pains as Dr. Morley; we have therefore selected his 'Outlines' for some comments dedicated to our younger school of chemical littérateurs.

The Preface contains a discussion of the plans at present in vogue, or scientifically possible, for constructing manuals of Organic Chemistry. Premising that "it was necessary that the book should include every substance upon which a student might expect to be examined," the author adduces and rejects two of the usual methods; and then proceeds as follows:—"I have, however, adopted a third arrangement. I have endeavoured to describe compounds in the order in which they may be synthetically produced, so that each compound should be a product of the one before and a producer of the one after. In this way the truth of the majority of the formulæ would be self-evident. I have adopted this order because I believe that a correct appreciation of structural formulæ, and the power to judge whether a given formula be correct or incorrect, is essential if chemical industry is to make any headway in England. The dogmatic teaching of structural formulæ has turned the hearts of many chemists against them altogether; the result has been that original research has ceased for want of original ideas, and the decline of chemical industry is the result." It is hardly necessary to say that the "arrangement" indicated breaks down; in by far the greater part of the work the plan of convenient successive grouping is adopted. Thus "Sugar and Starch Group," "Cyanogen Group," "Polybasic Acids," "Unsaturated Compounds," are consequent among the groups; and among individual members, phenol lies between diphenyl sulphide and phenyl acetate; the constitution of benzene is discussed between phenylic ether and bromaniline, &c., &c.

An author must be possessed by an exceptionally fervid zeal for chemical "structure" who supposes its neglect to be the cause of the decline of chemical industry in England. It has been contended, and with much reason, that chemical industry has not declined more in England than elsewhere; and that in England it has always been exceptionally characterized by original ideas. Of all departments of chemical theory, that of "structure" is the most infertile. The ideas that underlie it are, as Dr. Morley says, "very simple"; and this fact alone might induce us to suspect it.

On the other hand, industrial chemical processes are highly complex, and often extremely subtle; while their specially kinetic character imposes, as a frequent essential of success, the maintenance of a very recondite order of conditions. Upon these conditions the theory of chemical structure throws no light. All the great manufactures were founded, have grown, and are still maintained, in its absence. If structural language and formulæ are used in some of the minor industries, there is no case in which the terminology and symbols might not equally well be made non-structural without detriment to logical reasoning and the power of discovery. Structural formulæ, to be legitimate, are nothing but *multum in parvo* records of experimental transactions; but ever since the first of them was written by Higgins, there have been chemists who suppose them to have some extra virtue, to be pictures suggesting profounder insight into the constitution of matter. In these metaphysical paths the industrialist may, without blame, decline to wander. Indeed, Dr. Morley himself gives no practical demonstration of the value of chemical structure to manufacturers; in particular, under "fermentation," "paraffin," "soap," "coal-tar," not a hint of help from this source will be found, in fulfilment of the enthusiastic promise of the Preface. Apart altogether from the applications of Chemistry, it is notorious that the hypothesis of "structure" fails to explain the numerous instances of isomerism which it dismisses as "physical,"—admitted, in fact, on p. 125. Structure suggests nothing as regards colour in the region where it has been most employed, viz. that of the aniline colours themselves; for the few indications which have been made by Witt cannot be extended to "structures" in general. Structure presupposes all chemical change to be of a mechanical nature; but there is ample kinetic evidence that it is not. Hence we cannot agree with the author's extremely narrow definition of the object of Chemistry; which he states (p. 10) "is to study the relations which exist between the properties of bodies and their internal structure, so that we may be able to solve this problem; given the structure of a chemical compound to deduce all its properties, whether physical or chemical."

Among the earlier contents of the work, we may notice a few pages devoted, as is customary, to analysis. These are far too condensed to be of any real value for teaching purposes, and should be entirely omitted, as having nothing to do with the general scope of the book. Later on (p. 102) there is a discussion of Boiling-points, which would be much more appropriately placed in the terminal chapter on Physical Constants. The discussion itself is, by the way, very ancient history; Baeyer having shown long since that the properties of homologous series depend upon whether the coefficient of C is even or odd—a conclusion that has received much independent verification, and is, in fact, merely a derived form of the periodic law. This law must always be taken into account in the explanation of the properties of series. "Symmetry" (p. 108 and elsewhere) is a mechanical conception not derivable from a study of chemical reactions, and does not amount to a reason for the production, in any given case, of only a limited number of compounds. Again (p. 468) some decompositions are said to be possibly complete. No such decompositions are, however, known to modern chemistry. Reverting once more to the Preface, we should earnestly advise the author to withdraw from any future edition the concluding sentence. The slightest consideration must convince him of its extreme personal ungraciousness to all living chemists save one.

It remains to add that Dr. Morley's 'Outlines' is in most other respects deserving of much praise. The descriptive part of the work is concise and, so far as we have examined it, free from serious errors. It was a happy thought to place the chapter on Physical Constants near the end of the book; most of this is pithily written and brought down to date. But, like a skilful tactician, the author has kept his best to the last. The Summary of General Reactions, with references to the proper pages preceding, is an almost original feature, and cannot fail to be of the greatest advantage to students; it would well repay extension and classification.

Dr. Morley's text-book is undoubtedly a valuable and interesting work. If it is not quite the success that the author appears to have intended, we can only say, in the words of our neighbours, *il mérite bien de l'être.*

A Popular History of Astronomy during the Nineteenth Century. By AGNES M. CLERKE. Edinburgh: Adam and Charles Black. 1885.

SINCE the publication of Prof. Newcomb's 'Popular Astronomy' in 1878, this is undoubtedly the most remarkable work of a popular character that has appeared in this country on the subject of Astronomy. And being a history of Astronomy—that is, as Miss Clerke puts it, telling us in addition to *what* we know, *how* we came to know it,—it covers somewhat different ground from that traversed by Prof. Newcomb, and is to a considerable extent, especially in the domain of modern astronomical physics, supplementary to his treatise. The recent progress of Astronomy has been such as, in Miss Clerke's opinion, to lend itself with facility to untechnical treatment; and her endeavour has been to enable the reader to follow the course of modern astronomical inquiries, and to realize the full effect of the change introduced by the discovery of spectrum analysis. The author is evidently a practised writer, who has thought for herself on most of the astronomical problems of the day, and is not afraid of expressing her opinions on them, and she has certainly succeeded in making the work before us a very instructive as well as a very interesting one.

The book is divided into two parts. Part I. is concerned with the progress of Astronomy during the first half of the nineteenth century, and Part II. with the recent progress of Astronomy. In the first part, Miss Clerke sketches clearly and well the history of the foundation and progress of Sidereal Astronomy, including the life (special prominence being assigned to the biographical element) and work of the Herschels, Bessel, and the other pioneers of Astronomy of the time. She tells once more the story of the early struggles of the elder Herschel, and of Bessel, who "chose poverty and the stars, and went to Lilienthal with a salary of a hundred thalers annually," of Sir John Herschel's splendid work at the Cape, of F. G. W. Struve and the Pulkowa Observatory. The progress of our knowledge of the Sun during the first half of the century is related; and the Herschelian theory of the solar constitution explained and discussed in a way which shows that Miss Clerke is quite familiar with current ideas and theories on the constitution of the Sun and his appendages. The first discovery of minor planets and the circumstances which immediately led up to that event are gone into at length, as well as the great services rendered by Gauss in the emergency caused by these discoveries. We fear, however, that the method of Least Squares is not very felicitously referred to as that which "enabled him to extract the utmost amount of probable truth from a given set of observations;" but such subjects are avowedly outside the scope of Miss Clerke's book. The history of the discovery of Neptune is given with great impartiality, and a full discussion of the observations of, and theories relating to, Comets anterior to the application to them of the methods of spectrum analysis. The first part of the work concludes with a chapter on the important subject of the improvements effected in astronomical instruments during the period to which it refers.

Part II. may be divided into four sections, consisting of the chapters referring to (1) the Sun, (2) Planets and Satellites, (3) Comets, and (4) Stars and Nebulæ. Of these we think that the chapters devoted to the Sun are the best. Miss Clerke has evidently given much attention and thought to the subject, and has drawn a very clear and accurate picture of the state of our knowledge of, and of the various theories which have been advanced regarding, the Sun. Starting from Schwabe's discovery of a decennial Sun-spot period, she goes on to trace the rise and development of Spectrum Analysis, and to point out the various ways in which the spectroscope has increased or originated knowledge in the several departments of solar physics. Of the chapters on the Sun, that which pleases us best is the one on Recent Solar Eclipses. This, to our mind, gives a remarkably clear and able account of the various questions successively raised and answered, completely or partially, by the series of total solar eclipses extending from 1860 to 1883; and we know not where else, in popular literature, such an account is to be found. In discussing Sun-spot theories, Miss Clerke manages very judiciously to steer a middle course between "Sun-spottery" and scepticism. She even finds space for reference to the attempt which has been made to arrive at the period of an unknown planet through the observation of sun-spots; but, somewhat drily, adds, "The prediction still awaits fulfilment." We venture to think that the author is much more successful when discussing theories (*e. g.* when engaged on the subject of Mr. Lockyer's "basic lines") than when describing appearances: thus the chapters on the Planets and Satellites, which are mainly concerned with descriptive Astronomy, appear to us to be the least satisfactory of any in the book, and not calculated to fix the reader's attention in the same way as the following ones dealing with Comets or with Stars and Nebulæ, in which a much greater amount of speculative matter is introduced. In speaking of the rotation-period of Mars, Miss Clerke appears to claim for Mr. Proctor's result an undue amount of accuracy: it is undoubtedly five or six hundredths of a second too great. The chapter on Theories of Planetary Evolution is very interesting; but it is difficult for a writer not conversant with dynamics, to a knowledge of which Miss Clerke makes no claim, to discuss these subjects with perfect clearness, and a little obscurity is noticeable in one or two sentences. The book appropriately concludes with an account of the monster telescopes of the present day, special stress being laid on the necessity for placing them amidst suitable climatic conditions in order to reap the full advantages of their optical power.

All through the second part of the book, Miss Clerke brings prominently forward the great services which have been rendered to Astronomy in almost all its branches—Solar, Stellar, and Cometary—by the spectroscope; and to those of our readers who wish to have a clear view of the state of our knowledge before the invention of the spectroscope compared with what it was in the year 1885, we have no hesitation in recommending for their perusal this History of Astronomy during the Nineteenth Century.

The book has been printed with remarkable accuracy. We have noticed the following *errata*:—

Page viii, line 8, *for* Illinois *read* Wisconsin.
— 294, bottom line, *for* or *read* of.
— 314, line 5 from bottom (Notes), *for* N. G. Green *read* N. E. Green.

XXXIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 162.]

January 13, 1886.—Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. "On some Fish-remains from the Tertiary Strata of New Zealand." By James W. Davis, Esq., F.G.S.

2. "On a recent Section through Walton Common, exposing the London Clay, Bagshot Beds, and Plateau-gravel." By W. H. Hudleston, Esq., F.R.S., F.G.S.

During the past autumn the widening of the line between Walton and Weybridge stations has afforded a very interesting section in the above beds, showing their relations to each other with considerable clearness. Walton Station is 68 feet above O.D., and immediately to the westward the section described in the paper commences, the surface of the country gradually rising to a height of about 120 feet in the plateau which separates the drainage of the Mole from the drainage of the Wey. This plateau is connected on the south by a slope with the higher and far narrower plateau of St. George's Hill, having an elevation of 245 feet.

For convenience of reference the portion of the section more particularly described, and which has a length of 1070 yards, is divided into four blocks:—

Block A extends from Walton Station to where the unaltered London Clay is seen—313 yards.

Block B extends from this to the point where the Bagshot beds are first seen *in situ*—345 yards.

Block C extends from the above to the point where the Bagshots are first cut through to the level of the line, and the hollow filled up with Plateau-gravel—165 yards.

Block D exhibits the relations of the Bagshots to the Plateau-gravel, where the latter is most fully developed—247 yards.

Details of Block A.—This portion of the section rises from zero to 12 or 14 feet; the first bed which becomes visible is the "Top Sand," and on advancing further westward portions of a peculiar mixture of gravel and lumps of brown clay form the sides and floor of the cutting. This is evidently a disturbed series, and has peculiar relations with a mass of yellow sand, mainly false-bedded, which is 70 yards long, and from 12 to 14 feet high at the west end. The London Clay *in situ* rises very suddenly beyond this. Reasons were given for supposing this sand to be a superficial deposit against a steeply eroded surface of London Clay.

Details of Block B.—The London Clay of this block has yielded no fossils, nor are any Septaria visible. The bedding is difficult to distinguish, but recent weathering has made it more plain. This seems to establish a very slight dip towards the west. The surface of the London Clay is undulating, and it is overlain by from 6 to 7 feet of Plateau-gravel.

Details of Block C.—In this block, where the cutting has a depth of about 24 feet throughout, occurs the junction of the Lower Bagshots with the London Clay, and this is apparently an unconformable one. Both the lithology and the stratigraphy favour this view. Nothing in the nature of a lithological passage exists. The lowest bed of the Bagshots here is remarkably clear sand full of false-bedding, and is succeeded by an argillaceous series, also somewhat sandy. It was suggested that this latter might be the equivalent of the "Ramsdell Clay."

Details of Block D.—Here the Plateau-gravel attains its maximum thickness, since the Bagshots are cut through to the level of the line in three places—depth of cutting from 24 to 27 feet,—thus affording a fine opportunity for the study of this peculiar deposit. Three horizons were roughly made out, or, rather, three varieties occurring one above the other. Beyond the limits of the section there is more distinct evidence of at least two groups in these Plateau-gravels. No materials from the northern drift are found.

Other sections in the superficial beds were noticed, and more especially one about the 180-feet line on the north slope of St. George's Hill, where the contortions are of considerable interest.

January 27.—Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. "On the Fossil Mammalia of Maragha, in North-western Persia." By R. Lydekker, Esq., B.A., F.G.S., &c.

2. "On the Pliocene of Maragha, Persia, and its resemblance to that of Pikermi, in Greece; on Fossil Elephant-remains of Caucasia and Persia; and on the results of a Monograph of the Fossil Elephants of Germany and Italy." By Dr. H. Pohlig.

3. "The Thames Valley Surface-deposits of the Ealing District and their associated Palæolithic Floors." By John Allen Brown, Esq.

The author stated that his paper might be regarded as in some degree supplementary to that by Colonel Lane-Fox, published in the Quarterly Journal of the Society in November 1872. He referred to Mr. Whitaker's division of the Thames-valley deposits into three terraces, namely:—1. The lowest now seen in bends of the river, 10–20 feet above O. D.; 2. The middle terrace, 20–40 feet; and 3. The high-terrace gravel, 50–100 feet, extending up to the shoulders of the hills, and, according to the author, much higher. The high-terrace gravels near Ealing reach nearly to the top of the hills forming the inner valley-ridge, the highest point in which is the Mount at Ealing, 204 feet. The summit of this, when excavated for a reservoir, was found to be occupied by thick beds of gravel of different character from the valley-gravels, and not of fluviatile or estuarine formation; the same gravel occurs upon other elevations, and patches of it, appearing here and there, show that it probably once extended right along the ridge and over Hanger Hill. Similar materials to those forming this gravel also occur scattered over the surface of the ground. On the Mount these gravels filled a series of furrows or channels, beneath which were horizontally stratified deposits of white sand, loam, and loamy clay, which were pressed out of the line of deposit where the jagged furrows occurred; and from all the characters presented the author inferred that these deposits were due to the action of ice which had stranded and melted here, and deposited its burthen of glacial detritus. The author described the deposits of gravels, brick-earth, &c. at various points in the district, and noticed that the high-terrace gravels between 60 and 125 feet contain seams of black matter, apparently due to the decay of vegetable substances, which recur at more or less regular intervals, and serve to indicate three or four lines of old land-surfaces. In connection with these land-surfaces, especially in some pits excavated in the Creffield Road, about 100 feet above O. D., numerous worked flints were found, the characters and mode of association of which led the author to think that we have here traces of a regular manufactory of flint implements. He further indicated the conditions under which he considered their preservation in this locality had taken place.

February 10.—Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. "On a new species of *Psilotites* from the Lanarkshire Coal-field." By R. Kidston, Esq., F.G.S.

2. "The Melbourn Rock and the Zone of *Belemnitella plena*, from Cambridge to the Chiltern Hills." By W. Hill, Esq., F.G.S., and A. J. Jukes-Browne, Esq., F.G.S.

The "Melbourn Rock," which was first defined by one of the authors in 1880, is a band of rocky chalk which forms the base of the Middle Chalk in Cambridgeshire, and occurs about 80 feet above the "Totternhoe Stone." In the present paper it was shown, as the result of the mapping operations of the Geological Survey, to form a well-marked and constant feature in the counties of Hertford, Bedford, Buckingham, and Oxford. In the original description of the Melbourn Rock it was confounded with the "Zone of *Belemnitella plena* in a *remanié* condition," as described by Dr. Barrois; but it was now pointed out that the latter horizon is distinct from and underlies the latter. Although the zone of *Belemnitella plena* has been very largely removed by erosion in the district described, there is, nevertheless, evidence that this erosion has gone on to a different extent in each of the localities which have been particularly studied; and in some places some of the lower portions of the rocks of that horizon seem to have escaped denudation.

The microscopical characters of the several varieties of rock forming the Lower and Middle Chalk of the district were described, and it was shown that the beds containing nodules of a different variety of chalk which occur below the Melbourn Rock, may have been formed by the washing away of the finer particles from a disintegrating mass of chalk. This mottled chalk and the overlying Melbourn Rock are very similar to the bed found on the same horizon in the Richmond well. Somewhat similar beds occur, however, at other horizons in the Chalk over the district described in this paper.

3. "On the Beds between the Upper and Lower Chalk of Dover, and their comparison with the Middle Chalk of Cambridgeshire." By W. Hill, Esq., F.G.S.

In introducing the subject of this paper, the author referred to the divisions of the Upper Cretaceous series given in the 'Geology of the Neighbourhood of Cambridge' by Messrs. Penning and Jukes-Browne. The Middle Chalk was there described as separated from the Lower by the Melbourn Rock, which also appeared to coincide with a marked palæontological break, and from the Upper Chalk by the well-known Chalk Rock, this rocky bed, 10 feet in thickness, being included in the Middle Chalk. The division thus made corresponded exactly with the Turonian of French authors.

The author, giving a description of the Middle Chalk seen in the cliffs east and west of Dover, stated that the grit bed of Mr. Price, though much thicker, had all the appearance and structure of the Melbourn Rock, and this, with less hard, but still nodular, chalk above, appeared to be the equivalent of the zone of *H. Cuvieri* in Cambridgeshire. The zone of *Terebratulina gracilis* is well marked in the Dover cliffs, and is equal in thickness to that zone as described in the Cambr. Mem., viz. 150 feet. Above this zone the chalk became harder, withered, with lumpy projections, and finally passed into a series of rocky layers, separated by courses of softer chalk, containing, however, hard crystalline lumps. The passage to this rocky chalk was marked by the occurrence of *Holaster planus* (zone of *H. planus*). The rocky layers, extending upward for 80 feet, were marked by the presence of numbers of Micrasters, "Chalk with many Micrasters" of the author. His division included all the nodular chalk of Dover, the "chalk with many organic remains" of W. Phillips, and in it were found the fossils recorded as peculiar to Chalk Rock in the Geol. of Cambridgeshire. It appeared divisible into two zones; the lower, 15 feet, with *Micraster breviporus* (zone of *M. breviporus*), may be considered by some to be an extension of the zone of *H. planus*, the form which marks the passage from the soft to the hard chalk. In the remainder *M. cor testudinarium* was common (zone of *M. cor testudinarium*).

Seen in thin sections under the microscope, the structure of the hard beds which mark the limits of the Middle Chalk was stated to be very similar.

In conclusion, the author considered that the divisions of the Middle Chalk, as set forth in the Cambr. Memoir, are well shown in the cliffs of Dover; but the hard beds which appeared to him the equivalent of the Chalk Rock, and mark the upper limit of Middle Chalk, attaining a great development at Dover, it became necessary to examine the palæontological position of that bed to which the name "Chalk Rock" was given by Mr. Whitaker. Having studied Mr. Whitaker's description given in the 'Geology of the London Basin,' and having examined exposures of this rock between Cambridge and the Thames, he came to the conclusion that there was probably more than one bed to which the name Chalk Rock might be applied, and that these, probably not all persistent, may occur at different palæontological horizons. He therefore proposed to take the zone of *H. planus* as the top of the Middle Chalk; although this zone was difficult to identify inland, from the paucity of its fossils, the base of the overlying zone was well marked by the abundance of Micrasters and other forms, which appeared to him more closely allied to Upper than to Lower Chalk.

He believed that while the Chalk Rock seen at Henley may be considered the summit of the Middle Chalk, the Chalk Rock of Cambridgeshire, though convenient for marking the summit of the Middle Chalk of that county, included that which was really the upper part of the zone of *H. planus* and the base of the true Upper Chalk, the equivalent of chalk with many Micrasters of Dover.

He would therefore consider the Middle Chalk of Dover to be that included from the base of the grit-bed to the summit of the zone of *H. planus*. Its thickness was 242 feet at Shakespeare's Cliff. He was indebted to M. Curry, Esq., of Dover, for this accurate measurement.

XL. *Intelligence and Miscellaneous Articles.*

ON THE VELOCITY OF EFFLUX OF LIQUIDS. BY M. VAUTIER.

THE experiments which lead to the determination of the velocity of efflux generally depend on a measurement of the quantity, and on a coefficient of contraction of the jet. Bossut, however, verified Torricelli's law by two experiments, in which he measures the range of a horizontal jet of water (*Traité élémentaire d'Hydrodynamique*, vol. ii. p. 120).

In the course of researches on this subject, I have applied a graphic method which enables me to measure directly the velocity of efflux of liquids, and I have made use of this method for months.

In the flat horizontal bottom of a cylindrical vessel full of water, is an orifice in a thin plate, for which can be substituted an ajutage. Inside the vessel and in the line of its axis is placed a tube containing an emulsion of an insoluble liquid of the same density as water. This liquid is a mixture in suitable proportions of nitrobenzole and oil of turpentine. The very fine bubbles of emulsion pass along the axis of the jet, of which they take the exact velocity, as I have ascertained by modifying the density of the liquid; within pretty wide limits experiment shows a velocity independent of this density. This velocity is occasioned as follows.

The image of the jet, and therefore that of the bubbles, is formed on a photographic plate, which, by means of a suitable mechanism, is made to move at right angles to the trajectory of the jet. When the liquid begins to flow out the plate is exposed, and thus the sensitive plate receives the image of the jet during its passage.

The developed plate shows then one or more lines according as one or more bubbles have passed during the course of the plate. These lines are slanting; the direction of each is made up of two rectangular motions, that of the plate and that of the bubble. The velocity of the plate is determined by the vibrations of a tuning-fork, and the exact direction of the motion of the photographic plate is marked by a dotted line. The angle which one of the slanting lines of the photographic plate makes is measured; from this angle we easily deduce the velocity of the bubble, and hence that portion of the jet which is being investigated.

I have applied this method to the measurement of the velocity of efflux through an orifice in a thin plate 5·90 millim. in diameter under pressures varying from 0·15 metre to 0·30 metre of water. These experiments have been at first intentionally limited to such similar pressures, in order that we could settle by the constancy of the results the real accuracy of the method. With an imperfect apparatus, the mean error has remained below $\frac{1}{150}$.

I intend to investigate in this way, but under considerably different pressures, the efflux of different liquids, and particularly of viscous ones.—*Comptes Rendus*, Jan. 18, 1886.

A METHOD OF PRECISELY MEASURING THE VIBRATORY PERIODS OF TUNING-FORKS. BY PROF. A. M. MAYER.

The third volume of the Memoirs of the National Academy of Sciences contains a paper by Professor A. M. Mayer, embodying the results of a research recently carried on by him with funds from the Bache endowment. This research has as its object the elaboration of a method for measuring accurately the times of vibration of tuning-forks, and the determination of the laws of their vibrations with reference to the use of the tuning-fork as a chronoscope. The method employed was briefly to make a clock flash, at each second, a spark of induced electricity on a trace made by a style attached to the prong of the vibrating fork. To accomplish this the pendulum of the clock was armed with a triangular piece of platinum-foil, which each second cut through a globule of mercury contained in a small iron cup. To ensure the best results fresh mercury was taken with each experiment, and the height of the mercury was adjusted by a screw-collar in such a way as to make the globule as nearly as possible rigid and free from vibrations with each touch of the platinum point. The clock through this mercury connection was placed in the circuit of the primary coil of an inductorium, the current of which was given by a single voltaic cell. The tuning-fork, with one of its prongs armed with a light style of thin elastic copper-foil, was screwed to a board with a hinge which, with a screw-stop suitably placed, allowed of its being inclined so that the style was just in contact with a smoked surface of paper wound on a rotating cylinder. The secondary circuit of the induction-coil included the fork and cylinder. In the experiment the fork was raised on the hinge, set vibrating by a bow, and then depressed again, so that the style should write out its vibration on the smoked surface; at each second, as the platinum-pointed pendulum left the mercury, the primary circuit was completed and an induced current caused a spark from the point of the style, which made a single minute circular white spot on the blackened surface. The determination of the vibration-period of the fork is obviously given by counting the number of waves in the trace, and measuring the fraction of a wave with a microscope-micrometer. It was found to be essential to accuracy that the induction discharge should give a single spark only, and that the spot made by it should bisect the trace of the fork. A series of experiments with discharges, obtained on a rapidly rotating surface of blackened paper with currents of various strengths, showed that the discharge is ordinarily complex, and consists of a shower of sparks producing a large number of spark-holes on the paper. The proper conditions to be fulfilled to give the single spark-hole with a given induction-coil can only be obtained by a series of experiments varying the strength of the primary current and the area of the condenser in the secondary. In the experiments described the primary coil was 150 feet in length, the secondary 8 miles, and a condenser of plates of glass with tinfoil with 50 square inches of area was employed.

With the instrument which has been described a number of separate investigations were made. The first had to do with the question of the influence of varying amplitude on the time of vibration. With amplitudes varying in one case from 1·19 to 0·59 millim., in another from 2·39 to 0·61, and a third from 2·07 to 0·78, no variation in vibration-period greater than 0·5 of a vibration was noted. In a second series of experiments the effect of temperature was considered, and the result established with six Kœnig forks with Ut_2 and Ut_5 as extremes, that for all forks of the same steel and shape the effect of change of temperature was the same. A change of 1° F. produced a change of vibration-period of $\frac{1}{21561}$ part. In another series of experiments the law of the running down in the amplitude of a fork's vibration, and in another the numbers of vibrations per second of some European forks of various standards of pitch, were determined. In the latter determinations the probable errors in one of the mean cases was estimated to be $\pm·0053$ of a vibration; in another $\pm·004$ of a vibration.

Professor Mayer discusses further the use of the apparatus described as a chronoscope, and gives the results of some experiments with it on the velocity of fowling-piece shot of various sizes with various charges of powder. The degree of uniformity of rate of rotation of the cylinder is shown to be immaterial, and further it is shown that no correction is needed for the weight of the tracing-style nor for its scrape on the paper. With an A fork with 440 vibrations per second, it is stated that the number of vibrations can be determined by this method to at least $\frac{1}{100}$ of a vibration, and the time-record consequently to $\frac{1}{44000}$ of a second.—Silliman's *American Journal*, December 1885.

ON THE PERMEABILITY OF VARIOUS DIAPHRAGMS.

BY A. ZOTT.

The chief results of a long investigation on this subject are summed up by the author as follows:—

1. The most useful diaphragm for dialytic separation is goldbeater's skin. By its means twice as much, or in some cases, according to the way in which the experiment is arranged, a far greater separation is effected than with a dialysis of parchment paper, which it exceeds in homogeneity and in its capacity to hold water.

2. For mixtures of liquids which would attack organic diaphragms, ordinary porous cells are best; the separation which they effect is, however, 60 to 75 times less, that is to say slower, than that produced by goldbeater's skin.

3. All phenomena of diffusion are greatly increased when the diaphragm is first evacuated; the increase of volume of the solution in the dialysis is, however, far more considerable than the increase of the quantities of material which pass out; and the latter depends again on the relative velocity of diffusion of the substances in question. The more rapidly a substance of itself passes through a diaphragm, the more considerable is the acceleration which its velocity of diffusion experiences by exhausting the diaphragm.

4. The exhaustion of the diaphragm must from time to time be renewed, and this is best done after each experiment.

5. After previous exhaustion endosmosis takes place even with those diaphragms and porous plates which previously showed no increase in volume of the inner liquid.

6. Even substances which diffuse slowly, or what are called colloids, may bring about a considerable endosmosis, which, with a correspondingly long time of diffusion, may even exceed that of some crystals. Endosmosis is independent of the transit of the substance in solution, that is of the exosmosis, and when there is a mixture of solution in the dialyser, it does not differ much from that which the dissolved substances would separately bring about.

7. Solutions which contain two different substances may be more easily and completely separated in the dialyser, the further apart are the relative velocities of diffusion.

8. A dialytic separation is the more rapidly effected the more frequently the outer water is renewed.—Wiedemann's *Annalen*, February 1886.

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XLI. *On the Electromotive Forces developed during the Combination of Zinc and Iodine in presence of Water.* By A. P. Laurie, *B.Sc. Edin., B.A. Cantab.*[*]

THE following paper is a description of the measurements of the electromotive forces of certain constant voltaic elements, with a view to determine the heat of combination of zinc and iodine in presence of water.

As these measurements have been made in new voltaic combinations, a few words may be devoted to describing the forms of cells used. In the experiments described in the sequel, two cells have been used, namely the zinc-iodine cell and the zinc-cuprous-iodide cell.

The zinc-iodine cell consists of a zinc rod and a platinum wire immersed in a solution of iodide of zinc, in which free iodine has been dissolved. During the passage of a current the reactions which take place in the cell are very simple, zinc and iodine combining to form iodide of zinc, which dissolves in the water present. Thus as the zinc dissolves, the iodine combines with it, and as long as free iodine is present the cell is remarkably free from polarization.

The cuprous-iodide cell consists of a zinc rod, and a copper wire coated with cuprous iodide, immersed in a solution of iodide of zinc. During the passage of the current the zinc dissolves and the insoluble cuprous iodide is reduced to metallic copper.

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[*] Communicated by the Author. The substance of a considerable portion of this paper appeared in the 'Proceedings of the Royal Society of Edinburgh' for 1885.

With these two cells the following experiments have been made, with a view to determining the changes in electromotive force during the combination of zinc and iodine in presence of water.

These changes in E.M.F. no doubt correspond more or less closely to the changes in the heat set free during the reaction; and therefore before describing the experiments it is necessary to discuss the connection between these two phenomena from the point of view of the recent work on the subject by Prof. Helmholtz.

When a current passes through a given zinc-iodine cell, various changes take place requiring either the production or absorption of heat. In the first place, there is the combination of the zinc and iodine, producing heat; in the second place, there is the solution of the zinc iodide formed, producing heat. On the other hand, the disintegration of the zinc, the decomposition of the iodine molecule, and the removal of the free iodine from its solution in zinc iodide, absorb heat.

If now a series of cells is made up differing only in the strength of the zinc-iodide solution, the heat of solution of the zinc iodide formed in the cell during the passage of a current, will vary with the strength of the iodide of zinc solution, and that probably in a way familiar to chemists from the behaviour of sulphuric acid when added in larger and larger quantities to water.

On the other hand, the heat of combination of the zinc and iodine, and the heat absorbed in decomposing the iodine molecule and disintegrating the zinc, will probably remain the same. We shall, in fact, find that the small quantity of zinc iodide dissolved on passing a current has a definite heat of solution determined by the amount of zinc iodide already dissolved in the water contained in the cell.

Further, if a series of cells are made up differing only in the amount of free iodine dissolved in a given iodide of zinc solution, we shall find the heat absorbed in removing the iodine from its solution in zinc iodide diminish as the amount of free iodine present is increased.

It is also probable that the heat of solution of a constant quantity of iodine will vary with variations in the strength of the iodide of zinc.

Having thus stated what takes place in the cell, the question next to be decided is, whether the heat given out by these reactions corresponds exactly with the electromotive force of the cell.

Sir William Thomson, in publishing his formula connecting the electromotive force of a cell with the heat set free by the reactions taking place, assumed that this correspondence existed. Recent experiments have shown, however, that this is not a true assumption in many cases, and Helmholtz has recently treated the subject from a new point of view*.

The following is, as I understand it, the outcome of his work on chemical combination, in so far as it applies to finding the connection between the heats of combination and the electromotive force of the cell.

In general, when an infinitely small current de passes through a cell at a given absolute temperature θ, a certain amount of heat, dQ, must be supplied to or removed from the cell to keep its temperature constant, apart from the heat developed by the electric resistance of the liquid.

If the electromotive force of the cell corresponds exactly to the heat given out by the reaction taking place in the cell, then no heat need be added or removed.

Now the measurement of this cooling or heating of the cell would be difficult in practice, but, applying the second law of thermodynamics, Helmholtz obtains the following formula, showing that a measure of dQ can be obtained from the variations in electromotive force due to temperature—

$$\theta\frac{dp}{d\theta}de = \mathrm{J}dQ,$$

where dp is the variation in the electromotive force due to temperature.

It is necessary, then, in practice to measure the electromotive force of the cell experimented upon at different temperatures and to find the variation, if any, of the electromotive force.

In a cell of one volt electromotive force, at 300° ab. temp., a variation of ·0001 volt per deg. Cent. would mean a correction of ·03 volt or 3 per cent. to be applied before determining the heat of combination from the electromotive force.

The heat of combination can seldom be obtained with much accuracy from books on thermal chemistry, the conditions under which the reactions have been performed in the calorimeter differing considerably from the conditions in the cell.

For example, three numbers are given by Naumann as representing the heat of combination of zinc and iodine in presence of water—

1st. The heat of combination of zinc and iodine in water, 60540 calories.

2nd. The heat of solution of zinc iodide in water, 11310 calories ($ZnI_2, 400H_2O$).

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* *Die Thermodynamik Chemischer Vorgänger. Wissenschaftliche Abhandlungen*, von Hermann Helmholtz: Zweiter Band.

3rd. The heat of combination of zinc and iodine obtained by subtracting the second from the first, 49230 calories.

Now the first and second numbers are obviously average results, the zinc iodide formed dissolving in pure water at the beginning of the reaction, but in a strong zinc-iodide solution towards the end.

If care has been taken to use the same quantities of water and zinc iodide in both experiments, no doubt the third number represents fairly well the heat of combination of zinc and iodine.

The above criticism applies to Thomsen's book, though more details are usually given by him. It is consequently impossible to compare with exactness these numbers with those obtained by measuring the heats of combination in the iodine cell.

In the following experiments on the zinc-iodine and zinc-cuprous-iodide cell, I have used Professor Tait's Thomson electrometer to measure the electromotive forces obtained. Alder Wright recommends a high-resistance galvanometer for the purpose, which is certainly more delicate, but not more reliable, than this particular instrument.

About 50 divisions of the scale correspond to one volt, and it is possible to read to half a division.

As a standard of electromotive force a Daniell cell was used, made up according to the directions given by Alder Wright*, but specially constructed to make diffusion of the two liquids practically impossible. This cell has, according to Wright, an electromotive force of 1·107 volt.

To check this cell I used two Latimer-Clark cells, one made up to two years ago, the other made up quite recently. Taking Lord Rayleigh's recent determination of the electromotive force of this cell (1·454 volt), the three cells agreed with each other within the errors of experiment.

The electrometer was connected to a rocker so constructed that the zero of the instrument, the deflection due to the cell to be measured, and the deflection due to the Daniell cell could be noted one after the other. This was always done, and the numbers given at the end are always the mean of several readings. The Daniell did not alter at all from week to week.

When very small variations in electromotive force had to be measured, two or three cells were placed in series, and in some cases cells were connected to the electrometer through

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* 'Electrician,' Feb. 18, 1882. In recent papers Wright states the electromotive force of a Daniell cell, differing in some details, at 1·112 volt.

similarly constructed cells, especially to note the effects of temperature. No correction has been made for the new determination of the B.A. unit, as this affects both the electromotive force and the zinc dissolved by unit current. Consequently the error introduced in calculating from electromotive force to heat of combination is very slight*.

With the above apparatus the following experiments were made :—

1. Experiments to find the effect, on the electromotive force of the cell, of varying the nature of the zinc.

2. Experiments to find the effect, on the electromotive force of the cell, of varying the temperature of the cell.

3. Experiments to find the effect of varying the strength of the iodide of zinc solution. For these the cuprous-iodide cell was used, as simplifying the changes taking place in the cell.

4. Experiments on varying the strength of the free iodine present.

5. Experiments on varying the strength of the iodide of zinc solution in the iodine cell.

(1) In making measurements with the electrometer, the surface condition of the metals used is evidently of great importance, as so little current is drawn from the cell. If wet zinc is exposed to the air, it becomes coated with a film of hydrate, which perceptibly lowers the electromotive force of the cell.

I could find no difference between the deflections given by zinc electro-deposited from pure zinc, zinc "free from arsenic," zinc cleaned with sand-paper, zinc corroded by the iodine solution, and zinc with a freshly-broken crystalline surface. Probably, if two or three cells in series had been used, slight differences in electromotive force would have appeared, as is shown by Alder Wright's results with modifications of the Daniell cell†. It is well known that when a crystalline metal is treated with a weak acid, the crystalline structure is brought out by the dissolving of the crystals, which have been cut through in smoothing the surface of the metal, and there is, therefore, probably a slight difference of electromotive force between a smooth-filed zinc surface and a broken crystalline zinc surface. This difference, however, is too small to be shown on the electrometer with one cell.

(2) Two iodine cells in series, containing a dilute solution of iodine and of iodide of zinc, were raised from 10° C. to 50° C. No variation of electromotive force could be detected,

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* See Alder Wright's recent papers in the Phil. Mag. for 1885.

† Phil. Mag. Jan. 1885.

showing that the electromotive force does not vary ·0001 in 1° C.

Consequently the correction, if any, to be applied before calculating the heat of combination from the electromotive force is less than 2 per cent.

One iodine cell, made up with a saturated solution of iodide of zinc, was raised from 17° C. to 70° C. No variation of electromotive force could be detected.

(3) A series of measurements of the electromotive force of the zinc-cuprous-iodide cell, with varying strengths of iodide of zinc, was made. The amount of zinc iodide in each solution used was estimated by determining volumetrically the amount of combined iodine.

The temperature of the room during the experiments varied a little above and below 20° C.

The results of the observations are given in Table (*a*).

The lowest number given is that obtained in a saturated zinc-iodide solution; the highest is that obtained with only distilled water in the cell.

In every case zinc corroded in iodine solution, and then washed, was used. Some very minute traces of zinc iodide were therefore probably present in the distilled water, but probably this number should not be taken as being a trustworthy statement of the heat of solution of the first few molecules of iodide of zinc, until further experiments have been made. The next number obtained for a solution of ·003 grm. ZnI_2 in 1 grm. of water is probably safer as a starting-point for a curve.

Evidently the determination of the heat of solution of the first traces of a salt is difficult even by this method, though a much nearer approximation can be obtained than that possible in the calorimeter.

It was noticed, in the case of the stronger solutions, that on first placing the zinc rod, damp with distilled water, in the solution, the electromotive force of the cell was 2 or 3 per cent. too high, quickly falling to a constant value. This was no doubt due to the temporary dilution of a layer of liquid next the zinc, and the effect disappeared on drying the zinc with a filter paper.

On looking at the table, it is noticeable that the electromotive force falls off suddenly in a saturated solution. This is probably due to the separation of solid zinc iodide during the passage of the current.

(4) The variations in the electromotive force, caused by gradually increasing the amount of free iodine in a cell containing a constant amount of zinc iodide, are given in the Table (*b*).

The free iodine present was estimated with standard hyposulphite solution in the usual way.

This table requires no particular remark.

(5) Three determinations of the variation of the electromotive force of the zinc-iodine cell were made, due to varying the strength of the iodide of zinc, one in an iodine solution in distilled water, one in a zinc-iodide solution of medium strength, and one in a saturated iodide of zinc solution. The results are to be found in the Table (*c*)*.

If these numbers are subtracted from those obtained for corresponding solutions in the cuprous-iodide cell, the numbers obtained show that the curve for the zinc-iodine cell is slightly different, rising a little higher for distilled water, and not falling quite so low for saturated iodide of zinc.

TABLE (*a*).—Variations in Electromotive Force caused by varying the Zinc Iodide in solution as measured in the Zinc-Cuprous-Iodide Cell.

Electromotive Force in Volts.	Grms. of ZnI_2 in 1 grm. of Water.
·390	3·90
·415	3·90
·419	3·64
·425	2·87
·440	2·72
·454	2·49
·488	1·86
·545	·596
·607	·236
·637	·118
·656	·059
·696	·029
·771	·003
·894	D.W.

TABLE (*b*).—Variations in Electromotive Force caused by varying the amount of Iodine dissolved in a solution containing ·33 grm. of ZnI_2 in 1 grm. of water.

Electromotive Force in Volts.	Grms. of Iodine in 1 c. c.
1·287	·309
1·271	·155
1·271	·077
1·268	·037
1·259	·018
1·238	·005
1·221	·0006

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* Very similar results have been obtained for sulphates and chlorides by Alder Wright, Phil. Mag. 1884.

Table (*c*).—Variations in Electromotive Force caused by varying the strength of the Iodide of Zinc in a cell containing ·014 grm. of Iodine in 1 c.c.

Electromotive Force in Volts.	Grms. of ZnI_2 in 1 grm. of Water.
1·075	3·870
1·303	·118
1·594	D. W.*

On subtracting these from the cuprous-iodide numbers, we get

·686
·667
·719

Having now described the experiments, and given the results, I wish to make a few remarks upon them.

In the first place there are one or two points worth referring to with regard to this zinc-iodide curve. It will be noticed that the E.M.F. of solution for the first few traces of the salt is very high. This agrees with Prof. Helmholtz's experiments on zinc chloride, given in his second paper on the "Thermodynamics of Chemical Combination." In connection with that paper I may say that I propose to make measurements of the vapour-tension of zinc-iodide solutions, with the view of comparing them with the curve of E.M.F., as Prof. Helmholtz has done for zinc chloride.

One very curious point is the drop in E.M.F. for a saturated solution. This is no doubt due to the different physical conditions in the cell at this point, owing to the separation of solid zinc iodide; but it requires further investigation, as it is difficult to understand why the formation of the solid salt should lower the E.M.F. In all the calculations given below I have taken the value above ·390 volt, namely ·415 volt, as a starting-point for the values of y. With reference to this part of the curve, the two numbers, 3·9 grms., require explanation. The analysis of the very strong solutions with accuracy was difficult, and therefore, although the second solution was certainly just off the saturation-point, and the first solution contained solid zinc iodide (which was settled out before analysis), it seemed better to give the strength of the two solutions as the same, rather than to give numbers which lay within the errors of experiment.

I must also state that I have made no experiments to deter-

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* Iodine calculated to ·014 grm.

mine whether my strong solutions contained more complex compounds than ZnI_2.

In the next place, the electromotive force of an iodine cell containing an almost saturated solution of zinc iodide should correspond pretty closely with the calorimetric number for the heat of combination of zinc and iodine, as in this particular case the electromotive force due to the heat of solution of zinc iodide is eliminated.

Disregarding the portion of the iodine curve where the E.M.F. of solution of the iodine is considerable, as being too small a portion to affect materially the heat set free in the calorimeter, and taking the portion between 1·268 volt and 1·287 volt as being a straight line, we get the average E.M.F. of a cell containing ·33 grm. of ZnI_2 in 1 grm. of water as being 1·277 volt. This gives the E.M.F. of a cell with nearly saturated zinc iodide as 1·104 volt, a number probably too high, since the falling portion of the iodine curve has not been considered.

The value in volts of the number given by Naumann is 1·085 volt.

A more exact comparison is impossible as the strength of the iodine solution used in the calorimeter experiments is not given by Naumann.

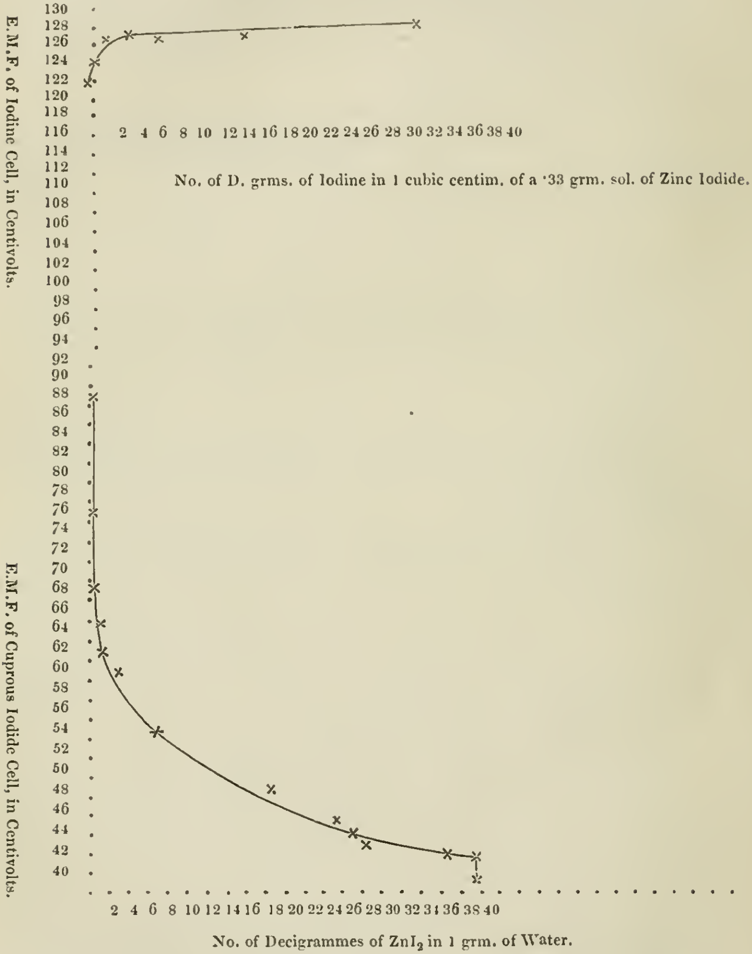
The calculation of the heat set free during the solution of a given quantity of zinc iodide in a given quantity of water can be easily made from the curve of E.M.F. If a cuprous-iodide cell be started with distilled water and allowed to run down, during the passage of the current zinc iodide will accumulate in the cell, and the E.M.F. will fall along the curve plotted in the diagram. At the same time the amount of zinc iodide dissolved during any time is a measure of the current that has passed through the cell.

We have only then to state percentages of zinc iodide in terms of unit current to calculate, by the integration of the curve, the quantity of heat set free during the solution of the zinc. It is necessary of course to take some value of E.M.F. as representing $y=0$, where y is the E.M.F. due to heat of solution only. It is probably best, as explained above, to take ·415 volt as the value corresponding to $y=0$.

If then $y=\phi x$ is the equation of this curve, then the heat of solution of ·044 grm. of zinc iodide in 1 grm. of water ($ZnI_2,400H_2O$) can be calculated from $\int_{\cdot 044}^{0} \phi x . dx$. Plotting this portion of the curve very carefully, and finding this area arithmetically, the value for the heat of solution ($ZnI_2,400H_2O$)

is found to be 13,000 calories. This is somewhat higher than Naumann's number.

Curves showing the E.M.F. of Solution of Zinc Iodide in Water, and of Iodine in Zinc Iodide.



It is evident from the above remarks and calculations, that any very close agreement between the numbers found in the calorimeter and those found in the voltaic cell, even on the assumption that Sir William Thomson's formula, $E = Je\theta$, is true, cannot as yet be expected, and that therefore any theories, based on the differences between these values, are at present meaningless.

Some of Dr. Alder Wright's recent work is thus open to criticism on account of his theoretical conclusions on the results of the comparison of his values with those found in the calorimeter. Another desideratum in his recent papers is the statement of the effects of temperature on the E.M.F. of his cells. Such measurements should always be made, especially since the publication of Prof. Helmholtz's mathematical researches already referred to.

This paper is only put forward as a preliminary investigation of the electromotive forces developed during the combination of zinc and iodine, and the difficulty of dealing with zinc iodide as a salt in solution must be my excuse for not producing final results on going over the ground for the first time.

XLII. *The Relations of Pressure, Temperature, and Volume in Saturated Vapours.* By W. C. Unwin, *M. Inst. C.E.*[*]

In the interesting and laborious paper of Messrs. Ramsay and Young, there are given four relations of a simple kind between the pressures, temperatures, and volumes of saturated vapours and the heat of vaporization of a number of substances. These relations are not given as exact relations, but as suggestive of laws approximately satisfied by very different substances over a very wide range of conditions.

Now long ago Hirn pointed out that, as for saturated vapours there exists only a single value of p and t corresponding to one specific volume v, there must be a direct relation between t and v, and between p and v, independent of p or t. But hitherto no exact relation has been found, and we remain still in the condition of being obliged in every thermodynamical calculation to fall back at every step on data either interpolated from tables of experimental values, or determined by the aid of purely empirical formulæ. Nor is this all: the formulæ are themselves cumbrous and are not interrelated.

Regnault's formula, giving p in terms of t for instance, cannot be inverted to get t in terms of p, though in practical calculations the pressure is almost always the given datum. Further, if differentiated to obtain $\frac{dp}{dt}$ an expression is obtained far too cumbrous for ordinary use. Rankine's formula is nearly as accurate, and is both simpler and gives an inverse function; but the expression for $\frac{dp}{dt}$ is cumbrous. The expression for latent heat is necessarily independent, but then

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[*] Communicated by the Physical Society; read February 27, 1886.

the density or specific volume ought to be expressed in terms of the formulæ for latent heat and pressure and temperature. But there being no simple expression for $\frac{dp}{dt}$ it is more common to resort to the quite independent empirical formula of Zeuner.

For purely scientific purposes no absolute difficulty or inaccuracy is caused, and no advance can be hoped for till rational expressions are found. When such expressions are found, also, it may probably prove, as Hirn surmises, that they will not have the simplicity which some people expect in all natural laws. The practical difficulty, again, can be surmounted by means of the tabulated values of p, t, $\frac{dp}{dt}$, calculated with great care and labour by Prof. Zeuner and Prof. Cotterill. Nevertheless the author thinks that some clearness would be introduced into the teaching of thermodynamics, and possibly some facility gained in practical calculations, if only amongst empirical expressions to which recourse must be had, one could be found accurate enough and yet so simple that all the related functions could be derived from it. The paper of Messrs. Ramsay and Young suggested an attempt in that direction.

It might be expected that the approximate relations stated by Profs. Ramsay and Young could be deduced from some of the empirical relations already established. This, however, is not strictly the case.

It is known for instance that the expression

$$p = \mathrm{AT}^{5\cdot 5},$$

where A is a constant and T is reckoned from an arbitrary zero, approximately satisfies the law connecting the pressure and temperature of saturated vapours.

Differentiating,

$$\frac{dp}{d\mathrm{T}} = 5\cdot 5\mathrm{A}\,\mathrm{T}^{4\cdot 5},$$

So that

$$\mathrm{T}\,\frac{dp}{d\mathrm{T}} = 5\cdot 5\mathrm{A}\mathrm{T}^{5\cdot 5} = 5\cdot 5p.$$

Consequently

$$\frac{\mathrm{T}}{p}\,\frac{dp}{d\mathrm{T}} = 5\cdot 5:$$

a relation which should be approximately satisfied for different vapours.

Thus, for instance, reckoning from the zeros given below we get from the values of $\frac{dp}{dt}$ in Messrs. Ramsay and Young's tables the following values of $\frac{\mathrm{T}}{p}\frac{dp}{dt}$:—

Substance ...	Bisulph. of Carbon.	Ethyl Alcohol.	Water.	Mercury.
Zero (Above −273°C)	144°.	208°.	210°.	322°.
Pressure in mm.				
100	5·913	5·323	5·183	5·243
500	5·749	5·616	5·794	5·598
1000	5·666	5·802	5·808	5·707
5000	5·201	5·540	5·645	......
10,000	......	5·429	5·503	......
20,000	......	5·291	5·302	......

At first sight it looks as if this were similar to the relation $t\frac{dp}{dt}$ = constant at any one pressure, given in Messrs. Ramsay and Young's paper. But, obviously, it is a quite different relation from the difference in the reckoning of temperature. It is, besides, a purely empirical relation, and the constancy of the values obtained may serve as a useful warning against accepting such correspondence of formula and data as indicating that the formula expresses a real law.

The principal relation discussed by Messrs. Ramsay and Young is that

$$t\frac{dp}{dt}$$

is constant for different vapours at the same pressure. In their table (Proc. Phys. Soc. vol. vii. p. 301*) values of this quantity, very carefully and laboriously calculated, are given for various vapours at pressures ranging from 10 to 20,000 mm. of mercury. It will easily be seen that the numbers in each horizontal line in their table approximate to constancy, varying in extreme cases by possibly 30 per cent.

If now these numbers are divided by the pressures so as to form values of

$$\frac{t}{p}\frac{dp}{dt}$$

the constancy of the horizontal lines of figures will remain unaffected, while the vertical columns will approach to constancy almost as nearly as the horizontal columns. The following table gives these values, with some of those for mercury corrected and with those for vapour of carbonic anhydride added:—

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* Phil. Mag. vol. xx. p. 526 (December 1885).

Values of $\frac{t}{p}\frac{dp}{dt}$ for different vapours.

Pressure in millims.	Carbon bisulphide, CS_2.	Ethyl bromide, C_2H_5Br.	Ether, $C_4H_{10}O$.	Chloroform, $CHCl_3$.	Mercury, Hg.	Sulphur, S.	Water, H_2O.	Ethyl alcohol, C_2H_5OH.	Carbonic anhydride, CO_2.
100	12·80	13·64	13·04	......	......	......	16·07	16·42	......
500	10·83	11·31	11·22	11·66	13·20	12·12	13·81	14·39	......
1000	10·10	10·37	10·51	10·85	11·89	11·20	12·95	13·83	......
3000	8·68	8·96	9·24	9·27	11·23	9·67	11·58	11·99	......
5000	8·22	8·26	8·66	8·46	9·73	......	10·89	11·29	......
10,000	......	......	......	......	......	......	10·03	10·39	7·62
15,000	.....	......	......	......	......	......	9·50	9·89	7·63
20,000	......	......	......	......	......	......	9·13	9·54	7·57
50,000	......	......	......	......	......	......	......	......	6·77

But now it may be pointed out that $\frac{t}{p}\frac{dp}{dt}$ is not a mere arbitrary expression for

$$\frac{t}{p}\frac{dp}{dt}=\frac{r}{Apu}$$

(Hirn, tom. i. p. 319). That is, it is the ratio between the total heat of evaporation and the heat expended in external work. What we have found, therefore, is that this ratio approaches constancy for widely different substances and under considerable differences of pressure. This approximation to constancy appears to me to lie at the basis of all the relations Messrs. Young and Ramsay have found.

The constancy of this ratio of internal and external work, for different vapours at one pressure, has been investigated by Messrs. Young and Ramsay from other data, but it does not seem to have occurred to them that it would be obtained in the simple way given above.

The author noticed that another relation, namely,

$$\frac{t^2}{p}\frac{dp}{dt},$$

gave values for each vapour, far more constant at different pressures than

$$\frac{t}{p}\frac{dp}{dt}.$$

The following table gives some of these values :—

Values of $\frac{t^2}{p}\,\frac{dp}{dt}$ for different vapours.

Pressure in millims.	Carbon bisulphide, CS_2.	Ether, $C_4H_{10}O$.	Mercury, Hg.	Sulphur, S.	Water, H_2O.	Ethyl alcohol, C_2H_5OH.	Carbonic anhydride, CO_2.
100	3426	3394	7053	......	5218	5049	......
500	3324	3329	7231	8437	4995	4909	......
1000	3313	3321	7247	8275	4932	4956	......
5000	3220	3233	......	7936	4745	4610	......
10,000	......	......	......	.....	4670	4528	1889
20,000	......	......	......	......	4570	4455	1991
50,000	......	......	......	......	......	......	2018

This suggested that probably an empirical relation of this kind could be found expressing the relation of pressure and temperature very simply and with considerable accuracy. Let, for instance, for steam the values of $\frac{t^{2\cdot25}}{p}\,\frac{dp}{dt}$ be formed. We get :—

t.	p.	$\frac{t^{2\cdot25}}{p}\,\frac{dp}{dt}$.
273	4·60	21660
298	23·55	21970
323	91·98	22020
348	288·5	21940
373	760·0	21870
398	1743·9	21830
423	3581·2	21790
448	6717·4	21770
473	11689·0	21950

Where the greatest and least values differ from the mean by only 0·7 per cent. But the expression, the values of which have been found, is integrable. Putting $n+1$ for the index of t, we get for a general approximate relation between the pressure and temperature of vapours,

$$\log_\epsilon p = a - \frac{\beta}{t^n}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

From this are easily derived the following equations, in which for convenience the logarithms are common logarithms.

$$\log p = a - \frac{b}{t^n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$t=\left(\frac{b}{a-\log p}\right)^{\frac{1}{n}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2\,a)$$

$$\frac{1}{p}\frac{dp}{dt}=2{\cdot}3025\,\frac{nb}{t^{n+1}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$=2{\cdot}3025n\frac{(a-\log p)^{\frac{n+1}{n}}}{b^{\frac{1}{n}}}. \quad . \quad . \quad . \quad (3\,a)$$

$$\frac{t}{p}\frac{dp}{dt}=2{\cdot}3025\,\frac{nb}{t^{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$=2{\cdot}3025n(a-\log p). \quad . \quad . \quad . \quad . \quad . \quad (4\,a)$$

For the latent heat, besides the ordinary formula,

$$\mathrm{L}=m-\frac{n}{(a-\log p)^{\frac{1}{n}}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

And consequently if v is the volume in cubic metres of the vapour and s that of the liquid,

$$v-s=\frac{\mathrm{JL}}{t\frac{dp}{dt}}$$

$$=\frac{13{\cdot}497\mathrm{L}}{pn(a-\log p)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In all these equations the quantity required is expressed simply in terms of the pressure or the temperature, a result not obtainable with the formulæ previously used.

Formulæ for Steam.

To test the value of these equations, the author has calculated the constants for steam most suitable for the complete range of Regnault's experiments, from −30° C. to 230° C., and from 0·4 millim. pressure to 20,000 millim. pressure. The proposal of a new empirical formula, and one not so accurate as Rankine's or Regnault's, for the relation of p and t in the case of steam, will probably appear the reverse of commendable. Still the fact that it gives a series of expressions, all directly derived from it, simple enough for ordinary use in engine calculations and accurate enough for practical purposes, is a strong reason in its favour. Its applicability can only be determined by testing its accuracy in a sufficient number of cases. In all the following calculations the calculated values are compared with the most accurate values thus far computed, over a range of pressure and temperature greater than would occur in practical cases.

The primary equation, derived from Regnault's data, for millimetres of mercury, Centigrade degrees reckoned from

$-273°$ C., and common logarithms is

$$\log p = 7{\cdot}5030 - \frac{7579}{t^{1{\cdot}25}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which gives

$$t = \left(\frac{7579}{7{\cdot}5030 - \log p}\right)^{\frac{4}{5}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

The following table gives the values of p calculated from t with Regnault's experimental values and values calculated by Rankine's formula for comparison :—

Temperature, Centigrade.	Temperature, absolute.	Pressure in millims. Regnault.	Pressure in millims. by formula.	Error in millims.	Pressure in millims. by Rankine.	Error in millims.
−30°	243°	0·386	·401	+ ·015	·35	−·036
−20	253	0·91	·982	+ ·072	·89	−·02
−10	263	2·08	2·229	+ ·149	2·07	−·01
0	273	4·60	4·709	+ ·109	4·47	−·13
5	278	6·53	6·69	+ ·16		
10	283	9·17	9·40	+ ·23	9·05	−·12
15	288	12·70	13·01	+ ·31		
20	293	17·39	17·83	+ ·44	17·33	−·06
25	298	23·55	24·07	+ ·52		
30	303	31·55	32·18	+ ·63	31·57	+·02
35	308	41·83	42·61	+ ·78		
40	313	54·91	55·72	+ ·81	55·05	+·14
45	318	71·39	72·24	+ ·85		
50	323	91·98	92·85	+ ·87	92·26	+·28
55	328	117·48	118·30	+ ·82		
60	333	148·79	149·48	+ ·69	149·15	+·36
65	338	186·94	187·50	+ ·56		
70	343	233·08	233·61	+ ·53	233·48	+·40
75	348	288·50	288·60	+ ·10		
80	353	354·62	353·59	−1·03	355·04	+·42
85	358	433·00	433·21	+ ·21		
90	363	525·39	523·48	−1·91	525·70	+·31
95	368	633·69	633·72	+ ·03		
100	373	760·00	757·35	−2·65	760·0	0
105	378	906·41	904·27	−2·14		
110	383	1075·4	1071·5	−3·9	1074·8	−·6
115	388	1269·4	1263·3	−6·1		
120	393	1491·3	1485·6	−5·7	1490·1	−1·2
125	398	1743·9	1735·4	−8·48		
130	403	2030·3	2020·2	−10·1	2028·0	−2·3
135	408	2353·7	2347·5	− 6·2		
140	413	2717·6	2710·2	− 7·4	2713·8	−3·8
145	418	3125·6	3114·6	−11·0		
150	423	3581·2	3564·5	−16·7	3575·5	−5·7
155	428	4088·6	4064·4	−24·2		
160	433	4651·6	4633·4	−18·2	4643·6	−8·0
165	438	5274·5	5262·6	−12·9		
170	443	5961·7	5941·6	−20·1	5951·2	−10·5
175	448	6717·4	6694·2	−23·2		
200	473	11689·0	11665·4	−23·6	11675·0	−14·0
230	503	20926·0	20951·7	+25·7	20945·0	+19·0

The following short table gives some values of t calculated from p :—

p.	t.	
	Calculated by (7a).	Observed.
4·60	272·7	273
91·98	322·8	323
760·00	373·2	373
3581·2	423·2	423
11689·0	473·1	473

The following are the derivative expressions. A few values are calculated from each and compared with the values very laboriously calculated by Zeuner from Regnault's formula.

$$\frac{1}{p}\frac{dp}{dt}=\frac{21815}{t^{2\cdot25}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$=\frac{(7\cdot5030-\log p)}{441\cdot3} \quad . \quad . \quad . \quad . \quad (8\,a)$$

t.	$\frac{1}{p}\frac{dp}{dt}$.	
	By formula (8).	From Zeuner.
273	·07201	·07150
323	·04932	·04979
373	·03567	·03577
423	·02688	·02685
473	·02090	·02083

$$\frac{t}{p}\frac{dp}{dt}=\frac{21815}{t^{1\cdot25}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$=2\cdot8782(7\cdot5030-\log p). \quad (9\,a)$$

t.	p.	$\frac{t}{p}\frac{dp}{dt}$.		From Zeuner.
		By equation (9).	By equation (9 a).	
273	4·60	19·659	19·69	19·52
323	91·98	15·929	15·94	16·08
373	760·00	13·304	13·30	13·34
423	3581·2	11·368	11·37	11·36
473	11689·0	9·890	9·89	9·85

The latent heat of vaporization has hitherto been expressed only in terms of the temperature by the empirical formula

$$L=796{\cdot}23-0{\cdot}695t, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

where t is the absolute temperature, and the smaller terms containing higher powers of t are omitted. From the relation between p and t we get

$$L=799-\frac{894}{(a-\log p)^{\frac{1}{5}}}. \quad . \quad . \quad . \quad . \quad . \qquad (10\,a)$$

t.	*p.*	L.		From Zeuner.
		By equation (10).	By equation (10 *a*).	
273	4·60	606·5	607·0	606·5
323	91·98	571·8	571·7	571·7
373	760·00	537·0	536·3	536·5
423	3581·2	502·3	501·0	500·8
473	11689·0	466·5	465·9	464·3

The new formula (10 *a*) is more accurate than the one (10) commonly used.

Let v be the volume in cubic metres of a kilogram of steam, and s the volume of the same quantity of water, usually taken at 0·001,

$$v-s=10{\cdot}821\,\frac{L}{p(a-\log p)}, \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

where p is still expressed in millimetres.

p.	*v—s.*	
	By equation (11).	From Zeuner.
4·60	208·7	210·6
91·98	12·14	12·05
760·00	1·652	1·650
3581·2	·3833	·3839
11689·0	·1255	·1257

Other Vapours.

The following equations may be useful. That for ether agrees extremely well. The mercury equation less well; but the errors are considerably less than those of Rankine's equation in his paper of 1850. The data are all from Regnault.

Alcohol:—

$$\log p = 7{\cdot}448 - \frac{8784}{t^{1\cdot29}}.$$

Ether:—

$$\log p = 6{\cdot}9968 - \frac{3047}{t^{1\cdot153}}$$

Mercury:—

$$\log p = 9{\cdot}8651 - \frac{597{\cdot}5}{t^{0\cdot69}}.$$

Carbonic acid:—

$$\log p = 8{\cdot}4625 - \frac{302{\cdot}8}{t^{0\cdot77}}.$$

XLIII. *The Law of Error and the Elimination of Chance. By* F. Y. Edgeworth, *M.A., Lecturer on Logic, King's College, London.*[*]

ONE of the principal uses of the Law of Error is to eliminate chance in cases like the following. The mean (or sum) of a set of observations[†] differs by a certain extent from an assigned value[‡]; usually that value which, upon the supposition that no disturbing cause other than chance had been at work, would be most likely to occur. It is required to determine the probability that the observed divergence is due to a disturbing cause rather than mere chance. The general method may be summarized as follows. Let x be the extent of observed divergence from the value most probable on the supposition of mere chance. The probability of this amount of divergence in an assigned direction (positive or negative) occurring by mere chance is approximately

$$\int_x^{\infty} \frac{1}{\sqrt{\pi}\,c} e^{-\frac{x^2}{c^2}} dx,$$

where c is a constant depending upon the number and character of the observations. To which is to be added a certain term outside the sign of integration, when we are dealing with discrete errors, as in Bernouilli's theorem, rather than with continuous quantity, as in the ordinary theory of errors of

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[*] Communicated by the Author.

[†] Or more generally *elements* subject to definite laws of facility; such as those which Mr. Galton supposes to obey individually the simplest binomial law, and by their composition to constitute an approximate probability-curve, such as we find *in rerum naturâ* (Phil. Mag. Jan. 1875).

[‡] Whether a fixed quantity or the mean (or sum) of another set of observations (or more generally *elements*).

observation. It is thus that Laplace determines the probability that the difference of a millimetre between the means of two sets of barometrical observations made at 9 A.M. and 4 P.M. respectively is due to a "constant cause," rather than mere chance. I have applied the method to a great variety of statistical inferences in a paper read before the Statistical Society this year.

In that paper[*], and elsewhere, I have discussed the general principles upon which the method is based. The subject of this paper is the particular case where the observed divergence is very great—so great as to raise a doubt whether the law of error upon which the whole theory turns is adequately fulfilled. For instance, in the example just cited from Laplace, the observed divergence much exceeds (as will presently[†] appear) the limit analogous to that which is ordinarily postulated in the application of the law of error to Bernouilli's theorem. It is attempted here to remove this scruple by proving the following propositions. The received formula is in general sufficiently accurate, or at least safe, in that it affords a superior limit to the probability of mere accident, an *à fortiori* argument in favour of law. But in a certain class of cases correction is required, and is attainable in a certain species of that class.

The subject may be divided according to the presence or absence of certain properties which frequently occur, and whose occurrence tends to the correctness or at least the corrigibility of the received formula. These properties are (α) the symmetry, (β) the finiteness, and (γ) the binomial character of that facility-curve, or more generally -locus, which represents the possible errors of an individual observation, or more generally of each of the *elements*[‡] of which the sum is our datum. The negatives of these attributes may be denoted thus :—$\bar{\alpha}, \bar{\beta}, \bar{\gamma}$.

$\alpha\,\beta\,\gamma$. According to this arrangement, the first case to be considered is that in which all the properties are present. This is that simple case of Bernouilli's theorem where the probability of both alternatives is the same, namely $\frac{1}{2}$. The interest of this theorem greatly transcends games of chance. For, as Mr. Galton has pointed out in this Journal[§], the laws

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[*] "Methods of Statistics," Journal of Statistical Society, Jubilee Number, 1885. "Observations and Statistics," Cambridge Phil. Soc. 1885. "On the Method of ascertaining Variations . . . . . ." read before the British Association, 1885; published in the Journal of the Statistical Society, January 1886; Proceedings of the Society for Psychical Research, parts viii. and x.

[†] Below, pp. 311, 317.

[‡] See note to p. 308.

[§] Phil. Mag. Jan. 1875.

of error which occur *in rerum naturâ* may very generally be regarded as Binomials.

It suits our purpose to take as the quæsitum not as usual * the probability of one of the events occurring within certain limits on either side the greatest term, but the probability that the divergence from the greatest term should exceed a given limit in an assigned direction; in short, one of the extremities rather than the body of the curve or locus under consideration. In this inquiry let us take Poisson † for our guide. And according to his notation let us call the total number of trials μ, the observed number of successes m, the number of failures n.

It is shown by Poisson that the probability of obtaining at least m successes, at most n failures, may be represented by a certain fraction, of which the numerator and denominator are both integrals; the subject of integration being the same for both, but the limits different. The subject of integration is of the form

$$\mathrm{H}e^{-t^2}(h' + 2h''t + 3h'''t^2 + \&c.),$$

where h', h'', &c. constitute a descending series, if, as usual, μ, m, and n are large. In order that the quotient of the integrals should converge, a further condition must be fulfilled by the inferior limit of the numerator, which Poisson calls k. This limit is found by substituting $\frac{1}{2}$ for p and q in the following expression—

$$n \log \frac{n}{q(\mu+1)} + (m+1) \log \frac{m+1}{p(\mu+1)},$$

and extracting the square root. If we actually perform the work of integration and division, we shall find that the result consists of two portions, one under the sign of integration which does not explicitly contain k, and one outside the sign of integration affected with k after this wise,

$$e^{-k^2}[\lambda' + \lambda''k + \lambda'''k^2 + \ldots],$$

where $\lambda', \lambda'', \lambda''' \ldots$ are of the same order respectively as $h', h'', h''' \ldots$, that is $\frac{1}{\mu^{\frac{1}{2}}}, \frac{1}{\mu}, \frac{1}{\mu^{\frac{3}{2}}} \ldots$ In order that the above expression should converge it is necessary that the order $\frac{k}{\mu}$ should be fractional.

If we have $\frac{k}{\mu}$ of the order $\frac{1}{\mu}$, k of the order unity, we shall

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* *E. g.* Todhunter, art. 993.

† *Recherches sur la probabilité*, chap. 3.

have the usual degree of approximation,* in which the lowest terms rejected are of the order $\frac{1}{\mu}$. This condition may be thus translated into the usual postulate, that the excess should not exceed the order $\sqrt{\mu}$. Expanding k in terms of ρ, where $\rho = \frac{\mu+1}{2} - n$, we have

$$\frac{\rho}{\sqrt{\frac{\mu}{2}}}\left\{1 + \frac{1}{12}\frac{\rho^2}{\left(\frac{\mu}{2}\right)^2} + \&c.\right\}.$$

Now, when ρ is of the order $\sqrt{\frac{\mu}{2}}$, since terms of the order $\frac{1}{\mu}$ may be neglected, we have k of the order unity. But, when ρ exceeds the order $\frac{1}{\sqrt{\mu}}$, since k increases with ρ, k exceeds the order unity. Hence the ordinary limitation is from this point of view perceived to be both sufficient and necessary.

It is more important for our purpose to show that the ordinary formulæ of approximation hold good far beyond the limit ordinarily prescribed, not of course with what may be called the regulation degree of precision (where the smallest order neglected is $\frac{1}{\mu}$), but with sufficient precision for practical purposes. Suppose ρ is of a higher order than $\sqrt{\mu}$, *e.g.* $\mu^{\frac{3}{4}}$; then k is of the order $\mu^{\frac{1}{4}}$. The series $\lambda' + \lambda'' k + \&c.$ is still convergent. It is still possible to simplify our formula by expanding k and neglecting terms of the order $\frac{k^2}{\mu^2}$. And the further simplification which is necessary to reduce Poisson's first formula to the more usual one given, *e.g.* by Mr. Todhunter, is still allowable. We have thus for a first approximation to the sought probability,

$$\dagger\ \frac{1}{\sqrt{\pi}}\int_{\tau}^{\infty} e^{-t^2}\,dt + \frac{1}{\sqrt{2\pi\mu}}\,e^{-\tau^2};\ \text{where } \tau = \frac{\rho}{\sqrt{\frac{\mu}{2}}}$$

(the Poissonian ‡ u for the case of symmetry).

For a second approximation we have the more rugged formula, from which Poisson reasons downwards,

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[*] *Cf.* Todhunter, *loc. cit.*

[†] This expression for the tail of the binomial locus is deducible from Mr. Todhunter's formula for its body (History, art. 993).

[‡] *Ibid.* art. 79.

$$\frac{1}{\sqrt{\pi}}\int_k^{\infty} e^{-t^2}\,dt + \frac{(\mu+n)\sqrt{2}}{3\sqrt{\pi\mu m n}}\, e^{-k^2};$$

where $k^2 = n\log\frac{2n}{\mu} + (m+1)\log\frac{2(m+1)}{\mu}$ and k is to be taken positively, when, as here supposed, n falls short of $\frac{\mu}{2}$.

Take for example $\mu=1000$, $m=700$, and therefore $n=300$, the divergence 200 far exceeding the regulation limit, which is the order $\sqrt{500}$. By the first approximation we have $\tau^2=80$, and for the *quæsitum*,

$$\frac{1}{\sqrt{\pi}}\, e^{-80}\left[\frac{1}{2\sqrt{80}}+\frac{1}{\sqrt{2000}}\right];$$

that is, about 10^{-36}, or (writing $\cdot 0^x$ for x ciphers following a decimal point) $\cdot 0^{36}7$. By the second approximation I find $\cdot 0^{37}6$. And by another method which will be explained[*] below I find for inferior and superior limits of the quæsitum $\cdot 0^{37}5$ and $\cdot 0^{37}67$.

In proving this conclusion we have had the advantage of knowing *explicitly* the probability of any degree of divergence. It is instructive to consider how we should have proceeded without this start. We should then have had to resort to methods of approximation analogous to those which are applied to the general theory of errors of observation. The following is, I think, the analogue of Laplace's procedure. Consider the expression

$$\left[\frac{e^{+\sqrt{-1}\theta}+e^{-\sqrt{-1}\theta}}{2}\right]^{\mu}\cos x\,2\theta \quad (\mu \text{ even}).$$

If it is integrated between the limits π and 0, all the terms other than the xth from the centre vanish. Hence we have

$$\frac{1}{\pi}\int_0^{\pi}(\cos\theta)^{\mu}\cos 2\theta x\,d\theta$$

for the probability of the particular divergence x. By the ordinary reasoning this expression is to be reduced to the form $\frac{1}{\sqrt{\pi\frac{\mu}{2}}}\, e^{-\frac{2x^2}{\mu}}$, which is to be summed between limits x and ∞; the process of summation, Σ, as contrasted with the usual $\int$, introducing a term outside the sign of integration.

There is another form perhaps better suited to the present purpose, the investigation of the limits of correctness. This

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[*] See p. 321.

is the method employed by the present writer in a former number of this Journal *, not without reference to the kindred work of Mr. Morgan Crofton. The essential feature of this method is a partial differential equation which must be fulfilled by the general expression for the probability of divergence x. In the case of a binomial let u_{sx} denote that probability, where s, an integer, $=\frac{1}{2}\mu$, and consider the formation of $u_{s+1,x}$. We have

$$u_{s+1,x}=\tfrac{1}{4}(u_{s,x-1}+2u_{sx}+u_{s,x+1}).$$

Whence

$$\Delta_s u=\tfrac{1}{4}\Delta_x^2 u_{x-1}\,;$$

an equation in finite differences which may under certain provisos be reduced to the differential equation

$$\frac{du}{ds}=\frac{1}{4}\frac{d_2u}{dx^2}\,;$$

an appropriate solution of which is found to be

$$\frac{1}{\sqrt{\frac{s}{2}\pi}}\,e^{-\frac{2x^2}{s}}.$$

In order that this solution should satisfy the equation in finite differences with a precision which retains quantities above the order $\frac{1}{\mu}$, it will be found necessary that x^2 should not exceed $\frac{s}{2}$. But in order that *some* degree of precision should be attained, it is sufficient that x be of an inferior order to $\frac{s}{2}$, *e.g.* $\left(\frac{s}{2}\right)^{\frac{3}{4}}$. Thus from this point of view also it is seen that the received formula is fairly accurate beyond the regulation limit.

And further, when it ceases to be accurate, it still remains safe: inasmuch as it affords a value *superior* to that of the real probability of mere accident; and therefore underrates the evidence in favour of the *demonstrandum*, the existence of a disturbing cause other than chance. To show this it is almost sufficient to compare the extreme term of the binomial locus with the corresponding ordinate of the probability curve. The Napierian logarithm of the former is $-\mu\log_e 2$; that of the latter $-\frac{\mu}{2}-\frac{1}{2}\log\frac{s}{2}-\frac{1}{2}\log\pi$. The latter is therefore greater than the former, and the curve has left the discontinuous locus *underneath* it before it reaches the extreme region of the locus.

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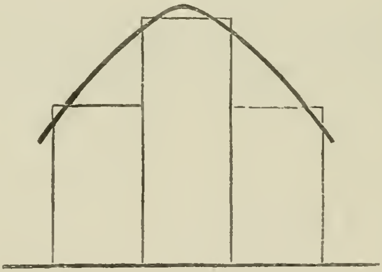
* Oct. 1883.

This conclusion may be confirmed by comparing the explicit expressions for the height of the respective loci at any point. Take the common centre of the two loci as origin of coordinates; then the binomial locus consists of a set of rectangular columns standing each on a base of unit length, the tallest at the centre. The general expression for the height of a column is

$$\frac{\underline{|\mu}}{\underline{|\frac{\mu}{2}+x}\;\underline{|\frac{\mu}{2}-x}}\;\frac{1}{2^{\mu}}.$$

This is to be compared with the corresponding ordinate of the probability-curve, or rather what that ordinate becomes when for x we put $x+\frac{1}{2}$. Otherwise, though the height of a column is less than the height of the ordinate, we cannot be sure that the curve has swept clear of the discontinuous locus. In fact it will be found that the centre of the central column (μ even, as in the accompanying figure) is less than the central ordinate of the curve, but that the curve strikes the column between $x=0$ and $x=\frac{1}{2}$. And for a long way the curve continues thus to hug the discontinuous locus. Put η for the logarithm of the ordinate at the point $x+\frac{1}{2}$, diminished by the logarithm of the height of column x; and let $x=\left(\frac{\mu}{2}\right)^{1-\alpha}$ $(\alpha<1)$. Expanding we have



$$\eta=\frac{1}{6}\left(\frac{\mu}{2}\right)^{1-4\alpha}-\frac{1}{4\mu}-\frac{1}{\left(\frac{\mu}{2}\right)^{2\alpha}}-\frac{1}{\left(\frac{\mu}{2}\right)^{\alpha}};$$

a quantity which, μ being large, is apt to become positive as soon as α is less than $\frac{1}{4}$; that is after x has attained the value $\left(\frac{\mu}{2}\right)^{\frac{3}{4}}$. This conclusion may be completed by observing the course of $\frac{d\eta}{dx}$ and $\frac{d_2\eta}{dx^2}$. It will be found that when μ is large the latter very early becomes positive, and the former after x has attained the value $\left(\frac{\mu}{2}\right)^{\frac{1}{2}}$. We thus conclude that the probability-curve disengages itself from the binomial locus long before the extreme region of the locus is attained, and sweeps on to infinity *above* the binomial locus. The approximation is therefore safe when it ceases to be accurate.

$\alpha\,\beta\,\bar{\gamma}$. The conclusions which have been proved for symmetrical binomials may be extended to the whole class of symmetrical finite facility-curves. Here we have not in general the advantage of starting from an explicit[*] knowledge of the probability that any particular degree of divergence would occur—the general term of what may be called the compound facility-curves. An explicit form may, however, be attained for some of the simpler cases by the method of Lagrange, which Mr. Todhunter cites[†]. Consider the simplest case of all (after the binomial), that in which the elementary facility-locus consists of a rectangle of base $2a$, and therefore of height $\frac{1}{2a}$—one value being as likely as another between the limits $\pm a$. Lagrange gives the facility-curve, which is formed by adding n values taken at random from under this elementary facility-curve, or according to this law of possibility[‡]. The general expression is somewhat

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[*] *Cf.* above.

[†] P. 301 and following.

[‡] Lagrange's theorem may thus be proved by way of an equation of mixed differences. Let Mr. Todhunter's $b=0$, and accordingly his $c =$ his t; $=$ our $2a$. Let his $K =$ our $\frac{1}{2a}$. The primary facility-curve consists of a rectangle whose base is $2a$ and height $\frac{1}{2a}$, and whose left base angle is at the origin. The compound facility-curve extending to the right is such that its ordinate u_{sx} represents the probability that, if s values be taken at random from the primary facility-locus, their sum will lie between x and $x+dx$; s and x corresponding to Mr. Todhunter's x and z respectively. Observing the transition from u_{sx} to $u_{s+1,\,x}$, we have

$$\frac{1}{2a}\int_x^{x+2a} u_{sx}\,dx = u_{s+1,\,x+2a}.$$

Put $$D_x u = u_{x+2a}; \quad D_s u = u_{s+1}.$$

Differentiating both sides of our equation, we have

$$\frac{1}{2a}(D_x - 1)u = \frac{d}{dx} D_s D_x u,$$

$$D_s u = \frac{1}{2a}(D_x - 1)\left(\frac{d}{dx}\right)^{-1} D_x^{-1}\,.\,u,$$

$$u = \left(\frac{d}{dx}\right)^{-s}\left(\frac{1}{2a}\right)^{s}.\,[1 - D_x^{-1}]^s \phi(x) =$$ (*cf.* Boole, 'Finite Differences,' chap. x. art. 2)

$$\left(\frac{1}{2a}\right)^{s}\left(\frac{d}{dx}\right)^{-s}\left\{\phi(x) - s\phi(x-2a) + \frac{s(s-1)}{1\,.\,2}\phi(x-4a) - \&c.\right\}$$

Observing the initial case when $s=2$, we shall find that this expression reduces to Lagrange's.

unmanageable, but it reduces to a few and ultimately to a single term at the extremity of the compound curve. That term is (*mutatis mutandis*)

$$\frac{1}{(2a)^n\ \underline{n-1}}\left[\frac{n}{2}-x\right]^{n-1},$$

for the equation of the curve between the points $x=\frac{n}{2}$ and $x=\frac{n}{2}-1$, the origin being taken at the central point of the curve, and n supposed even. Let us compare now the height of this portion of curve with the height at the same region of the ancillary probability curve, of which the equation is

$$y=\frac{1}{\sqrt{n\frac{2}{3}a}}\ e^{-\frac{x^2}{n\frac{2}{3}a^2}}.$$

Put for x $\frac{n}{2}a$, and the extreme ordinate becomes

$$\frac{1}{\sqrt{n\frac{2}{3}a}}\ e^{-\frac{3}{8}n}.$$

The logarithm of the reciprocal of this quantity is of the order n; while the logarithm of the compared quantity's reciprocal is of the order $(n-1)\log(n-1)+n\log(2a)$. Neglecting the second of these terms, since $2a$ may be supposed of the order unity, we see that the representative probability-curve is well above the real facility-locus. And this being true of the particular case under consideration, the rectangle, is *à fortiori* true for all other finite symmetrical facility-curves which fulfil the usual condition of descending from the centre. Hence it is safe for extreme degrees of divergence to use the tail of the probability-curve as the measure of the probability in favour of mere chance.

To investigate the accuracy of the approximative form for moderate degrees of divergence, we must leave the explicit expression, and have recourse to the analogues of the methods employed at p. 313. If the elementary facility-curve be $y=f(z^2)$ between limits $\pm b$, then the general term of the compound fulfils the condition

$$u_{s+1,x}=\int_{-b}^{+b}f(z)\,u_{sx}dx.$$

And this condition (with the other requisites of a symmetrical* facility-curve) is approximately satisfied by the expression

$$\frac{1}{\sqrt{\pi s}\,c}\ e^{-\frac{x^2}{sc^2}};$$

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* See my paper on "Observations and Statistics," Cambridge Philosophical Society Transactions, 1885, p. 142.

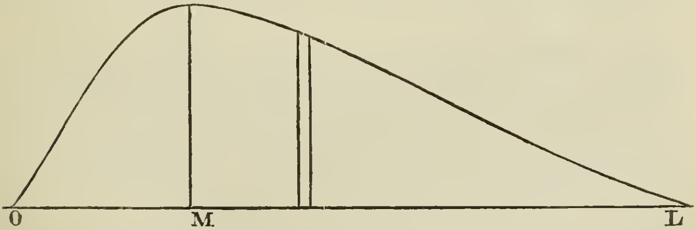
provided that the powers of $\frac{x}{s}$ constitute a descending series. Hence it may be concluded that the probability-curve is for a long way a fairly accurate representative of the real locus.

It continues for a long way accurate and it is ultimately safe; and though we have not proved that between the accurate tract and the safe tract there may not intervene a tract without either of those attributes, still I think the analogy of the binomial-curves may justify us in jumping over this interval, and asserting generally that the received formula is either accurate or at least safe.

In forming this conclusion for symmetrical finite facility-curves, we have proved the greater part of our thesis*. For it will be admitted that the remaining cases are exceptional. The most important remaining class is that of finite unsymmetrical $\alpha\bar{\beta}$. This may, like the symmetrical finite class, be divided into binomial and non-binomial.

$\alpha\bar{\beta}\gamma$. The binomial species has an interest beyond games of chance in so far as it may be regarded as the type of the laws of error which occur *in rerum natura.* Here arises the question: given a set of observations unsymmetrically grouped (such as the entries in the column d_x of a Life-table between the ages of 50 and 100), how shall we reason back from this composite datum to the elementary binomial from which it is assumed to have sprung? How shall we perform the analogue of the operation which Mr. Galton† performs for symmetrical binomials, when he calculates the number and extent of the elements which underlie a given set of statistics.

Let us first get a clear idea of the problem. What we are given is a set of n observations grouped unsymmetrically as in the accompanying figure, where the ordinates of the curve represent the number of measurements corresponding to each degree of the base. Let the observations range from O, which we will call zero, over a length l to OL. It is assumed



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* P. 309.

† Phil. Mag. Jan. 1875, p. 43.

that the phenomenon observed is thus generated; there are taken at random n elements, each of which may have either the value zero or a, but not with equal probability; the chance of zero being p, the chance of a (say greater) q. The probability that the sum of n such elements should have the value na would of course be given by the binomial law. Now we have to determine, upon the hypothesis made, both n and a. For a first equation we have (1) $na=l$. A second equation is afforded by the *probable error* of the observed group; for, as will appear presently, any binomial locus is accurately represented by the ancillary probability-curve up to the probable error, and indeed as far as what Mr. Galton calls the decile. Therefore we may equate the observed probable error to $\cdot 475c$, where c is the modulus of the ancillary probability-curve. But the modulus of this curve is in terms of n and a $\sqrt{2pqn}\,a$, p and q are given when M, the point of maximum ordinate, is observed; for $p:q::\text{OM}:\text{ML}$. Thus then we are given the value of $\sqrt{n}\,a$; let it $=k$. From this equation combined with the first we have $a=\frac{k^2}{l}$, $n=\frac{l^2}{k^2}$.

It may be objected to this reasoning that one of the data, the distance between extreme limits, l, is apt to be very inaccurate. It will be found, however, that the error introduced is on the safe side, causing the evidence in favour of law to appear less than it really is.

It may be assumed then that a large proportion of unsymmetrical cases are reducible to the general form of Bernouilli's theorem. In discussing this form, let us again take Poisson as our guide. By parity of reasoning we shall still find Poisson's* formula (15) a sufficiently good approximation, provided that the powers of $\frac{k}{\sqrt{\mu}}$ constitute a descending series. But the further reductions by which we descend from k to the Poissonian u, the Todhunterian τ, must now be employed with great caution; in fact the formula given in most of the derived authorities is confessedly applicable only to the *body*, not the extremity, of the binomial-curve. Applied to the latter it gives a value which is neither accurate to the *extent*, nor in the *degree*, which might be supposed. It is accurate over a range of divergence, not so much of the order $\sqrt{\mu}$, but $\sqrt{2pq\mu}$—a serious correction when the asymmetry is very great. And the degree of accuracy is measured not by the

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* Art. 77.

neglect of terms of the order $\frac{1}{\mu}$, but terms of the order $\frac{1}{\sqrt{2pq\mu}}$. For that is the order of the first term* of k's expansion, which vanished in the symmetrical case, but now makes itself felt. Among derived authorities the only one known to me who has called attention to this point is Prof. Lazarus, in a paper "*On some Questions* . . ." in the 15th vol. of the 'Assurance Magazine' †. In short for other than small divergences the formulæ in the text-books are apt to be unsuited to our purpose ‡, the determination of the probability that a given divergence in an assigned direction would have occurred by mere chance.

The conclusion that asymmetry diminishes the range and the degree of accuracy may be verified by that method of approximation which proceeds by way of a partial differential equation§.

Let the odds be $\alpha : \beta$ where α and β are integers. Let $\mu = s(\alpha + \beta)$; and put u_{sx} for the xth term from that which is the greatest. Consider the formation of $u_{s+1,\,x}$; it is thus made up:

$$u_{s+1,\,x} = u_{s,\,x-\alpha} \times \alpha^{\alpha+\beta} + (\alpha+\beta)\, u_{s,\,x-(\alpha-1)} \times \beta\alpha^{(\alpha-1)+\beta} + \&\text{c.}$$
$$+ (\alpha+\beta) u_{s,\,x+(\beta-1)} \times \alpha\beta^{\alpha+(\beta-1)} + u_{s,\,x+\beta}\beta^{\alpha+\beta}.$$

Expanding as before, we have

$$u + \frac{du}{ds} = u(\alpha+\beta)^{\alpha+\beta} + \mathrm{B}\,\frac{du}{dx} + \tfrac{1}{2}\mathrm{C}\frac{d_2u}{dx^2};$$

where B is the mean error of the binomial $(\alpha+\beta)^{\alpha+\beta}$ about its centre of gravity, and C is the mean square of error about the same point. The first coefficient vanishes ||, and the second

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[*] Poisson, art. 78.

[†] The correction which he derives from Poisson is accurate only for a very limited extent of divergence.

[‡] I have treated the case of unsymmetrical Binomials more fully in the 'Journal for Psychical Research,' part x.

[§] Above, p. 313.

[||] These propositions, if they are not already known, may thus be proved. Put

$$p = \frac{\alpha}{\alpha+\beta}, \quad q = \frac{\beta}{\alpha+\beta}, \quad \mu = \alpha+\beta.$$

The centre of gravity of the binomial locus $(p+q)^{\mu}$, measured from one extremity is

$$\Sigma \frac{|\underline{\mu}}{|\underline{m}\;|\underline{\mu-m}}\, p^{m} q^{\mu-m} \times m,$$

[Over.

is equal to $\frac{\alpha\beta}{\alpha+\beta}$. Whence it follows that the modulus of the representative probability-curve tends to be small when $\alpha:\beta$ is very small; and therefore that the range throughout which the approximation holds is, *cæteris paribus*, less. Also for the same range the degree of approximation is less. For in the case of symmetry the equation above written is satisfied up to and inclusive of the term involving $\frac{d_3u}{dx^3}$ by the solution of $\frac{du}{ds}=\frac{1}{2}\text{C}\frac{d_2u}{dx^2}$. But in the case of asymmetry that term does not vanish. Hence, even though x is within the regulation limits, yet u_{x_s} is accurate only up to the order $\frac{1}{\sqrt{s}}$, not $\frac{1}{s}$. In order to obtain the latter degree of accuracy we should have to add together the nth terms on both sides of the greatest term of the binomial, as is done in the books (*e. g.* Mr. Todhunter). For in that case the third term of expansion would vanish.

But though apt to be incorrect, the received formula is in the case of the binomial corrigible. With regard to the degree of accuracy, it is necessary, in order to obtain the regulation precision, to add to the argument of the probability-curve the τ[*] of Mr. Todhunter, the second[†] term of the expansion of k; and this even when the regulation extent of range is

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(where m has every integer value from 0 to μ),

$$=\mu p\times\Sigma\frac{|\underline{\mu-1}}{|\underline{m-1}\,|\underline{\mu-m}}p^{m-1}q^{\mu-m}=\mu p.$$

Whence the first proposition.

Again,

$$\Sigma\frac{|\underline{\mu}}{|\underline{m}\,|\underline{\mu-m}}p^{m}q^{\mu-m}\times m^2$$

$$=\mu p\Sigma\frac{|\underline{\mu-1}}{|\underline{m-1}\,|\underline{\mu-m}}p^{m-1}q^{\mu-m}\times m$$

$$=\mu p\,\Sigma\frac{|\underline{\mu-1}}{|\underline{m-1}\,|\underline{\mu-m}}p^{m-1}q^{\mu-m}\times(m-1)+\mu p\Sigma\frac{|\underline{\mu-1}}{|\underline{\mu-1}\,|\underline{\mu-n}}p^{m-1}q^{\mu-m}$$

$$=\mu(\mu-1)p^2+\mu p=\mu^2p^2+\mu p(1-p)$$

$$=(\text{C. G.})^2+\mu pq.$$

Whence the second proposition.

[*] Or more exactly to Poisson's u, which is not quite the same as Mr. Todhunter's τ.

[†] Poisson.

not exceeded. With regard to the range or extent of divergence with which we are here more particularly concerned, when this is large it will be found necessary to desert altogether the neighbourhood of the received formula, and revert to Poisson's earlier formula *, where the argument of the probability-curve is the unreduced k (written above, p. 310), and the expression outside the sign of integration is the unreduced one written on p. 312. This incorrectness and corrigibility may be illustrated by the following example. Let $\mu=999$, $p=\frac{1}{10}$, $m=299$, $n=100$. Here the current, as contrasted with the unreduced formula, exaggerates by trillions of times the improbability of the observed divergence being due to accident—the odds in favour of a disturbing cause. For the τ^2 of the former formula is 222·4, giving as the value of the probability of mere chance about 10^{-98}. Whereas k^2, which measures the order of the sought probability according to the unreduced formula, is 153·7. And the corresponding value of the quæsitum is 10^{-68}, which is correct to its last decimal.

I have verified this calculation by the following simple process, which has the advantage of being most efficacious just when the received methods are least so: when the asymmetry and the divergence are great. The sought probability may be written

$$p^m q^n \times \frac{\underline{|\mu}}{\underline{|m}\,\underline{|n}}\left[1+\frac{p}{q}\times\frac{n}{m+1}+\frac{p^2}{q^2}\,\frac{n(n-1)}{(m+1)(m+2)}+\&c.\right].$$

If p is small and n less than μq, m greater than μp, as in the case which presents difficulty, that of the longer limb, the second term within the brackets is fractional, say $=r$. The third term is less than r^2. Hence we have a convergent series, which converges the more rapidly the less p and n are, the greater the asymmetry and divergence. For a superior limit we have the geometric series $1+r+r^2$ &c. multiplied by the term outside the brackets; for an inferior limit that term alone.

The formula given in the text-books is quite inadequate to deal with such extreme cases. And not only is it accurate only for a short range, but also when it ceases to be accurate, it ceases to be secure. For, as before, compare the extreme term with the corresponding ordinate of the probability-curve. The former is now p^μ. The (Napierian) logarithm of the latter is

$$-\frac{q}{2p}\mu-\tfrac{1}{2}\log 2pq\mu-\tfrac{1}{2}\log\pi.$$

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* *Ibid.* (15)

If we compare $-\frac{1-p}{2p}\mu$ with $\mu\log_e p$, we see that as p diminishes from $\frac{1}{2}$, the first exponent soon becomes, and constantly continues, of a lower order than the second. Hence at the extremity of the longer limb of the binomial the probability-curve does not escape free from the binomial. It is otherwise at the extremity of the shorter limb. These conclusions may be verified by examining the explicit general terms of the compared *loci*. It will be found now that, as regards the longer limb, it is not in general possible to expand in terms of $\frac{\rho}{\mu p}$ (where ρ is the divergence from the central point, the position of the largest term). For ρ may be greater than μp. And if we examine* the differentials of η, we shall find that $\frac{d_2\eta}{d\rho^2}$ is apt to be continually negative and large.

$\alpha\bar{\beta}\bar{\gamma}$. The inaccuracy and insecurity which have been proved for the binomial species of asymmetry may be extended by parity of reasoning to the other species, multinomials and continuous facility-curves. But the attribute of corrigibility is less easily generalized. First, it is to be observed that in case of asymmetry the modulus of the ancillary probability-curve is apt to be small. This may be shown by induction from particular hypotheses, like that which is indicated by the accompanying figure, where O is the centre of gravity, and the sum of the rectangles erected on O P and O Q is unity. The modulus squared = twice sum of squares of error

$$=\tfrac{2}{3}(OQ^3Qq + OP^3Pp),$$

where $\frac{1}{2}OQ^2Qq = \frac{1}{2}OP^2Pp$ and $OQ \times Qq + OP \times Pp = 1$. Also PQ, the total range, is finite, say of the order unity. Whence if OP is small, the modulus is small. This proof may be thus generalized:—The curve being huddled asymmetrically, the mean error for the short limbs must be small. But it is equal to the mean error for the other limb. Therefore the total

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* See above, p. 314.

mean error is small. But if the total range is unity, the mean square of error is less than the mean error. Whence the proposition. Also the Lagrangian * method may be applied to the investigation of explicit expressions for the extreme terms of the compound facility-curve. Comparing these extreme terms with the corresponding ordinates of the representative probability-curve, we see that the former are apt to be of a higher order than the latter. Hence the representative curve does not in general disengage itself from the real locus before the extremity of the latter has been reached. The received formula, therefore, does not afford a superior limit to the probability of the observed divergence occurring by chance. Again, by parity of reasoning, by way of a partial differential equation, it may be seen that when the modulus is small, *cæteris paribus*, the range and degree of accuracy is diminished. But a remedy for this defect is not attainable, owing to the unmanageability of the explicit expression for the general term.

α. There remains the class of infinite facility-curves. This is of the less importance in that the attribute infinity must be construed strictly in order that the class should be exceptional. If it is merely meant that the range of the elementary facility-curve is *very large*, then the peculiarities which I have elsewhere † ascribed to this class will not occur. Consider, for example, the curve $y=\frac{1}{\pi(1+x^2)}$. If it is merely meant that this form holds for a long way, then it constitutes no exception to the law of convergence that the arithmetical mean has a less dispersed facility-curve than the primary or elementary curve. Convergence will set in at once and continue until any assigned extent of the original form has been converted into that of the probability-curve. It is not easy to understand how such strictly infinite errors as here postulated can exist in observations or statistics. The only case in which it occurs to me that such forms might arise is where the registered "errors" or variations are not the raw material of observations, but *functions* of a datum given by observation, and where the function becomes infinite for certain finite values of its variable. Suppose, for example, an angle θ to be the direct object of observation; and that it is as likely to have one value as another between limits $\pm\frac{\pi}{2}\alpha$ ($\alpha \angle 1$). Then it may be shown that the facility-curve which represents the possible

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* Above.

† Phil. Mag. Oct. 1883; Camb. Phil. Trans. 1885.

variations of $\tan\frac{\theta}{\alpha}$ is

$$y=\frac{1}{\pi}\,\frac{1}{(1+y^2)},$$

extending from $+\infty$ to $-\infty$.

In such cases the general proof of the law of error breaks down. The general formula for the modulus, that it is the double sum of squares of the apparent errors, is apt to yield an infinite result. We must fall back upon the explicit methods. If, for instance, the law of facility above written, or rather the more general form

$$y=\frac{1}{\pi}\,\frac{s}{s^2+y^2},$$

held good for any species of phenomena, then, in order to determine the improbability of a chance deviation to the extent of y', we must integrate y from ∞ to y'.

In view of the rarity of such cases, I think we are justified in concluding that the received formula enounced at the outset is in general either accurate or at least safe; and that, in the exceptional case where it is neither correct nor safe, it is still corrigible, so far as the laws of error which exist in nature may be regarded as binomials.

XLIV. *Experimental Error in Calorimetric Work. By* SPENCER UMFREVILLE PICKERING, *M.A., Professor of Chemistry at Bedford College*[*].

THE determination of the heat of dissolution of a solid in water is an operation which will always occupy a most important position in the majority of calorimetric determinations; and it is therefore desirable to ascertain what the experimental error involved in this process is, and in what direction we must look for a reduction of this error. The large number of these determinations which I have had occasion to make during the last two years will give the means requisite for an investigation of this error.

The *modus operandi* in the experiments was as follows:—The given salt was weighed out into test-tubes on feet, which were placed in an open metal beaker carefully guarded from radiation and draughts by screens; in this was suspended a delicate thermometer, a companion instrument to that used in the calorimeter itself, the exact difference in the readings

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[*] Communicated by the Physical Society: read February 13, 1886.

between the two instruments being known throughout the extent of their scales.

It was found that one hour * was a sufficient interval to allow for the salt to assume the temperature of the surrounding atmosphere, provided this latter remained constant during this time. In order to diminish the error in measuring the rate of cooling (or heating) during the dissolution of the salt, the temperature of the air was always maintained as nearly as possible at the temperature of the calorimetric water, the difference in the majority of cases not exceeding ·1° C., or at the most ·2° C. The correction to be applied, owing to the temperature of the salt not being exactly the same as that of the calorimetric water, was thus rendered very small, and in most cases quite negligible.

The alteration in the temperature of the salt during its removal to the calorimeter can scarcely be appreciable, since this operation does not take more than ten or fifteen seconds.

The calorimeter employed was an open calorimeter similar to that devised by Berthelot (*Mécanique Chimique*, vol. i. p. 140); a pounder such as Berthelot uses to crush salts which cake (*ibid.* vol. i. p. 183) being employed in all cases, not only as a pounder, but also as a stirrer, and the platinum vessel in which the operations were performed being always used without its cover; indeed, free circulation of air round the calorimeter is most important in all delicate determinations. It was found that an annular cardboard disk, covering in a most imperfect manner the space between the calorimeter and the surrounding water-jacket, enclosed the air to an extent sufficient to make it act as so much calorimetric water, and introduced a very appreciable error into the results.

In dissolving an anhydrous salt, when caking generally occurs, the calorimeter proper cannot be placed on the cork tripod as in other cases, but must be supported on a cork disk covered with cardboard; and, inasmuch as this disk was found to absorb an appreciable amount of heat from the calorimeter, the quantity thus absorbed had to be determined by performing a series of experiments in which a reaction of known calorimetric value was effected in the calorimeter when supported on the tripod and on the disk alternately. The use of this disk unfortunately introduces a small experimental error, since from continual pounding the form of the bottom of the

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* A hygroscopic substance may be left in a tube well closed with an india-rubber stopper for two or three hours with safety; but a longer exposure should be avoided, as moisture is gradually absorbed from the air permeating the stopper.

platinum vessel is altered, and consequently this vessel may not be in such intimate contact with the disk at one time as at another, and the amount of heat absorbed by the latter will therefore not always be the same. The error thus introduced, however, cannot be very large, since the disk was never found to be equivalent to more than one hundredth of the contents of the calorimeter.

It was thought possible that an error might also arise in the following manner. Before the introduction of any salt into the calorimeter, all the parts of the apparatus are at the same temperature; but as soon as a reaction takes place, involving, say, the evolution of heat, the radiation from the calorimeter will raise the temperature of the vessel which is interposed between it and the water-jacket (owing to its great bulk the water-jacket itself remains practically unaltered in temperature). During the rest of the time allowed for the experiment this vessel will therefore be at a higher temperature than it was initially; and consequently the rate of cooling during the last intervals will be less than during the first one, the correction to be applied for cooling will be under-estimated, the intermediate vessel having in reality acted as so much calorimetric water. In order to ascertain whether the error from this source attained appreciable dimensions, four experiments with potassium sulphate were performed; in two of these the intermediate vessel was present as usual, while in the other two it was dispensed with. The results obtained were as follows:—

A. With the intermediate vessel:—

$$\left.\begin{array}{ll} 1.\ \ldots\ldots & -7215 \text{ calories} \\ 2.\ \ldots\ldots & -7181 \quad ,, \end{array}\right\} \text{Mean} \quad -7198 \text{ cal.}$$

B. Without the intermediate vessel:—

$$\left.\begin{array}{ll} 1.\ \ldots\ldots & -7157 \text{ calories} \\ 2.\ \ldots\ldots & -7185 \quad ,, \end{array}\right\} \text{Mean} \quad -7171 \text{ cal.}$$

Showing that the use of the intermediate vessel had no appreciable effect on the results obtained*. Where, however, large heat-disturbances take place in the calorimeter, it is safer to dispense with it entirely; and indeed the employment of it is in no case attended by any advantage.

The time required to complete the dissolution of the salt varied, of course, in different cases, but rarely exceeded 5 minutes. The loss (or gain) of heat by radiation &c. during this interval was determined separately in each experiment.

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* If otherwise, the results of A would be smaller than those of B.

It was found that with the apparatus employed, and with a difference between the temperature of the calorimetric liquid and that of the surrounding air not exceeding 2°·5 C., the rate of cooling was practically constant throughout the 20–30 minutes (and even for a considerably longer period) during which the experiment lasted; whereas for accurate measurements it was never safe to trust to the results of one experiment to determine the rate of cooling in another experiment, even though the two were performed within 10 minutes of each other, and apparently under exactly similar conditions. To determine the rate of cooling, therefore, all the operations (pounding, stirring, &c.), performed during the first 5 minutes to effect the dissolution of the salt, were imitated as nearly as possible during a second, third, and sometimes even fourth and fifth similar intervals, the temperature being read at the end of each interval. The actual rate of cooling (or heating) rarely exceeded 0°·04 C. for 5 minutes, and was generally much less.

In these experiments the proportion of salt to water taken was 1 : 400 molecules*, the actual volume of the latter being about 600 cub. centim. The chief salts operated on were the sulphates of sodium, potassium, lithium, copper, magnesium, potassium-magnesium, and potassium-copper, both hydrated and anhydrous.

The thermometers were all read by estimation by means of a lens to the twentieth part of the marked divisions, *i. e.* to 0·05 millim.†; and one such estimation-figure, being equivalent to ·002° C., makes a difference of about 16 cal. in the molecular heat of dissolution. I should not put the estimation-figure at less than one tenth of the marked divisions were it not that these experiments afford ample proof that some reliance can be placed on smaller amounts than this.

The heat-disturbance in the calorimeter varied between *nil* and 2°·3 C., the average being rather less than 1° C.

Out of some 600 determinations of this nature, I may

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* With double salts 1 : 800; but, for the sake of comparison, these are here reduced so as to be comparable with the other experiments.

† The divisions in some of the instruments measured rather more than 1 millim., namely 1·2 millim.; but, provided sufficient attention be paid to a certain proportion between the breadth of the mercurial column and the distance between the divisions, there is no appreciable difference between estimating the fractional portions of these two quantities. Besides practice, and uniformity in the lines themselves, nothing conduces so much to accuracy in estimation as a just proportion between the breadth of the mercurial column and the distance between the divisions. I find the best proportion to be 1 : 10; 1 : 15 is too great, and 1 : 5 too small. Different ratios, however, might suit different observers.

discard the first hundred as consisting chiefly of preliminary and imperfectly conducted experiments; the next century of determinations was also found to give an experimental error decidedly higher than the rest; these also I have therefore omitted, and will confine myself to the remaining 400 experiments. Out of these, however, it will only be the ones which were performed in duplicate which will be available for the present purposes.

Now the average difference between two such duplicate experiments, performed on the same day and with one thermometer only in the calorimeter, was found to be 26·6 calories (deduced from 76 separate experiments), giving a probable error in each experiment of ±13·3 cal.; this corresponds to an error in the thermometric column of considerably less than ±·05 millim.; and as the results involve not only four or five readings of the thermometer, but also the correct reproduction of every action performed in dissolving the salt during the intervals allowed for the determination of the rate of cooling, the correct determination of the salt temperature, and many other points where serious experimental error may occur, I consider that I am fully justified in concluding that the thermometers can be read to ·05 millim., and that even a certain amount of reliance can be placed on such estimation figures.

Where the duplicate experiments were not performed on the same day, the error was found to be greater than in the previous case; on an average, deduced from such experiments, it amounted to ±19·6 cal. This number is, however, somewhat bigger than it should be for strict comparison with the previous one; for the experiments which yielded it belonged chiefly to the earlier ones amongst the 400 under consideration, and an increase of accuracy appeared to be made with increased practice throughout the whole series.

In what follows I deal with those duplicate experiments which were performed consecutively only. We thus have so far:—

I. Difference of two experiments where one thermometer was employed, 26·6 cal.

Now in a large number of cases two thermometers were used in the calorimeter at the same time; from these was deduced,

II. Difference of two experiments where two thermometers were employed, taking the results obtained with the same instrument in the two experiments, 41·9 cal. (from 72 experiments).

Subtracting I. from II., we get

III. 15·3 cal. as the increase of difference in two experiments due to the increased difficulty of manipulation when two thermometers are used instead of one.

IV. Difference in two experiments when two thermometers are used, comparing the results obtained with the one instrument in the one experiment with those of the other instrument in the other experiment, 53·02 cal. (from 76 experiments).

V. Difference in the results obtained from the two different thermometers in the *same* experiment, 33·95 cal. (from 142 experiments).

Now, subtracting II. from IV., we get

VI. That portion of the difference in the results given by two thermometers in any single experiment which is due to the instruments not being absolutely concordant, 11·12 cal.

(This amount will represent the sum of the errors in the calibration and standardization of the instruments. As it is dependent on two readings of each instrument, the amount attributable to each reading will be 3·7 cal., corresponding to ·014 millim., or 0·00056° C.)

Subtracting this amount from V. gives

VII. Difference due to the error inherent in reading the two thermometers, 22·83 cal., and therefore a difference due to error in reading each thermometer of 11·42 cal.

Subtracting these two quantities from I. and II. respectively, and halving the results, we obtain :—

A. In a single experiment where one thermometer is used:—

(1) Error of reading	±5·71 cal.*
(2) Error due to manipulation ...	±7·59 „
Total	±13·3 „

B. In a single experiment where two thermometers are used:—

(1) Error of reading	±11·42 cal.
(2) Error due to manipulation ..	± 9·53 „
Total	±20·95 „

These duplicate experiments being performed at exactly the same temperature, no difference will appear between them due to errors of calibration or standardization ; but in regarding the absolute value of the numbers deduced from them, this source of error must also be taken into account. The amount of this error has already been shown to be 11·12 cal. when the results of two instruments are compared (VI.) ; the total

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* Corresponding to ·021 millim. of the mercurial column.

error, therefore, in experiments where one thermometer is used will have to be increased by half this amount, thus becoming ±18·86 cal. This number, then, represents the probable divergence from the truth of any one experiment; and, from the manner in which the various thermometers were standardized (by comparison with each other), this error will probably be as great when two experiments performed at different temperatures are compared, whether they were performed with the same or with different instruments.

Perhaps, for the purpose of determining this probable error, the calculations ought to be based on the difference between duplicate experiments performed *not* on the same day, in which case the error would be somewhat larger. I have not done so, however, chiefly owing to uncertainty in the number given for this quantity (see above). Many causes also which tend to increase the difference when the experiments are not performed consecutively might not apply in general. Amongst these I may mention the very hygroscopic nature of many of the salts taken, where a difference in the state of moisture of the atmosphere would affect the extent to which traces of water were absorbed during their exposure while being transferred to the weighing-tubes: these substances, again, were often kept in sealed tubes containing sufficient for two or three determinations only, and the contents of the various tubes may not have been dried to precisely the same degree.

XLV. *On Delicate Calorimetric Thermometers. By* SPENCER UMFREVILLE PICKERING, *M.A., Professor of Chemistry at Bedford College*[*].

IN the foregoing communication it has been shown that the average error of a determination of the heat of dissolution of a salt in $400H_2O$ amounts to ±18·86 cal.; but this is only an *average*, and it must not be overlooked that the error in some cases may exceed this very considerably. It is not uncommon to find a difference of 40 or 50 cal. between two duplicate experiments (although the average error in such cases is only ±13·3 cal.), and a proportionately larger error must therefore be expected occasionally in the comparison of two experiments at different temperatures.

The determinations from which these conclusions were drawn consisted of a series of experiments with various salts at temperatures ranging from 1° to 26° C., where it was imperative that the greatest possible accuracy should be attained, and also that the experiments at the different temperatures should all be strictly comparable with each other. The ther-

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[*] Communicated by the Physical Society: read February 13, 1886.

mometers employed had a range of 15° C., and a total length of 600 millim.; it was therefore impossible to increase their length sufficiently to make one instrument embrace the whole range of 25° C., and any increase in the delicacy (by increasing the size of the bulb) would have involved a diminution in their range, so that more than two instruments would have been required, while in such experiments it is obviously of the greatest importance that as few instruments as possible should be used.

With a view to overcoming these difficulties the following expedient was adopted, whereby the delicacy of the instrument was increased six- or sevenfold, its range was made to embrace that of all temperatures at which a mercurial thermometer can be used, and its registration was rendered (for these purposes) practically independent of calibration and standardization error.

The principle on which it was worked consisted in removing a portion of the mercury, by the application of heat, into the upper chamber, and thus adjusting any particular point in the instrument so as to register any required temperature. Experiments on the same substance at different temperatures were thus made absolutely comparable, exactly the same portion of the scale being used in each case.

The zero point of the thermometer being thus altered for each experiment, the actual temperature in degrees Centigrade which it registers will not be known with any great degree of accuracy; but this is not necessary in calorimetric work: the heat of chemical combination is affected to such a small extent by temperature, that an error of ·05° or ·1° C. in this will be unimportant; and by a rough comparison of the thermometer with some standard instrument after each adjustment of the mercury, the temperature which it registers can be easily ascertained within ·01° or ·02° C.

This thermometer (No. 62839) possessed a total length of 746 millim., of which 565 millim. constituted the divided portion of the stem, each division being 1 millim., and ten such divisions being termed 1 degree. The bulb measured 72 millim. in length, and was made out of glass cylinder instead of being blown, a detail which is rarely attended to in the construction of delicate thermometers, but one which is most important in giving the bulb greater stability and greater uniformity of action. The weight of mercury in the bulb was 36·23* grams,

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* In the other instruments, with a range of 15° C., the weight of mercury varied between 13·6 and 15·6 grams; the bore of the tube of No. 62839 would be considerably more than twice as fine as in these. Fuller details respecting these instruments will be found in the Phil. Mag. March 1886.

and the total range of the instrument only 3°·4 C., giving 166 millim. to each degree C.; one estimation figure (·05 millim.) would therefore represent ·0003° C.

In using this thermometer it is first suspended in the calorimeter containing water at a temperature a certain known degree above that at which the experiments are to be made; a very small flame is then applied to a point just below the upper chamber (which in such instruments must be of considerable size), by which means the column of mercury is broken off at the part thus heated, and the separated portion remains in the upper chamber, the tube being much too fine to permit of it being shaken down again. After cooling it is put into a bath at the required temperature, and compared with some standard instrument. In this way the registration of the thermometer can be adjusted to any required temperature within ·05° C. without the least difficulty; but greater accuracy could be obtained if necessary.

This thermometer was employed in a large number of experiments, and the general results, as will be shown below, proved to be satisfactory. But it possessed one serious imperfection, or, more properly speaking, its delicacy brought into light an imperfection which must be inherent, although it has hitherto been unnoticed in all mercurial thermometers.

As is well known, the bulb of a thermometer does not expand regularly when heated; "en effet," to quote Berthelot's words, "la marche de l'instrument est intermittent, c'est-à-dire que le niveau n'est souvent atteint qu'après une série de petites oscillations" *. To obtain a state of equilibrium the thermometer must be tapped on the top with the finger, or some such means adopted to overcome the inertia of the bulb before each reading. The larger the bulb and the finer the bore of the tube, the more apparent does this inertia become: with instruments such as the less delicate ones here mentioned a dozen or less taps are sufficient to overcome it, but with No. 62839 it was found that continuous tapping for two or

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* *Méc. Chim.* i. p. 178. It is curious to note that even while Berthelot is warning his readers against this source of error he appears to have fallen into it himself. On p. 163 he gives the results of a comparison of two thermometers placed in a bath of water, the temperature of which was rising, and read simultaneously at intervals of ten minutes; from this and other closely concordant comparisons he finds 6·702 degrees of the one instrument are equivalent to 14·827 of the other; but, on looking more closely at each reading, it will be found that

(1) a rise of 0°·9 in the one corresponds to a rise of 1°·1 in the other.
(2) „ 0·7 „ „ „ 2·2 „
(3) „ 0·6 „ „ „ 1·5 „
(4) „ 1·1 „ „ „ 0·9 „
(5) „ 1·2 „ „ „ 1·1 „

Vastly discordant numbers.

three minutes was absolutely necessary. The extent to which error from this source may accumulate may be drawn from the fact that this instrument, when the mercury is *rising* to the temperature of the bath in which it is placed, will register 6 millim. lower than when *falling* to the same temperature, however long it be left in the bath, if it be not tapped (the temperature of the bath in this case was such that the mercury stood at about the middle point of the stem). Again, it was found, by means of a series of experiments in which the height of the column was read when the instrument was inclined at different angles, that with thermometer 55082, which possessed a blown bulb containing 15·6 grams of mercury, a difference of 6·6 millim. in the reading was made when the instrument was placed horizontally instead of vertically; making due allowance for the greater size of the bulb and greater fineness of the bore in 62839, this latter instrument would probably exhibit a difference of at least ten times this quantity under similar treatment. This will give some adequate idea of how great an effect the expansion of the bulb under pressure may have on the reading.

Now, besides the inertia of the bulb, which may be overcome by a sufficient amount of tapping, there appears to be another and more serious imperfection, due to what may be termed a permanent alteration in size, as opposed to the other, which may be called temporary, and one which no amount of tapping will overcome. It would seem that the bulb of this, and every thermometer, has two different shapes, one when the column is rising, the other when it is falling. The following simple experiments will serve to show this.

The thermometer being suspended in the calorimeter full of water, the contents of this were heated or cooled slightly, and the rate of cooling (or heating) determined during consecutive intervals.

In the first column the time is entered, in the second the reading of the instrument, and in the third the rate of cooling or heating.

A. Experiments in which a rate of *heating* was determined.

I.

Time.	Reading (arbitrary).	Rate.	
0	-1°		
Hot water added.			
1 min.	19·96		
4 ,,	20·07	·11	
7 ,,	20·165	·095	
10 ,,	20·245	·08	
13 ,,	20·38	·135	mean = ·10.
16 ,,	20·47	·09	

II.

Time.	Reading.	Rate.	
0	−5°		
Hot water added.			
2 min.	20·685		
5 „	20·76	·075	
8 „	20·855	·095	
11 „	20·94	·085	mean ·09.
14 „	21·03	·09	

In this case the rate of heating is constant from the very beginning: during the first three minutes it differs from the mean of the other intervals by +·01 in Exp. 1 and by −·015 in Exp. 2, both of these quantities being well within the limits of experimental error.

III.

Time.	Reading.	Rate.	
0	54°		
Cold water added.			
2 min.	20·555		
5 „	20·56	·005	
8 „	20·65	·09	
11 „	20·735	·085	mean ·093.
14 „	20·84	·105	

IV.

Time.	Reading.	Rate.	
0	54°		
Cold water added.			
2 min.	19·45		
5 „	19·465	·015	
8 „	19·555	·09	
11 „	19·645	·09	mean ·103.
14 „	19·775	·13	

In these two experiments, however, this is not so; the rate of heating (as registered) during the first interval is almost *nil*, in each case exactly ·088 less than the mean deduced from the other intervals. Thus, when the column of mercury rises to any temperature it will go on rising regularly afterwards, indicating the rate of heating correctly, but when it *falls* to that temperature a certain time elapses before it will begin to rise afterwards; although the mercury must be expanding during this interval, the column is stationary, and therefore the bulb must be expanding, and assuming a new form.

The following experiments are complementary to the preceding ones and illustrate the same fact.

B. Experiments in which a rate of *cooling* was measured.

I.

Time.	Reading.	Rate.	
0	55°		
Cold water added.			
3 min.	22·16		
6 „	21·76	·41	
9 „	21·41	·34	
12 „	20·99	·42	mean ·39.
15 „	20·59	·40	

II.

Time.	Reading.	Rate.	
0	53°		
Cold water added.			
3 min.	22·21		
6 „	21·84	·37	
9 „	21·48	·37	
12 „	21·155	·325	mean ·342.
15 „	20·815	·34	

The difference between the rate of cooling measured during the first interval and that during the remaining ones being +·02 in the one experiment, and +·028 in the other, *i. e.* practically *nil.*

III.

Time.	Reading.	Rate.	
0	0		
Hot water added.			
2 min.	20°·65		
5 „	20·45	·20	
8 „	20·09	·36	
11 „	19·79	·30	mean ·34.
14 „	19·42	·37	

IV.

Time.	Reading.	Rate.	
0	−3°		
Hot water added.			
1 min.	25·58		
4 „	25·36	·22	
7 „	24·935	·425	
10 „	24·52	·415	mean ·40.
13 „	24·16	·36	

The difference between the first and remaining intervals being −·14 and −·18 in the two experiments. Thus whichever be the direction of the motion of the mercury it will continue in that direction, giving correct results, but, if the direction be changed, an interval elapses before the motion becomes apparent, and a considerable error will be introduced.

The above are but typical experiments out of a large number performed, and all of which gave the same results; indeed, every determination of the heat of dissolution of a salt afforded a fresh exemplification of the fact.

Of course the alteration in the size of the bulb will invalidate any experiment unless its effect be counteracted. This was always done in every experiment by taking care that, if a rate of cooling was to be measured after the salt had been dissolved, the liquid should be cooling also before its introduction, and *vice versâ*; the motion of the mercury, and therefore the shape of the bulb, being the same at the beginning and end of the experiment, no error would occur. In such an experiment, where for instance a rate of cooling obtained, and the salt dissolved with absorption of heat, no period of inertia in the column would occur; but if the salt dissolved with evolution of heat, two such periods would occur, and, though this would not affect the accuracy of the results, a certain time would elapse before the apparent rate of cooling became constant, extending often to three intervals of 3 or 5 minutes each (for the whole of these intervals cannot be spent in tapping the thermometer as in the experiments quoted above, but are chiefly occupied in reproducing the actions performed in effecting the dissolution of the salt), thus creating a serious increase in the duration of an experiment. This was obviated by removing the thermometer from the calorimeter, touching the bulb with some warm object, when, on replacing it, the column fell to the temperature of the calorimeter, and proceeded to give the rate of cooling at once; where a rate of heating was to be determined, the thermometer was cooled (by evaporation from the surface) instead of heated. As a few millim. rise or fall are sufficient for the purpose, the heating or cooling of the contents of the calorimeter in such an operation is quite negligible *.

The change of size in the bulb, as deduced from the experiments already quoted, is, perhaps, somewhat exaggerated, owing to an under-estimation at the time of the amount of

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* The water-equivalent of the immersed portion of this thermometer was 2·09 grams, that of the calorimeter and contents about 610 grams. A heating of the former sufficient to produce a rise of 5 mm. would raise the temperature of the latter only 0·0001° C.

tapping which was necessary to overcome the temporary inertia of the bulb. The following, even more simple, experiments are free from such an error, and bring to light other facts concerning this phenomenon.

The method of procedure here consisted in suspending the thermometer in a calorimeter containing a much larger volume of water than the one generally used, taking the instrument out, heating and cooling it alternately, when, on its being replaced, readings of the same temperature were obtained, the column having fallen or risen to that temperature respectively.

As it was found to be impossible to keep the temperature of the bath constant during the requisite time, any observed reading, say when the column was rising to the temperature, was compared with a theoretical reading consisting of the mean of the previous and subsequent readings, both of which were obtained when the column was falling to the temperature. The differences here quoted will represent the total difference between the readings with rising and falling columns. After the thermometer had been replaced in the bath, it was tapped continuously and read at intervals of one minute till it became quite stationary; between five and seven such readings were made in the series here given, although it will be necessary to quote the final reading only in each case. An interval of about 8 minutes elapsed between these final readings, all the intervals in each separate series being exactly equal.

I.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being heated 10°.........	14·08		
,, ,, cooled 10	14·08	14·103	−·023
,, ,, heated 10	14·125	14·118	+·097
,, ,, cooled 10	14·155	14·185	−·030
,, ,, heated 30	14·245	14·233	+·012
,, ,, cooled 10	14·310	14·313	−·003
,, ,, heated 10	14·380		
		Mean	·015

II.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being cooled 10°.........	26·83		
,, ,, heated 10	26·86	26·845	+·015
,, ,, cooled 10	26·86	26·908	−·048
,, ,, heated 10	26·955	26·918	+·037
,, ,, cooled 10	26·975	27·008	−·033
,, ,, heated 10	27·06	27·038	+·022
,, ,, cooled 20	27·10	27·123	−·023
,, ,, heated 20	27·185	27·175	+·010
,, ,, cooled 10	27·25		
		Mean	·027

III.

			Registered.	Theory.	Difference.
			°	°	
Immersed after being		heated 10°	45·845		
,,	,,	cooled 10	45·755	45·804	−·049
,,	,,	heated 10	45·763	45·718	+·045
,,	,,	cooled 10	45·680	45·717	−·063
,,	,,	heated 10	45·670	45·643	+·027
,,	,,	cooled 10	45·605	45·655	−·045
,,	,,	heated 10	45·640	45·595	+·045
,,	,,	cooled 10	45·585	45·635	−·050
,,	,,	heated 10	45·630		
				Mean	·046

Without exception, therefore, a reading when the thermometer is falling to a given temperature is higher than when it is rising to this same temperature, and the difference between these two readings appears to be independent of the extent of the foregoing fall or rise; a fact which will be shown more clearly in a series of similar experiments with another thermometer to be quoted below. The difference in the two readings, however, is considerably influenced by the position of the mercury in the stem; from these experiments it would appear to be directly proportional to the height of the column, the total difference in each case being $\frac{1}{1000}$ of this height.

Although this difference is very appreciable, it must be remembered that it corresponds to a difference of very small dimensions in the capacity of the bulb. The 0°·015 measured in the first series is equivalent to 0°·0009 C., and represents but 0·0000004 c.c., or but little over one millionth part of the total capacity of the bulb (2·64 c.c.), a quantity so small that there is no wonder in its having hitherto escaped observation. The considerable force necessary to push a column of mercury through a long very fine tube is, I should say, quite sufficient to account for this expansion of the bulb; it is well illustrated by the fact that a quick fall of but a small amount causes the mercury to separate at the neck of the bulb.

The question now arises whether this instrument, possessing such serious imperfections, is really workable, or whether we have not pushed thermometric delicacy beyond the limits compatible with accuracy.

The various determinations of the heat of dissolution of salts which were made with this thermometer give the means of answering this question.

As shown in the previous communication, ±13·3 cal. is the average error of each experiment when compared with a duplicate one performed under the same conditions; of this 7·59 cal. are error due to manipulation and 5·71 cal. to error of reading. The manipulation-error will be independent of the thermometer employed, but the reading-error will be smaller in direct proportion to the delicacy of the instrument. As an estimation-figure with No. 62839 represents about $\frac{1}{6\cdot4}$ of what it does in the case of the instruments to which these numbers refer, the reading-error with it ought to be only $\frac{5\cdot71}{6\cdot4}$, or about ·9 cal., giving a total error for each experiment of $\pm(\cdot9+7\cdot59=)8\cdot49$.

Now the average difference of two duplicate experiments with this thermometer was found to be 14·84 cal. (deduced from 38 experiments), giving an error of only ±7·42 * cal. for each experiment, a quantity even smaller than that which would have been anticipated, proving conclusively that such an instrument can be worked with just as much certainty as the less delicate ones. The fact that the total error here is even less than the manipulation-error alone in the other experiments is due to greater care being taken in manipulation, a larger number of intervals being allowed for the determination of the rate of cooling. It must be remembered, however, that this diminution of the difference between two duplicate experiments by no means represents the total advantages accruing from the use of this thermometer, for, the same portion of the instrument being used for experiments with the same substance at all the different temperatures, these will be on the same footing as duplicate experiments themselves. We shall, therefore, have to make no addition to this error when comparing different experiments in a series, and we thus get rid at once of the additional error of ±5·56 cal., which had to be admitted with the other instruments †.

The extra time required for experiments with such an instrument is considerable; the determination itself occupies two or three times as long as with an ordinary thermometer, and the preliminary adjustment of the mercury ‡ and the

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* I am probably very much overstating the error here; this number is deduced from *all* the experiments in which this thermometer was used. Several of these were performed before the peculiarities of the instrument were thoroughly known, and contained known sources of error; eliminating these, the average error of the remaining experiments (24 in number) is only ±3·33 cal., a surprisingly small quantity.

† From what has been mentioned in the Phil. Mag. March 1886 as to the error of standardizing this thermometer, the divergence of any measurement from the absolute value will probably not be more than ·00045° C. for each degree C. measured, or ±3–4 cal.

‡ In one instrument which I possess a small particle of dust has become fixed in the tube just below the upper chamber, the result of which is that the column of mercury, whenever it has passed a few millimetres beyond this point, breaks off there and shoots up into the upper chamber. If it were possible to introduce such an obstacle at will, the time expended in separating the mercury by heat, and the danger thereby incurred, would be obviated. I am not without hopes of succeeding in effecting this.

comparison with a standard occupies the greater part of an hour. It is possible to do three determinations at different temperatures with it in a day; but this means a very hard day's work, and could only be effected after much practice.

Although the results obtained with this thermometer may appear satisfactory as measured by the average error, they still leave much to be desired. It is impossible to feel absolute confidence in an instrument which possesses such serious imperfections; and, apart from this, I was desirous of investigating the matter further for its own sake, and producing an instrument in which delicacy did not involve the sacrifice even of convenience.

It occurred to me that the substitution of a double bulb for the single bulb of No. 62839 would probably result in a considerable increase in strength under pressure. Such an instrument, therefore, I had constructed. Considerable difficulty was met with in boiling the mercury in a double bulb thoroughly, but this was overcome in a masterful manner, while at the same time the other parts of the instrument were so perfect that I believe it is the finest thermometer of its kind ever constructed, in this country at any rate. The stem was of the required stoutness, and the bore, while being flat, was well rounded at the edges, thus exposing no crevices into which the mercury would find it difficult to enter, as is usually the case with flat bores, and as was so with No. 62839. The length of each bulb of this instrument, No. 63616, was 55 mm., the total weight of mercury in them being 30·5 grams, considerably less therefore than in the other thermometer and less than double that in the bulbs of some of the less delicate thermometers. The scale was rather less open than in 62839, the total range of 60 cm. representing 3°·85 C., or 154·3 mm. to each degree, one estimation-figure representing therefore $\frac{1}{3000}$°.

The results of two series of experiments with this instrument similar to those with 62839, last described, gave the following results :—

I.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being cooled 1°	45·69		
,, ,, heated 1	45·765	45·688	+·077
,, ,, cooled 1	45·685	45·790	−·105
,, ,, heated 1	45·815	45·703	+·112
,, ,, cooled 10	45·720	45·733	−·113
,, ,, heated 10	45·850	45·768	+·082
,, ,, cooled 10	45·815	45·899	−·084
,, ,, heated 10	45·947		
		Mean	·096

II.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being heated 10°	13·985		
" " cooled 10	13·95	14·00	−·05
" " heated 10	14·015	13·93	+·085
" " cooled 10	13·91	14·029	−·119
" " heated 10	14·043	13·933	+·110
" " cooled 10	13·955	14·044	−·089
" " heated 10	14·045		
		Mean	·091

Thus, contrary to expectation, this instrument not only shows a difference in reading when the column is rising or falling to any temperature, but that difference is even greater, and considerably so, than with No. 62839. This is certainly remarkable, and tends to show that a full explanation of this difference has not yet been obtained, for the double bulb would undoubtedly possess a greater rigidity than the single bulb of the other instrument; although the combined length of the two bulbs is 110 millim. as opposed to 72 millim., the diameter of the tubing of which they were made was considerably less, 4·83 millim. instead of 6·86 millim. (internal measurements), and the wall of the tubing also was considerably stouter, 0·76 millim. instead of 0·635 millim., and a small improvement in these last two items would cause a very considerable increase in the rigidity. Another peculiarity in this instrument is that the difference in the readings is independent of the height of the column of mercury; or at any rate very nearly so.

Series I. of the above experiments affords good proof that the difference in readings is independent of the distance through which the column has fallen or risen; the mean difference of the first three numbers in the last column being ·098, and that of the last three ·093; numbers practically identical, although the fall or rise was 1 degree in the former, and 10 degrees in the latter.

Although this difference, due to what I have termed the permanent alteration in the size of the bulb, is greater with 63616 than with 62839, it is otherwise with the temporary alteration. An experiment similar to the above, but the tapping of the instrument being omitted, gave a difference of 0°·23 in the mercury standing at 45·8, whereas with 62839 it amounted to 0°·6 (at 27°); these numbers representing the sum of the permanent and temporary alterations, the latter only will be represented by (·23−·096=) 0°·13, and (·6−·027=) 0°·57 in the two instruments respectively. This tends to confirm an opinion expressed by Mr. Casella, that a considerable portion of this temporary alteration is due, not to the bulb, but to the mercury not entirely filling the bore of tube of its own accord, owing to the extreme flatness of this latter at the edges. The tube of which 63616 was made presented no such imperfections. However, neither the permanent nor temporary difference can be in any degree attributed to the action of the tube in this latter instrument, but is wholly due to the bulb itself; for the thermometer was first made up with a small bulb*, containing only 3 grams of mercury, in which state it showed no difference whatever in the readings obtained under different conditions, with or without tapping. The comparative smallness of this temporary alteration in the case of 63616 renders this instrument far more convenient and satisfactory than the other. Instead of requiring two or three minutes continuous tapping in order to obtain a correct reading, less than one minute is sufficient, and this must very materially increase accuracy in calorimetric determinations. I have not as yet used this thermometer in a sufficient number of experiments to ascertain the experimental error with it; but the uniformity of its action and the increased concordance of the rate of cooling registered in successive intervals, leads me to feel confident that the error with it will be considerably less than with 62839.

From what has already been said as to the smallness of the reading-error in this instrument, it may be stated that we have pushed thermometric delicacy quite as far as is desirable with regard to calorimetric work, and that to produce a further degree of accuracy in this branch of study, the methods employed, and not the thermometers, must be improved.

In conclusion, I wish to take this opportunity of expressing my warmest thanks to Mr. Casella and to his assistants for the scientific interest which they have shown in this investigation, and the ungrudging manner in which they have spared no pains to help me in attaining my object.

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* Where the bulb is to contain as much as 20 or 30 grams of mercury, it is well to have the instrument made up temporarily with a small bulb, for the purpose of calibration, as with fine tubes some rough handling is often necessary to pass a short thread of mercury along them.

It would appear that 30 grams of mercury is not an uncommon amount in the instruments used by Berthelot (*Méc. Chim.* i. 165), although they are far less delicate than those described in the present communication. He even refers to thermometers containing 250 grams! (p. 156).

XLVI. *On the Foundations of the Kinetic Theory of Gases.* *By* Prof. TAIT [*].

THE attempt to account for the behaviour of gases by attributing continuous pressure to exceedingly numerous, but nearly infinitesimal, impacts on the containing vessel is probably very old. It certainly occurs, with some little development, in Hooke's tract of 1676, "*Lectures de potentiâ restitutivâ, or of Spring*"; and, a little more fully developed, in the *Hydrodynamica* of D. Bernouilli, 1738. It was recalled to notice in 1847 by Herapath in his *Mathematical Physics*, and applied, in 1848, by Joule to the calculation of the average speed of the particles in a mass of hydrogen at 0° C.

In and after 1857 Clausius greatly improved the theoretical treatment of the problem by taking account of the mutual impacts of the particles and the rotations which they communicate to one another, at the same time introducing (but only to a limited extent) the statistical method. In this series of papers we find the first hint of the length of the mean free path of a particle, and the explanation of the comparative slowness of the process of diffusion of one gas into another. But throughout it is assumed, so far as the calculations are concerned, that the particles of a gas are all moving with equal speeds.

In this Magazine for 1860 Clerk-Maxwell published his papers on the "Collision of Elastic Spheres," which had been read to the British Association in the previous year. In this very remarkable investigation we have the first attempts at a numerical determination of the length of the mean free path. These are founded on the observed rate of diffusion of gases into one another; and on the viscosity of gases, which here first received a physical explanation. The statistical method is allowed free play, and consequently the law of distribution of speed among the impinging particles is investigated, whether these be all of one kind or a mixture of two or more kinds. In the ardour of his research, Maxwell here and there contented himself with very incomplete proofs (we can scarcely call them more than illustrations) of some of the most important of his results. This is specially the case with the investigation of the law of ultimate partition of energy in a mixture of smooth spherical particles of two different kinds. He obtained,

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[*] Abstract of Papers read to the Royal Society of Edinburgh, Dec. 7th, 1885, and subsequently: communicated (by permission of the Council) at the request of Sir W. Thomson.

in accordance with the so-called *Law of Avogadro*, the result that the average energy of translation is the same per particle in each system; and he extended this in a corollary to a mixture of any number of different systems. This proposition, if true, is of fundamental importance. It has since been extended by Boltzmann and others to cases in which the individual particles are no longer supposed to be hard smooth spheres, but complex systems having great numbers of degrees of freedom. And it is stated, as the result of a process which is rather of the nature of playing with symbols than of reasoning by consecutive steps, that in such groups of systems the ultimate state will be a partition of the whole energy in equal shares among the classes of degrees of freedom which the individual particle-systems possess. This, if accepted as true, at once raises a formidable objection to the kinetic theory. For there can be no doubt that each individual particle of a gas has a very great number of degrees of freedom besides the six which it would have if rigid:—the examination of its spectrum while incandescent proves this at once. But if all these degrees of freedom are to share the whole energy (on the average) equally among them, the results of theory will no longer be consistent with our experimental knowledge of the relations between the two specific heats of a gas.

Hence it is desirable that Maxwell's proof of his fundamental Theorem should be critically examined, and improved where it may be found defective. If it be shown in this process that certain preliminary conditions are absolutely necessary to the proof even of Maxwell's Theorem, and if these *cannot* be granted in the more general case treated by Boltzmann, it is clear that Boltzmann's Theorem must be abandoned.

1. The chief features, besides too great conciseness, in respect of which Maxwell's proof is objectionable are:—

(*a*) He *assumes* that the transference of energy from one system to the other can be calculated from the results of a single impact between particles, one from each system, each having the average translational energy of its system.

Thus (so far as this step is concerned) the distribution of energy in each system may be any whatever.

(*b*) In this typical impact the velocities of the impinging spheres are taken as at right angles to one another, so that the relative speed may be that of mean square as between the particles of the two systems. The result obtained is fallacious because, in general, the directions of motion after impact are found not to be at right angles to one another, as they would certainly be (on account of the perfect reversibility of the motions) were this really a typical impact.

(*c*) Maxwell proceeds as if every particle of one system impinged upon one of the other system at each stage of the process—*i. e.* he calculates the transference of energy as if each pair of particles, one from each system, had simultaneously a typical impact. This neglect of the immensely greater number of particles which either had no impact or impinged on others of their own group makes the calculated rate of equalization far too rapid.

(*d*) Attention is not called to the fact that impacts between particles are numerous in proportion to their *relative* speed, nor is this consideration introduced in the calculations.

(*e*) Throughout the investigation each step of the process of averaging is performed (as a rule) before the expressions are ripe for it.

2. In seeking for a proof of Maxwell's Theorem, I found it absolutely essential to the application of the statistical method to premise :—

(A) That the particles of the two systems are thoroughly mixed.

(B) That, in any region containing a very large number of particles, the particles of each kind acquire and maintain the error-law distribution of velocities. This will be referred to as the "special" state. The disturbances of this arrangement produced in either system by impacts on members of the other are regarded as being promptly repaired by means of the internal collisions in the system itself. This is the sole task assigned to these internal collisions. We assume that they accomplish it, so we need not further allude to them.

[The warrant for these assumptions is sought in the fact that only a small fraction of the whole particles are at any instant in collision ; *i. e.* that each particle advances, on the average, through a considerable multiple of its diameter before it encounters another.]

(C) That there is perfectly free access for collision between each pair of particles, whether of the same or of different systems ; and that, in the mixture, the number of particles of one kind is not overwhelmingly greater than that of the other kind.

[This is one of the essential points which seem to be wholly ignored by Boltzmann and his commentators. There is no proof given by them that one system, while regulating by its internal collisions the distribution of energy among its own members, can also by impacts regulate the distribution of energy among the members of another system, when these are not free to collide with one another. In fact, if (to take an extreme case) the particles of one system were so small, in comparison with the average distance between any two contiguous ones, that they practically had no *mutual* collisions, they would behave towards the particles of another system much as Le Sage supposed his ultra-mundane corpuscles to behave towards particles of gross matter. Thus they would merely alter the apparent amount of the molecular forces between the particles of a gas. And it is specially to be noted that this is a question of *effective diameters* merely, and not of masses.]

3. With these assumptions we may proceed as follows:—Let P and Q be the masses of particles from the two systems respectively; and when they impinge, let u, v be their velocity-components measured towards the same parts along the line of centres at impact. If these velocities become, after impact, u′, v′ respectively, we have at once

$$P(u'-u)=-\frac{2PQ}{P+Q}(u-v)=-Q(v'-v);$$

an immediate consequence of which is

$$P(u'^2-u^2)=-\frac{4PQ}{(P+Q)^2}\left(Pu^2-Qv^2-(P-Q)uv\right)$$
$$=-Q(v'^2-v^2).$$

Hence, denoting by a bar the average value of a quantity, we see that transference of energy between the systems must cease when

$$P\overline{u^2}-Q\overline{v^2}-(P-Q)\overline{uv}=0, \quad . \quad . \quad . \quad . \quad (1)$$

and the question is reduced to finding these averages.

I thought at first that $\overline{uv}$ might be assumed to vanish, and that $\overline{u^2}$ and $\overline{v^2}$ might each be taken as one third of the mean-square speed in its system. This set of suppositions would lead to Maxwell's Theorem at once. But it is clear that, when two particles have each a *given* velocity, they are more likely to collide when they are moving towards opposite parts than when towards the same parts. Hence $\overline{uv}$ must be an essentially negative quantity, and therefore $P\overline{u^2}$ necessarily less than $Q\overline{v^2}$, if P be greater than Q. Thus it seemed as if the greater masses would have on the average less energy than the smaller.

4. But these first impressions are entirely dissipated when we proceed to calculate the average values. For it is found

that if we write (1) in the form

$$\mathrm{P}\overline{\mathrm{u}^2-\mathrm{uv}}-\mathrm{Q}\overline{\mathrm{v}^2-\mathrm{uv}}=0, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the terms on the left are equal multiples of the average energy of a P and of a Q respectively. Thus Maxwell's Theorem is rigorously true, though in a most unexpected manner. There must surely be some extremely simple and direct mode of showing that $\overline{\mathrm{u}^2-\mathrm{uv}}$ is independent of the mean-square speed of the system of Qs. Meanwhile I give the heads of the investigation by which I arrived at the result just stated.

5. It is shown that, if a particle move constantly with velocity v among a system of other particles which are in the "special" state, the fraction of the whole of its encounters which take place with particles whose velocity is from v_1 to v_1+dv_1, and whose directions of motion are inclined to its direction at angles from β to $\beta+d\beta$, is proportional to

$$\epsilon^{-qv_1^2}v_1^2v_0dv_1\sin\beta\,d\beta\;;$$

where

$$v_0=\sqrt{v^2+v_1^2-2vv_1\cos\beta}$$

is the relative velocity, and $3/2q$ is the mean-square speed of the spheres of the system.

The line of centres at impact depends for its positions upon the condition that the line of relative motion of the centre of one of the impinging particles may pass, with equal probability, perpendicularly through all equal areas of a diametral plane of the sphere, whose radius is the sum of the radii, and which is concentric with the other particle.

The number of particles of the first system which have speeds between v and $v+dv$ is proportional to

$$\epsilon^{-pv^2}v^2\,dv,$$

where the mean-square speed of the system is $3/2p$.

Taking these things into account, it is found that

$$\overline{\mathrm{u}^2}=\frac{p+2q}{2p(p+q)}$$

and

$$\overline{\mathrm{uv}}=-\frac{1}{2(p+q)},$$

so that

$$\overline{\mathrm{u}^2-\mathrm{uv}}=\frac{1}{p},$$

which gives the result stated above.

These values are deduced from particular cases of the curious expression

$$\int_0^\infty \epsilon^{-px^2} x\,dx \left(\int_0^x \epsilon^{-qy^2} y\,dy \left(\overline{x+y}^{2n+1} - \overline{x-y}^{2n+1} \right) + \int_x^\infty \epsilon^{-qy^2} y\,dy \left(\overline{y+x}^{2n+1} - \overline{y-x}^{2n+1} \right) \right)$$

$$= \frac{\sqrt{\pi}}{4} n!(2n+1) \frac{(p+q)^{\frac{2n-1}{2}}}{(pq)^{n+1}},$$

which, in its turn, may be made to depend upon the following pair of fundamental theorems :—

$$\int_0^\infty \epsilon^{-px^2} x\,dx \int_0^x \epsilon^{-qy^2} dy = \frac{\sqrt{\pi}}{4p\sqrt{p+q}},$$

$$\int_0^\infty \epsilon^{-px^2} dx \int_x^\infty \epsilon^{-qy^2} y\,dy = \frac{\sqrt{\pi}}{4q\sqrt{p+q}}.$$

6. Another question of importance in the theory regards the proper definition of the *Mean Free Path.* From the point of view adopted by Maxwell, and since taken by Meyer, Watson, and others, the mean free path in a system of equal spheres is

$$\frac{\text{average speed of a sphere}}{\text{average number of collisions per sphere per second}}.$$

It seems to be more in accordance with the usual sense of the word "mean" to define the mean path as the sum of the products of the mean path for each speed into the chance of that speed. And those who adopt the above deviation from the ordinary usage must, I think, face the question,—Why not deviate in the opposite direction, and define the mean path as (average time of describing a free path) × (average speed)?

The numerical values deduced from these three definitions bear to one another, in the above order, the ratios

0·707 : 0·677 : 0·647 ;

unit being the length of the mean path of a particle (whatever its speed) if all the others were reduced to rest, and evenly distributed throughout the space which they occupied while in motion.

XLVII. *On the Diurnal Period of Terrestrial Magnetism.*
By Arthur Schuster, *F.R.S.*[*]

THE explanation of the daily variation of the magnetic forces observed on the surface of the earth will, in all probability, lead to the explanation of the mysterious connection between solar phenomena and terrestrial magnetism. For the increase in amplitude of the diurnal variation of the horizontal components of magnetic force forms one of the most striking effects accompanying the increase in sunspot activity. The daily variation, then, seems a most important symptom of solar influence, and its investigation becomes a matter of great interest.

In the remarks which I wrote out for the Report of the Committee appointed by the British Association, for the purpose of considering the best means of comparing and reducing magnetic observations, I pointed out the importance of adopting a suggestion, made already by Gauss, to apply the analysis of surface harmonics to the diurnal oscillations. It is well known that such an analysis would allow us to decide the question whether the immediate cause of the disturbance was inside or outside the surface of the earth; nor can there be two opinions as to the importance of definitely settling that question. At the time I wrote out my suggestions, however, it seemed to me, as the causes of the disturbance had their seat in all probability close to the surface, whether outside or inside, that we should require a large number of terms in the expansion before we could arrive at a definite result.

In this I was mistaken; and it is one of the principal objects of this paper to show that the periodic variations adapt themselves with great facility to the analysis, and that, even with the very limited quantity of material at our disposal, we shall be able to arrive at most important results; results which within a short time might be made absolutely certain, if additional observations were taken at a few well-selected stations. My results, as far as they go, point definitely to the region *outside* the surface of the earth as the locality of the periodic cause of the variation.

It is easy to see that if electric currents parallel to the earth's surface produce any disturbance, we can readily find out whether these currents are outside or inside the earth. As we pass through any current sheet the normal magnetic

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[*] Communicated by the Author, having been read before the Literary and Philosophical Society of Manchester, January 26, 1886.

force remains continuous, but that tangential component which is at right angles to the current suffers a discontinuity depending on the intensity of the current. For a spherical current sheet these components will always be of opposite sign on the two sides. If we then find the distribution of magnetic potential on the surface of the earth from the horizontal components only, we should get by calculation a vertical component of different sign, according as the cause is inside or outside. A comparison with the observed values will at once decide the question. A more careful analysis is necessary if the causes are partly outside and partly inside, and we wish to determine their relative importance.

I believe that few practical magneticians at the present day read Gauss's memoir, 'On the General Theory of Terrestrial Magnetism'*; and the loss which cosmical physics has suffered in consequence is, as far as our generation is concerned, quite irretrievable. The memoir is a model of scientific reasoning and full of suggestions, which are as valuable now as they were fifty years ago. The investigations of Gauss are founded on the assumption of a magnetic potential on the surface of the earth; and he deduces from this assumption the theorem, now well known, that if on every place of the earth we know the component of magnetic force tending towards the west, we can determine from that component the direction and magnitude of total horizontal force, leaving only a quantity undetermined which may depend on the latitude, but which cannot depend on the longitude, and which therefore is easily found. It appears on investigation that the quantity in question, if it has a diurnal variation at all, must vary on each circle of latitude with the solar time of some particular meridian, and not with local time. There can only be a very small fraction of the observed diurnal variation changing in this fashion. We may then say that, assuming the variation of the westerly component of magnetic force to be known over the surface of the earth, the knowledge of the northerly component will follow. This is of importance, considering the ease with which changes in declination are observed compared to change of horizontal force. Nevertheless changes of horizontal force ought to be observed wherever possible, as the two records at any one station will be equivalent to the record of declination only, at two stations.

Moreover, we cannot assume without proof that the magnetic changes of diurnal variation are subject to the existence of a potential. If there is any actual discharge through the earth's surface it will not be the case; and if there is only a variation of electric charge it would be equivalent to an electric current.

[* See Taylor's Scientific Memoirs, vol. ii. pp. 184, 313.]

The following calculations will show the order of magnitude of the vertical currents required to produce a sensible effect on the magnetic needle. But, in the first place, we may estimate the intensity of the displacement-current, consistent with electrostatic observations. The numbers given in the following quotation from Sir Wm. Thomson* may serve as a basis :—" Even in fair weather the intensity of the electric force in the air near the earth's surface is perpetually fluctuating. The speaker had often observed it, especially during calms or very light breezes from the east, varying from forty Daniell's elements per foot to three or four times that amount during a few minutes."

We may then take ·01 volt per centimetre in a second as a variation not unfrequently occurring. Reduced to C.G.S. units, this gives 10^6 as the rate of variation of displacement.

The current intensity C is measured by $\frac{de}{dt}\Big/4\pi v^2$, where v is the velocity of light ; and for $\frac{de}{dt}$ we put, as just found, 10^6. We thus obtain $C=10^{-16}$ nearly. This means that the total current through a surface of a million square kilometres is equal to unity. Charges such as described by Sir William Thomson, if occurring simultaneously over a surface of 600 miles square, would thus be equivalent to a unit current. If occurring over an area about 20 per cent. larger than Ireland, therefore, the current would be equivalent to one ampere.

Let us ask next how large the current through an area like that of Ireland would have to be in order to show itself in magnetic observations. A deflection of one minute of arc in the declination, if recurring periodically, would no doubt show itself. This means, in our latitudes, a force of 5×10^{-5} C.G.S. Assuming, for simplicity's sake, the surface to be a circular disk of radius 16×10^6, we get 400 units of current, or 4000 amperes ; which is 4000 times stronger than the displacement-currents observed by Sir William Thomson. We may then leave out of account the variations of electrification on the earth's surface ; for although the conditions are somewhat more favourable over larger surfaces, and especially near the equator, the possible effects seem to me always to fall outside the observable limits. It is difficult to estimate the possible values of actual discharge, especially in the polar or equatorial regions. It must therefore be one of our first objects to find out whether the line-integral of magnetic force does or does not vanish when taken round a closed curve

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* Reprints of Papers on Electrostatics and Magnetism, xvi. p. 219.

taken on the earth's surface. In our latitudes we should almost certainly find that it does vanish; but the observations of Sabine near the magnetic pole tend to show an appreciable effect.

It is, then, to circumpolar and equatorial observations that we must look for an answer; and as the point is of importance, steps ought to be taken to settle it. Accurate and uniform observations over a limited area will be more valuable than less uniform observations over a more extended area. Two or three declination-magnetographs distributed over the northern frontier of India, together with one additional vertical-force instrument in Central India, would, I believe, when taken together with the Madras and Bombay observations, give definite results in the course of one year, and the instruments might then become available for other work.

The following calculation, however, seems to justify us in neglecting, until we have more definite information, the vertical discharges through the earth.

In the first place it is necessary to draw attention to the fact that, as concerns the subject of discussion, everything that holds for any set of observations taken over the earth's surface at any particular time, must also be true of the average values taken over a certain period of time; and hence we may deal with the averages which give us the daily variations exactly in the same manner as we should deal with the whole components of force at any particular time. All we assume is, that no part of the mean magnetic force is due to vertical currents crossing the earth's surface.

Suppose the periodic forces on which the diurnal variation depends to be expressed all over the earth in terms of longitude, latitude, and the time of a given meridian. Observation tells us, that all over a given circle of latitude we may take the variation to be very nearly the same for a given local time; that is to say, we may write

$$\frac{dX}{dt}=\frac{dX}{d\lambda},\quad \frac{dY}{dt}=\frac{dY}{d\lambda};$$

where X and Y are the components of force towards the geographical north and west respectively, and λ the longitude measured towards the east. If u is the co-latitude, we have, assuming the existence of a potential,

$$\frac{d}{du}\,Y\sin u=\frac{dX}{d\lambda}=\frac{dX}{dt};$$

Y, considered as a function of the time, is nearly of the same type at places differing widely in latitude; and we may therefore, as a first approximation, put Y equal to the product of two quantities, one depending on the latitude, the other on the time only. This seems true approximately, but only approximately. Writing, therefore,

$$\mathrm{Y}\sin u=\mathrm{U}\frac{d\mathrm{T}}{dt},$$

where U is a function of u, and T a function of the time, we get

$$\mathrm{X}=\mathrm{T}\frac{d\mathrm{U}}{du},$$

where no constant is added, as we only consider periodic terms.

The result I wish to draw from this equation, which can easily be tested, is this :—If our assumptions are all justified, X will be a maximum or a minimum as far as the time is concerned, whenever T is a maximum or a minimum ; that is to say, whenever $\frac{d\mathrm{T}}{dt}$, and therefore also Y, vanishes. In other words, the northerly component of horizontal force ought to be a maximum and a minimum, whenever the westerly component vanishes.

At Greenwich, X has a maximum at 7 o'clock in the evening and a minimum at noon ; while Y vanishes a little after 7 o'clock, and between 12 and 1 in the afternoon.

At Bombay the declination-needle seems to pass its mean position on the average a little after 10 in the morning and about 10 in the evening. The horizontal force has its maximum a little after 11 in the morning, and the minimum at a quarter past 9 o'clock in the evening. Considering that, owing to the southerly position of Bombay, the type in the declination-range differs considerably from that in our own latitude, the agreement is satisfactory, and so far tends to disprove the existence of vertical currents through the earth's surface.

The observations taken at Lisbon and Hobarton show an equally good agreement, those at St. Helena and the Cape of Good Hope less so ; but in these two latter places the observations taken at different months show a considerable difference of behaviour.

We may now attempt another step, and try to gain an idea, however imperfect, as to the direction and intensity of the currents which may produce the diurnal variation. The variation in westerly force increases with the latitude, and we shall not go far wrong in taking it as a first approximation proportional to the sine of the latitude. I write therefore, with an arbitrary unit of force,

$$Y = \cos u \cos (t + \lambda),$$

where t is reckoned in arc from 2 o'clock Greenwich time.

It is well known that in the expression for Y there is an important term having a double period each day; but it is not my intention to enter into any details at present, and we may see what we get with the above expression.

Applying the equation

$$\frac{dY \sin u}{du} = \frac{dX}{d\lambda},$$

we obtain

$$X = \cos 2u \sin (t + \lambda).$$

The important point here is the factor $\cos 2u$, which changes sign at a latitude of 45°. If our equation is approximately right the northerly force ought to be a maximum in the morning, a minimum in the afternoon in the equatorial regions, where $\cos 2u$ is negative; while in the latitudes above 45° the minimum ought to take place in the morning. This is exactly what happens, with the exception that the change seems to take place in latitudes smaller than 45°. At Bombay the *maximum* of horizontal force takes place at 11 o'clock A.M. At Greenwich the *minimum* takes place a little after that time. At Lisbon ($u = 51°$) the minimum lies, as at Greenwich, in the morning, but the range is considerably reduced*.

It is surprising that the above equation represents so well the general type of character of the horizontal-force variation, both in the northern and southern hemispheres. Considerable importance is to be attached to the fact that the maxima and minima of horizontal force agree in sign with the observed phenomena, for, as regards magnitude, all these variations might equally well be due to currents crossing the surface of the earth; but the *sign* of X would have to be reversed, so that the minima and maxima would be inverted. This is another argument in favour of the supposition that no appreciable part of the diurnal variation is due to currents crossing the surface of the earth.

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* I find, since writing the above, that in the winter months Lisbon agrees in phase with Bombay: so that it is very likely near the line at which the change takes place.

Now as regards the vertical force and the localization of the currents, we must in the first place obtain an expression for the potential V. We may take either

$$X=-\frac{dV}{adu}, \text{ or } Y=-\frac{dV}{a\sin u d\lambda},$$

where a is the radius of the earth, and find

$$V=-a\sin u\cos u\sin(t+\lambda).$$

This expression for V happens to be a tesseral harmonic; and the potential, if it exists, must therefore be either

$$-V=\frac{r^2}{a}\sin u\cos u\sin(t+\lambda)$$

or

$$-V'=\frac{a^4}{r^3}\sin u\cos u\sin(t+\lambda).$$

For the vertical force we obtain in the first case, putting $r=a$,

$$-\frac{dV}{dr}=\sin 2u\sin(t+\lambda);$$

and in the second case,

$$-\frac{dV'}{dr}=-\frac{3}{2}\sin 2u\sin(t+\lambda).$$

Both expressions have their minima and maxima coincident with those for the northerly components of horizontal force, a fact which finds its confirmation in actual observation. They also give us the phase of vertical force to be the same for each hemisphere, and not to change as in the case of the horizontal force. But there is an important distinction, while $-\frac{dV}{dr}$ has its maxima and minima coincident with the maxima and minima of horizontal force at latitudes greater than 45°, and in the equatorial regions the maximum of horizontal force ought to be coincident with the minimum of vertical force, and *vice versâ*, just the opposite holds for $-\frac{dV'}{dr}$.

At Greenwich the maximum of northerly force takes place at 7 P.M., the minimum at noon; the maximum of vertical force takes place at 7 P.M., the minimum at 11 A.M.

At Bombay the maximum of northerly force takes place at 11 A.M., the minimum at 9 P.M.; there is a very decided minimum of vertical force at 11 A.M.; but there is no pronounced maximum; two minor maxima occur, one at 6 A.M. and the other at midnight.

As far as these results go, they give an emphatic answer in favour of the supposition that a great part, at any rate, of the disturbing currents lie outside the earth's surface; a view which Prof. Balfour Stewart has often supported in the last few years.

The results seem to me very encouraging, and I hope soon to be able to make use of more material, and to obtain more accurate expressions for the various forces concerned.

It would help considerably all those who, like myself, wish to obtain some knowledge on the subjects of terrestrial magnetism without the aid of a staff of computers, if the directors of magnetical observatories were to reduce their observations so as to give us changes in the components of force directed towards the geographical north and west, rather than, as is customary, changes in horizontal force and declination. In all reductions such as I have attempted, and indeed in all comparisons of the results obtained at different stations, what interests us most is the two components of force resolved along two definite directions like north and west, and not the components of force resolved, as at present, in directions changing sometimes rapidly from place to place.

It may ultimately appear that some variations of terrestrial magnetism are expressed most simply according to a system of large and small circles, having the points of intersection of the magnetic axis with the surface of the earth as poles; but the present system seems to me quite arbitrary, and until we know more accurately the position of the magnetic axis, the latitude and longitude circles seem to me to be the only possible lines of reference for the magnetic forces.

Supposing we have, by expansion in spherical harmonics, obtained the distribution of potential, representing some periodic variation we wish to investigate, we may easily, should it be considered desirable, obtain such a distribution of electric currents on any sphere concentric with the earth's surface, inside or outside as the case may be, as might cause the observed variation. Such a representation would always be instructive, although the actual currents causing the disturbance may be distributed in a very different manner if they have any vertical components. The simplest plan would be, in the first place, to take the sphere on which we draw the currents close to the earth's surface, either just outside or just inside, according to the result obtained for the vertical force.

If the magnetic potential is distributed over the earth's surface, according to a surface harmonic of order i, Y_i, the current function will be given by

$$\phi = \frac{(2i+1)A}{4\pi\alpha} Y_i{}^{*} ;$$

the potential just inside the sphere,

$$V = -(i+1)\frac{A}{\alpha} Y_i ;$$

that just outside,

$$V = i\frac{A}{\alpha} Y_i ;$$

or, if the current-sheet is just outside the earth, therefore (which supposition would, as we have seen, give a good agreement for the vertical force), we find

$$\phi = -\frac{2i+1}{i+1} \cdot \frac{1}{4\pi} V.$$

It follows from this, that the currents flow at right angles to the magnetic force at the point. If, however, the distribution of potential cannot be represented by a single surface harmonic, then, as the coefficient of V differs for harmonics of different orders, the currents need not necessarily be at right angles to the magnetic force. If i is infinitely large, the fraction depending on i is 2; if i is 2, the fraction is $\frac{5}{3}$; and it must always lie between those limits if i varies between 2 and infinity. There seems for diurnal variation no term of the first order; and we may therefore take very approximately the currents to be at right angles to the magnetic force at any place. In order to obtain the currents in C.G.S. measure from the magnetic force we have to apply a factor, which, as we have seen, is approximately obtained by putting $i=2$, and therefore is equal to $5/12\pi$.

In the following table I give the direction and intensity of the currents at Greenwich and Bombay for the local solar hours. The direction of the current is as accurate as the observations will permit; the intensity is calculated, as explained above, by multiplying the magnetic force by $5/12\pi$, and is therefore approximate only as far as its absolute value is concerned, but the relative value of the numbers ought to be correct. The Greenwich result applies to the year 1882, that for Bombay is founded on the mean values during a succession of years.

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* Maxwell, 'Electricity and Magnetism, vol. ii. p. 281.

GREENWICH.			BOMBAY.		
Time (astronomical).	Intensity (amperes 10^{-6}).	Direction.	Direction.	Intensity (amperes 10^{-6}).	Time (astronomical).
h		°	°		h m
0	366	+ 53	− 67	556	0 12
1	398	+ 36	− 65	442	1 12
2	364	+ 24	− 65	282	2 12
3	282	+ 14	− 75	125	3 12
4	184	− 2	+ 0	8	4 12
5	128	− 29	+ 88	92	5 12
6	126	− 72	+ 85	165	6 12
7	136	− 87	+ 85	229	7 12
8	146	−104	+ 85	253	8 12
9	149	−117	+ 88	261	9 12
10	149	−121	+ 90	251	10 12
11	146	−124	+ 86	231	11 12
12	138	−159	+ 98	211	12 12
13	120	−132	+100	201	13 12
14	110	−136	+100	188	14 12
15	110	−136	+ 97	177	15 12
16	118	−132	+ 94	165	16 12
17	124	−134	+ 98	152	17 12
18	136	−149	+127	132	18 12
19	168	−169	+139	181	19 12
20	219	+170	−152	223	20 12
21	263	+145	−113	348	21 12
22	277	+116	− 90	462	22 12
23	289	+ 80	− 76	569	23 12

The table well repays a careful study. The Bombay observations on magnetic declination refer, as regards time, to twelve minutes past each hour; the observations at the same place on horizontal force to fourteen minutes past each hour. This is only one of the many little devices by means of which the heads of magnetical observatories try to enliven the time of those who want to compare their results.

The direction of the currents is reckoned from the geographical north towards the west as positive, and towards the east as negative. It is very remarkable how very nearly at the same local hours the currents flow north and south at Bombay and at Greenwich, namely at 4 in the afternoon and between 7 and 8 in the morning. It is curious, moreover, how very quickly the current turns through the meridian at Bombay; at 3 o'clock it flows at an angle of 15° from the east, and at 5 already it flows due west, and remains almost unaltered in direction till 5 o'clock in the morning. At Greenwich the currents turn much less sharply, but they always flow east when the currents at Bombay flow west.

The system of currents indicated by these numbers is that approximately shown by the equations given above, the phase, however, being different. Along the meridian, on which the local time is 4, the currents flow from the equator towards the north, they turn round in our latitude towards east and west, join on either side again to go south, where the local time is half-past 7 in the morning, and come back along the equator.

The numbers given in the columns as intensity become amperes when multiplied by 10^{-6}. They are approximately of the same magnitude as the currents we are accustomed to send through our vacuum-tubes; but as the thickness of layer through which they are distributed must be very large compared to that on which we experiment, the current-intensity at such place is very small, far too small to cause luminosity. The currents, on the whole, are weaker at Greenwich than at Bombay; but while they almost vanish at one time at Bombay, making the ratio of the strongest to the weakest current equal to 73, that ratio is only $3\frac{1}{2}$ at Greenwich. The minimum at Greenwich in the early morning is as pronounced at the afternoon minimum, but much less so at Bombay.

On the whole the numbers, both as regards direction and intensity, show such a remarkable regularity that there is good hope of obtaining a good mathematical representation of their distribution.

But more detailed investigations will require much time and consideration. They can hardly upset the conclusion arrived at in this paper, that the greater part of the diurnal variation is due to disturbing causes outside the earth's surface. I forbear at present from entering into some very curious conclusions to which we seem almost forced if we adopt this view.

It will be interesting to apply the method here used to the other periodic variations of terrestrial magnetism which have been discovered.

XLVIII. *On the Peltier Effect at different Temperatures*[*]. *By* G. Gore, *LL.D., F.R.S.*[†]

IN order to examine this question I made the following experiments:—A current of about ·10 ampere was passed, during five minutes, through a thermoelectric pile,

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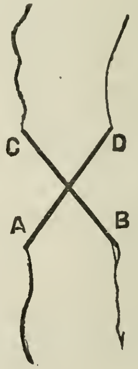
[*] See Campbell, Proc. Roy. Soc. Edin. vol. xi. 1882–83, p. 807, and vol. xii. 1883–84, p. 293; consult also a paper by Naccari and Bellati on the same subject, Wiedemann's *Beiblätter*, 1878, vol. ii. p. 223; and one by Bellati, *ibid.* vol. iii. p. 638.

[†] Communicated by the Author, having been read before the Birmingham Philosophical Society, February 11, 1886.

composed of thirty-six pairs of bismuth and antimony, at a uniform temperature of 8° Centigrade. The current was then stopped, and the terminals of the pile at once connected with an astatic galvanometer of 100 ohms resistance: the needles gave a swing of 8 degrees. The pile was then heated in a hot-water jacketed chamber to a uniform temperature of 65° C., and the experiment exactly repeated with the current of its original strength: the needles now gave a swing of 17 degrees. These experiments were again exactly repeated, but with the pile at 9° C. and 85° C.: the deflections were 8 degrees at 9° C. and 20 at 85° C.

These results indicate that the difference of temperature produced at and near the two junctions of a bismuth and antimony thermo-couple, by the passage of an electric current through them, is more than twice as great at 85° C. as at 8° C. As the amount of resistance of the galvanometer was large in comparison with that of the pile, the increased strength of current was due to increase of electromotive force.

In order to examine the amount of Peltier effect produced at the two junctions of the pile separately, a current of ·2 ampere was passed, during about twenty seconds, from A to B, through a cross composed of two wires; A D being of iron, ·5 millim. diameter, and B C of German-silver, ·4 millim. diameter, whilst their opposite ends, C, D, were attached to a galvanometer, of about 2·0 ohms resistance, by means of slender wires of copper.



With the entire cross and the adjoining portions of its conducting wires at 10° C., on passing the current from iron through the junction to German-silver, a deflection of 3 degrees was produced, showing that the junction was heated; and on passing it from German-silver to iron, the deflection was 2 degrees in the same direction, showing that the junction was again heated, but in a less degree. These results were obtained several times. On repeating these experiments carefully in a similar manner, but with the cross and its attachments at 90° C., the current from iron through the junction to German-silver produced a deflection of 4 degrees, indicating heat at the junction; and on passing it from German-silver to iron, the deflection was 2 degrees in the same direction, the junction being again heated.

These results show—1st, that with a thermo-couple composed of iron and German-silver, a current of uniform strength, passed from iron to German-silver, evolved more heat than when passed in the opposite direction, whether the pile was at 10° C. or 90° C. 2nd, that when the current was passed from iron to German-silver, it evolved more heat at and near the junction when the couple was at 90° C. than when it was at 10° C. And 3rd, that when it was passed from German-silver to iron, the amounts of heat evolved were about the same when the couple was at 90° as when it was at 10° C.

With the same strength of current, and a cross formed of bismuth and antimony, with the cross and its connections at 12° C., on passing the current from the bismuth through the junction to the antimony, a deflection of 8 degrees was produced, showing that the junction was cooled ; and on passing it in the opposite direction, the deflection was 8 degrees in the opposite direction, showing a heating effect. With the cross, &c., at 93° C., passing the current from the bismuth through the junction to the antimony produced a deflection of 10 degrees and a cooling effect ; and passing it in an opposite direction produced a deflection of 10 degrees and a heating effect.

From these results it appears that the Peltier effect, both of heating and cooling, with a thermo-couple of bismuth and antimony, was considerably larger at 93° than at 12° C. Also that the amounts of heating and cooling effect were about equal, whether the couple was at 12° or 93° C.

Similar experiments were made with a cross formed of bismuth and silver, and with one composed of antimony and silver, the silver wire being ·5 millim. diameter, with the same strength of current as before. The results were as follows (the direction of current given in each case is that through the junction) :—

Bismuth and Silver at 12° C.

Direction of Current.	Deflection.	Thermal Effect.
From Bi to Ag	2·0	Junction cooled.
„ Ag to Bi	2·0 to 2·5	„ heated.
	Bismuth and Silver at 92° C.	
From Bi to Ag	3·0	Junction cooled.
„ Ag to Bi	3·0	„ heated.
	Antimony and Silver at 12° C.	
From Sb to Ag	1·5	Junction heated.
„ Ag to Sb	1·5	„ cooled.
	Antimony and Silver at 95° C.	
From Sb to Ag	1·5	Junction heated.
„ Ag to Sb	1·5	„ cooled.

These results show—1st, That with a bismuth and silver thermo-couple, the total Peltier effect was larger at 92° than at 12° C.; 2nd, with an antimony and silver couple it was about the same at 95° as at 12° C.; 3rd, that it was less with an antimony-silver than with a bismuth-silver couple at each temperature; 4th, with a bismuth-silver couple, the heating-effect at 12° C. was somewhat greater than the cooling one, and at 92° C. the heating and cooling effects were about equal; and 5th, that with an antimony-silver pair, the heating and cooling effects both at 12° and 95° C. were all about alike.

With the couples formed of bismuth-antimony, iron-German-silver, and bismuth-silver, the total Peltier effect was greater in each case at the higher temperature than at the lower one, but with the antimony-silver one, the effects at the two temperatures were about equal.

All the results were probably affected to some extent by the influence of "electric convection of heat."

The whole of the results obtained (after making due allowance for differences in the specimens of metals employed by different experimentalists) agree with the thermo-electric diagram given in the manual on "Heat," by P. G. Tait.

XLIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 285.]

February 24, 1886.—Prof. J. W. Judd, F.R.S., President, in the Chair.

THE following communications were read:—

1. "On two Rhætic Sections in Warwickshire." By Rev. P. B. Brodie, M.A., F.G.S.

The sections noticed in this paper were (1) one exposed on a railway at Summer Hill, near Binton, between Stratford and Alcester, and (2) one, 13 miles further to the south-east, at Snitterfield, 3 miles north of Stratford-on-Avon, in excavations for a tunnel connected with a supply of water to that town.

At the first-named locality a bed with insect remains overlies the firestone and *Estheria*-bed, and this is succeeded in descending order by a considerable thickness of black and grey shales with the usual Rhætic fossils. The bone-bed is not exposed.

At the second locality, in borings and shafts, black Rhætic shales were found in three places resting upon a denuded surface of new Red Marl, and covered by between 40 and 50 feet of drift. *Avicula contorta* and other typical fossils were obtained from the shales. In other shafts the Rhætic beds were wanting, so that apparently those met with were merely small portions remaining of a larger mass which had been denuded away.

2. "On the Basement-beds of the Inferior Oolite of Gloucestershire." By E. Witchell, Esq., F.G.S.

The author observed that few papers have appeared lately on this subject in the Quarterly Journal, and admitted that the work done between 1847 and 1860 was of such excellent character that there seemed to be but little left to do in the Cotteswolds. Still he considered, after twenty-five years of experience, that there is room for another paper on the lower beds:—

(1) Because the Pea Grit of Leckhampton is made to include too much.

(2) Because this use of the term has led to confusion.

(3) Because the Pea Grit proper has a greater extension than has hitherto been supposed.

Thus has arisen the mistaken notion that the oolitic limestone at Frocester and Haresfield Hills is part of the freestone series *above* the Pea Grit. The author proposed to call the beds underlying the Pea Grit the "Lower Limestone," and gave sections at Crickley Hill and Ruscombe, near Stroud, in explanation of his views.

Summarizing the results—(1) the Pea Grit is well developed in the Cheltenham area, thinning towards the south, is no more than from three to five feet thick in the Stroud area, extending as far as Uley Bury, where it occurs as a thin band, having lost its ferruginous aspect. (2) Underlying this are several beds of white oolitic limestone, having layers of freestone alternating with layers of shelly detritus, and locally small quartz-pebbles, thickness from 20 to 30 feet. Attention was especially drawn to the contrast which these beds present, both lithologically and palæontologically, to the Pea Grit; and to their poverty in entire organic remains, limited chiefly to a few very small and peculiar Gasteropods. (3) Brown sandy limestones, locally coarse ferruginous gritty beds from 5 to 9 feet, fossiliferous in the lower portion. These are within the *Opalinus*-zone, and repose directly on the Cephalopoda-beds.

3. "On the Pliocene Beds of St. Erth." By Percy F. Kendall, Esq., and Robert G. Bell, Esq., F.G.S.

This paper consisted of a description of the beds exposed at St. Erth, a list of the Molluscan fossils identified, and some preliminary considerations of the evidence afforded by the Mollusca, and may be considered a continuation of that by the late Mr. S. V. Wood, read to the Society in November 1884.

The beds consist of sand and clay dipping about 5° to N.N.W. The only important fossiliferous bed is a blue clay, and fossils have only been obtained in one spot, though the beds have been traced over an area of about 120 acres. The fossils are well preserved, and with a few unimportant exceptions, are of invertebrate forms, chiefly Mollusca, Polyzoa. Ostracoda, and Foraminifera; remains of Crabs, Cirripedes, Echinoderms, Annelida, Sponges, and even of

Holothurians and Tunicata (*e.g. Leptoclinum tenue?*) have been detected.

The list of the Mollusca showed the range of each species in Miocene and Pliocene beds and in the present seas. The authors considered that the fossils agree in age with the middle or lower portion of the Red Crag, but that whilst many species having a southern character are present at St. Erth, and wanting in the Crags of the east coast, the Boreal and Arctic forms found so abundantly in the Crag are absent at St. Erth.

In explanation of this remarkable fact, it is suggested that when the St. Erth beds were deposited, although the North-Sea area was in direct communication with the Arctic Ocean, the western part of the British Channel was not, that the British Isles were joined to the continent of Europe on one side and to Greenland on the other, the Shetland and Faroe Islands and Iceland being the remnants of the barrier that formerly divided the Atlantic from the Arctic Sea. Evidence is given in support of this view from the present submarine configuration of the North Atlantic. It was also shown to be probable that the St. Erth area, in Pliocene times, was more directly connected with the Mediterranean than at present, by a marine channel that traversed France.

March 10.—Prof. J. W. Judd, F.R.S., President, in the Chair.

The following communications were read:—

1. "On the Alteration of coarsely spherulitic Rocks." By Grenville A. J. Cole, Esq., F.G.S.

The author stated that the pitchstone of Zwickau, Saxony, contains large spherulites, remarked on by Cotta in 1847, which are devoid of radial structure, and are traversed by the fine lines of flow that characterize the glassy matrix. The centre of each of these has been hollowed out by decomposition along cracks, as may be seen at the ends of the branches into which the cavity divides, and infiltration of chalcedony and calcite has occurred. The lines of flow correspond on opposite sides of this secondary mass, and do not bend round as if the spherule had formed about some calcareous inclusion or about a vesicle. Similar excavation and infiltration have occurred extensively among the coarsely spherulitic layers of the Precambrian rhyolites of Lea Rock, Wrekin, and in these the cracks traversing the rock are seen, under the microscope, as mere lines when passing through the matrix, but widen out at once, probably through more ready decomposition along their walls, when they enter spherulitic matter. In the white rock (Silurian rhyolite) of Digoed, near Penmachno, N. Wales, similar alteration has converted the closely set spherulites (often three inches in diameter) into mere shells filled with quartz and chlorite; while a black slate-like decomposition-product, with a hardness of 2·5 and a specific gravity of 2·77, occurs occasionally here, and very frequently in the less coarse but similar rock of Conway Mountain. In the latter place spherulites may be found containing this product in alternate concentric layers. Analysis shows it to be allied to pinite; but the formation in it, when it tends to become crystalline, of microlites of various kinds opposes its being regarded as a simple mineral. The rock of Digoed itself contains 83 per cent. of silica, the black product only 50 per cent. The great nodular masses of quartz and these contrasted soft, black, cleavable layers form striking features of alteration, especially as the residual spherulitic matter closely resembles the matrix, and may in time become undistinguishable from it. A consideration of the pyromerides of the continent makes it appear probable that they also are altered coarsely spherulitic rhyolites, and the comparisons made by Delesse in 1852 strongly support this view.

2. "Account of a Well-sinking made by the Great Western Railway Company at Swindon." By Horace B. Woodward, Esq., F.G.S. With Lists of Fossils, by E. T. Newton, Esq., F.G.S.

This well-sinking was made under the direction of Captain William Dean, while fossils were collected and notes of the strata were made by Messrs. W. H. Stanier and A. R. Elliott, to whom the authors were greatly indebted. The object of the sinking was to seek a supply of water for use in the works at Swindon. The strata proved were as follows:—

	ft.	in.
Made ground	8	0
Kimeridge Clay	64	1
Corallian Beds	40	1
Oxford Clay and Kellaways Rock	572	9
Cornbrash	18	3
Forest Marble	33	0
	736	2

Unfortunately for the Company, saline waters were met with in the Corallian rocks and again in the Forest Marble.

Few fossils were obtained from the Kimeridge and Corallian rocks; but those from the Oxford Clay and Kellaways Rock indicated the upward succession of the Callovian *ornatus*-, and *cordatus*-forms of Ammonites. It was shown that at least 44 feet of clays, sands, and sandstones might be assigned to the Kellaways Rock, which should be regarded as an irregular and impersistent basement-bed of the Oxford Clay. Turning to the subject of the saline waters, it was shown from analyses by Mr. F. W. Harris that the Corallian water contained 144 grains per imperial gallon, consisting chiefly of sodium chloride and sodium carbonate. In the Forest-Marble water, which had a temperature of 64°, the saline ingredients amounted to 2131 grains per gallon, consisting chiefly of sodium chloride, calcium chloride, &c.

Attention was then drawn to the occurrence of saline waters in the Jurassic rocks, at Melksham, Holt, Trowbridge, St. Clement's, Oxford, and other localities in the neighbourhood; and also to the occurrence of saline waters in the Coal-measures and older rocks of the Bristol Coal-basin, &c. It was shown that the occurrence of saline waters was not necessarily connected with the proximity of saliferous New Red rocks, and it was suggested that the saline waters at Swindon escaped from a ridge of Palæozoic rocks against which the Lower Jurassic rocks abutted, as they do on the Mendip Hills.

Mr. E. T. Newton said the fossils had been collected with great care by Mr. Stanier and Mr. Elliott, an exact record of depths being kept. He noticed some of the more important species that had been met with and their distribution, especially mentioning that the Ammonites from the Oxford Clay were nearly all from greater depths than 400 feet.

L. *Intelligence and Miscellaneous Articles.*

ON THE RESISTANCE IN THE VOLTAIC ARC. BY E. EDLUND.

If we measure the apparent resistance of the voltaic arc in the ordinary way, we find that it consists, as it were, of two parts, one of which is independent of the length of the arc, and the other is proportional to it. If we call the resistance w, the length of arc l, while a and b are two constants, then $w = a + bl$. This holds if the current strength is kept constant while the length of the arc is changed. The behaviour of the constants a and b is in so far different that b is less when the current increases, while a is almost independent of the strength of the current, and of the electromotive force of the source of electricity; it is only when this is so much diminished that an arc light is scarcely formed that the value of a becomes less. These observations of mine* have been confirmed by experimenters in recent times.

The question may be put whether this constant a represents a resistance of transition, which takes place at the surface of contact of the electrodes and the air, or whether it has its origin in an electromotive force, for the diminution in the strength of the current expressed by a might be explained by either of these assumptions. From the reasons given in the researches in question, and to which we here refer, it follows that a represents an electromotive force, which acts in opposition to the principal current.

Of all investigations on this subject published in the last few years, we shall only call attention to the following.

Frölich†, who in his investigation made use of observations made in the laboratory of Siemens and Halske, came to the conclusion that either of the assumptions are reconcilable with these observations, though he seems inclined to think that the constant a represents an electromotive force, as well as a re-

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* Pogg. *Ann.* vol. cxxxi. p. 586 (1867); vol. cxxxiii. p. 353; vol. cxxxiv. pp. 250, 337 (1868); and vol. cxxxix. p. 354 (1870).

† *Electrotechn. Zeitschrift*, vol. iv. p. 150 (1883).

sistance of transition. Frölich probably considers that a cannot be exclusively an electromotive force, for in this case it would have what, in his opinion, is the absurdly high value of 39 volts. Peukert* has made a series of observations on this subject, in which the strength of the current varied from 10 to 30 amperes. As follows from my older observations, Peukert found that the apparent resistance of the luminous arc may be represented by the formula $w = a + bl$. If it be assumed that the constant a is an electromotive force, its value according to Peukert must amount to 35 volts; a value which appeared to him so high that he did not venture to assume it could have its origin in an electromotive force, but that, partly at least, it represents a resistance of transition.

From my investigations cited above it follows that a is independent both of the magnitude of the source of the current and of the strength of the current, provided this does not sink to the lowest limit in which a voltaic arc may be formed. In my first experiments on this subject I have calculated a as an electromotive force, expressed in Bunsen's elements. Seven successive experiments made with a current of 53 to 79 Bunsen's elements gave the following results:—

a=24,416; 25,962; 25,354; 20,951; 21,637; 21,483; 23,119;

the mean of which is=23·315. This holds when the light is produced between carbon points of the ordinary kind.

If it be assumed that 1 Bunsen's element is equal to 1·7 Daniell's, and that this is 1·08 volt, 1 Bunsen=1·8 volt. If this number be multiplied by the mean in question, we obtain 41·97 volts. The mean of this number and of that found by Frölich and Peukert (39 and 35) gives 38·66 volts.

The view favoured by some experimenters, that the constant a partly represents a resistance of transition, is in fact disproved by the investigations of Victor von Lang†. By an ingenious method Lang succeeded in proving that the voltaic arc does contain a counter electromotive force which is equal to 39 volts. As this value of the counter force in the arc is almost equal to the value of the constant a above given, it follows that *there is no resistance of transition in the voltaic arc, and that therefore the entire diminution of the strength of the current which results from the production of the arc-light is caused by the resistance of the arc bl, and by the electromotive force contained in it.*

It must, however, be remarked here, that since the determinations of the values of a and of the electromotive counter force contained in it may possibly have been made with carbon electrodes of different kinds, it would be desirable to repeat both determina-

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* *Electrotechn. Zeitschrift*, vol. vi. p. 111 (1885).

† V. von Lang, *Wien. Ber.* April 1885; Wiedemann's *Annalen*, vol. xxvi. p. 145 (1885).

tions with one and the same voltaic arc.—*Annalen der Physik*, vol. xxvi. p. 518.

ON THE DEVIATION OF OXYGEN FROM BOYLE AND MARIOTTE'S LAW UNDER LOW PRESSURES. BY CHRISTIAN BOHR, OF COPENHAGEN.

In a series of absorptiometric determinations which I made in the course of the last few years, on the loosely combined oxygen in oxyhæmoglobin, the experiments made under low pressures of oxygen always showed irregularities, which, notwithstanding all the trouble I expended, could not be eliminated. In inquiring after the cause of these irregularities, I was led to look for it in the calculations necessary, in all such experiments, for converting the volume of the gas from the pressure before the absorption to the smaller pressure after the absorption.

This calculation was made of course by Boyle and Mariotte's law. The object was therefore to investigate with what accuracy oxygen follows the law in question under low pressures, in order, if possible, to obtain data for the experiments on dissociation. In this way arose the present series of experiments, in which it is indisputably proved that oxygen differs considerably from the law under the conditions in question. In the course of the experiments, the unexpected phenomenon was met with that the curve which expresses the relation between volume and tension exhibits a strongly marked discontinuity at a certain tension, which seems to suggest that here there is an alteration in the molecular composition of oxygen. Hence in the experiments great weight was laid on an accurate determination of this point.

After describing the experiments, the author sums up his conclusions as follows:—

I. At a temperature between 11° and 14° C. oxygen deviates from Boyle's law within the limits in question. The dependence between volume and pressure for a value of the latter which is greater than 0·70 millim. may be approximately expressed by the formula

$$(p+0{\cdot}109)v=k;$$

while the formula for values of the pressures which are less than 0·70 millim. is

$$(p+0{\cdot}070)v=k.$$

II. If the pressure sinks below 0·70 millim., oxygen undergoes a change of state; by raising the pressure above 0·70 millim. it may be restored to its original condition.—Wiedemann's *Annalen*, No. 3, 1886.

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AND
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[FIFTH SERIES.]

MAY 1886.

LI. *The Reaction upon the Driving-Point of a System executing Forced Harmonic Oscillations of various Periods, with Applications to Electricity. By* Lord RAYLEIGH, *D.C.L., F.R.S.*[*]

THE object of the present communication is to prove some general mechanical theorems, which may be regarded as in some sort extensions of that of Thomson relating to the energy of initial motions. The question involved in the latter may be thus stated[†]:—

"Given any material system at rest. Let any parts of it be set in motion suddenly with any specified velocities possible, according to the connections of the system; and let its other parts be influenced only by its connections with these. It is required to find the motion." And the solution is "that the motion actually taken by the system is that which has less kinetic energy than any other motion fulfilling the prescribed velocity conditions." On the other hand, if the impulses are given, a theorem of Bertrand tells us that the kinetic energy is the *greatest* possible.

For our present purpose we suppose the system to be set in motion by an impulse of one particular type, which we may call the first. The impulse itself may be denoted by $\int \Psi_1 \, dt$, and the corresponding velocity generated by $\dot{\psi}_1$. Under any given circumstances as to constraint, the velocity and the impulse are in proportion to one another; and the

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[*] Communicated by the Author.

[†] Thomson and Tait's 'Natural Philosophy,' §§ 316, 317.

resulting kinetic energy T is proportional to the square of either, being equal to $\frac{1}{2}\dot{\psi}_1\int\Psi_1\,dt$. Now Thomson's theorem asserts that the introduction of a constraint can only increase the value of T when $\dot{\psi}_1$ is given. Hence, whether $\dot{\psi}_1$ be given or not, the constraint can only increase the ratio of $\frac{1}{2}$T to $\dot{\psi}_1^2$, or of $\int\Psi_1\,dt$ to $\dot{\psi}_1$. This form of the statement virtually includes both Bertrand's and Thomson's theorems, which are thus seen to be merely different aspects of the same truth. If the velocity be given, the impulse is a minimum in the absence of constraint. If the impulse be given, the velocity is under the same circumstances a maximum. Calling the ratio of $\int\Psi_1\,dt$ to $\dot{\psi}_1$ the moment of inertia of the system when subjected to forces of the type in question, we may say that this moment can only be increased by the introduction of a constraint forcing the motion to follow a different law from that natural to it.

In close analogy to this theorem there are two others, relating to equilibrium and to steady motion resisted by viscous forces, of at least equal importance*. They may be thus stated.

Conceive a system to be displaced from stable equilibrium by a force of specified type. If the corresponding displacement be given in magnitude, the force is a minimum—or if the magnitude of the force be given, the displacement is a maximum,—when there is no constraint. Or we may say that the *stiffness* of the system, with respect to the kind of force in question, is increased by constraint. Examples, in illustration of the general proposition, are given in the papers already cited.

The third theorem depends upon the properties of the dissipation-function, and its most interesting application is to the conduction of heat and electricity. To take the latter case, if an electromotive force be applied to any system of conductors, the "resistance" to steady currents can only be increased by the imposition of a constraint, such for example as the rupture of a contact.

Hitherto we have supposed the forces to be either instantaneous or steady; and the three theorems depend upon the functions T, F, and V, expressing respectively kinetic energy, dissipation, and potential energy, only one of them being supposed to come into consideration at a time. We have now

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* Phil. Mag. Dec. 1874, "A Statical Theorem"; March 1875, "General Theorems relating to Equilibrium and to Initial and Steady Motion." See also 'Theory of Sound,' ch. iv.

to inquire under what conditions the theorems remain intact when the impressed force is a harmonic function of the time.

As regards the first theorem, the justification for the neglect of F and V may be that they are non-existent, as in many problems of ordinary hydrodynamics. In such cases the motion is at any instant of the same character as if it had been generated impulsively from rest, and the moment of inertia is a minimum. But even when F and V are generally sensible, their influence tends to diminish as the frequency of alternation increases, and we approach at last a state of things in which they may be neglected. From this point onwards we may say that the moment of inertia is a minimum in the unconstrained condition. Thus in a system of electrical conductors subject to a rapidly periodic electromotive force, the distribution of currents is ultimately independent of the resistances, and the *self-induction* is a minimum in the absence of constraint.

In like manner, even when T and F are sensible, the motion tends to be more and more determined by V, as the frequency of the vibrations is imagined to *diminish*. An "equilibrium theory" ultimately becomes applicable, and the "stiffness" is a minimum when there are no constraints.

The theorem in which F is mainly concerned stands in a somewhat different position. If T and V are both sensible, we cannot find an extreme case, in respect of the frequency of the vibration, which shall annul their influence. If, however, V vanish, we can make F paramount by taking the period sufficiently long; and if T vanish, we can attain the same object by limiting ourselves to the case when the period is very short. If T and V both vanish, the theorem of minimum resistance in the absence of constraint holds good for all periods of vibration. In the application to a system of electrical conductors which possess resistance and induction, but no capacity for *charge* needing to be regarded, we find that while (as already stated) the induction becomes paramount when the vibrations are very rapid, on the other hand when they are very slow the distribution is determined ultimately by the resistances only. In the first case the self-induction, and in the second the effective resistance, is a minimum in the absence of constraints.

We are now prepared to enter upon the consideration of the problem which is the main subject of the present paper, viz. the behaviour of systems in which F, and one or other of the two remaining functions T and V, are sensible, but without the restriction to very rapid or to very slow motions by which the influence of the second function may be got rid of. The investigation is almost the same whether it be T or V that enters; for the sake of definiteness I will take the first alternative.

Consider then a system, devoïd of potential energy, in which the coordinate ψ_1 is made to vary by the operation of the harmonic force Ψ_1, proportional to e^{ipt}. The other coordinates $\psi_2, \psi_3, \ldots$ may be chosen arbitrarily, and it will be very convenient to choose them (as may always be done) so that no product of them enters into the expressions for T and V. They would be in fact the principal or normal coordinates of the system on the supposition that ψ_1 is constrained (by a suitable force of its own type) to remain zero. The expressions for T and F thus take the following forms:—

$$\begin{aligned} \mathrm{T} &= \tfrac{1}{2}a_{11}\dot{\psi}_1{}^2 + \tfrac{1}{2}a_{22}\dot{\psi}_2{}^2 + \tfrac{1}{2}a_{33}\dot{\psi}_3{}^2 + \ldots \\ &\quad + a_{12}\dot{\psi}_1\dot{\psi}_2 + a_{13}\dot{\psi}_1\dot{\psi}_3 + a_{14}\dot{\psi}_1\dot{\psi}_4 + \quad . \quad . \quad . \qquad (1) \\ \mathrm{F} &= \tfrac{1}{2}b_{11}\dot{\psi}_1{}^2 + \tfrac{1}{2}b_{22}\dot{\psi}_2{}^2 + \tfrac{1}{2}b_{33}\dot{\psi}_3{}^2 + \ldots \\ &\quad + b_{12}\dot{\psi}_1\dot{\psi}_2 + b_{13}\dot{\psi}_1\dot{\psi}_3 + b_{14}\dot{\psi}_1\dot{\psi}_4 + \quad . \quad . \quad . \qquad (2) \end{aligned}$$

from which we get the equations of motion

$$\begin{aligned} & a_{11}\ddot{\psi}_1 + a_{12}\ddot{\psi}_2 + a_{13}\ddot{\psi}_3 + \ldots + b_{11}\dot{\psi}_1 + b_{12}\dot{\psi}_2 + \ldots = \Psi_1, \\ & a_{12}\ddot{\psi}_1 + a_{22}\ddot{\psi}_2 + b_{12}\dot{\psi}_1 + b_{22}\dot{\psi}_2 = 0, \\ & a_{13}\ddot{\psi}_1 + a_{33}\ddot{\psi}_3 + b_{13}\dot{\psi}_1 + b_{33}\dot{\psi}_3 = 0, \\ & . \quad . \quad . \quad . \quad . \quad . \quad . \end{aligned}$$

since there are no forces other than Ψ_1. We now introduce the supposition that the whole motion is harmonic in response to Ψ_1. Thus the above equations may be replaced by

$$\begin{aligned} & (ip\,a_{11} + b_{11})\dot{\psi}_1 + (ip\,a_{12} + b_{12})\dot{\psi}_2 + (ip\,a_{13} + b_{13})\dot{\psi}_3 + \ldots = \Psi_1, \\ & (ip\,a_{12} + b_{12})\dot{\psi}_1 + (ip\,a_{22} + b_{22})\dot{\psi}_2 = 0, \\ & (ip\,a_{13} + b_{13})\dot{\psi}_1 + (ip\,a_{33} + b_{33})\dot{\psi}_3 = 0. \\ & . \quad . \quad . \quad . \quad . \quad . \quad . \end{aligned}$$

By means of the second and following equations, $\dot{\psi}_2, \dot{\psi}_3, \ldots$ are expressed in terms of $\dot{\psi}_1$. Introducing these values into the first, we get

$$\frac{\Psi_1}{\dot{\psi}_1} = ip\,a_{11} + b_{11} - \frac{(ip\,a_{12} + b_{12})^2}{ip\,a_{22} + b_{22}} - \frac{(ip\,a_{13} + b_{13})^2}{ip\,a_{33} + b_{33}} - \ldots \quad . \qquad (3)$$

The ratio $\Psi_1 : \dot{\psi}_1$ is a complex quantity, of which the real part corresponds to the work done by the force in a complete period, and dissipated in the system. By an extension of electrical language we may call it the *resistance* of the system and denote it by the letter R′. The other part of the ratio is imaginary. If we denote it by $ip\mathrm{L}'\dot{\psi}_1$, or $\mathrm{L}'\ddot{\psi}_1$, L′ will be the moment of inertia, or self-induction of electrical theory. We write therefore

$$\Psi_1 = (\mathrm{R}' + ip\mathrm{L}')\dot{\psi}_1 \, ; \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the values of R′ and L′ are to be deduced by separation of the real and imaginary parts of the right-hand member of (3).

Now the real part of $\dfrac{(ip\,a_{12} + b_{12})^2}{ip\,a_{22} + b_{22}}$

$$= \frac{b_{12}{}^2 b_{22} + p^2 a_{12}(2\,b_{12}a_{22} - a_{12}b_{22})}{b_{22}{}^2 + p^2 a_{22}{}^2}$$

$$= \frac{b_{12}{}^2}{b_{22}} - \frac{p^2(a_{12}b_{22} - a_{22}b_{12})^2}{b_{22}(b_{22}{}^2 + p^2 a_{22}{}^2)} \, ; \quad . \quad . \quad . \quad . \quad (5)$$

so that

$$\mathrm{R}' = b_{11} - \Sigma \frac{b_{12}{}^2}{b_{22}} + p^2 \, \Sigma \frac{(a_{12}b_{22} - a_{22}b_{12})^2}{b_{22}(b_{22}{}^2 + p^2 a_{22}{}^2)} . \quad . \quad . \quad (6)$$

This is the value of the resistance as determined by the constitution of the system, and by the frequency of the imposed vibration. Each component of the latter series (which alone involves p) is of the form $\alpha p^2 / (\beta + \gamma p^2)$, where α, β, γ are all positive, and (as may be seen most easily by considering its reciprocal) increases continuously as p^2 increases from zero to infinity. We conclude that as the frequency of vibration increases, the value of R′ increases continuously with it. At the lower limit the motion is determined sensibly by the quantities b (the resistances) only, and the corresponding resultant resistance R′ is an absolute minimum, whose value is

$$b_{11} - \Sigma \frac{b_{12}{}^2}{b_{22}} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

At the upper limit the motion is determined by the inertia of the component parts without regard to resistances, and the value of R′ is

$$b_{11} - \Sigma \frac{b_{12}{}^2}{b_{22}} + \Sigma \frac{(a_{12}b_{22} - a_{22}b_{12})^2}{b_{22}a_{22}{}^2} . \quad . \quad . \quad . \quad (8)$$

That the resistance in this case would exceed that expressed by (7) might have been anticipated from the analogue of Thomson's theorem; but we now learn in addition that at every stage of the transition, during which in general the motions of the various parts disagree in phase, every increment of frequency of vibration is accompanied by a corresponding increment of resistance.

Again, the imaginary part of $\frac{(ip\,a_{12}+b_{12})^2}{ip\,a_{22}+b_{22}}$

$$=ip\,\frac{b_{12}(2a_{12}b_{22}-a_{22}b_{12})+p^2a_{22}a_{12}{}^2}{b_{22}{}^2+p^2a_{22}{}^2}$$

$$=ip\,\frac{a_{12}{}^2}{a_{22}}-ip\,\frac{(a_{12}b_{22}-a_{22}b_{12})^2}{a_{22}(b_{22}{}^2+p^2a_{22}{}^2)}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

so that

$$L'=a_{11}-\Sigma\frac{a_{12}{}^2}{a_{22}}+\Sigma\frac{(a_{12}b_{22}-a_{22}b_{12})^2}{a_{22}(b_{22}{}^2+p^2a_{22}{}^2)}. \quad . \quad . \quad . \quad (10)$$

In the latter series each term is positive, and continually diminishes as p^2 increases. Hence every increase of frequency is attended by a diminution of the moment of inertia, which tends ultimately to the minimum corresponding to disappearance of the dissipative terms.

Certain very particular cases in which R′ and L′ remain constant do not require more than a passing allusion. If T and F are of the same form, every such quantity as $(a_{12}b_{22}-a_{22}b_{12})^2$ vanishes.

As examples of the general theorem may be mentioned the problems considered by Prof. Stokes in his well-known paper upon "The Effect of the Internal Friction of Fluids on the Motion of Pendulums"*. Consider, for instance, the result for a sphere of radius a, vibrating (according to e^{ipt}) in a fluid for which the kinematic coefficient of viscosity is μ'. M′ denoting the mass of the fluid displaced by the sphere, Prof. Stokes's results may be written

$$R'=\frac{9M'}{4a}\left\{\frac{2\mu'}{a}+\surd(2\mu'p)\right\},$$

$$L'=M'\left\{\frac{1}{2}+\frac{9\surd(2\mu')}{4a\surd p}\right\}.$$

When p is zero, which represents uniform motion of the sphere,

$$R'=\frac{9\mu'M'}{4a^2}, \qquad L'=\infty\,\dagger.$$

As p increases, the expressions show that, in agreement with the theorem, R′ continually increases and L′ continually diminishes. In fact R′ tends to become infinite, and L′ to

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* Camb. Trans. vol. ix., 1850.

† That the energy of the motion is infinite in this case does not appear to have been noticed.

assume the value ($\frac{1}{2}M'$) given by ordinary hydrodynamics, in which viscosity is not regarded.

The use of the principal coordinates would not often be advantageous when the object is a special calculation of L' and R', rather than the establishment of a general theorem. In one very important case—that of two degrees of freedom only—the question does not arise, since but one other coordinate ψ_2 enters in addition to ψ_1. Under this head we may take the problem of the reaction upon the primary circuit of the electric currents induced in a neighbouring secondary circuit. In this case the coordinates (or rather their rates of increase) are naturally taken to be the currents themselves, so that $\dot\psi_1$ is the primary, and $\dot\psi_2$ the secondary current.

In usual electrical notation we represent the coefficients of self and mutual induction by L, N, M, so that

$$T=\tfrac{1}{2}L\dot\psi^2+M\dot\psi_1\dot\psi_2+\tfrac{1}{2}N\dot\psi_2^2,$$

and the resistances by R and S. Thus

$$a_{11}=L,\quad a_{12}=M,\quad a_{22}=N\,;$$
$$b_{11}=R,\quad b_{12}=0,\quad b_{22}=S\,;$$

and (6) and (10) become at once

$$R'=R+\frac{p^2M^2S}{S^2+p^2N^2}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$L'=L-\frac{p^2M^2N}{S^2+p^2N^2}. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

These formulæ were given long ago by Maxwell*, who remarks that the reaction of the currents in the secondary has the effect of increasing the effective resistance and diminishing the effective self-induction of the primary circuit.

If the rate of alternation be very slow, the secondary circuit is without influence. If, on the other hand, the rate be very rapid,

$$R'=R+\frac{M^2S}{N^2},\qquad L'=\frac{LN-M^2}{N}.$$

The formulæ (11) and (12) may be applied to deal with a more general problem of considerable interest, which arises when the secondary circuit acts upon a third, this upon a fourth, and so on, the only condition being that there must be no mutual induction except between immediate neighbours in

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* Phil. Trans. 1865; M is misprinted for M^2.

the series. Thus a_{13}, a_{14}, a_{24}, . . . (or, as we should here call them, M_{13}, M_{14}, M_{24}, . . .) are supposed to vanish, as would usually happen in experiment. For the sake of distinctness we will limit ourselves to four circuits.

In the fourth circuit the current is due *ex hypothesi* only to induction from the third. Its reaction upon the third, for the rate of alternation under contemplation, is given at once by (11) and (12); and if we use the complete values applicable to the third circuit under these conditions, we may thenceforth ignore the fourth circuit. In like manner we can now deduce the reaction upon the secondary, giving the effective resistance and self-induction of that circuit under the influence of the third and fourth circuits; and then, by another step of the same kind, we may arrive at the values applicable to the primary circuit, under the influence of all the others. The process is evidently general; and we know by the theorem that, however numerous the train of circuits, the influence of the others upon the first must be to increase its effective resistance and diminish its effective inertia, in greater and greater degree as the rapidity of alternations increases.

In the limit, when the rapidity of alternation increases indefinitely, the distribution of currents is determined by the induction-coefficients irrespective of resistance, and it is of such a character that the currents are alternately opposite in sign as we pass along the series*.

As another example under the head of two degrees of freedom, we will take the case of two electrical conductors in parallel. It is not necessary to include the influence of the leads outside the points of bifurcation. Provided there be no mutual induction between these parts and the remainder, their induction and resistance enter into the result by simple addition.

Under the operation of resistance only, the total current $\dot{\psi}_1$ would divide itself between the conductors R and S in the parts

$$\frac{\mathrm{S}\dot{\psi}_1}{\mathrm{R}+\mathrm{S}}, \quad \text{and} \quad \frac{\mathrm{R}\dot{\psi}_1}{\mathrm{R}+\mathrm{S}}.$$

We may conveniently take the second coordinate $\dot{\psi}_2$ so that the currents in the two conductors are

$$\frac{\mathrm{S}}{\mathrm{R}+\mathrm{S}}\,\dot{\psi}_1+\dot{\psi}_2, \quad \text{and} \quad \frac{\mathrm{R}}{\mathrm{R}+\mathrm{S}}\,\dot{\psi}_1-\dot{\psi}_2,$$

$\dot{\psi}_1$ still representing the total current.

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[*] See a paper, "On some Electromagnetic Phenomena considered in connection with the Dynamical Theory," Phil. Mag. July 1869.

Thus,

$$F=\tfrac{1}{2}R\left(\frac{S}{R+S}\,\dot{\psi}_1+\dot{\psi}_2\right)^2+\tfrac{1}{2}S\left(\frac{R}{R+S}\,\dot{\psi}_1-\dot{\psi}_2\right)^2$$

$$=\tfrac{1}{2}\dot{\psi}_1^{\,2}\,\frac{SR}{R+S}+\tfrac{1}{2}\dot{\psi}_2^{\,2}(R+S);$$

and if L, M, N be the induction-coefficients of the two conductors,

$$T=\tfrac{1}{2}\dot{\psi}_1^{\,2}\,\frac{LS^2+2MSR+NR^2}{(R+S)^2}$$

$$+\dot{\psi}_1\dot{\psi}_2\,\frac{(L-M)S+(M-N)R}{R+S}+\tfrac{1}{2}\dot{\psi}_2^{\,2}(L-2M+N)\cdot$$

Accordingly,

$$a_{11}=\frac{LS^2+2MSR+NR^2}{(R+S)^2},\qquad a_{12}=\frac{(L-M)S+(M-N)R}{R+S},$$

$$a_{22}=L-2M+N;$$

$$b_{11}=\frac{SR}{R+S},\qquad b_{12}=0,\qquad b_{22}=R+S;$$

and thus by (6), (10),

$$R'=\frac{SR}{R+S}+\frac{p^2}{R+S}\;\frac{\{(L-M)S+(M-N)R\}^2}{(R+S)^2+p^2(L-2M+N)^2},\quad .\quad (13)$$

$$L'=\frac{LS^2+2MSR+NR^2}{(R+S)^2}-\frac{\{(L-M)S+(M-N)R\}^2}{(R+S)^2(L-2M+N)}$$

$$+\frac{\{(L-M)S+(M-N)R\}^2}{(L-2M+N)\{(R+S)^2+p^2(L-2M+N)^2\}}\quad .\quad (14).$$

It should be remarked that $(L-2M+N)$ is necessarily positive, representing twice the kinetic energy of the system when the current in the first conductor is $+1$ and in the second -1.

Of the three terms in (14) the second and third cancel one another when p vanishes, and when p is very great the third term tends to disappear. The first and second terms together may be put into the form

$$\frac{LN-M^2}{L-2M+N},\quad .\quad .\quad .\quad .\quad .\quad .\quad .\quad (15)$$

independent (as it should be) of the resistances. In this $(LN-M^2)$ is necessarily positive, but may be relatively small when the wires are wound together. The energy of the system is then very small, when the currents are so rapid that their distribution is determined by induction.

There is an interesting distinction to be noted here dependent upon the manner in which the connections are made. Consider, for example, the case of a bundle of five contiguous wires wound into a coil, of which three wires connected in series (so as to give maximum self-induction) constitute one of the branches in parallel, and the other two, connected similarly in series, constitute the other branch. There is still an alternative in respect to the manner of connection of the two branches. If steady currents would circulate opposite ways (M negative), the total current is divided into two parts in the ratio of 3 : 2, in such a manner that the more powerful current in the double wire nearly neutralizes at external points the magnetic effects of the less powerful current in the triple wire, and the total energy of the system is very small. But now suppose that the connections are such that steady currents would pass the same way round in both branches (M positive). It is evident that the condition of minimum energy cannot be satisfied if the currents are in the same direction, but requires that the smaller current in the triple wire should be in the opposite direction to the larger current in the double wire. In fact the ratio of currents must be $3:-2$; so that (as on the same scale the total current is 1) the component currents in the branches are both numerically greater than the total current which is divided between them. And this peculiar feature becomes more and more strongly marked the nearer L and N approach to equality*.

When there are several conductors in parallel, the results would in general be very complicated. When, however, there is no mutual induction between the various members, a simplification occurs. If the currents be denoted by $\dot{\psi}_1$, $\dot{\psi}_2$, $\dot{\psi}_3$ . . . , the difference of potentials at the common terminals is

$$\mathrm{E}=(ip\mathrm{L}_1+\mathrm{R}_1)\dot{\psi}_1=(ip\mathrm{L}_2+\mathrm{R}_2)\dot{\psi}_2= \ .\ .\ .\ .\ ,$$

so that

$$\frac{\mathrm{E}}{\dot{\psi}_1+\dot{\psi}_2+\dots}=\frac{1}{\Sigma(ip\mathrm{L}+\mathrm{R})^{-1}}.$$

But if R′ and L′ be the effective resistance and self-induction respectively of the combination,

$$\frac{\mathrm{E}}{\dot{\psi}_1+\dot{\psi}_2+\dots}=\mathrm{R}'+ip\mathrm{L}',$$

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* The reader who is interested in this subject is referred to my papers in the Phil. Mag. July 1869, June 1870, "On Some Electromagnetic Phenomena," &c.

so that

$$\frac{1}{\mathrm{R}'+ip\mathrm{L}'}=\Sigma\frac{1}{\mathrm{R}+ip\mathrm{L}}. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Now

$$\Sigma\frac{1}{\mathrm{R}+ip\mathrm{L}}=\Sigma\frac{\mathrm{R}-ip\mathrm{L}}{\mathrm{R}^2+p^2\mathrm{L}^2};$$

or, if we write

$$\Sigma\frac{\mathrm{R}}{\mathrm{R}^2+p^2\mathrm{L}^2}=\mathrm{A}, \quad \Sigma\frac{\mathrm{L}}{\mathrm{R}^2+p^2\mathrm{L}^2}=\mathrm{B}, \quad . \quad . \quad . \quad (17)$$

$$\Sigma\frac{1}{\mathrm{R}+ip\mathrm{L}}=\mathrm{A}-ip\mathrm{B}=\frac{1}{(\mathrm{A}+ip\mathrm{B})/(\mathrm{A}^2+p^2\mathrm{B}^2)}.$$

Hence

$$\mathrm{R}'=\frac{\mathrm{A}}{\mathrm{A}^2+p^2\mathrm{B}^2}, \quad \mathrm{L}'=\frac{\mathrm{B}}{\mathrm{A}^2+p^2\mathrm{B}^2}. \quad . \quad . \quad (18)$$

Equations (17) and (18) contain the solution of the problem. When $p=0$,

$$\mathrm{R}'=\frac{1}{\Sigma(\mathrm{R}^{-1})}, \quad \mathrm{L}'=\frac{\Sigma(\mathrm{LR}^{-2})}{(\Sigma\mathrm{R}^{-1})^2}. \quad . \quad . \quad (19)$$

When $p=\infty$,

$$\mathrm{R}'=\frac{\Sigma(\mathrm{RL}^{-2})}{(\Sigma\mathrm{L}^{-1})^2}, \quad \mathrm{L}'=\frac{1}{\Sigma(\mathrm{L}^{-1})}. \quad . \quad . \quad (20)$$

These examples will suffice.

The relation between Ψ_1 and $\dot{\psi}_1$ expressed in (4) may be exhibited in another way in terms of the phase difference (ϵ) and the ratio of maxima. Thus if

$$\Psi_1=\mathrm{P}e^{i\epsilon}\dot{\psi}_1,$$

we have

$$\mathrm{P}=\sqrt{(\mathrm{R}'^2+p^2\mathrm{L}'^2)}, \qquad \tan\epsilon=\frac{p\mathrm{L}'}{\mathrm{R}'}. \quad . \quad . \quad (21)$$

As p increases from 0 to ∞, ϵ usually ranges from 0 to $\frac{1}{2}\pi$. At first sight it might appear probable that every increment of p would involve an increment of ϵ, but this seems not to be generally true. For consider a case in which

$$a_{11}=0, \quad a_{12}=0, \quad a_{13}=0, \ldots .$$

so that by (10)

$$p\mathrm{L}'=\Sigma\frac{a_{22}b_{12}{}^2p}{b_{22}{}^2+p^2a_{22}{}^2}.$$

Here $p\mathrm{L}'$ begins (as usual) at zero and ends at zero. During part of the range, therefore, it falls; and thus since R' rises throughout, it follows that ϵ does not rise throughout.

It may be worth while to remark that in some cases, where we cannot deal with phases, we are concerned principally with the value of $\surd(\mathrm{R}'^2+p^2\mathrm{L}'^2)$, a quantity which practical electricians are then tempted to call the resistance of the system. This temptation should be overcome, and the name reserved for R′, on which depends the amount of energy dissipated. It must be admitted, however, that a name for $\surd(\mathrm{R}'^2+p^2\mathrm{L}'^2)$ is badly required. Perhaps it might be called the "throttling."

The corresponding theorem in cases when T vanishes is deduced in a similar manner with use of the potential energy,

$$\mathrm{V}=\tfrac{1}{2}c_{11}\psi_1{}^2+\tfrac{1}{2}c_{22}\psi_2{}^2+\tfrac{1}{2}c_{33}\psi_3{}^2+\ldots.$$
$$+c_{12}\psi_1\psi_2+c_{13}\psi_1\psi_3+c_{14}\psi_1\psi_1+\ldots$$

Thus, if we write

$$\Psi_1=\mu'\psi_1+\mathrm{R}'\frac{d\psi_1}{dt}\ldots \quad . \quad . \quad . \quad (22)$$

we find

$$\mu'=c_{11}-\Sigma\frac{c_{12}{}^2}{c_{22}}+p^2\,\Sigma\frac{(b_{12}c_{22}-b_{22}c_{12})^2}{c_{22}(c_{22}{}^2+p^2b_{22}{}^2)}, \quad . \quad . \quad (23)$$

$$\mathrm{R}'=b_{11}-\Sigma\frac{b_{12}{}^2}{b_{22}}+\Sigma\frac{(b_{12}c_{22}-b_{22}c_{12})^2}{b_{22}(c_{22}{}^2+p^2b_{22}{}^2)}. \quad . \quad . \quad . \quad (24)$$

As p^2 increases, the "stiffness" (represented by μ') increases, and the "resistance" diminishes.

After what has been said it will not be necessary to occupy space with illustrations of the present theorem. Indeed its applications seem to afford less interest. It is curious that here, again, the easiest examples would be taken from electricity, although the principle itself is one of general mechanics. These (relating to the periodic charge and discharge of condensers through high resistances) may be left to the reader who wishes to pursue the subject further. The application to the theory of the conduction of heat may also be noticed.

When the three functions T, F, and V are all sensible, it is not generally possible to make the transformation to sums of squares upon which our process was founded. There are, however, special cases in which the same transformation which is required to simplify T and V is successful also as regards F. Among these are of course to be reckoned cases in which F does not appear, and those where there is but one other coordinate besides ψ_1. Assuming that $b_{23}, b_{34}, \ldots$ vanish, we have

$$\frac{\Psi_1}{\psi_1}=c_{11}-p^2a_{11}+ip\,b_{11}-\frac{(c_{12}-p^2a_{12}+ip\,b_{12})^2}{c_{22}-p^2a_{22}+ip\,b_{22}}-. \quad . \quad . \quad (25)$$

If we put

$$\Psi_1 = \mu' \psi_1 + \mathrm{R}' \frac{d\psi_1}{dt}, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

we obtain the values of μ' and R' by writing in (23) and (24) throughout $c_{11} - p^2 a_{11}$, $c_{22} - p^2 a_{22}$, $c_{12} - p^2 a_{12}$, . . . for c_{11}, c_{22}, c_{12}, . . . respectively.

A simpler case, which may be worth special mention, arises when all the coefficients b_{12}, b_{13}, . . . vanish. We have then

$$\mu' = c_{11} - p^2 a_{11} - \Sigma \frac{(c_{12} - p^2 a_{12})^2 (c_{22} - p^2 a_{22})}{(c_{22} - p^2 a_{22})^2 + p^2 b_{22}{}^2}, \quad . \quad . \quad (27)$$

$$\mathrm{R}' = b_{11} + \Sigma \frac{(c_{12} - p^2 a_{12})^2 b_{22}}{(c_{22} - p^2 a_{22})^2 + p^2 b_{22}{}^2}. \quad . \quad . \quad . \quad . \quad (28)$$

This case, when there are two degrees of freedom, is considered in my book on the 'Theory of Sound,' § 117.

If all the frictional coefficients b_{22}, b_{33}, . . . disappear, we have

$$\mathrm{R}' = b_{11}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

and

$$\mu' = c_{11} - p^2 a_{11} - \Sigma \frac{(c_{12} - p^2 a_{12})^2}{c_{22} - p^2 a_{22}}. \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Whenever, during its increase, p approaches and passes through one of the values proper to the free vibrations of the system supposed to be vibrating under the condition that ψ_1 is constrained by a suitable force Ψ_1 to remain zero, μ' rises to $-\infty$ and passes through to $+\infty$.

LII. *On the Self-induction and Resistance of Straight Conductors.* *By* Lord Rayleigh, *Sec. R.S., D.C.L.*[*]

IN connection with the experimental results of Professor Hughes[†], I have recently been led to examine more minutely the chapter in Maxwell's 'Electricity and Magnetism' (vol. ii. ch. xiii.) in which the author calculates the self-induction of cylindrical conductors of finite section. The problems being virtually in two dimensions, the results give the ratio L : l, where L is the coefficient of self-induction, and l the length considered. And since both these quantities are linear, the ratio is purely numerical. In some details the formulæ, as given by Maxwell, require correction, and in some directions the method used by him may usefully be

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[*] Communicated by the Author.

[†] Inaugural Address to the Society of Telegraph Engineers, January 1886.

pushed further. The present paper may thus be regarded partly as a review, and partly as a development of Maxwell's chapter.

The problems divide themselves into two classes. In the first class the distribution of the currents is supposed to be the same as it would be if determined solely by resistance, undisturbed by induction; in particular the density of current in a cylindrical conductor is assumed to be uniform over the section. The self-induction calculated on this basis can be applied to alternating currents, only under the restriction that the period of the alternation be not too small in relation to the other circumstances of the case. If this condition be not satisfied, the investigation must be modified so as to include a determination of the distribution of current. A problem of this class considered by Maxwell (§ 689) relates to the "Electromotive Force required to produce a Current of Varying Intensity along a Cylindrical Conductor."* In connection therewith another problem of the same class will here be treated, in which the mathematical conditions are simpler, and the results more readily apprehended.

In § 685 Maxwell takes the problem of two cylindrical conductors, the first of which conveys the outgoing and the second the (numerically equal) return current. The external radii are a_1, a_1'; the internal radii a_2, a_2'; b the distance between the centres. A possible difference in the magnetic quality is contemplated, the permeabilities for the material composing the cylinders being denoted by μ, μ', and that of the intervening space by μ_0.

The first correction I have to note relates merely to a slip of the pen. The result (22) should run

$$\frac{\mathrm{L}}{l}=2\mu_0\log\frac{b^2}{a_1a_1'}+\tfrac{1}{2}\mu\left[\frac{a_1^2-3a_2^2}{a_1^2-a_2^2}+\frac{4a_2^4}{(a_1^2-a_2^2)^2}\log\frac{a_1}{a_2}\right]$$
$$+\tfrac{1}{2}\mu'\left[\frac{a_1'^2-3a_2'^2}{a_1'^2-a_2'^2}+\frac{4a_2'^4}{(a_1'^2-a_2'^2)^2}\log\frac{a_1'}{a_2'}\right].$$

As printed in Maxwell's book the square brackets are omitted. This error does not affect the following formula (23), in which the cylinders are supposed to be solid. By putting a_2, a_2' equal to zero, we get

$$\frac{\mathrm{L}}{l}=2\mu_0\log\frac{b^2}{a_1a_1'}+\tfrac{1}{2}(\mu+\mu').$$

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* That some of the results arrived at experimentally by Hughes might be attributed to unequal distribution of current in the conductors was pointed out by Prof. Forbes in the course of a discussion which followed the delivery of Prof. Hughes's address.

It must, however, be remarked that in the derivation of (22) Maxwell appears to have overlooked the effect of the matter composing one conductor in disturbing the lines of induction due to the current in the other. On this account the formula is correct only when the permeabilities μ are all equal, and the results cannot be applied to iron wires without reservation. It would seem, however, that the error is of small importance when the wires are distant. The application to wires in contact, contemplated in § 688, will hold good only for the non-magnetic metals.

If we write c^2 for $(a_1^2-a_2^2)$, so that c is the radius of the solid cylinder of equal sectional area, we have in (22),

$$\frac{a_1^2-3a_2^2}{a_1^2-a_2^2}+\frac{4a_2^4}{(a_1^2-a_2^2)^2}\log\frac{a_1}{a_2}$$

$$=\frac{3c^2-2a_1^2}{c^2}-\frac{2(a_1^2-c^2)^2}{c^4}\log\left(1-\frac{c^2}{a_1^2}\right)$$

$$=\frac{2}{3}\frac{c^2}{a_1^2}+\text{terms in }\frac{c^4}{a_1^4}.$$

Hence, when the thickness of the cylinders is relatively small,

$$\frac{\mathrm{L}}{l}=2\mu_0\log\frac{b^2}{a_1a_1'}+\frac{\mu}{3}\frac{c^2}{a_1^2}+\frac{\mu'}{3}\frac{c'^2}{a_1'^2}.$$

If b, c, c' be given, the self-induction diminishes with increase of a_1, a_1', especially when μ, μ' are much greater than μ_0.

When μ is constant throughout, the "geometric mean distance" (§§ 691, 692) may conveniently be introduced. If A_1, A_2 be the areas occupied by the outgoing and return currents, we have

$$\frac{\mathrm{L}}{l}=4\mu_0[\log\mathrm{R}_{\mathrm{A}_1\mathrm{A}_2}-\tfrac{1}{2}\log\mathrm{R}_{\mathrm{A}_1}-\tfrac{1}{2}\log\mathrm{R}_{\mathrm{A}_2}],$$

where $\mathrm{R}_{\mathrm{A}_1}$, $\mathrm{R}_{\mathrm{A}_2}$ are to be understood as in (5), (6), (9) § (692).

For two circular areas,

$$\log\mathrm{R}_{\mathrm{A}_1\mathrm{A}_2}=\log b,\quad \log\mathrm{R}_{\mathrm{A}_1}=\log a_1-\tfrac{1}{4},\quad \log\mathrm{R}_{\mathrm{A}_2}=\log a_1'-\tfrac{1}{4},$$

if a_1, a_1' be the radii and b the distance between the centres; so that

$$\frac{\mathrm{L}}{l}=2\mu_0\log\frac{b^2}{a_1a_1'}+\mu_0,$$

as before.

In § 692 the value of R_A is given for rectangles and circular rings. For an ellipse of semi-axes a and b Prof. J. J. Thomson gives*

$$\log R = \log \frac{a+b}{2} - \tfrac{1}{4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which of course the case of the circle is included.

It is evident that for a given area R is least when the figure is circular. In that case we have

$$R = \cdot 4393 \, \surd(A). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In the case of the square,

$$R = \cdot 44705 \, \surd(A). \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For the ellipse, Prof. Thomson's result leads to

$$R = \cdot 4393 \, \surd A \, . \, (1 + \tfrac{1}{32} e^4 + \ldots), \quad . \quad . \quad . \quad (4)$$

showing the small effect of moderate eccentricity when the area is given.

As examples of very elongated forms we may take the ellipse or the rectangle. In the latter case the value approximates to that applicable to a line given by Maxwell (5) § 692. If the length be a,

$$R = a e^{-\frac{3}{2}} = \frac{A e^{-\frac{3}{2}}}{b}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

increasing without limit for a given area as b decreases.

It has been pointed out that Maxwell's result (22) § 685 is not rigorous, unless μ be constant. In order to put a case in which the lines of induction follow a simple law in spite of the presence of iron, we may suppose that the conductors are co-axal cylindrical shells. The outgoing current of total strength C travels in the interior cylinder of radii a_2, a_1; the return current of strength $-C$ in the outer cylinder of radii a_2', a_1'.

In Maxwell's notation we have the equations

$$\frac{dH}{dr} = -\mu\beta, \qquad \beta r = 4\pi \int_0^r w \, r \, dr,$$

so that

$$\iint H \, w \, dx \, dy = 2\pi \int_0^\infty H \, w \, r \, dr = \tfrac{1}{2} \int H \, d(\beta r)$$

$$= \tfrac{1}{2} [H \beta r] + \tfrac{1}{2} \int_0^\infty \mu \beta^2 r \, dr.$$

Now βr vanishes both at zero and infinity, so that we may

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* In a private letter.

take

$$\iint \mathrm{H}\, w\, dx\, dy = \tfrac{1}{2}\int_0^\infty \mu\, \beta^2\, r\, dr, \quad . \quad . \quad . \quad . \quad (6)$$

in which β represents the magnetic force, everywhere perpendicular to r.

In the integration from 0 to ∞ there are five regions to be considered. In the first, from 0 to a_2, there is no magnetic force. In the second, from a_2 to a_1, the magnetic force depends upon the total current travelling through the strata which are internal with respect to the point in question. In terms of the total current C we have

$$\beta = \frac{2\mathrm{C}}{a_1^2 - a_2^2}\left(r - \frac{a_2^2}{r}\right). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The permeability is here supposed to be μ.

In the third region, between the cylinders, the permeability is μ_0, and the magnetic force is given by

$$\beta = \frac{2\mathrm{C}}{r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Within the second cylinder the permeability is μ', and

$$\beta = \frac{2\mathrm{C}}{r} - \frac{2\mathrm{C}}{a_1'^2 - a_2'^2}\left(r - \frac{a_2'^2}{r}\right). \quad . \quad . \quad . \quad . \quad (9)$$

In the fifth region, from a_1' to ∞, $\beta = 0$.

Effecting the integrations, as indicated in (6), we obtain the value of

$$\iint \mathrm{H}\, w\, dx\, dy,$$

which gives $2\mathrm{T}/l$; and (if L be the coefficient of self-induction) $\mathrm{T} = \frac{1}{2}\mathrm{LC}^2$. The result is

$$\begin{aligned}\frac{\mathrm{L}}{l} &= 2\mu_0 \log \frac{a_2'}{a_1} \\ &+ \frac{2\mu}{a_1^2 - a_2^2}\left\{\frac{a_1^2 - 3a_2^2}{4} + \frac{a_2^4}{a_1^2 - a_2^2}\log\frac{a_1}{a_2}\right\} \\ &+ \frac{2\mu'}{a_1'^2 - a_2'^2}\left\{\frac{a_2'^2 - 3a_1'^2}{4} + \frac{a_1'^4}{a_1'^2 - a_2'^2}\log\frac{a_1'}{a_2'}\right\}. \quad . \quad (10)\end{aligned}$$

Perhaps the most interesting application of the general result is to trace the diminution of self-induction as the two currents are brought into closer and closer proximity. Let us suppose that the intervening space is reduced without limit, so that $a_2' = a_1$. Suppose further that $\mu' = \mu$, and that both conductors have the same sectional area πc^2, so that

$$a_1^2 - a_2^2 = a_1'^2 - a_2'^2 = c^2.$$

Under these circumstances we have

$$\frac{L}{l}=\frac{2\mu}{c^4}\left\{-r^2c^2+(r^2-c^2)^2\log\frac{r}{\sqrt{(r^2-c^2)}}\right.$$
$$\left.+(r^2+c^2)^2\log\frac{\sqrt{(r^2+c^2)}}{r}\right\}, \quad . \quad . \quad (11)$$

in which r is written for the radius of the common surface.

If c is small in comparison with r, (11) becomes

$$\frac{L}{l}=\frac{2\mu c^2}{3r^2}\left\{1+\frac{1}{10}\frac{c^2}{r^2}+\ldots\right\}, \quad . \quad . \quad . \quad (12)$$

showing that when the sectional areas are given, the self-induction diminishes without limit as the radius (r) increases.

If b denote the thickness of the walls, we have ultimately

$$c^2=2br,$$

and

$$\frac{L}{l}=\frac{4\mu b}{3r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

If the material composing the conductors be soft iron, the self-induction will be several hundred times greater than in the case of copper or other non-magnetic metal.

I now pass on to § 689, in which Maxwell solves a problem of the second class, relative to the self-induction of a cylindrical conductor, regard being had to the disturbance from uniformity in the distribution of the current over the section, due to induction. I will introduce the permeability μ, which in this question Maxwell treats as unity. His equations (14), (15), thus become

$$\mu C=-\left(\alpha\mu\frac{dT}{dt}+\frac{2\alpha^2\mu^2}{1^2.2^2}\frac{d^2T}{dt^2}+\ldots\right.$$
$$\left.+\frac{n\alpha^n\mu^n}{1^2.2^2\ldots n^2}\frac{d^nT}{dt^n}+\ldots\right),$$

$$AC-S=T+\alpha\mu\frac{dT}{dt}+\frac{\alpha^2\mu^2}{1^2.2^2}\frac{d^2T}{dt^2}$$
$$+\ldots+\frac{\alpha^n\mu^n}{1^2.2^2\ldots n^2}\frac{d^nT}{dt^n}+\ldots\Big),$$

where α, equal to l/R, represents the conductivity (for steady currents) of unit of length of the wire.

If $\phi(x)$ denotes the function

$$1+x+\frac{x^2}{1^2.2^2}+\ldots+\frac{x^n}{1^2.2^2\ldots n^2}+\ldots, \quad . \quad (14)$$

these equations may be written

$$\frac{dS}{dt}=AC-\phi\left(\alpha\mu\frac{d}{dt}\right)\cdot\frac{dT}{dt},$$

$$C=-\alpha\,\phi'\left(\alpha\mu\frac{d}{dt}\right)\cdot\frac{dT}{dt}.$$

Moreover, if E denote "the electromotive force due to other causes than the induction of the current upon itself,"

$$\frac{E}{l}=\frac{dS}{dt}.$$

To apply this to periodic currents following the harmonic law, where all the functions are proportional to e^{ipt}, we may replace d/dt by ip. Hence, eliminating $\frac{dT}{dt}$, we get

$$\frac{\alpha E}{lC}=\frac{E}{RC}=ip\alpha\,.\,A+\frac{\phi(ip\alpha\mu)}{\phi'(ip\alpha\mu)}. \quad . \quad . \quad . \quad (15)$$

To interpret (15), we have to separate the real and imaginary parts of ϕ/ϕ'. Now if x be small, we get in ascending powers of x by ordinary division,

$$\frac{\phi(x)}{\phi'(x)}=1+\frac{1}{2}x-\frac{1}{12}x^2+\frac{1}{48}x^3-\frac{1}{180}x^4+\frac{13}{8640}x^5-\ldots; \quad (16)$$

so that

$$\frac{\phi(ip\alpha\mu)}{\phi'(ip\alpha\mu)}=1+\frac{1}{12}p^2\alpha^2\mu^2-\frac{1}{180}p^4\alpha^4\mu^4+\ldots$$
$$+i\left\{\frac{1}{2}p\alpha\mu-\frac{1}{48}p^3\alpha^3\mu^3+\frac{13}{8640}p^5\alpha^5\mu^5-\ldots\right\}. \quad . \quad (17)$$

Thus, if we write

$$E=R'C+ipL'C, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

we find

$$R'=R\left\{1+\frac{1}{12}p^2\alpha^2\mu^2-\frac{1}{180}p^4\alpha^4\mu^4+\ldots\right\}$$
$$=R\left\{1+\frac{1}{12}\frac{p^2l^2\mu^2}{R^2}-\frac{1}{180}\frac{p^4l^4\mu^4}{R^4}+\ldots\right\}, \quad . \quad . \quad . \quad (19)$$

$$L'=l\left\{A+\mu\left(\frac{1}{2}-\frac{1}{48}p^2\alpha^2\mu^2+\frac{13}{8640}p^4\alpha^4\mu^4-\ldots\right)\right\}$$
$$=l\left\{A+\mu\left(\frac{1}{2}-\frac{1}{48}\frac{p^2l^2\mu^2}{R^2}+\frac{13}{8640}\frac{p^4l^4\mu^4}{R^4}-\ldots\right)\right\}, \quad (20)^*$$

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* For the case $\mu=1$, (19) and (20) follow readily from Maxwell's equation (18) § 690.

in which R′ represents the effective resistance and L′ the effective self-induction.

If the rate of alternation be very slow, so that p is small, these equations give (as was to be expected), R′ = R, and

$$L' = l\{A + \tfrac{1}{2}\mu\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

representing the self-induction for steady or slowly alternating currents. If we include the next terms, we see that as the frequency increases, the self-induction begins to diminish. At the same time the resistance begins to increase.

These results are merely very special cases of a general law*, from which we may learn that as the frequency of alternation gradually increases fron zero to infinity, there is a steady rise of resistance and accompanying fall of self-induction. The application of the general idea to the present case is very simple. At slow rates of alternation the distribution of current, being such as to make the resistance a minimum, is uniform over the section; and this distribution, since it involves magnetization of the outer parts of the cylinder, leads to considerable self-induction, especially in iron. On the other hand, when the rate of alternation is very rapid, the endeavour is to make the self-induction a minimum irrespective of resistance. This object is attained by concentration of the current into the outer layers. The magnetization of the conductor is thus more and more avoided, but of course at the expense of increased resistance. We may gather from the general argument, what (19) and (20) in their actual forms do not tell us, that as p increases without limit, R′ also becomes infinite, while the part of L′ depending upon the magnetization of the conductor tends to zero.

The increase of resistance proper (not merely of the "throttling" due to the combined effect of resistance and self-induction) in iron wires of moderate diameter subjected to varying currents, is one of the most striking of Prof. Hughes's results. So far as I am aware, neither Maxwell nor any other theorist had anticipated that the alteration of resistance would be important under such circumstances†.

In order to see under what conditions the alteration of resistance (and of self-induction) would become sensible, we have to examine the value of $\frac{1}{12}\frac{p^2l^2\mu^2}{R^2}$. We will take first

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[*] See preceding article.

[†] In the paper referred to I have quoted Maxwell's calculation of increased resistance and diminished self-induction due to the operation of currents in a *secondary* circuit.

the case of an iron wire of ·4 centim. diameter. The specific resistance of iron in C.G.S. measure is about 10^4; so that

$$\frac{R}{l}=\frac{10^4}{\pi\times\cdot04}.$$

Thus, if $p=2\pi/\tau$, τ being the complete period,

$$\frac{1}{12}\frac{p^2l^2\mu^2}{R^2}=\frac{5\cdot2\,\mu^2}{10^{10}\tau^2}. \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

The value of μ is more difficult to assign. It must be remembered that it is only in a very rough sense that μ can be treated as a constant at all. For small degrees of magnetization and for solid iron we may perhaps take $\mu=300$. In the case of the hissing sounds of a microphone-clock, working by a scraping contact, τ must be less than $\frac{1}{1000}$ second. Taking it, however, at this value, we get

$$\frac{1}{12}\frac{p^2l^2\mu^2}{R^2}=47 \text{ nearly},$$

which shows that under these circumstances the resistance and self-induction are entirely different from what they would be for slow rates of alternation.

We will now consider the case of copper, where $\mu=1$. The specific resistance may be taken to be 1640. If a be the radius in centimetres,

$$\frac{1}{12}\frac{p^2l^2\mu^2}{R^2}=\frac{\pi^4}{3}\frac{a^4}{1640^2\tau^2}=\frac{1\cdot2\,a^4}{10^5\tau^2}. \quad . \quad . \quad . \qquad (23)$$

From an alternate-current machine we may have currents of period ·01 second (100 positive and 100 negative pulses per second). In such a case our fraction becomes $\cdot12\,a^4$. This shows that for diameters of 1 centim. and over, the augmentation of resistance in the mains of an alternate-current system will rapidly become of commercial importance. A remedy may be found in the use of a more elongated section, or in subdivision of the main into a number of detached parts.

In physical experiments, such as those in which absolute resistance is determined by the method of the revolving coil*, (23) may be neglected, as we may see by supposing $a=\frac{1}{10}$, $\tau=\frac{1}{4}$.

The ultimate form of (15), when p is very great, may be

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* See for example Phil. Trans. 1882. Experiments to Determine the Value of the B.A. Unit of Resistance in Absolute Measure.

arrived at analytically. The series (14) may be then replaced by

$$\frac{1}{2\sqrt{\pi}}\,\frac{e^{2\sqrt{x}}}{x^{\frac{1}{4}}}, \quad \ldots \ldots \ldots \quad (24)$$

from which we find

$$\frac{\phi(x)}{\phi'(x)}=x^{\frac{1}{2}},$$

or

$$\frac{\phi(ip\alpha\mu)}{\phi'(ip\alpha\mu)}=\sqrt{(\tfrac{1}{2}p\alpha\mu)}\,.\,(1+i). \quad \ldots \quad (25)$$

Accordingly, the limiting values of resistance and self-induction are given by

$$\mathrm{R}'=\mathrm{R}\sqrt{(\tfrac{1}{2}p\alpha\mu)}=\sqrt{(\tfrac{1}{2}pl\mu\mathrm{R})}, \quad \ldots \ldots \quad (26)$$

$$\mathrm{L}'=l\left\{\mathrm{A}+\frac{\sqrt{\mu}}{\sqrt{(2p\alpha)}}\right\}=l\left\{\mathrm{A}+\sqrt{\left(\frac{\mu\mathrm{R}}{2pl}\right)}\right\}, \quad (27)$$

the first of which increases without limit with p, while the second tends to the finite value lA.

In the preceding problem the return current is supposed to be at a distance. As an example in which the self-induction of the whole circuit may become small, it would be natural to imagine the currents to travel in co-axal cylindrical shells, the interval between which might be considered to diminish indefinitely. The interest of the solution would, however, centre in the extreme case arrived at by supposing the radii of the cylinder to be great in comparison with the thickness of the walls ; and if we limit ourselves to this from the first, the analysis will be a good deal simplified.

Neglecting then the curvature, we treat the walls as plane, and the width of the strips (corresponding to the circumference of the cylinders) as infinite ; so that our functions, while remaining, as hitherto, independent of z (measured parallel to the axes of the cylinders), now become also independent of the second rectangular coordinate y, and may be treated as functions only of the time and of x, the coordinate measured perpendicularly to the walls. The problem is thus the distribution of currents in a circuit composed of two parallel infinitely long, infinitely wide, and equally thick strips, one of which conveys the outgoing and the other the return current. The thickness of each conducting strip will be denoted by b, and that of the intervening insulating layer by $2a$. The origin of x may conveniently be taken at the central point, in the middle of the insulating layer.

We might commence with the investigation of steady currents; but it will be sufficient to regard them as alternating (e^{ipt}). The results applicable to steady currents can always be deduced by simply putting p equal to zero.

Assuming, then, that the component currents u, v vanish, as well as the components of magnetic force γ, α, we have, in Maxwell's notation, the equations

$$\rho w = -\frac{d\Psi}{dz} - \frac{dH}{dt} = -\frac{d\Psi}{dz} - ipH, \quad . \quad . \quad . \quad (28)$$

$$\frac{d\beta}{dx} = 4\pi w, \qquad \mu\beta = -\frac{dH}{dx}; \quad . \quad . \quad . \quad . \quad (29)$$

so that

$$w = \frac{1}{4\pi}\frac{d\beta}{dx} = -\frac{1}{4\pi\mu}\frac{d^2H}{dx^2}, \quad . \quad . \quad . \quad . \quad (30)$$

and

$$\frac{d^2H}{dx^2} = \frac{4\pi\mu}{\rho}\frac{d\Psi}{dz} + i \,.\, \frac{4\pi\mu p}{\rho} \,.\, H. \quad . \quad . \quad . \quad (31)$$

We will now apply (31) to that conducting strip which lies on the positive side of the origin. Since, by hypothesis, $\frac{d\Psi}{dz}$, the rate at which the potential varies, is independent of x, the solution for regular periodic motion may be written

$$H = \frac{i}{p}\frac{d\Psi}{dz} + Ae^{m(x-a)} + Be^{-m(x-a)}, \quad . \quad . \quad . \quad (32)$$

$$\mu\beta = -mAe^{m(x-a)} + mBe^{-m(x-a)}, \quad . \quad . \quad . \quad (33)$$

in which A and B are constants, so far arbitrary, and

$$m^2 = \frac{4\pi\mu p i}{\rho}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

One relation between A and B is supplied by the condition that the magnetic force β must vanish at the external surface, where $x = a + b$. Hence

$$Ae^{mb} = Be^{-mb}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

If C be the total current corresponding to width y, we have

$$\frac{C}{y} = \int_a^{a+b} w\,dx = \frac{1}{4\pi}(\beta_{a+b} - \beta_a) = -\frac{1}{4\pi}\beta_a = \frac{m}{4\pi\mu}(A - B),$$

by (33); so that

$$A - B = \frac{4\pi\mu C}{my}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

These equations determine A and B.

Another condition is afforded by the consideration that, on account of the symmetry, H must vanish when $x=0$, or $H_0=0$. Within the insulator, whose permeability we take to be unity, $w=0$, so that by (29) $\beta=\beta_a$, and

$$H_a-H_0=-\int\beta\,dx=-\beta_a a.$$

Hence from (32), by equating the values of H_a,

$$\frac{4\pi aC}{y}=\frac{i}{p}\frac{d\Psi}{dz}+A+B. \quad . \quad . \quad . \quad . \quad (37)$$

Now by (35), (36),

$$A+B=-\frac{4\pi\mu C}{my}\,\frac{e^{mb}+e^{-mb}}{e^{mb}-e^{-mb}},$$

so that

$$-\frac{d\Psi}{dz}=ipC\frac{4\pi a}{y}+\frac{4\pi\mu ipC}{my}\,\frac{e^{mb}+e^{-mb}}{e^{mb}-e^{-mb}}. \quad . \quad . \quad (38)$$

In (38) the first term represents a part of the effective self-induction, and contributes nothing to the effective resistance. This self-induction, per unit length, is simply $4\pi a/y$, and is independent of p. The second term, being neither wholly real nor wholly imaginary, contributes both to self-induction and to resistance. If, separating the real and imaginary parts of the right-hand member of (38), we write

$$-l\frac{d\Psi}{dz}=R'C+L'.\,ipC\,; \quad . \quad . \quad . \quad . \quad (39)$$

then R′ represents the resistance and L′ the self-induction of length l of the conductor measured parallel to z.

From (34)

$$m=\sqrt{\left(\frac{2\pi\mu p}{\rho}\right)}\,.\,(1+i)=q(1+i), \quad . \quad . \quad (40)$$

if we write for brevity

$$q=\sqrt{\left(\frac{2\pi\mu p}{\rho}\right)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

The general expressions for R′ and L′ are somewhat complicated. If the rate of alternation be slow, p, and with it m and q, are small. In this case (38) may be written approximately

$$-\frac{d\Psi}{dz}=ipC\frac{4\pi a}{y}+\frac{\rho C}{by}\left(1+i\frac{4\pi\mu pb^2}{3\rho}\right);$$

so that

$$R'=\frac{\rho lC}{by}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

in accordance with Ohm's law, and

$$L' = \frac{4\pi a l}{y} + \frac{4\pi}{3}\frac{\mu b l}{y}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (43)$$

If $a=0$, the first term in (43) disappears, and we get a simplified result which should agree with one found previously (13). We may compare them by replacing y with $2\pi r$. The apparent discrepancy that the self-induction by (13) is twice as great as by (43) depends merely upon a slight difference in the way of reckoning. The result in (13) refers to a *double* length l, one part from the outgoing and the other from the return conductor.

At the other extreme, when p is very great, a simple result again applies. In that case $(e^{mb}+e^{-mb})/(e^{mb}-e^{-mb})$ may be replaced by unity, and (38) becomes

$$-\frac{d\Psi}{dz} = ipC\frac{4\pi a}{y} + (1+i)\frac{C\sqrt{(2\pi\mu p\rho)}}{y}.$$

Thus

$$R' = \frac{l\sqrt{(2\pi\mu p\rho)}}{y}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (44)$$

$$L' = \frac{4\pi a l}{y} + \frac{l\sqrt{(2\pi\mu\rho)}}{y\sqrt{p}}. \quad . \quad . \quad . \quad . \quad . \qquad (45)$$

These formulæ show that the resistance increases without limit with p, being proportional to $\sqrt{p}$, and that the self-induction diminishes towards the limit $4\pi a l/y$. If a be zero, that is if the insulating layer be infinitely thin, the self-induction diminishes without limit as p increases, being proportional to $p^{-\frac{1}{2}}$. Another important point is that when p is great enough, the values of R′ and L′ are independent of b, the thickness of the strips. The meaning of this is, of course, that, under such circumstances, the currents concentrate themselves more and more towards the inner parts, in the endeavour to diminish the effective self-induction.

The distribution of current in the extreme case, where it is not limited by the thinness of the strips, is readily expressed. We have in general

$$w = \frac{mC}{y}\frac{e^{m(x-a-b)}+e^{-m(x-a-b)}}{e^{mb}-e^{-mb}}, \quad . \quad . \quad . \quad . \qquad (46)$$

becoming, when $b=\infty$,

$$w = \frac{mC}{y}e^{-m(x-a)}; \quad . \quad . \quad . \quad . \quad . \quad . \qquad (47)$$

or, on introducing the value of m from (40),

$$w=\frac{\sqrt{2}\,.\,q\mathrm{C}}{y}e^{-q(x-a)}\left\{\cos\left(\tfrac{1}{4}\pi-qx+qa\right)+i\sin\left(\tfrac{1}{4}\pi-qx+qa\right)\right\}. \quad (48)$$

The thickness through which the current is important is found from

$$q(x-a)=1,$$

or

$$x-a=\sqrt{\left(\frac{\rho}{2\pi\mu p}\right)}, \quad . \quad . \quad . \quad . \quad (49)$$

diminishing as p increases.

It should be remarked in conclusion that when a is very small and l very great, there may be a sensible accumulation of electricity upon the inner surfaces of the strips acting as plates of a condenser. In such a case u will no longer vanish, w will become a function of z, and our results will require modification.

April 3, 1886.

LIII. *Observations on Invisible Heat-Spectra and the Recognition of hitherto Unmeasured Wave-lengths, made at the Allegheny Observatory. By* Prof. S. P. Langley, *Allegheny, Pa.*[*]

[Plate IV.]

IT is known to all that the surface-temperature of this planet depends upon the properties of radiant heat and the relation to them of the action of its atmosphere. It has been usual to compare this action to that of the glass cover of a hot-bed; for glass, it is also well known, grows opaque to dark heat, and continuously so as its wave-length increases, thus letting the solar light-heat pass freely through it to the soil, while it is comparatively impervious to the dark heat returned from the latter. But this analogy must not be interpreted too literally. Whether the atmosphere is pervious to the soil's heat we do not here discuss, but it has of late [†] been shown that the air does not behave otherwise like glass, as it was supposed to do, but, except for the absorption-bands, grows—not more opaque—but more transmissible, to *solar* heat, up to its greatest observed wave-length, and that hence our views of the nature of the yet uncomprehended heat-storing action which maintains organic life on the earth must be modified. The little that the spectroscope tells us about the atmospheres of other

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[*] Communicated by the Author, having been read before the American Association for the Advancement of Science, at Ann Arbor, 1885.

[†] See Amer. Journ. of Science, March 1883; Professional Papers of U.S. Signal Service, No. 15, Expedition to Mount Whitney.

planets, leads us to think that we can best understand their relations to solar energy by studying the atmosphere of our own; for our non-comprehension of these relations is largely due to our ignorance of certain physical data which have never yet been obtained.

While the general question for the physical astronomer, then, is "What kind of transformation does the solar energy suffer at the surface of any planet?" we here seek a reply to the simpler preliminary one, "What are the wave-lengths of heat from non-luminous sources, such as the soil of this planet?"—a question which has never been answered, because there have been no means of recognizing this heat when drawn out into a spectrum; indeed, we so habitually associate the idea of a spectrum with that of light, that there is a certain strangeness at first in the idea even of a "spectrum" formed by a cold body like, for instance, ice. Yet the ice surface must not only be capable of radiating heat to a still colder body, but, according to our present conceptions of radiant energy, be capable of giving a spectrum, whether we can recognize it or not. It is the object of the present paper to describe the actual formation of such spectra, and the recognition of their heat in approximate terms of wave-lengths.

To distinguish between these new regions of research and the older ones, let us briefly summarize our actual information about wave-lengths, since on the latter the whole question largely turns, and each extension of it, we may agree, is a step toward an interpretation of everything about the constitution of the universe which radiant energy may have to tell us. Thus there is no exact relation known between the periods of vibration of certain molecules in the sun and the angles through which the rays announcing them are refracted by a prism, while the wave-lengths of these rays, if known, are capable of giving us quite other intelligence.

Yet our knowledge even of the wave-lengths of light is comparatively recent, since it was only at the beginning of this century that the labours of Thomas Young brought the undulatory theory itself from the disfavour in which it had lain; and the memoirs in which Fraunhofer gave the first relatively full and accurate measures of the wave-lengths of light date no further back than 1814.

The measures of Newton, interpreted in terms of the present theory, gave the length of the extreme violet waves at $\frac{167}{10,000,000}$ of an inch, and of the extreme red at $\frac{266}{10,000,000}$, or in millimetres 0·00042 millim. and 0·00067 millim. respectively—numbers nearly corresponding with the lines H and B, while Fraunhofer's own values are comprised between 0·00036 millim. and 0·00075 millim. More recently the range of vision has been still more extended, by the use of the fluorescent eyepiece of Soret; while by the aid of photography and the employment of quartz trains, solar radiations of a wave-length of about 0·29 μ have been observed *, and rays whose wave-length is as little as 0·185 μ have, it is said, been observed from the induction spark.

Our atmosphere cuts off the ultra-violet rays of a length less than about 0·29 μ, while I have found it not very difficult to *see* below Fraunhofer's great A, lines whose wave-length is about 0·81 μ. The extreme range of the normal eye, then, is from about 0·00036 to 0·00081 millim. or a little over one octave, though the statement that the range of the eye is less than one octave is still commonly made.

Fraunhofer's first measures were made with a literal grating composed of parallel strands of wire; while the successive labours of Nobert, Rutherfurd, and Rowland have placed in the hands of physicists instruments of constantly increasing power, which have finally reached what seems nearly theoretical perfection at the hands of the two latter. It is with the now so well-known gratings of Prof. Rowland that the direct measures of wave-lengths in the solar-heat spectrum I have already made public † have been chiefly executed.

In Plate IV. fig. 1 we have a necessarily condensed representation of the whole spectrum, visible and invisible, on the normal scale, the distances being proportional to the wave-lengths observed. The inferior limit being 0, we have at (*a*) the number 0·18 μ (eighteen one-hundred-thousandths of a millimetre), which represents the shortest measured in the electric spark from aluminum. Next, near 0·29 μ (*b*) we have, according to M. Cornu, the shortest solar ray which penetrates our atmosphere; near 0·35 μ (*c*), in the ultra-violet, is the shortest wave which can be seen by the naked eye, and nearly the shortest which can pass through glass; while near 0·81 μ (*d*), in the extreme red, is nearly the longest which the eye can observe. The entire visible spectrum on the normal scale is, it will be seen, insignificant in comparison with that great infra-red region which is so important to us, and of which we know so very little. It has been known since the time of the first Herschel that heat-rays existed

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* 1·0 μ=0·001 millim.

† *Comptes Rendus*, Sept. 11, 1882; National Academy of Science, 1883; Amer. Journ. of Science, March 1884; Phil. Mag. March 1884.

Fig. 3.

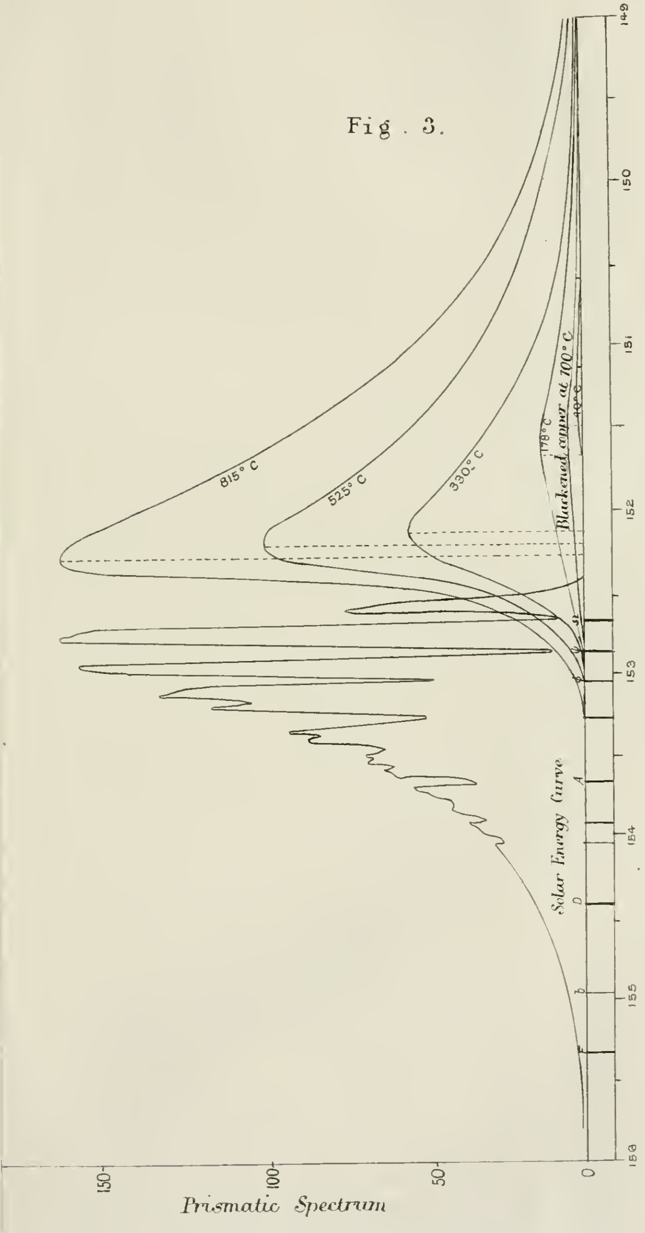
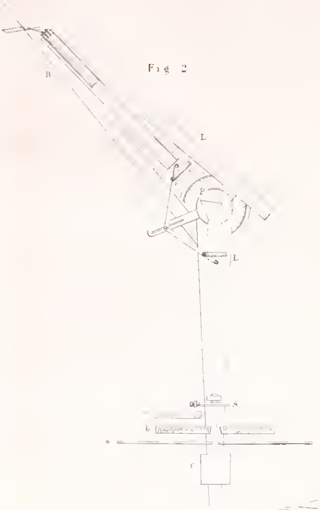
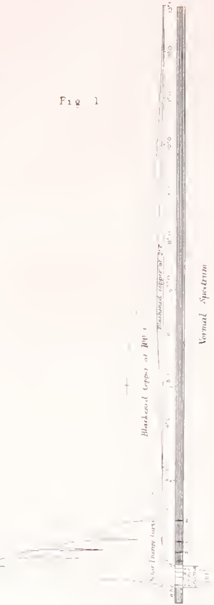

815° C
525° C
330° C
178° C
40° C
Blackened copper at 100° C
Solar Energy Curve
Ω
ψ
ф
A
D
b
149
150
151
152
153
154
155
156
150
100
50
0
Prismatic Spectrum

Fig. 2.



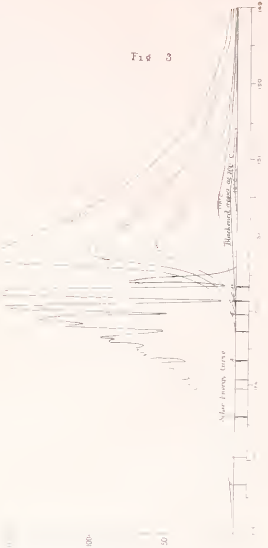
Spectro-bolometer with rock salt train

Fig. 1.



Normal Spectrum

Fig. 3.



Prismatic Spectrum

below the range of vision, but of their wave-lengths nearly nothing has, till lately, been ascertained, partly for want of sufficiently delicate heat-recognizing apparatus, and still more from the fact that it is difficult to use the grating here, owing to the overlapping spectra, and to the consequent necessity we have till lately been under of separating these rays only by the prism, which gives no measure of their wave-lengths. Physicists have accordingly attempted to find these, by observing what deviations correspond to known wave-lengths in the visible portion, and by trying to determine from theoretical considerations what relations should obtain in the infra-red ; but the various formulæ by which these supposed relations have been expressed have not till lately been tested. The difficulty has been partly overcome in the last few years by the application of the linear bolometer to the spectrum formed by the concave gratings with which Prof. Rowland has furnished us ; the deviations of the heat-rays having first been observed and the principal lines of the infra-red region mapped by the joint use of the bolometer and a flint-glass prism, in 1881. It will be remembered that one of the best known formulæ on which physicists till lately relied for determining the relations of wave-lengths to deviations was Cauchy's ; that this set an absolute limit to the wave-length which any prism could under any circumstances discriminate, and that this supposed extreme wave-length was somewhere between 10,000 and 15,000 on Ångstrom's scale. Besides this theoretical limit, it was supposed that glass absorbed dark heat to such an extent that the longer solar heat-waves would be stopped in the substance of the prism, even were there no other obstacle.

In 1881, however, we found at Allegheny by actual trial that heat-waves, whose wave-length was far in excess of the theoretical limit, passed through a flint-glass prism, so that it was ascertained both that this supposed limit did not exist and that common glass was nearly diathermanous to all the dark heat which comes to us from the sun. By means of a glass prism and the bolometer, we were thus able to pursue our researches and map the infra-red or invisible solar spectrum to a point where it actually came to an end. What the wave-length of this point was we could not tell, for it lay entirely outside of what theory had till then pronounced possible.

Next, using the grating, we have at Allegheny determined the wave-lengths of most of the newly discovered solar-heat region, by direct observation, and shown that it extended to the unanticipated length of $2{\cdot}7\,\mu$ (*e*, Pl. IV. fig. 1) (*i. e.* 27,000 on Ångstrom's scale). I cite these facts, which have already been published, to bring us up to the point where the present researches begin.

The question now arises, "Does this ultimate observable wave-length of solar heat of 2·7 μ, which our atmosphere transmits, correspond to the lowest which can be obtained from any terrestrial source, or are the wave-lengths emitted from our planet towards space even greater, and conceivably such that our atmosphere is nearly athermanous to them?" To answer this, it becomes necessary to do what I think has not been attempted before—to take a source of very low temperature, comparable to that of the soil, and not only to measure its extremely feeble invisible heat, but to draw this out into a spectrum by means of the prism or grating, and to determine the indices of refraction of its prominent parts, and, by inference, their wave-lengths. We have now been engaged on this research at Allegheny at intervals for two years, a time which will not appear extravagant to one acquainted with its extreme difficulties. Not to dwell on these in detail, I will mention only that the grating cannot well be used on account of its overlapping spectra, if for no other reason, and that the most transparent glass, which we have found to be comparatively diathermanous to dark solar heat, turns out to be almost absolutely athermanous to the heat from a surface at the temperature of boiling water.

Glass being useless here, almost the only material of which we can form our prism is rock-salt, and we must have not only an entire train of lenses (both collimating and observing) of salt, as well as the prism, but the pieces must be of exceptional size, purity, and perfection of figure, to contend with these special difficulties, and they must be maintained in condition, in spite of the incessant deterioration of this substance. Finally, as we wish to determine wave-lengths, these measures must be very accurate, and the prism be capable of giving fixed points of reference like the visible Fraunhofer lines. The prism we are now using is made by Mr. Brashear of Pittsburgh, and when freshly polished gives a spectrum not only filled with hundreds of Fraunhofer lines, but which shows distinctly the nickel line between the D's, and is probably the finest one ever produced from this material.

Such measures on the collective heat of black bodies as those of Melloni and Tyndall have been made on large radiating surfaces, like those of the Leslie cube; but in order to form a spectrum, of this as of any other source, we must, of course, take only such a limited fraction of the side of the cube as is represented by a narrow spectroscope slit; so that both from its minute amount and feeble intensity (even if we can pass it through a prism, to form a spectrum), it is absolutely inappreciable, in anything like homogeneous portions, to the most delicate thermopile, and difficult of attack even by the bolometer.

We have employed as radiating surfaces, Leslie cubes covered with lampblack and filled with boiling water or aniline, the former giving a radiating surface of a temperature of 100° C., the latter one of 178° C.; and also cubes filled with freezing-mixtures, with the latter of which Mr. F. W. Very, of this Observatory, conducted in the cold days of last March one series of measures in which the radiator was the bolometer itself, at a temperature of −2° C., and the source radiated to, a vessel filled with a mixture of salt and snow at the temperature of −20° C., thus determining the distribution of energy in the *spectrum* of a surface below the freezing-point of water. The Leslie cube used in these experiments was filled either with a freezing-mixture or with water, kept gently boiling by a Bunsen burner underneath; or, again, when measurements from a source at an exactly determinable higher temperature were desired, with aniline, which has a boiling-point of about 178° C. A condensing apparatus connected with the cube in the latter case prevented the escape of the aniline vapour. It was also found possible to keep the cube at any intermediate temperature within sufficiently narrow limits by properly adjusting the flame.

The apparatus is shown in Pl. IV. fig. 2. Between the blackened side of the Leslie cube C and the spectrometer-slit S were interposed a large pasteboard screen (*a*) and a flat copper vessel (*b*) filled with broken ice, both pierced with apertures slightly larger than the slit, to allow the passage of the rays; and the exposures were made by withdrawing a third hollow screen (*c*) made of copper and filled with ice, which cut off the radiation of the cube from the slit when it was in place.

The train for forming the spectrum upon the bolometer-face consisted of two rock-salt lenses L, L, and the rock-salt prism P. Each lens is 75 millim. in diameter, and 350 millim. focus for visible rays. For the infra-red rays measured on, the focus is from one to two centimetres greater than this. The prism is made from an unusually perfect piece of rock-salt, and is 64 millim. on a side. With this train, composed entirely of rock salt, and an ordinary eyepiece, the Fraunhofer lines are very distinctly visible in either sunlight or moonlight. The lenses, prism, slit, and other parts of the train were mounted upon the large spectrometer (described in the Amer. Journ. of Science, vol. xxv. 1883, and the Mt. Whitney Report, chap. xi.).

To illustrate the use of the apparatus, we give below in detail the observations of March 20, 1885, for determining the form of the energy-curve in the spectrum of a Leslie cube at 178° C. The temperature of the room was −7° C.; so that the excess of the temperature of the cube over that of the room was 185° C.

The reading of the circle was made 0° 0′ 0″ when the spectrometer-arms were in line, and the direct image of the slit fell on the bolometer. The prism was then placed on its table, the automatic minimum deviation apparatus connected, and the prism set to minimum deviation by a sodium-flame held in front of the slit. The deviation of the ray falling upon the bolometer was then given directly by the circle reading to 10″.

The bolometer used was 2 millim. wide, and consequently subtended an angle of about 20′ in the spectrum. After adjusting the prism, the slit was opened to the same width. A secondary object of the experiment was the determination of the transmission of rock-salt in different parts of the spectrum, and for this purpose a plate of polished rock-salt, whose thickness was 9·1 millim., was interposed at the slit, after each deflection obtained in the ordinary manner, the plate being allowed to remain in each case till the bolometer had registered the heat due to radiations from the salt itself, when the screen was withdrawn and the radiations from the Leslie cube allowed to pass through it.

The results are given below in the form of a table.

Deviation.	Deflection.	Deflection with rock-salt plate interposed.	Transmission of plate.
40° 30′	12		
40 00	72		
39 30	214		
39 00	364		
38 30	420	360	·857
38 00	365		
37 30	269	251	·933
37 00	196		
36 30	137	122	·891
36 00	96		
35 30	62	63	1·02
35 00	48		
34 30	29	27	·931
34 00	26·5		
33 30	18	14	·778
33 00	10·5		

The "transmission" of the plate of rock-salt (here uncorrected for heat lost by reflection at the anterior surface) appears to be shown by subsequent experiments to slightly diminish for extreme heat-rays in the Leslie cube-spectrum; but to remain so nearly constant through the range of these experiments, as to show that the present approximate values need no correction on this account. More exact ones decisive of the point in question will be given in a subsequent memoir.

The following series was then taken for fixing more accurately the position of the maximum:—

Deviation.	Deflection.
39° 00′	365
38 50	406
38 40	430
38 30	428
38 20	414
38 10	401
38 00	371

From curves representing these observations, it was concluded that the maximum was at 38° 35′. It will be shown further on, how an attempt may be made to estimate the wave-lengths in these regions.

Measurements were also made with surfaces of copper heated to much higher temperatures, and with the cube at different lower temperatures, for the purpose of determining whether the position of the maximum of the energy curve varies with the temperature, and if so to determine if possible the relation. Experiments of this kind have been made by Mr. W. W. Jacques [*], who found that "the distribution of heat in the spectrum of a solid or liquid source of radiation is nearly independent of the temperature of the source." It was evident from the care with which Mr. Jacques's experiments were conducted, that the shifting of the maximum must be slight and difficult of quantitative determination; but with the pure spectrum and delicate heat-measuring apparatus at our command, it was thought possible that this might be effected. Accordingly, measurements similar to those just described were made with a radiating surface of lampblacked copper at the approximate temperatures of 815° C., 525° C., and 330° C.; and with the Leslie cube at temperatures of 178° C., 100° C., 40° C., and −20° C.; the excess over the temperature of the room being in the latter

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[*] "Distribution of Heat in the Spectra of various sources of Radiation," by William W. Jacques, Ph.D., Proceedings of American Academy.

cases respectively 185° C., 88° C., 46° C., and −18° C. In the last instance, the cube was colder than the bolometer strips, and the deflections obtained were negative; though small, they were distinctively measurable, the greatest being −12 divisions of the galvanometer-scale. The position of the maximum in the ice-curve is indicated, but the curve itself is, on this scale of ordinates, sensibly coincident with the straight line. (See Pl. IV. fig. 1.) We have in fig. 3 the curves representing the radiation from these sources, in which the abscissæ are proportional to the indices of refraction in the rock-salt prism, but the ordinates only approximately so to the deflections of the galvanometer due to the heat at the corresponding points; since we are not here principally concerned with the relation of the amounts of heat emitted to the temperatures of the sources of emission, but chiefly with the secondary effect of the progressive movement of the maximum which is clearly shown.

Date of observation.	Approximate temperature of source.	Approximate temperature of excess.	Deviation of maximum ordinate in heat curve.
1885.			
October 7 ………	815° C.	803° C.	39° 08′
,, 3 ………	525	505	39 03
,, 7 ………	330	318	39 01
,, 3 ………	330	310	39 00
September 26 …	300	275	38 42
March 20 ………	178	185	38 35
August 19………	179	152	38 35
March 20 ………	119	126	38 25
October 7 ………	100	88	38 22
,, 3 ………	99	79	38 27
March 21 ………	40	46	38 00
,, 24 ………	−02	−18	37 40*

It is to be observed of each of the curves in fig. 3 that though nearly all the *area* is seen, yet, owing to the extension of the heat-curve toward the right, the length shown is limited here by the size of the plate, whereas the extremity measured in each curve (except of course the solar one) does, in fact, correspond to an index of less than 1·45. We give above a table showing the dates of observation, the approximate temperatures of excess, and the approximate deviations of the ordinate corresponding to the point of maximum heat in the (rock-salt) prismatic spectrum. We should observe that the higher temperatures are here only determined with an approximation sufficient to make it certain that there is a

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* The position of the maximum in this last case depends upon a single observation of some delicacy and is liable to subsequent correction.

progression in the direction of the shorter wave-lengths of the position of the maximum ordinate, as the temperature rises. These results, both in the table and as represented in the plates, are given as preliminary, not as final, for we hope soon to be able to offer other and more exact ones, deduced from the heat-spectra of bodies at all temperatures between that of melting platinum and melting ice. We are entitled, however, even at present, to draw the following conclusions, which are of special interest in connection with the spectra of dark bodies, of which almost nothing has been hitherto known.

(1) The heat represented by the areas of these curves is *almost altogether of a character not observed in that of the sun*, these wave-lengths, in general, not being transmissible by glass, which is comparatively permeable to the lowest solar heat-waves that penetrate our atmosphere *. To show this more clearly we have drawn the solar spectrum given by the rock-salt prism in its true position (though not in its true amount) relatively to that of the heat-curves cited. The maximum of the latter lies in every case, it will be seen, far below the very lowest part of the solar invisible heat.

(2) In spite of the compression of the infra-red by the prism, these heat-curves extend almost indefinitely in the direction of the smaller indices, so far that we can, in fact, represent only a part of this extent in our plate. The measures already cited in case of the curve for the Leslie cube at 178°, for instance, show very measurable heat at a deviation of 33°, which corresponds to an index of refraction of 1·4511, while the smallest index given in the plate is 1·49.

(3) An increase of temperature increases every ordinate, but not in like proportions, ordinates corresponding to the heat in the more-refrangible parts always growing more rapidly than those for less-refrangible heat.

(4) As a necessary consequence of this, follows the (independently observed) fact of the progressive movement of the maximum ordinate toward the more-refrangible end as the temperature rises.

(5) These prismatic curves are not symmetrical, the greater portion of the area in every case lying below the maximum, *i. e.*, toward the greater wave-length, and the descent being always most abrupt on the more-refrangible side.

As the heat-spectra from surfaces at the temperature of

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* The distinctive character of these radiations is also well shown by the fact that we have found that a thick film of lampblack, which is nearly as impervious to the dark solar heat as to light, transmits more than 50 per cent. of some of the rays in question.

boiling water or melting ice are those to which the chief interest attaches, in connection with the temperature of the soil, and as these are not well shown on the same scale of ordinates with that of the red-hot copper, we give an independent representation of these two in fig. 1, but upon the wave-length, not the prismatic scale. Their maxima of heat fall at points in the normal spectrum which (as we explain later) are only approximately determinate on *this* scale, but which are probably at least as low as the points (*f*) corresponding to the boiling-water maximum, and (*g*) corresponding to the position of the maximum ordinate in the spectrum of ice at the melting-point, or lower. No attempt is made in this figure to represent the relative amounts of heat in the solar and Leslie-cube curves, but only their positions on the wave-length scale ; and here also it will be understood that the latter curves really extend far further to the right than the limits of the plate admit of showing them.

These observations, then, show a real though slight progression of the point of maximum heat toward the shorter wave-lengths as the temperature rises. The position of the maximum ordinate of the lower curves is of course more difficult to determine, on account of their flatness.

The whole heat-spectrum from most of these sources, it is interesting to note, passes through the prism at angles which the theories of our text-books have heretofore pronounced impossible. The existence of these radiations, and the relative amounts of heat for each deviation, are certain, for these deviations are determined by the spectro-bolometer, in most cases with a probable error of less than a minute of arc ; but when we pass to the next stage of our work, the determination of the corresponding wave-lengths, we cannot speak with such confidence. We have calculated the wave-lengths for some of the observations by means of Wüllner's new formula*. This formula,

$$n^2-1=-\mathrm{P}\lambda^2+\mathrm{Q}\frac{\lambda^4}{\lambda^2-\lambda_m{}^2}$$

where P, Q and λ_m are constants, depending upon the nature of the refracting substance, to be determined by observation, is founded on Helmholtz's theory, but he has tested it by our own observations with the glass prism. We have found the calculated values to agree with similar ones obtained directly from the curve representing the relation between n and λ for rock-salt, which is shown in the woodcut, by measurements on points whose wave-lengths were known from our prior

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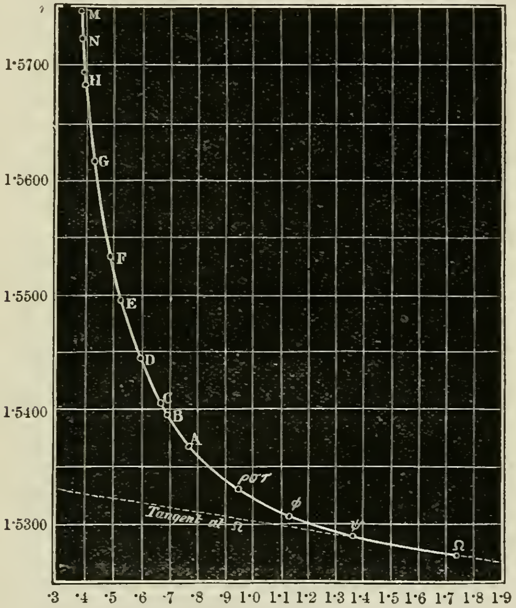
* Wiedemann's *Annalen*, Band 33, S. 307.

observations up to about 20,000 of Ångstrom's scale. Beyond this point we have continued the curve both by computation and by graphical extrapolation. We do not disguise from ourselves the danger of all extrapolations, although ours rest, it will be seen, on a wholly different basis from the ones depending on formulæ derived from the visible spectrum alone, since our curve has been already followed by direct observations until it is almost coincident with a straight line. Up to this point then (within the limits of error already elsewhere given) there is no doubt, and unless there is some utter change in the character of the curve, such as we have no reason to anticipate, a tangent from the last part will not differ very greatly from the immediate course of the curve itself, and will at any rate meet the axis of abscissæ sooner than the curve can. If we assume, then, the prolongation of the curve to agree with this tangent, we evidently assume a minimum value for all the wave-lengths measured by it, and that is what we have done.



Showing $n=f(\lambda)$ for Rock-salt.

We are not prepared yet to speak of these wave-length values as exactly determinate, and they are here given as first approximations. They are indeed sufficiently startling to make us inclined to proceed with caution; but, speaking with the reserves indicated by the conditions referred to, I may say that we have every reason to believe that the minimum wave-length assignable to the maximum ordinate of the heat-curve, in the spectrum of a source whose temperature varies from 100° to 0° Centigrade, is a little less than 5μ and a little over 6μ, and that these may be indefinitely greater. This refers, it will be remarked, only to the position of the maximum ordinate, while the extreme portions of the curve measured on (corresponding to an index of 1·45) have probably at least three times this wave-length. I shall be better understood, perhaps, if I say that some of the heat radiated by the soil has probably a wave-length of *over* 150,000 of Ångstrom's scale, or about twenty times the wave-length of the lowest visible line in the solar spectrum, as known to Fraunhofer.

These investigations are still going forward, and I hope soon to give more exact values. But I have presented the present ones, though imperfect, because they give us at least some knowledge of a region of which we are at present quite ignorant, and because they are thus, I think, of some interest both to the physicist and to the astronomer: to the physicist, as showing that the wave-lengths which Newton measured to the $\frac{1}{40,000}$ of an inch are so far from being the limits of nature's scale, that the existence of measurable wave-lengths of something greater than $\frac{1}{2000}$ of an inch is rendered at least highly probable; to the astronomer, because we find that *the heat radiated from the soil is of an almost totally different quality from that which is received from the sun*, so that the important processes by which the high surface-temperature of the planet are maintained can now be investigated with, we may hope, fruitful results in connection with the researches here described.

I should not close this preliminary account without stating that I have in these observations been throughout and at every stage indebted to Messrs. F. W. Very and J. E. Keeler, of this Observatory, for a collaboration without which it could not have appeared in its present form.

ADDENDUM.

Reduction of Observations made with the Rock-salt Prism to a Standard Refracting Angle; with a Table of Refractive Indices of Rock-salt.

The surfaces of the rock-salt prism and lenses undergo a deterioration when exposed to the air, which is more or less rapid according to the greater or smaller relative humidity of the atmosphere at the time. In ordinary dry weather they may be used several times before they become spoiled, while in damp or rainy weather three or four seconds is a sufficiently long time to cover them with condensed moisture, and work under these circumstances is of course impossible. After the surfaces have in this way become unfit for use they are repolished, and the refracting angle of the prism is thereby unavoidably altered. The change is usually small, generally not exceeding 1′, so that for most of our heat-measures it may be neglected altogether. The changes have, however, tended on the whole to reduce the refracting-angle, so that it is now about 4′ smaller than when the prism was first used.

To make all observations strictly comparable, they are reduced to one value of the refracting-angle, for which the deviations of the Fraunhofer lines, and the wave-lengths corresponding to given deviations in the infra-red, have been determined with the greatest possible accuracy. This standard value of the refracting-angle is 59° 57′ 54″. A series of observations for fixing the positions of the Fraunhofer lines was made by Mr. J. E. Keeler, of this Observatory, on Sept. 14, 1885. One arm of the spectrometer, which was firmly clamped, carried a glass collimating-lens of 25 feet focus, and the other an achromatic observing-telescope of nearly four feet focus, with a micrometer-eyepiece. The double deviations of the C, D_1, b_1, and F lines were observed, and also the differences of deviation between these and the other lines whose positions were determined. For observing the M and N lines a Soret fluorescent eyepiece was used, and in the infra-red a bolometer, having a single strip $\frac{1}{10}$ millimetre in width. In the two last cases the prism was automatically kept in the position for minimum deviation. The spectrometer-circle reads by two opposite verniers to 10″, but on account of the construction of the instrument (for whose principal purpose arms whose length is inconsistent with absolute rigidity had to be used), care is necessary to measure an angle with this degree of precision, as the arms are liable to spring slightly on the application of lateral pressure. The deviations given in our table were obtained by Mr. Keeler by setting on the line with the micrometer-eyepiece, after the telescope had been directed upon it and freed from strain by a light tap; and applying the micrometer-correction to the circle-reading. It was found by a careful comparison of the solar spectrum given by the rock-salt prism with that by a fine prism of flint glass, that, in spite of the greater dispersion of the latter, no lines could be seen in its spectrum which the rock-salt prism would not also show. The probable error of one setting of the micrometer was less than 1″. From the agreement of the different measurements made in this way, it is believed that the deviations throughout the visible spectrum are correct to within 5″. Those in the ultra-violet and infra-red cannot of course pretend to this degree of accuracy. The positions of ρ ς τ (invisible) given by two independent series with the bolometer differed by 30″; those of φ (invisible) by 1′, those of φ (invisible) by 30″, and those of Ω (invisible) agreed exactly.

We have thus obtained incidentally the data for constructing a table of refractive indices of rock-salt throughout the entire range of the solar spectrum, with an accuracy which we believe to be greater than has heretofore been attained, and which we deem of sufficient interest to give in full below, for the convenience of others having occasion to work with this material, and for testing theories of dispersion.

REFRACTING ANGLE OF PRISM = 59° 57′ 54″.

Line.	Wave-length.	Deviation.	Δ	Refractive Index.
	μ	° ′ ″		
M ……	0·3727	43 50 57	1·21	1·57486
L ……	0·3820	43 35 27	1·20	1·57207
H_2 ……	0·3933	43 19 32	1·19	1·56920
H_1 ……	0·3968	43 14 44	1·19	1·56833
G ……	0·4303	42 36 7	1·16	1·56133
F ……	0·4861	41 51 47	1·13	1·55323
b_4 ……	0·5167	41 33 43	1·12	1·54991
b_1 ……	0·5183	41 32 52	1·12	1·54975
D_1 ……	0·5889	41 2 41	1·10	1·54418
D_2 ……	0·5895	41 2 29	1·10	1·54414
C ……	0·6562	40 42 56	1·09	1·54051
B ……	0·6867	40 35 49	1·09	1·53919
A ……	0·7601	40 22 25	1·08	1·53670
ρ ς τ …	0·94	40 1 26	1·07	1·5328
φ ……	1·13	39 49 11	1·06	1·5305
ψ ……	1·38	39 39 56	1·05	1·5287
Ω ……	1·82	39 29 21	1·05	1·5268

Temp. = 24° C. Barometer, 733·1 mm.

The wave-lengths of the M and L lines are from Cornu, those of the lines between H and A inclusive from Ångstrom, and those of the infra-red bands from the Allegheny observations. The column headed Δ was prepared at the suggestion of Mr. Keeler, and is for the purpose of facilitating the reduction of observations made with a different prism-angle from that for which the table is computed and for which our wave-length curves are drawn. If we differentiate the ordinary formula for a prism,

$$n = \frac{\sin \frac{1}{2}(\mathrm{A}+d)}{\sin \frac{1}{2}\mathrm{A}}$$

with respect to A, which we now regard as a variable, we have

$$\frac{dd}{d\mathrm{A}} = \frac{n \cos \frac{1}{2}\mathrm{A}}{\cos \frac{1}{2}(\mathrm{A}+d)} - 1 = \Delta,$$

or

$$dd = \Delta d\mathrm{A}.$$

The values of Δ for the different lines of the spectrum are readily computed from the table of deviations and refractive indices. To find, then, the deviation of a line after any repolishing of the prism, we have merely to multiply the change of the angle by the approximate value of Δ taken from the table, and we obtain the change in the deviation of the line, and hence also the deviation required. Thus, if the new angle is found on measurement to be 59° 57′ 44″, $d\mathrm{A} = -10''$, and the deviation of the F line (say) will have been changed by $10'' \times 1{\cdot}13 = -11''{\cdot}3$. That is, the deviation of the F line is now 41° 51′ 36″. The reduction from the new to the standard angle is of course the reverse of this; and that the use of the table saves much labour in redetermining the constants of the prism will be understood when it is added that ours has been entirely refigured and repolished by the maker as many as ten times during the present year.

LIV. *On Measurements of the Electromotive Force of a Constant Voltaic Cell with moving Plates. By* A. P. Laurie, *B.Sc. Edinb., B.A. Cantab.*[*]

In the last number of the Philosophical Magazine I described some experiments made with the view of determining the electromotive forces developed during the combination of zinc and iodine in presence of water.

Since obtaining the above results I have been engaged on similar experiments with voltaic cells in which the zinc is replaced by cadmium, the cell consisting of a cadmium plate, and a platinum plate immersed in a solution of cadmium iodide in which a little free iodine is dissolved. This work not being as yet completed, I do not propose to describe it here, but merely to give an account of a special set of experi-

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[*] Communicated by the Author.

ments made with this cadmium cell, for a special purpose. The object which the investigator has in view in such researches as these, is to determine the electromotive force developed by a given set of chemical reactions; and he therefore first devises a voltaic cell in which the given reactions will occur on using the cell as a source of electricity, and then measures its electromotive force.

As examples of this kind of measurement it is only necessary to refer to the papers by Dr. Alder Wright in the back numbers of this Magazine. I know of no other set of experiments approaching these in accuracy and completeness.

These measurements, then, of electromotive force can be made by two or three different methods: for instance, by means of the quadrant-electrometer, or by means of a very high-resistance galvanometer, with a few megohms in the circuit. These methods of measurement, however, have one point in common: an infinitely small current is drawn from the cell which is being tested, whether it be to charge the quadrants of the electrometer or to deflect the galvanometer-needle. Unfortunately the use of these very small currents leads one to doubt how far such measurements are reliable; for, be it remembered, it is not the measurement of the E.M.F. of a given voltaic cell with an enormous resistance in the circuit which is required, but the measurement of the electromotive force due to a definite chemical reaction.

Now an infinitely small current means an infinitely small amount of chemical change; and to take the cell at present under consideration, how can we be sure that the source of this current is the formation of cadmium iodide, and that it is not due to impurities in the metal or the solution, or to a film of gas or coat of oxide on the cadmium plate? To this it may be answered that experiments such as those of Dr. Wright with a great variety of voltaic combinations, and the remarkable agreement of the results one with another, give a considerable confidence in such measurements. This is no doubt correct, though it is still possible that constant sources of error may occur. Then the approximate agreement of the electromotive force found with that calculated from the thermal data in so many cells confirms the measurements for those cells at any rate.

But in many cases Dr. Wright has found that not only do the calculated and measured electromotive forces differ considerably, but in several voltaic combinations the current actually flows the opposite way to that calculated from the thermal data.

Such a result, if *proved*, is of the greatest interest; but I think that we are justified in refusing to accept such a result until not only the E.M.F. of the given voltaic combination has been accurately measured, but it has also been clearly shown to what chemical changes this electromotive force is due.

To show this it is necessary to draw a considerable current for some time from the cell in order to find by analysis what chemical changes have taken place ; and, further, it is necessary to measure the E.M.F. during the passage of this current. Unfortunately, as soon as we attempt to draw a considerable current per square centimetre of plate surface from a so-called constant cell the E.M.F. immediately falls off considerably. To give an example : Dr. Alder Wright finds that a current of 30 or 40 microamperes per square centimetre is quite sufficient to cause an appreciable fall in the E.M.F. of the cell experimented on. Now a current of 30 microamperes running for an hour from a cadmium cell would dissolve about ·00006 grm. of metallic cadmium, an amount hardly sufficient for analytical purposes.

Now this fall in E.M.F., on taking an appreciable current per square centimetre from a constant voltaic cell, is usually ascribed to "polarization," "transition resistance," &c. On considering it more carefully, it seems to be largely due, possibly entirely due, to alterations in the layers of liquid next the plate.

To keep to the cadmium cell, an increase of cadmium iodide in the layer of liquid next the cadmium plate, or a diminution of the free iodine in the layer of liquid against the platinum plate, would cause a considerable diminution of E.M.F.

If, then, we suppose the plates immersed in a sufficient amount of solution to remain of practically constant strength though a considerable current be running from the cell for some time, the amount of current per square centimetre which we can draw from the cell without a fall in E.M.F., will be largely, perhaps entirely, a question of the rate at which diffusion of the cadmium iodide and free iodine takes place.

It follows, then, obviously that if we wish to draw a considerable current from a voltaic cell under conditions similar to those during the measurement of E.M.F. in the usual way, the liquid contents of the cell must be kept well stirred.

I determined therefore to make some experiments on a cadmium-iodine cell with moving plates, drawing from the cell a considerable current per square centimetre ; a sufficient current, in fact, to enable me to estimate quantitatively at the end of about two hours the nature and amount of the salts formed in the cell.

Although it is well known that blowing air through the liquid enormously increases the current from bichromate cells (probably because it thoroughly mixes the liquid), I do not know of any measurements having been made with cells with moving plates; and even if such measurements have been made, additional results are nevertheless of interest.

The arrangement I adopted was as follows:—A shallow glass jar was lined inside with platinum foil to which platinum wires had been welded. This platinum-foil formed the one electrode of the cell, and amounted to 90 square centimetres in surface. This jar was placed under a horizontal wooden pulley with a deep groove cut in its upper surface. A binding-screw was screwed into the pulley from below until the end of the screw emerged in the bottom of the groove above mentioned. To this binding-screw a little cadmium plate was attached, having 10·6 square centim. of its surface immersed in the liquid. (This is counting the surface of both sides of the plate.)

The groove in the pulley was half-filled with mercury, and an amalgamated flattened copper wire, fixed to the framework of the apparatus, dipped into the mercury in the groove. In this way metallic connection was made with the cadmium plate. The cadmium plate was driven through the liquid by an old clock, altered for the purpose, at the rate of about two or three revolutions a second*.

In order to check a little the moving of the liquid, little glass pillars were cemented at short intervals to the surface of the platinum plate. The cell held about 100 cubic centim. of liquid. In order to measure the current from this cell it was connected to the Helmholtz galvanometer in Prof. Tait's laboratory.

Taking into consideration the amount of accuracy with which the constant of this instrument has been determined, and the amount of accuracy possible in the readings of the galvanometer-needle, I believe the following measurements of E.M.F. may be taken as having a possible maximum error of 1 per cent.

The method of experimenting was as follows:—

The cadmium plate was weighed, both before and after the experiments, the loss of weight amounting to ·8275 grm., and the solution analyzed. Before weighing after the experiments, the plate was washed in water, then in alcohol, and

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* This apparatus was a copy of a similar arrangement used by Dr. Gibson, of Edinburgh University, in some experiments on Electrolysis.

dried at a gentle heat. The solution contained about 5 per cent. of cadmium iodide and ·0032 grm. of free iodine in 1 cubic centim. A little solid iodine was added to the cell to keep up the strength of the iodine solution.

It is sufficient to state that the weight of cadmium used and the weight of combined iodine found corresponded to the formation of cadmium iodide, as the result of the reactions in the cell. Probably about one third of the cadmium iodide formed was due to the direct action of the iodine on the cadmium plate.

After setting up the cell its E.M.F. was measured on the electrometer against a standard Latimer-Clark. This measurement, it was found, was not affected by setting the plates in motion.

The plate being now started moving, the cell was connected to the galvanometer, and a deflection obtained corresponding to ·1054 ampere. The external resistance did not amount to ·5 ohm, showing the internal resistance of the cell to be somewhere about 10 ohms. I next proceeded to measure this internal resistance by interpolating known resistances in the circuit.

Now, as is well known, it is impossible to measure the internal resistance of an ordinary voltaic cell in this way, because every variation in external resistance alters the E.M.F. of the cell. It was necessary therefore to determine whether internal resistance, as calculated from different sets of two interpolated resistances, was the same.

It is to be noted here that the calculation of the resistance in the rest of the circuit by this method is not capable of great accuracy, as is at once obvious from an examination of the formula used,

$$\frac{ir - i'r'}{i' - i} = x;$$

where x is the unknown resistance, r, r' the interpolated resistances, and i, i' the respective current measurements. In fact, when the resistance of the whole circuit is varied one third of its whole amount, an error of 1 per cent. in the galvanometer-reading becomes about 10 per cent. in the calculated resistance of the circuit. Keeping this in mind, the differences in the following numbers are within the errors of experiment; and it is further to be noticed that they are quite irregular, and that the resistance of the cell shows no tendency to increase with diminishing external resistances.

Interpolated resistance, stated in ohms.	Calculated resistance of rest of circuit.
10 and 20	10·3 ohms.
10 „ 15	10·0 „
10 „ 5	10·3 „
5 „ 0	9·9 „

This gives as the resistance of the circuit, 10·12 ohms. Adding this number to the interpolated resistance in each experiment, and calculating the E.M.F. of the circuit for each, we get as the mean, 1·084 volt. The number obtained on the electrometer was 1·076 volt.

After these measurements were completed, the current was allowed to run through the galvanometer for nearly two hours. The deflection remained very steady, slightly increasing and then slightly diminishing. At the end of this time the deflection corresponded to a current of ·1068 ampere. On again interpolating resistances, the following results were obtained:—

Interpolated resistance.	Calculated resistance.
0 and 5	10·1
5 „ 10	9·9
10 „ 15	10·0
Mean	10·0 ohms.

The E.M.F. calculated from these results is $=1·067$ volt.

The E.M.F. on the electrometer amounted to 1·072 volt, a number about as much higher as the first number was lower than that calculated from the current measurements.

Experiments are evidently capable of being made of far greater accuracy than these, but they are sufficient to show that the E.M.F. of the cadmium-iodine cell as measured on the electrometer is really due to the formation of cadmium iodide.

Similar experiments should, I feel sure, be made for all cells which are not well known, before any attempt is made to base important conclusions on the differences between the calculated and measured E.M.F.

As already stated, the area of the plate used amounted to 10·6 square centim. Probably one side of the plate supplied most of the current; but, considering the current as equally shared between both sides, this means ·01 ampere per square centim. of surface steadily supplied for two hours, about 500 times what could have been drawn from the cell with stationary plates, without causing a serious fall in E.M.F.

Whether the platinum plate could have been safely diminished in size to the same extent I do not know: probably not, as the iodine solution was so dilute.

A striking experiment is to suddenly stop the movement of the plate while the cell is connected to the galvanometer. The needle at once begins to move, falling in less than a minute to about a quarter of its original deflection. On now allowing the plate to start off again, the needle rushes up to its old position.

These experiments then, though rough, are, I think, sufficient to show that we have here a method of comparing measurements of E.M.F. made with open circuit with those made while a considerable current is being drawn from the cell, that the fall in E.M.F. when the plates are stationary is entirely due to the alterations in the strength of the solutions next the plates, and that the particular piece of apparatus experimented with deserves the title of a constant voltaic cell.

LV. *A Map of the World on* Flamsteed's *Projection.*

By WALTER BAILY, *M.A.*[*]

[Plate V.]

IN Flamsteed's *Atlas Cœlestis* the projection used is one invented by him and described in the Preface to that work as follows :—

"Conceive the globe or sphere to be compassed about with an infinite number of infinitely fine threads all exactly parallel to the equator. Let all the circles usually drawn upon the globe, as the equator, the ecliptic, the meridians, &c., be supposed drawn and divided, and let the constellations also be formed upon them, and the stars laid down in their proper places. Let also the meridian passing through the middle of any constellation be conceived drawn on the globe, and covered with a fine thread with as many of the adjacent circles as you may think convenient. Conceive the threads on which the constellation is painted to be cut off from the surface of the globe; and that which passes through the middle being extended straight on the middle of some paper or perfectly plane superficies, let the rest be placed on it at right angles to the middle meridian, but reverted."

Flamsteed used his projection only for maps of portions of the celestial sphere, and he did not apply it to the polar

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[*] Communicated by the Physical Society: read February 27, 1886.

regions, as the distortion which would otherwise have been produced would have been inconvenient to an astronomer.

The Preface points out the advantages of the method as follows:—"So will you have the picture of the Constellation projected upon it, in which the parallels of declination will be straight lines and their distances exactly equal, the same as they are on the globe, as will also the distances and differences of the right ascensions of any two stars that are equally distant from the pole." The advantage in Geography of a map in which the parallels of latitude are equidistant straight lines parallel to the equator is obvious, as the position with regard to latitude is seen at a glance. There is, moreover, a property of this projection which is evident at once from the way in which the projection is constructed, viz. that the area of every part is preserved unaltered. The imaginary threads have simply slipped over one another, like the cards in a pack, without altering their distances, so that only a distortion of form has occurred. This property is not referred to by Flamsteed, either because he did not notice it, or because it was of no importance in Astronomy. I venture to submit, however, that in Physical Geography it is a property of considerable importance, and that it would be advisable in many physical maps to use this projection. For instance, in maps showing rainfall, depth of the sea, height of the land, ocean currents, prevailing winds, distribution of plants and animals, &c., it is essential to take account of the area occupied, and maps in which this is correctly shown could not fail to be of use. In Plate V. is shown a map of the World on Flamsteed's projection, the small square at the side representing 1,000,000 square miles on the same scale.

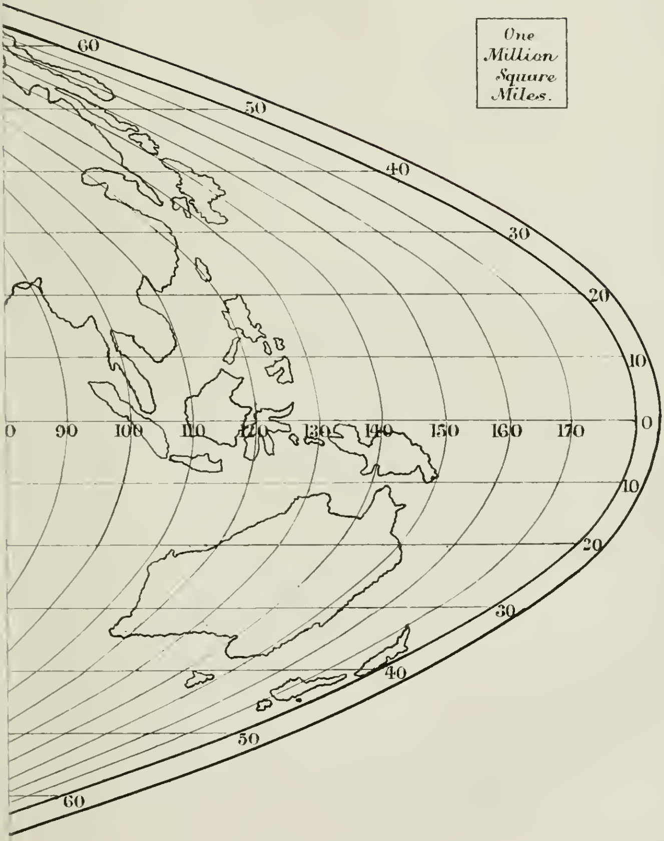
The formulæ for constructing the map are readily obtained. Take the equator as the axis of x, and the central meridian (say the meridian of Greenwich) for the axis of y. Let x, y be the coordinates of a point m° of longitude from the central meridian, and n° of latitude from the equator. Then if α is the length of a degree of latitude in the scale adopted,

$$y/\alpha = n, \quad x/\alpha = m \cos n^\circ.$$

Hence the equation to a meridian m degrees from the central meridian is

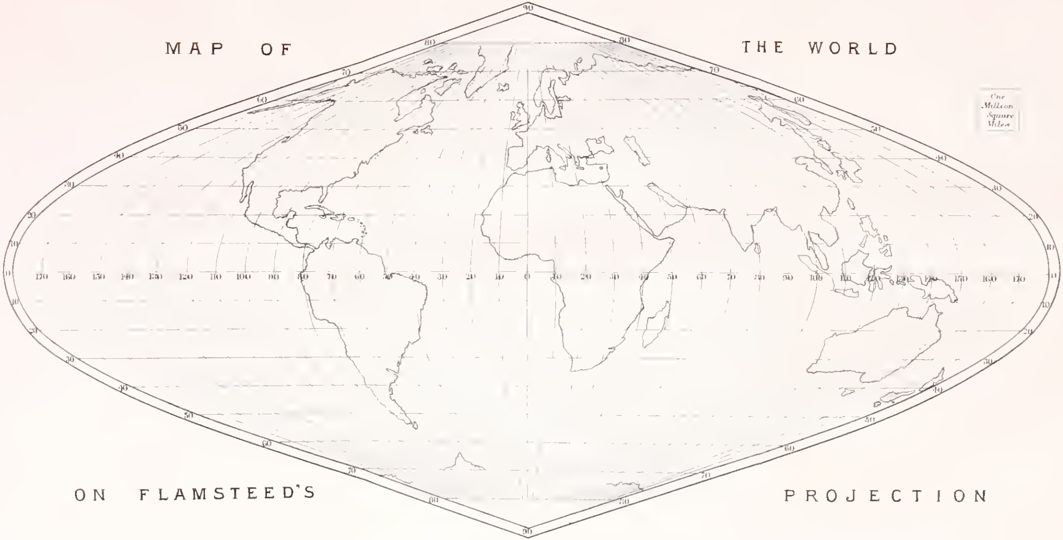
$$\frac{x}{\alpha} = m \cos\left(\frac{y}{\alpha}\,.\,1^\circ\right).$$

HE WORLD



PROJECTION.

MAP OF THE WORLD



ON FLAMSTEED'S PROJECTION

Mintern Bros. lith.

LVI. *Note on Supersaturated Saline Solutions.*

By CHARLES TOMLINSON, *F.R.S.*[*]

THE current number of the Journal of the Chemical Society has called my attention by its abstracts to two most interesting papers on the above subject by Dr. Nicol, contained in the Philosophical Magazine, 5th series, xix. p. 453, and xx. p. 295.

With Dr. Nicol's main conclusion, that a supersaturated solution is a solution of the anhydrous salt, I cordially agree, and expressed such an opinion in my paper read before the Royal Society in 1868. I also brought together in the 'Chemical News' of December 1869 various opinions of some French chemists on the constitution of sodium sulphate in solution. These are somewhat contradictory. The favourite view of supersaturation in French, English, German, and American textbooks long continued to be Löwel's, viz. that a solution (say of sodium sulphate) saturated at a high temperature, and left to cool out of contact with air, does not actually become supersaturated, but undergoes a molecular change, in which the 10-atom salt becomes the more soluble 7-atom; so that, instead of having a supersaturated solution of the 10-atom salt, we have only a saturated solution of the 7-atom salt.

Now it is remarkable that in Löwel's five memoirs, which appeared the first in 1850 and the fifth in 1855, the above theory is maintained in the case of sodium sulphate, and a similar theory with respect to sodium carbonate and magnesium sulphate. But in his sixth and last memoir, published in 1857, he maintains that between the boiling-point of a saturated solution of sodium sulphate (103°·17 C.) and the point at which the 7-atom salt begins to be deposited (18°), it is not this modified salt, but the anhydrous variety, which is held in solution. He is led to this conclusion by considering:—

1. That the 10-atom salt parts readily with its water of crystallization by mere exposure to the air.
2. That Faraday found, on evaporating a solution of the 10-atom salt below 100° C. (or, according to Mitscherlich, below 40°), that the anhydrous salt was deposited.
3. That in boiling for some time a saturated solution of the

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[*] Communicated by the Author.

10-atom salt, small hard granular crystals of the anhydrous salt are formed as the solution becomes concentrated.

Löwel's speculations as to the formation of the 7-atom salt need not be gone into here; nor need I repeat my own experiments, conducted in 1867, which led me to the conclusion that it is the anhydrous salt that is in solution; but I do wish to repeat the following consideration by which the same conclusion was arrived at.

In the experiments for determining the elasticity of steam from pure water, the elasticity is diminished for any given temperature if a small portion of a salt, such as soda, soluble in water, and not capable of rising in vapour with it, be allowed to ascend to the top of the mercurial column; the column rises, thereby indicating a diminished elasticity of steam. The adhesion of the soda to the water tends to restrain the water from evaporating, and this tendency is a measurable force and here measured; for it partly balances the tension of the water or its tendency to emit steam, and it thus makes the steam-emitting tension of a solution of soda measurably less than that of pure water at the same temperature.

Now it is clear that if, instead of soda, Glauber's salt be used in experiments of this kind, there will be a smaller amount of diminution in the elasticity of the steam if the salt in solution retain its water of crystallization than if it entered into solution in the anhydrous form. In a valuable series of experiments by Wüllner (Pogg. *Ann.* ciii. p. 529, and cx. p. 564) it appears to have been established for solutions of various strengths (such as 10, 20, 30, &c. per cent. of Glauber's salt in pure water), and at various temperatures from 10° to 100° C., that the diminution in the elasticity of the steam is proportional to the quantity of *dry* salt in solution; and, further, that at the point of maximum solubility of this salt no molecular change takes place, or it would have impressed itself on the curve which represents the elasticity of the steam. The general conclusion for the salts tried is that the action of efflorescent salts is expressed in terms of the dry salt, while for deliquescent salts it is in terms of the hydrated salts.

Dr. Nicol's papers are so admirable, that I trust he will continue his researches into other matters connected with this difficult subject.

Highgate, April 15, 1886.

LVII. *Discharge of Electricity in an Imperfect Insulator.* *By* J. H. POYNTING, *M.A., Professor of Physics, Mason College**.

MAXWELL has shown that the phenomena known as the Residual Discharge may be accounted for on the supposition that the dielectric is an imperfect insulator in which the conductivity varies in different parts. His theory is really quite simple and straightforward and free from any hypothesis beyond the fundamental one of electric displacement. But its very generality makes it, I believe, difficult to grasp. The idea of a yielding of displacement in the dielectric, accompanied by a conduction-current in the opposite direction, gives us no help in forming a mental picture of the process actually going on in the dielectric. A hypothesis as to the nature of electric current, which will shortly be published in the 'Philosophical Transactions,' seems to me to render the theory easier to follow; and I propose in this paper to arrange Maxwell's account of the Residual Discharge in accordance with it.

I shall first give some account of the hypothesis referred to in the special case of the discharge of a condenser. Let us suppose that we have two conductors, A and B, which we may suppose to be the two plates of a condenser charged with equal and opposite amounts of electricity, that of A being positive. Then the lines of force will run from A to B through the medium, the condition of the medium being described by saying that there is "electric displacement" from A to B. Or we may describe it without introducing the confusing term "displacement" by returning to Faraday's term "induction." We may then say that tubes of electric induction pass through the medium, each tube starting from $+1$ of electricity on A and ending in -1 on B. The total induction across any section of a tube is then always equal to 1. If we draw the level surfaces at unit differences of potential, the tubes will be divided up into cells; and if we suppose each cell to contain half a unit of energy, then the whole energy of the electrified system is accounted for. Maxwell has called these *unit cells* ('Elementary Treatise on Electricity,' p. 47). According to the views of Faraday and Maxwell, the charges on the conductors bounding the dielectric are to be regarded as the surface manifestations of the altered state of the dielectric

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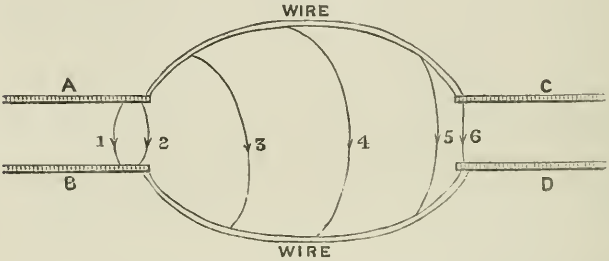
* Communicated by the Author, having been read before the Birmingham Philosophical Society, December 10, 1885.

corresponding to the energy put into it, somewhat as the pressure on a piston in the wall of a closed vessel of compressed water might be regarded as the surface-manifestation of the strained condition of the water.

In order to follow out the process of discharge in the medium, *i. e.*, the mode in which it is relieved from its strained condition, we will first take a simpler case in which we connect the two plates, A and B (fig. 1), of one condenser to the two plates, C and D, of another condenser previously uncharged, and so far from A and B that there is no appreciable direct inductive action on C and D. When equilibrium is again restored, the + charge is shared between A and C, the − charge between B and D, while the difference of level has decreased. There is the same total number of tubes of induction, but each contains fewer unit cells than before, the energy corresponding to the decrease having been transferred to the wires, where it has been dissipated as heat. I shall use the term energy-length to indicate the line-integral of the electric intensity along its axis, this being the same as the difference of potential when there is equilibrium. We may say then that the energy-length of the tubes has decreased. During the change some of the electric energy was converted into magnetic energy in the medium. This might be observed if sufficiently delicate means were used.

Fig. 1.



If we confine our attention to the charges on the conductors we must say that equal quantities of + and − have moved respectively from A to C and B to D along the wires.

But taking into account the condition of induction in the medium described by the induction-tubes, we must say that the induction-tubes move sideways out from the space between A and B into the space between C and D, the motion of the charges along the wires being really the motion of the ends of the induction-tubes. (See fig. 1, where 1–6 may be taken as successive positions of a tube.) During the motion of the tubes, some of their energy was converted into the magnetic form, the coexistence of the two forms, electric and magnetic, being a necessary condition of motion. We may illustrate this from the analogous case of a strained incompressible solid which can be sheared. If there is any mode of escape given to the strain-energy by a slipping of the surface against the constraint, then the state of strain will be propagated outwards from the interior of the solid, but some of the strain-energy will be converted into kinetic energy, and the presence of the two is a necessary condition for the propagation of the strain.

Since the energy-length of a tube diminishes as its ends move along the connecting-wires, we may represent this by supposing that parts of the tubes move into the wire. If a similar motion of electric induction took place into a dielectric, it would remain, and the dielectric would become electrically strained; but in the wire the strain breaks down rapidly, the energy being converted into heat. I think there is good reason to suppose that it is the electric energy which thus breaks down, the magnetic only being dissipated after it has been reconverted to the electric form.

We may now consider the case in which the total discharge of a condenser takes place through a connecting wire. Considering merely the conducting plates and the wire, we say that the charges move along them towards each other and finally unite, neutralizing each other and producing heat in the wire. Regarding the medium, we must suppose the tubes of induction to move sideways towards the wire, shortening as their ends, which are represented by the charges, approach each other, and finally disappearing into the wire. Faraday describes the process by saying that "when current or discharge occurs between two bodies, previously under inductrical relations to each other, the lines of inductive force will weaken and fade away, and, as their lateral repulsion-tension diminishes, will contract and ultimately disappear in the line of discharge" (Exp. Res. vol. i. p. 529, § 1659). The so-called velocity of electricity is merely the velocity of the ends of the tubes, and this may evidently vary according to the nature of the circuit. It is quite conceivable that if the wire be in a neutral medium, *i. e.* one in which there is no surface-difference of potential, say gold in air, and if it follow the direction of a tube of induction, then a tube may move into the wire throughout its whole length at once. In this case the "velocity of electricity" would be infinite.

We know from experiment that if a galvanometer be inserted on the connecting wire then the same magnetic impulse is observed wherever in the circuit the galvanometer be placed, the impulse depending on the galvanometer-constant and on the total discharge. The same experimental result may be stated in an equivalent form, viz. that the line-integral of the magnetic intensity round a closed curve encircling the wire, if integrated for the time of discharge, is the same for all positions of the curve. On the hypothesis here described all the electric induction-tubes of the system finally pass sideways from the medium into the wire. They must, therefore, on their way pass inwards across any curve encircling the wire, so that the total number of induction-tubes cutting such a curve is the same for all positions of the curve. In the paper above referred to, I have sought to connect these two constants by supposing that the magnetic effect is due to, or, more correctly, accompanies, the motion inwards of the condition of electric induction. As soon as motion commences some of the electric energy is converted into magnetic, and the magnetic induction may be represented by ring-shaped closed tubes surrounding the wire. The two inductions, electric and magnetic, coexisting, will propagate the energy onwards till it finally arrives in the wire and is dissipated as heat, the induction there losing its directed condition.

The flowing of electric charges along the wire, which is usually considered as the essential part of the phenomena, or at least that to which attention is to be chiefly directed, becomes on this hypothesis merely the last stage of the process, which consists of a propagation from the surrounding dielectric towards the wire of electric and magnetic induction, which we may symbolize by the motion inwards of two sets of tubes, the electric tubes being, on the whole, more or less in the direction of the wire, the magnetic tubes being closed rings surrounding it. The wire plays the part of the refrigerator in a heat-engine, turning the energy it receives into heat—a necessary condition for the working of the machinery.

Let us now take the case of a condenser in which the dielectric, though homogeneous, is imperfectly insulating, so that the charge gradually disappears. According to Maxwell, in this case "induction and conduction are going on at the same time." Though Maxwell gave no precise account of the process of discharge, his theory and the mechanical illustration accompanying it are based on the supposition that two processes are going on at the same time in every part of the medium, viz. :—(1) a yielding of the electric strain or "displacement" in the dielectric equivalent to a displacement current from the negative towards the positive plate, and (2) a conduction-current from the positive plate to the negative equal to (1) in amount. This latter is accompanied by dissipation of energy. The two equal and opposite currents, being superposed, have no external magnetic effect.

But it seems to me that we may equally well and more simply represent the facts by considering the first process alone, viz. the yielding of the electric strain, the medium being incapable of bearing it permanently. The electric energy is gradually converted into heat in the same part of the dielectric where it was previously electric, *i. e.* there is here no transfer of energy. The decrease of induction in the medium is accompanied by a corresponding decrease of charge on the plates, not by conduction of + or − electricity either way through the medium, but simply because there is a decrease of the induction in the medium of which the charges on the plates are the surface manifestations. The induction decreases equally through the whole length of a tube, so that the tube "weakens" at the same rate throughout its length.

There will be no magnetic effect in the surrounding space, for there is no movement inwards of electric induction-tubes to supply the place of those which decay.

Perhaps we may take the following as illustrating the two modes of regarding the process. Suppose that a solid is submitted to some strain and kept in the strained position, but that the energy of the strain gradually dissipates; then we may confine ourselves simply to the statement that, owing to some rearrangement of the molecules, they cease to have molecular-strain energy, the energy in each portion of the mass being transformed to heat in that portion; or we may imagine that there is a continual return from the strained towards the original position, accompanied by an equal reverse flow of the matter towards the strained position, this latter not storing up energy, but dissipating the energy given up by the yielding of the strain. The ultimate result according to each is the same, but the latter account is purely hypothetical. We may at once obtain the equation giving the value of the charge at any time in terms of the initial charge when the condenser is left insulated.

Let σ be the charge per unit area, this being equal to the electric induction across unit area in the dielectric;
a be the thickness of the dielectric;
K be the specific induction-capacity;
c be the capacity per unit area;
X be the electric intensity in the dielectric, *i. e.* force per unit electricity on a small electrified body.

We have

$$X=\frac{4\pi\sigma}{K}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now we know that the rate of decrease of charge on the ends is proportional to the charge σ, and therefore to X.

The decrease of charge or of induction in the medium is therefore

$$\frac{d\sigma}{dt}=-\frac{X}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where r is a constant, which we may term the specific resistance.

Hence from (1),

$$\frac{d\sigma}{dt}+\frac{4\pi\sigma}{Kr}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

$$\sigma=\sigma_0 e^{-\frac{4\pi t}{Kr}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If we use p to denote the decrease of induction per second,

$$p=-\frac{d\sigma}{dt}=-\frac{K}{4\pi}\frac{dX}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The energy per unit volume is $\frac{KX^2}{8\pi}$; its rate of decrease is therefore

$$-\frac{KX}{4\pi}\frac{dX}{dt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

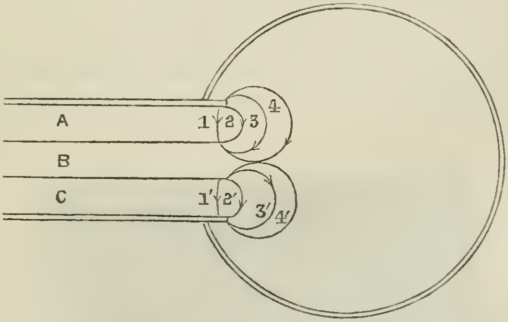
Substituting from (2) and (5), we get the expression which here corresponds to Joule's law for the heating effect, viz. rate of decrease of electric energy per unit volume $=p^2r$.

If at any moment the two end plates be connected by a wire, transfer of induction will at once take place into the wire, and the whole system will be completely discharged. During this discharge there will be magnetic energy accompanying the motion of electric induction.

We will now investigate the more complicated case of a stratified dielectric in which the different layers have different specific resistances. Before proceeding to the mathematical account, we shall consider the process generally, taking the simple case in which K is the same throughout. Let the condenser be charged very rapidly and then insulated. At the first moment there will be equal and opposite charges on the two end plates, and the number of induction-tubes running through unit area parallel to the plates will be the same in each layer. But decay of induction and dissipation of energy at once sets in, the rate of decay varying in different layers, so that after a time the number of induction-tubes in contiguous layers will differ and there will be charges on the separating surfaces. In those layers where the rate of decay is most rapid, there will be negative charges on the surface nearer the + plate, and + charges on the surface nearer the − plate; but still the induction in all is in the same direction.

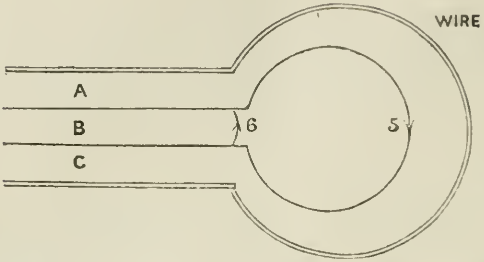
Now let the two end plates be connected by a wire. At once induction is propagated into the wire and transference takes place from the space between the plates until they are at the same potential, *i. e.* until the line-integral of the electric intensity, or, since K is constant, that of the induction from plate to plate is zero. The same number of tubes must have entered all parts of the wire, otherwise there would be charges at points along its length. Hence the same number of tubes running in the positive direction must have passed out from each of the layers. The result must be a reversal of the induction of some of the layers, viz. those in which the induction decayed most rapidly. This, of course, means that after their positive induction has all flowed out and they are quite discharged, tubes from the other layers have bent round and entered them, now charging them in the opposite direction. We may imagine the process to be somewhat as in figs. 2 and 3, representing a condenser with three layers, A, B, C, the decay having been most rapid in the middle one, so that it has become completely discharged, while there is still positive induction in A and C. 1, 2, 3, 4 (fig. 2) represent successive positions of a tube moving out from A towards the wire: $1'$, $2'$, $3'$, $4'$ successive positions of a tube moving out from C. When they have taken up the positions 4 $4'$ they come in contact, and where they overlap they will neutralize each other and break up into two portions, the outer part of each

Fig. 2.



forming one positive tube, as 5 (fig. 3), which will move off

Fig. 3.



to the wire, the inner parts uniting to form a negative tube 6 in B.

When the difference of potential between the end plates is zero, suppose the wire to be removed. The induction still remaining decays. If it decayed in the same proportion throughout, the difference of potential would always remain zero. But it decays in greater proportion in the negative layers, since in these the dissipation is by hypothesis most rapid. Hence in the line-integral of the induction from plate to plate the negative terms decrease more rapidly than the positive, and so the total value becomes positive. Then on again connecting with a wire, another positive discharge occurs. The process may evidently be repeated, the discharge always being positive, until finally it becomes insensible.

The analogy between the residual discharge and the phenomenon of elastic recovery in strained solids, pointed out by Kohlrausch, suggests a simple illustration.

Suppose that we build up a cube with successive layers of substances with the same instantaneous rigidity but with different viscosities. Let this be placed between two plates, A, B (fig. 4), the lower plate being fixed. Let rigid trans-

Fig. 4.

verse partitions, *r*, *r*, be passed through the layers and attached by hinges to the two plates, and then let the upper plate be acted on by a force in a direction perpendicular to the partitions, so that a shearing-strain is given to the whole cube. The partitions *r*, *r* are merely put so that the distortion from the original position shall always be the same throughout. When a given strain has been produced, let the upper plate be also fixed. Now if the rate of dissipation of strain-energy were the same throughout the layers the stress would also be the same throughout, though gradually decreasing, and on removing the constraint the upper plate would return by a certain amount and then remain in its new position. But the dissipation is not uniform, and after a time the stress in some of the layers is greater than in others. Hence, on removing the constraint from A and allowing it to return, when those in which dissipation has been most rapid have become entirely free from strain-energy, there is still some remaining in the other layers. These latter will therefore strain the former, and we shall have a reverse stress in some of the layers. Thus A will come to a new position of equilibrium; not so far, however, as its first position. Suppose that it is now again fixed. At first no force is necessary to keep it in position; but the stress exerted by the negative layers decays more rapidly than that exerted by the positive, and soon, on releasing A, it will return still further towards its original position. The process may be repeated, the successive discharges of momentum imparted to A being always in the same direction.

[*Added April* 15, 1886.—The supposition of stratification made by Maxwell is, no doubt, very artificial, and was made for the sake of simplicity in the mathematical treatment. He states that "an investigation of the cases in which materials are arranged otherwise than in strata would lead to similar results, though the calculations would be more complicated; so that we may conclude that the phenomena of electric absorption may be expected in the case of substances composed of parts of different kinds, even though these individual parts should be microscopically small.

"It by no means follows that every substance which exhibits this phenomenon is so composed. . . . . ." (*Electricity and Magnetism*, 2nd ed. vol. i. p. 419.)

Probably in the case of blown glass or any dielectric made up of heterogeneous parts, which has been flattened by rolling, there is more or less approach to the stratified condition; but in other cases, such as shellac or paraffin, we might fairly expect the dielectric to be similarly constituted in all directions. We can only therefore take Maxwell's investigation as showing in a general way that heterogeneity would introduce absorption phenomena ; and we cannot expect the results obtained on the supposition of such a special arrangement to agree with those of experiment. We may regard the stratified arrangement as giving a superior limit, as it were, this being the constitution most favourable to the production of the phenomena in the way supposed. The inferior limit would be given by an arrangement in which each portion of the substance of the same kind stretched from plate to plate with the same cross section throughout. In this case there would be no residual discharge produced. Using Maxwell's notation (see below), the resistance per unit cross section may be shown to be

$$R' = \frac{(a_1 + a_2 + \dots)^2}{\frac{a_1}{r_1} + \frac{a_2}{r_2} \dots}$$

instead of

$$R = a_1 r_1 + a_2 r_2 + \dots,$$

and R′ is always less than R. In any intermediate composition, in which portions of more conducting matter are insulated from each other by less conducting matter, we shall have residual discharge.

It appears probable, from experiments of Dr. Schulze-Berge ('Nature,' March 4, 1886, p. 432), that the resistance of certain dielectrics is not proportional to the thickness, but is much less for thin layers than might be expected. May this not possibly arise from the size of the heterogeneous portions being comparable with the thickness of the dielectric, so that the more easily conducting portions may stretch in some parts from plate to plate? If so, we approximate more nearly to the inferior limit.]

The mathematical account of the residual discharge on this hypothesis is practically the same as Maxwell's ; but it may perhaps be worth while to give it with the necessary alterations, as these seem to make it somewhat more straightforward and evident.

We shall suppose with Maxwell, "for the sake of simplicity, that the dielectric consists of a number of plane strata of different materials and of area unity," and that the induction is in the direction of the normal to the strata.

Let a_1, a_2, &c., be the thickness of the different strata ;
X_1, X_2, &c., be the electric intensity within each stratum;
p_1, p_2, &c., be the amount of decay of induction per second in each stratum ;

Let f_1, f_2, &c., be the induction in each stratum ;
u_1, u_2, &c., be the total number of tubes of electric induction entering each layer sideways, *i. e.* crossing in through its boundary per second ;
r_1, r_2, &c., be the specific resistance referred to unit of volume ;
K_1, K_2, &c., be the specific inductive capacity ;
k_1, k_2, &c., be the reciprocal of the specific inductive capacity ;
E be the electromotive force due to a voltaic battery placed in the part of the circuit leading from the last stratum towards the first, which we shall suppose good conductors ;
Q be the total number of induction-tubes which have left the battery and entered the wires and dielectric up to the time t.

Then, since the same number of tubes enter all parts of the circuit in a given time,

$$u_1 = u_2 = u_3 = \ldots . = u \text{ say.} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

These tubes tend to increase the induction in the layers. But at the same time decay is going on, so that we have

$$u_1 = p_1 + \frac{df_1}{dt}, \quad u_2 = p_2 + \frac{df_2}{dt}, \text{ \&c.,} \quad . \quad . \quad . \quad (2)$$

whence

$$p_1 + \frac{df_1}{dt} = p_2 + \frac{df_2}{dt} = \text{\&c.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We also have by Ohm's law,

$$p_1 = \frac{X_1}{r_1}, \text{ \&c.;} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and by the relation between induction and intensity,

$$X_1 = 4\pi k_1 f_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

whence

$$u = \frac{X_1}{r_1} + \frac{1}{4\pi k_1} \frac{dX_1}{dt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Let us suppose that at first there is no charge, and that suddenly the E.M.F., E is made to act. Then, if at once Q tubes enter the dielectric,

$$X_1 = 4\pi k_1 Q, \text{ \&c.;} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and since

$$E = a_1 X_1 + a_2 X_2 + \ldots ; \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$E = 4\pi(k_1 a_1 + k_2 a_2 + \ldots)Q.$$

The instantaneous capacity C, which is equal to $\frac{Q}{E}$, is given by

$$C = \frac{1}{4\pi(k_1a_1 + k_2a_2 + \ldots)}. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

But dissipation at once sets in, and if the electromotive force E be continued uniform, a steady state will ultimately be reached in which the dissipation in each layer is equal to the number of fresh tubes reaching that layer. The number of tubes entering being the same throughout, the dissipation p is also the same throughout.

We have then

$$p = \frac{X_1}{r_1} = \frac{X_2}{r_2} = \text{ \&c.} \ . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and substituting in (8)

$$E = (r_1a_1 + r_2a_2 \ldots \ldots)p.$$

Hence, if $R = r_1a_1 + \ldots$

$$p = \frac{E}{R} \cdots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In this state we have the induction given by

$$f_1 = \frac{X_1}{4\pi k_1} = \frac{r_1}{4\pi k_1}p = \frac{Er_1}{4\pi k_1 R}. \quad . \quad . \quad . \quad (12)$$

If we now suddenly connect the extreme strata by means of a conductor of small resistance, E will be suddenly changed from the value E_0 to zero, and Q' tubes will pass out from each layer of the dielectric into the wire. If then X^1 be the new value of the intensity,

$$Q' = \frac{X_1}{4\pi k_1} - \frac{X_1^1}{4\pi k_1};$$

whence

$$X_1^1 = X_1 - 4\pi k_1 Q'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Since, then, the difference of potential is zero,

$$a_1X_1^1 - a_2X_2^1 + \ldots = 0;$$

substituting from (13) we get

$$a_1X_1 + a_2X_2 + \ldots \ldots = 4\pi(a_1k_1 + a_2k_2 + \ldots)Q';$$

or

$$Q' = \frac{a_1X_1 + a_2X_2 + \ldots}{4\pi(a_1k_1 + a_2k_2 + \ldots)} = CE = Q, \text{ from (8) and (9)} . \ (14)$$

Hence the instantaneous discharge is equal to the instantaneous charge.

By (10) and (11) we may put (13) in the form

$$X_1^1 = pr_1 - 4\pi k_1 Q,$$

$$= \frac{Er_1}{R} - 4\pi k_1 Q. . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Let us next suppose the connection broken immediately after the discharge. No fresh tubes enter any layer; so that putting $u=0$, we have from (6)

$$u=\frac{X_1}{r_1}+\frac{1}{4\pi k_1}\frac{dX_1}{dt},$$

or

$$X_1=X_1{}^1 e^{-\frac{4\pi k_1}{r_1}t},$$

where X_1 is now the value of the electric intensity at any time t after the connection is broken.

Substituting from (15) and putting E_0 for the initial value of E,

$$X_1=E_0\left(\frac{r_1}{R}-4\pi k_1 C\right)e^{-\frac{4\pi k_1}{r_1}}. \quad . \quad . \quad . \quad . \quad (16)$$

The value of E at any time is

$$E=a_1X_1+a_2X_2+\dots$$

$$=E_0\left\{\left(\frac{a_1r_1}{R}-4\pi a_1k_4C\right)e^{-\frac{4\pi k_1}{r_1}t}+\left(\frac{a_2r_2}{R}-4\pi a_2k_2C\right)e^{-\frac{4\pi k_2}{r_2}t}+\text{\&c.}\right.$$

$$=E_0\left\{\left(\frac{r_1}{R}-4\pi k_1C\right)a_1e^{-\frac{4\pi k_1}{r_1}t}+\left(\frac{r_2}{R}-4\pi k_2C\right)a_2e^{-\frac{4\pi k_2}{r_2}t}+\dots\right\}. \quad (17)$$

$$=E_0\left\{\left(\frac{r_1}{k_1}-4\pi CR\right)\frac{a_1k_1}{R}e^{-\frac{4\pi k_1}{r_1}t}\dots\right.$$

The instantaneous discharge obtained at any time t will be, as before, .CE.

If the terms be arranged in descending order of magnitude of $\frac{r_1}{k_1}$, then the exponentials are also in descending order of magnitude, or the negative terms decrease more rapidly than the positive, and E is positive.

LVIII. *Note on a "Relation between the Critical Temperatures of Bodies and their Thermal Expansions as Liquids."* By T. E. THORPE, *Ph.D., F.R.S.*, and A. W. RÜCKER, *M.A., F.R.S.**

A PAPER bearing the above title was published by us in the Journal of the Chemical Society of London for April 1884, and has recently been discussed by MM. A. Bartoli and E. Stracciati†. As these gentlemen have done us the honour to make use of a formula deduced by us from the

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* Communicated by the Physical Society: read April 10, 1886.

† *Ann. Chim. Phys.* Mars 1886, p. 384.

simple expression given by Mendelejeff for the expansion of liquids, we should like to state exactly the position which we ourselves think ought to be assigned to it, and the use which may legitimately be made of it.

Prof. Mendelejeff has shown* that the expansion of liquids under constant pressure between 0° C. and their boiling-points may be expressed by means of the very simple formula

$$V_t = \frac{1}{1-kt};$$

where V_t is the volume at $t°$ (that at 0° C. being unity), and k is a quantity which differs for different substances, but which may for any one substance be considered invariable between 0° C. and the neighbourhood of the boiling-point.

The great merit of Mendelejeff's law is that it is proved by him to express the law of expansion to within the limits of the differences between the results of different observers experimenting on the same liquid. Thus, if the results of any one observer alone are considered, they may no doubt be most accurately expressed by a formula of the type

$$V_t = 1 + a't + b't^2 + ct^3.$$

Another equally reliable observer will, however, obtain for the same liquid a formula

$$V_t = 1 + a''t + b''t^2 + c''t^3,$$

where a', b', c' differ appreciably from a'', b'', c''. These slight differences depend on the *unavoidable errors of experiment*, which may perhaps in the future be diminished, but which at present affect the work of the best observers using the best known methods. Hence formulæ such as those given above can only be considered as approximations to the true law of the expansion of the liquid to which they refer. That law will be most nearly given by combining the results of several physicists whose methods and observations are equally good, rather than of relying upon those of any one.

Now Mendelejeff has shown that the volumes calculated at different temperatures by means of the formula

$$V_t = \frac{1}{1-kt}$$

differ less from the results of good observers than they do from one another. It might in any given case be possible to obtain another more complex formula which would express the *mean result* more accurately, but it would remain very doubtful whether the greater mathematical accuracy obtained

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* Journ. Chem. Soc. April 1884.

represented the physical facts more closely. Mendelejeff (as we think rightly) considers that the simplicity of the formula which he has suggested gives it a special claim upon our attention; and he proves that it expresses, at all events as a first but very close approximation, all *that we certainly know* about the expansion of liquids.

It is therefore no argument against Mendelejeff's formula to remark, as MM. Bartoli and Stracciati have done, that

$$V_t = \frac{1}{1-kt} = 1 + kt + k^2t^2 + k^3t^3 + \&c.;$$

and that in the formulæ given by Pierre, Kopp, Hirn, Thorpe, &c., the constants a, b, and c do not differ by a constant ratio, as the expression would require. This criticism would only hold good if all these observers had obtained the same, or closely identical, values of a, b, and c; whereas, as a matter of fact, the values of b and c given by different observers may differ very widely. The very merit of Mendelejeff's remark is that, although the results of no one physicist are expressed by

$$V_t = 1 + kt + k^2t^2 + k^3t^3,$$

yet that this formula in its simpler form,

$$V_t = \frac{1}{1-kt},$$

expresses the results of all as accurately as those results will allow; and that since it is thus sufficiently accurate and extraordinarily simple, it may claim to be the best general formula hitherto proposed for expressing the laws of liquid expansion.

These remarks are subject to the conditions which Mendelejeff made clear, that the formula was only applied to the range of temperature between 0° and the neighbourhood of the boiling-point, and that the constant k increases slightly as the temperature rises. This latter fact indicates that the law, though very accurately expressing the known facts, is only an approximation to the truth.

Mendelejeff's formula, then, appears to us to stand in somewhat the same position as Boyle's or Charles's laws. It is a first approximation, which expresses the facts, under given conditions of temperature and pressure, with great accuracy. The difference between the cases is that, whereas the deviation of each of the principal gases from Boyle's law has been studied, Mendelejeff has shown that the most careful researches do not enable us to state with certainty what is the magnitude of the error caused by applying his formula to any particular liquid. They show only that k increases very slightly as the temperature rises.

Having thus defined as accurately as we can the position which we think that Mendelejeff's law holds, we need hardly say that we do not claim any higher status for our own formula connecting the law of expansion and the critical temperature. We were most careful to express in our paper our appreciation of the fact that our expression was based upon Mendelejeff's, and therefore it ranked only as a theoretical deduction from an extremely close approximation to the truth, and is to be employed only under the conditions for which that approximation was valid.

Thus we have shown that the critical temperature of a liquid (T_c) is given very approximately by the formula

$$T_c = \frac{TV_t - 273}{a(V_t - 1)};$$

where V_t is the volume at $t°$ C., $T = 273 + t$, and a is a constant which we proved is nearly $= 2$.

We should, however, never have thought of applying this formula to determine the critical temperature of water from the expansion up to 200° C. We have not applied it to water at all, on account of the well-known peculiarities of the expansion of that substance; but had we done so, we should have regarded it as holding only between 0° C. and the boiling-point. We have distinctly laid it down that it is under these conditions *k* is to be determined*. In proving, therefore, that the values of the critical temperature, calculated from the expansions at temperatures above the boiling-point, vary very widely from those obtained under the conditions adopted by Mendelejeff and ourselves, MM. Bartoli and Stracciati have only shown that the formula does not hold good under circumstances to which its authors never intended it to be applied.

We are, however, gratified to find that these gentlemen, notwithstanding their criticisms, show a reliance upon our formula even greater than that which we feel ourselves. The values of the constant *a* given in our paper prove that its true value is uncertain, at all events to 1 per cent. or more. MM. Bartoli and Stracciati, however, give in their second paper a number of critical temperatures calculated by the formula to tenths of a degree. If the tenth of a degree is to be determined with accuracy, the constant *a* must be known to 0·025 per cent. We beg, therefore, those who may do us the honour to use our formula, neither to outrage it under conditions to which it does not apply, nor to use it as though it were more accurate than it pretends to be.

* Journ. Chem. Soc. *loc. cit.* p. 139.

LIX. *On the Cause of the Solar-Diurnal Variations of Terrestrial Magnetism.* *By* Professor BALFOUR STEWART, *LL.D., F.R.S.*[*]

IN attempting to account for the Solar-diurnal inequalities of Terrestrial Magnetism, scientific speculators have ranged over the whole field of likely explanations. Some of them think that they have now finally driven the truth into a corner, and are in hopes of ultimately securing the object of their pursuit.

I shall begin by enumerating the chief hypotheses which have been proposed.

(1) There is, first, that of the direct magnetic action of the Sun upon the Earth. There are, however, many serious objections to this hypothesis. One of these is the great difficulty attending the supposition that the Sun is capable of acting as a powerful magnet, since terrestrial analogies would lead us to infer that matter at the high temperature of the Sun is quite incapable of possessing magnetic properties. Again, we have strong evidence that changes in the range of the daily variation of magnetic declination lag behind corresponding solar changes in point of time. This kind of behaviour is apparently inconsistent with direct magnetic action, and points rather to some indirect influence probably caused by the radiant energy of the Sun, inasmuch as the changes and turning-points of such indirect influences due to radiation are well known to lag in respect of time behind the corresponding changes and turning-points in their cause. Finally, Dr. Lloyd and Mr. C. Chambers [†] have both shown that direct solar magnetic action will not account for the peculiarities of the diurnal magnetic variation. We may therefore perhaps dimiss this hypothesis.

(2) The next hypothesis which I shall introduce is that of Faraday. Reasoning from his discovery that oxygen is magnetic and becomes weaker in its power when heated, he concludes that when the Sun heats a certain portion of the Earth's atmosphere, this renders that portion less magnetic than those other portions not subjected to solar influence. This kind of action is thus seen to be equivalent to a displacement by means of solar influence of the magnetic matter of the Earth, and hence implies a corresponding displacement of the lines of magnetic force. Now there is unquestionably truth in this hypothesis, but yet there is very great

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[*] Communicated by the Physical Society: read April 10, 1886.

[†] Proc. Royal Irish Academy, Feb. 22, 1858, and Phil. Trans. 1863.

doubt whether it will account for the diurnal oscillation as we know it. It will form *a cause*, but yet it will not be *the chief cause*. It is obviously one prominent peculiarity of Faraday's hypothesis, that in it the action of the Sun must, to ensure its probability, be associated with the great mass of the Earth's atmosphere, that is to say with the lower strata as well as with the upper; or rather with the lower strata in preference to the upper, bearing in mind the superior mass of the former and their greater nearness to the magnetic Earth. Now we know both from observations of the declination and horizontal force (Proc. Roy. Soc. March 22, 1877, and Phil. Trans. 1880, p. 541) that the action of the Sun in producing diurnal variations of these elements is one and a half times as powerful at epochs of maximum as it is at epochs of minimum sun-spot frequency.

But it is very difficult, if not impossible, to imagine that the great mass of the atmosphere can be heated by the Sun one and a half times as much at epochs of maximum sun-spot frequency as it is at epochs of minimum sun-spot frequency; and yet we must imagine this if we suppose that Faraday's hypothesis accounts for the diurnal variation. Certainly the facts of meteorology are strongly against any such belief. Again, during our summer the heating influence of the Sun is considerably greater in the Northern than in the Southern Hemisphere, while during our winter the reverse will be the case. Totally apart from the diurnal variation we ought therefore, if Faraday's hypothesis be true, to find a very perceptible difference in the mean magnetic condition of the Northern Hemisphere between summer and winter, and a like difference too in the Southern Hemisphere, the one being at the same moment differently affected from the other. But there are no traces of such a phenomenon, the annual and semi-annual variations being quite of a different nature and none of them very large.

(3) Let me now discuss the hypothesis that these variations are caused by earth-currents. These currents were first detected by W. H. Barlow, and were at a later period observed and studied by C. V. Walker. They are now continuously recorded by photography at the Royal Observatory, Greenwich, and at the Central Russian Observatory.

With respect to these currents, I have always maintained that in type they bear all the marks of being secondary currents generated in the moist conducting crust of the Earth, and caused by small but abrupt changes in the magnetism of the Earth. Whether this be the true explanation or not, it is at any rate, I venture to think, consistent with what we know of electrical action. But while I should thus feel disposed to regard these phenomena as effects rather than causes, in their primary sense at least, it is manifest that, when once generated, such currents will influence the needle; and the results of the Greenwich observers induce us to think that such influence is very great and forms perhaps the chief immediate cause of those oscillations of the needle called disturbances, which are quite different from the solar diurnal variation. In one sense therefore such currents may be effects, while in another they are causes, but causes of disturbances rather than of the daily variation.

It may, however, be replied that earth-currents may be complex phenomena, and that while their most important manifestations may be due to induction, thus being primarily effects rather than causes, yet another portion of them may operate as a true cause producing the solar-diurnal variation. Now there are two objections to this hypothesis; and one of these is, that we know of no physical agency that will produce in the Earth's crust currents of this nature, which, in order to account for the solar-diurnal variation, must be one and a half times more powerful at times of maximum than at times of minimum sun-spot frequency. Another objection is that Sir George Airy has not been able to detect any resemblance in form between the regular diurnal progress of the magnet and that of the earth-currents. We think therefore that we may dismiss this hypothesis.

Now, if it be unlikely that these magnetic variations are caused either by the direct magnetic action of the Sun, or by earth-currents, or by the heating effect of the Sun on the chief mass of the Earth's atmosphere, we seem to be driven by the method of exhaustion to look for their cause in the upper atmospheric regions. We shall, however, have to show that there is no improbability in locating their cause in these elevated regions, otherwise our method of exhaustion will have done us no service. In the first place, I need hardly say that if the cause we are in search of be in these upper regions, it must either be in the shape of a set of electrical currents, or in some other shape with which we are quite unacquainted; but the nature of this discussion precludes us from entertaining the latter supposition; and we are therefore driven to regard electrical currents as being the only conceivable cause, if this cause is to be located in the upper atmospheric regions.

I shall now attempt to reply to two imaginary objections that may be raised as to the possibility of such currents. In the first place, it may be said that while undoubtedly rarified air is a conductor of electricity, yet it is not a good conductor; and where can we look for sufficient potential to drive currents through these upper atmospheric regions? To this I would reply that *as a matter of fact* we know that there are visible electric currents in the upper atmospheric regions which occur occasionally at ordinary latitudes, and which are very frequent, if not continuous, in certain regions of the Earth. I allude to the Aurora, which is unquestionably an electric current, and must therefore influence the magnetic needle. Furthermore, both with respect to its times of occurrence and to the disposition of its beams, the Aurora manifests a close connection with the phenomena of terrestrial magnetism, occurring at ordinary latitudes only when there are great magnetic disturbances, and the disposition of its beams having a distinct reference to lines of magnetic force. We are therefore justified in asserting that there is no impossibility in conceiving a set of electrical currents, intimately associated with certain phenomena of terrestrial magnetism, to exist in the upper region of the Earth's atmosphere.

In the next place, the objection may be raised, How is it possible to suppose any cause that will make such currents one and a half times more powerful at times of maximum than at times of minimum sun-spot frequency? Can it be imagined that the radiant energy of our luminary varies in this proportion? Now it has been remarked by Professor Stokes that an increase in the radiative power of the Sun would most probably imply, not only an increase in general radiation, but a special and predominant increase in such actinic rays as are probably absorbed in the upper regions of the Earth's atmosphere. These regions will therefore greedily absorb the new rays, their temperature will rise, and, as is known to be the case for gases, the electrical conductivity of the strata will be increased*. Thus, even if we imagine the general atmospheric current to remain constant, a greater proportion of it would be thrown at such times into those heated regions which had become good conductors; but then it is likewise probable that the current itself would be increased as well as increasingly diverted into a particular channel.

Such an explanation appears to receive support from the curious and suggestive fact that the lunar influence on the

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* It seems not impossible, too, that the constitution of these strata with respect to aqueous vapour, may be different at times of maximum and at times of minimum sun-spot frequency; hence their absorbing power may be different.

Earth's magnetism, as observed at Trevandrum, is greater during the day than during the night, and greater perhaps, too, at times of maximum than at times of minimum sun-spot frequency. If the arguments now advanced be generally assented to, we may presume that, while it is unlikely that the cause of the daily variation exists anywhere else than in the upper regions of the Earth's atmosphere, there is no objection to our imagining that it resides there in the form of a set of electric currents. Such currents will of course affect the needle directly, but they will also affect the magnetic earth, and any affection of the magnetic earth will again influence the needle. The question thus arises, To what extent do these hypothetical currents act directly upon the needle, and to what extent do they act upon it indirectly by influencing the magnetism of the Earth? That this question is not unimportant will be manifest by considering what takes place when a powerful electromagnet influences a needle. In this case probably only a small portion of the influence is due to the direct action of the current, while a large portion is due to the iron of the electromagnet that has been magnetized by the current. In order to study this point it will perhaps be desirable that we limit ourselves to the solar diurnal variations of declination, as these are of a simple definite type in each hemisphere, the type in the one hemisphere being the reverse of that in the other. Let us therefore consider the peculiarities of this variation, particularly in the regions on either side of the magnetic equator.

Here we find, speaking generally, that north of the equator the extreme westerly deflection of the marked pole of the needle is reached at 2 P.M., while south of the equator this pole reaches its extreme easterly deflection at the same hour. Now, if we attempt to picture to ourselves any general change in the magnetic system of the Earth that will produce these results, it will be one of a very artificial character. On the other hand, these motions of the needle, which cannot well be explained by any easily conceivable temporary change of the Earth's magnetic system, can very easily be explained by a system of atmospheric currents. In the northern hemisphere we should have a set of positive currents flowing from the equator northwards, while in the southern we should have in like manner a similar set of positive currents flowing southwards. And, therefore, since positive currents flow out from the equator on both sides of it, we should have to contemplate a vertical stream of positive electricity at the equator which there splits itself up into two portions—one for each hemisphere.

The argument as I have now advanced it is of a general nature and is twofold.

(1) In the first place it brings forward objections to the localization of the cause of the diurnal variations anywhere else than in the higher regions of the Earth's atmosphere; then points out that if this cause exist in these regions it must be in the shape of a system of electric currents; and finally endeavours to show that there are no valid objections to such a system of currents.

(2) It endeavours to show that, if we take the diurnal variation of the declination-needle, which is of a remarkably simple type, we have great difficulty in imagining that it can be brought about by any temporarily induced displacement of the magnetic system of the earth, while we can with the greatest ease account for it by means of a system of currents in the upper regions of the Earth's atmosphere.

At this point Dr. Schuster has endeavoured to apply mathematical analysis to the subject, and he has obtained results which are very satisfactory and encouraging *. He had previously, in the Report of the Magnetic Committee of the British Association for the year 1885, pointed out the existence of a test † which will enable us to decide whether or not the diurnal variation can be caused by a series of electric currents which embrace both the upper atmospheric regions and the Earth, and complete themselves by electric discharges through the lower regions of the Earth's atmosphere into the ground; and he now endeavoured to ascertain whether the supposed vertical currents at the equator, to which allusion has been made, could possibly be of this nature. If this were the case, he argues, and if a unit pole were carried from a position A at the Earth's surface in a path which should return again to A, and in the centre of which there should exist such a vertical current, then through all its course work would be done either by or against this pole, inasmuch as there would be a continued effort of the vertical current to turn the pole round it in one direction. In other words, the pole and the point A being immersed in the system of currents, there would be a potential having multiple values. On the other hand, if the system which produces the daily variation be outside of A, whether above or below it, there will be at A a true potential, and if the unit pole be carried as before, in any path from A and back to A again, as much work will be done against the pole as will be done by it. Let us consider, now, a little path embraced between two parallels of latitude near each other,

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* Proc. Lit. & Phil. Society of Manchester, January 12, 1886; Phil. Mag. April 1886, p. 349.

† The reader will find a complete discussion of this subject in Maxwell's 'Electricity and Magnetism.'

and two meridians of longitude likewise near each other, and imagine our pole to be carried round this boundary. On the supposition that there is no vertical current in the centre of the path, the work done upon the pole will be equal to that done by it. This will at once give us an equation between X and Y; that is to say, between the components of the solar-diurnal periodic force towards the geographical north and west respectively. From this equation, and by means of certain legitimate assumptions regarding the type of Y, which represents very nearly the force influencing the declination (and this we know to be of a simple uniform type), Dr. Schuster is able to obtain certain relations between the solar-diurnal variations of the declination and of the horizontal force which ought to hold, *if there be no vertical currents between the upper regions and the Earth*, or, rather, if such vertical currents are inoperative as an element in producing the solar-diurnal variation. One of these is that the northerly or horizontal-force component of the daily variation ought to have a maximum or a minimum at the time when the westerly or declination component vanishes, that is to say attains its mean position.

Now at Greenwich, X or the horizontal-force component has a maximum at 7 o'clock in the evening and a minimum at noon; while Y or the declination component vanishes a little after 7 o'clock and between 12 and 1 in the afternoon. At Bombay the declination-needle is at its mean value on an average a little after 10 in the morning and about 10 in the evening. The horizontal force has its maximum a little after 11 in the morning and the minimum at a quarter past 9 in the evening.

The observations at Lisbon and Hobarton show an equally good agreement, those at St. Helena and the Cape of Good Hope less so; but in these two latter places the observations taken at different months show a considerable difference of behaviour. On the whole, Dr. Schuster regards the agreement as satisfactory, and as so far tending to disprove the existence of vertical currents through the Earth's surface. Pursuing his analysis, he comes to the conclusion, from certain approximate expressions which he obtains, that the northerly force ought to be a maximum in the morning and a minimum in the afternoon in the equatorial regions; while in latitudes above 45° the minimum ought to take place in the morning. Now this is almost exactly what happens. At Bombay, for instance, the *maximum* of horizontal force takes place at 11 A.M., while at Greenwich the *minimum* takes place a little after that time.

Having thus obtained results which lead him to infer that the unit pole we are observing is not immersed in the attracting system, Dr. Schuster next proceeds to discuss the question whether this system is above us or beneath us. To do this it is necessary first of all to obtain an approximate value for the potential at the surface of the earth, and from it to derive the general potential. To aid in determining this we must bear in mind that, since the unit pole is now assumed not to be immersed in the attracting system, the potential V will be subject to the condition

$$\frac{d^2V}{dx^2}+\frac{d^2V}{dy^2}+\frac{d^2V}{dz^2}=0$$

or to an equivalent condition adapted to the system of coordinates employed. From this Dr. Schuster deduces two possible expressions for the potential ; the one referring to a system above our heads and having powers of (r) the radius in its numerator, the other referring to a system beneath our feet and having powers of the radius in its denominator. Now the expression for the vertical force as derived from the potential will be $-\frac{dV}{dr}$, the sign of which will be manifestly different according as r appears in the numerator or in the denominator of the potential in question. Which, therefore, of these two possible (approximate) forms of V agrees best with observation? In the first place, both expressions found by Dr. Schuster have their turning-points coincident in epoch with those for X, or the northerly component of the disturbing force ; and this is a fact confirmed by actual observation. But while the expression for the vertical force derived from a system above us has its maxima and minima coincident with those of horizontal force at latitudes greater than 45°, in the equatorial regions the maximum of horizontal force ought to be coincident with the minimum of vertical force, and *vice versâ*. Precisely the opposite arrangement should hold if the attracting system be beneath our feet.

Now at Greenwich the maximum of northerly force takes place at 7 P.M. and the minimum at noon ; while the maximum of vertical force takes place at 7 P.M. and the minimum at 11 A.M.

At Bombay the maximum of northerly force takes place at 11 A.M. and the minimum at 9 P.M. ; there is a very decided minimum of vertical force at 11 A.M., but there is no pronounced maximum ; two minor maxima, however, occur, one at 6 A.M. and the other at midnight.

On the whole it must be said that the results of this first and praiseworthy attempt are very encouraging, and point to the supposition that the greater portion of the disturbing currents lies outside the Earth's surface.

I now come to consider another aspect of the subject. It seems quite possible to conceive a set of currents to exist in the Earth's atmosphere without exhibiting a considerable diurnal variation. Let us take, for instance, an ordinary electric circuit, say of a circular shape and horizontal, and heat it by causing some source of heat, such as a lamp, to travel slowly around it with a definite rate of progress. It will be evident that we shall have (assuming the current to be otherwise constant) no variation in flow due to this heating effect. In like manner, if there be electric currents in the atmosphere which circulate round the Earth in the direction of parallels of latitude, such currents will not be subject to a considerable solar diurnal variation. For while the conductivity of a given region would vary according to the position of the Sun with regard to it, yet the whole circuit round the Earth, which would always embrace a region affected by the Sun, would not have its total resistance altered, at least not greatly altered ; and as there would be no cause for much alteration of the total electromotive force, there would be no great reason for inconstancy of current—in other words, no great solar diurnal variation.

It may, however, be asked if there are any grounds for imagining the existence of such a set of currents. To this I would reply that, assuming the existence of currents in the upper regions of the atmosphere, their disposition would certainly be to some extent subject to magneto-electric considerations. If we bear in mind the distinct connection between auroral beams and lines of magnetic force, we must certainly, I think, be prepared to admit the possibility of perhaps even a marked reference to magneto-electric considerations in the disposition of the currents in question.

For the purpose of the following argument we may consider the Earth to be at rest (*i. e.* devoid of rotation), and imagine that the Sun circulates round the equator in twenty-four hours. As a consequence of solar influence, we shall have convection-currents in the upper regions of the atmosphere flowing from the equator northwards and southwards towards the poles. Whether these currents reach the poles or come down in some intermediate region may be left an open question. Now such currents will not only be conductors, but they will form a movable system of conductors, which we may suppose to be created at the equator when they rise into the upper regions, and destroyed at the poles or those intermediate regions where they descend.

Again, for the purpose of this argument we may, without sensible error, look upon the magnetic Earth as similar to the class model that is sometimes used to represent it; that is to say, as a globe wrapped round continuously with insulated wires in the same direction which convey an electric current, the circles of such wires being small near the poles, and of course large at the equator. Now if an external insulated circuit of wire a trifle larger than the diameter of this globe be supposed to travel from the equator to either of the poles, it will leave behind more convolutions of the primary globe-current than it approaches, and will therefore be traversed by an induced current in the same direction as that of the primary; and the continuous travelling of such an external insulated system might be supposed to increase the magnetic power of the globe. Applying the same sort of reasoning to the Earth and to the convection-currents under consideration, these may be imagined to be traversed by equatorial currents, the tendency of which in both hemispheres would be to increase the general magnetism of the globe. From the reason already given such currents would have no solar-diurnal variation, but yet they would be dependent upon the state of the Sun and would vary with it. For imagine a change to take place in the radiation of our luminary producing an excess of such rays as are greedily absorbed by the upper atmospheric regions; there would be (as I have before remarked) a sensible increase in the conductivity of these regions even if the electromotive force remained altered, and hence there would be an increase in the supposed equatorial current. In other words, such currents, while presenting no great diurnal variation, due to the carriage of a constant Sun round the Earth, would yet be eminently susceptible to any inconstancy in the sun itself. Now have we any such phenomenon connected with terrestrial magnetism? I think we have. The late John Allan Broun has, I believe, proved that we have changes in the mean daily value of the horizontal force which are simultaneous, and in the same direction at places on the Earth's surface very far removed from each other; and I have endeavoured to show that the changes of this nature recorded by him depend, as far as we can judge from somewhat imperfect records, upôn the state of the Sun's surface, an increased area of spotted surface coinciding apparently with increased values of the daily means of horizontal force all over the Earth. But my chief object in giving prominence to this part of the subject is with the view of advocating that the Gaussian method of analysis should not be applied merely to the solar diurnal variations of the three magnetic elements, but that they should likewise embrace a consideration of the simultaneous variations in the mean daily values of the elements at various stations. We must, in fine, consider the possibility at least of there being in the upper atmospheric regions, not merely currents which present a solar-diurnal variation, but others that have no such variation, while yet they may be highly susceptible to changes in the Sun. The double method of treating mathematically not merely the solar-diurnal variation, but likewise the simultaneous changes in the mean daily values of the elements, would thus appear to be necessary, and sufficient for giving us the required information. Already the Greenwich scheme of publication embraces not merely information connected with the solar-diurnal variation, but gives us likewise the mean daily values of the three elements; and if a complete system of this nature be pursued by a sufficient number of well-equipped magnetical observatories, we may hope soon to obtain reasonably complete information regarding the existence and distribution of currents in the upper regions of the Earth's atmosphere.

LX. *Notices respecting New Books.*

On the Sensations of Tone as a Physiological Basis for the Theory of Music. By H. L. F. Helmholtz, *M.D., &c. Second English Edition. Translated with additions by* A. J. Ellis, *F.R.S., &c., &c.* Longmans, Green, & Co.: 1885.

IT is now nearly a quarter of a century since the first appearance of this book, the most recent English edition of which lies before us. It ought to be possible by this time to form a fairly grounded judgment as to the permanent position the work is likely to occupy in the discussion of the matters of which it treats. And the verdict must, as it seems, be, that while errors have been committed on a certain number of points, and there are deficiencies here and there in detail such as must be inevitable in a work of such magnitude, yet the great bulk of the book holds its own to a most surprising extent, and bears minute investigation in a manner characteristic of the work of a master hand. Within the limits of a notice it would be impossible to attempt to convey an analysis of the work, and I will only endeavour to emphasize a few points of present importance.

The first great controverted point is that dealt with at pp. 125–6. This purports to be an experimental proof of the law that "the quality of the musical portion of a compound tone depends solely on the number and relative strength of its partial simple tones, and in no respect on their differences of phase." Now I do not think that the experiments described in support of this law are sufficient, if opposed by other experiments, in which apparent differences in quality due to phase can be shown. Koenig has, I believe, attacked the supposed law in this way. And it can undoubtedly be shown by very simple experiments that apparent differences of quality do arise from the differences of phase. Take two notes sounding an octave, and put them very slightly out of tune; then there will be a slow heavy beat consisting of variations of intensity of the lower note (if the tones are pure). By putting the notes in tune again the effect at any instant may be arrested and maintained; and thus we may obtain either a combination with a heavy lower note, or one with a light lower note, according to the relative phase. Whether we explain this phenomenon by difference tones or by Koenig's hypothesis of beat notes is a question on which I do not enter. But I point out the fact that this supposed law of non-dependence of quality on phase is certainly not true in fact; for the combinations with heavy and light lower notes obtained as above, by varying the phase, present quite different qualities in the resulting compound, as might be expected.

And yet I have no doubt that the above law of Helmholtz divines correctly what would happen if we could get rid of the difference tones; that is, if we could reduce the case to one of infinitely small displacements, in which terms of the second order could be entirely neglected. But I suppose that those who take Koenig's view would not admit this.

While on this point I may mention that the absence of formulæ accompanying the little tables which deal with the mathematics of sympathy makes it very difficult to find out how they were calculated, notwithstanding the explanations in the Appendix. In the table of Resonance and Phase for instance (p. 125) it would be convenient to add, "If x be the number in the column for resonance, and τ the angle, then $x^2=\cos\tau$." According to the notation in the Appendix (p. 401), the amplitude is taken to represent the resonance (evidently by a slip of the pen), whereas the square is intended.

This whole question of representing intensity of sound by the square of the amplitude of a stationary vibration seems very doubtful. There is perhaps hardly any other mode of treatment actually ready for use; but there can be no doubt that a correct treatment of the question of loudness of sound must (1) deal with the portion of sound that reaches the ear, and not merely with the vibration of the vibrating body (which may and generally does give to the surrounding medium vibrations very much less than its own), and (2) must base the theory of perception of loudness on assumption consistent with Fechner's law, such as the arrangement of sounds in magnitudes, in a manner analogous to that practised in the case of stars.

I have long thought that the best basis for the hypothesis as to the constitution of the resonant mechanism of the ear is afforded by the complete explanation of the musical phenomena thus attainable. No doubt, however, great interest attaches to the connection of this with the actual anatomy of the ear, and the hypothesis as to the function of the basilar membrane. I was, therefore, interested to hear not long ago from an eminent physiologist that Helmholtz's main hypothesis in this direction must be abandoned, on the ground that birds have no cochlea; and we know that birds have an accurate perception of musical pitch, as they can sing tunes. I have therefore made inquiry, and I am satisfied that the most recent work on the subject presents accounts of such essential organs, including the membrana basilaris in remarkably complete development, in the case of birds, as are at all events sufficient to prevent this point being taken as a conclusive objection *in limine*. Of course on the detail of an anatomical question I should not venture an opinion.

I have always thought that the account of the origin of difference tones of the higher orders given in the text is unsatisfactory. It is inconceivable that where, for instance, the primary difference tone is so faint as to be inaudible, a higher tone should be due to its reaction with one of the original notes. Elsewhere I have attempted to give what I believe to be a correct account of this matter. This point has certainly been one of those which have been seized upon with most success by those who have objected to Helmholtz's doctrines in general.

Passing over many points which deserve mention, we may endeavour to form an opinion as to the nature of the general results, as embodied in ch. xix., headed "Results of the Investigation," and "Esthetical Relations." I cannot help feeling that on this ground the results of the physical investigation, highly interesting as they are in themselves, seem to fail us. After all we cannot get behind the natural feeling for the beauty of melodic phrase. Or, as Helmholtz says (pp. 366–7). "What is esthetically beautiful is recognized by the immediate judgment of a cultivated taste, which declares it pleasing or displeasing, without comparison with any law or any independent conception." This last phrase represents the meaning of the original as I understand it. The version in the present edition seems to me not quite correct; and it is hard to understand, as the sense in which the word 'conception' is used is not sufficiently indicated by the context. I think that the education of the ear by custom plays a much more important part in the whole subject than is assigned to it in this work. And important as the esthetics of melody may be as expounded in ch. xix., I cannot feel that I am much the wiser for them, in the sense of knowing to which of the endowments of the organism I am to look for the secret of the perception of melodic beauty as expressed in the above quotation.

Mr. Ellis's part of the work is, as usual, very complete. If a remark is admissible, I should say that the notes are a little overdone. However, no doubt it is better to err on the side of copious information. Mr. Ellis's Appendix contains a quantity of matter of interest. I may particularly mention the complete history of musical pitch, well known as a paper read before the Society of

Arts. Also on temperament, the combination or beat note controversy, and other matters, very full information is given.

A trifling point of translation:—The heading of chap. ix. should be, "*Depth* and Deepest Tones;" not "*Deep* and Deepest Tones." And on this subject I say, as I have said before, that none of the experiments here mentioned are comparable for a moment with such experiments as can be made with large open 32 feet organ-pipes, on account of the comparatively enormous amounts of power that can be employed in connection with such pipes. And it can be shown, by a simple process of analysis by beats of consecutive semitones, that the notes of such pipes are generally free from octave, and form something of the nature of sound right down to the lowest notes (16–17 per second). Even with stopped 16's which purport to give the same notes, the fundamentals thus tested generally prove to be absent in the lower octave; and I cannot believe that with any less amount of power these notes can really be produced in perceptible magnitude.

This volume supplies the critical student of the subject not only with references up to date, but also with a large amount of new matter. It is a perfect library in itself.

R. H. M. Bosanquet.

LXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 366.]

March 24, 1886.—Prof. J. W. Judd, F.R.S., President,
in the Chair.

THE following communications were read:—

1. "On the Genus *Diphyphyllum*, Lonsdale." By James Thomson, Esq., F.G.S.

2. "On additional Evidence of the Occurrence of Glacial conditions in the Palæozoic Era, and on the Geological Age of the Beds containing Plants of Mesozoic type in India and Australia." By Dr. W. T. Blanford, F.R.S., Sec. G.S.

After recapitulating briefly the principal facts known as to the correlation of the Karoo formation of South Africa, the Gondwána system of India, and the Coal-measures and associated beds of Eastern Australia, and especially noticing those phenomena in the different strata that had been attributed to the action of ice, the author proceeded to describe the additions recently made to previous knowledge by various members, past or present, of the Geological Survey of India, and especially by Mr. R. Oldham and Dr. Waagen. These additions had recently been published in the Records of the Geological Survey of India.

Mr. R. Oldham, in a recent visit to Australia, had come to the same conclusion as all other geologists who had visited the country, and clearly showed, as the Rev. W. B. Clarke and many others had done, that beds containing *Glossopteris*, *Phyllotheca* and *Næggerathiopsis* were intercalated among marine beds with Carboniferous fossils. The age of these marine beds was shown by Dr. Waagen to be that of the European Coal-measures. Mr. Oldham had, however, further ascertained the presence in abundance of smoothed and striated boulders, evidently transported by ice, in the marine Carboniferous beds north of Newcastle, N.S.W., and he consequently considered these beds, and not the overlying Hawkesbury, the equivalents of the Bacchus-marsh beds of Victoria, and of the Talchirs of India, a view which was in accordance with the relations of the fossil flora.

Meantime Dr. Waagen had received from Dr. H. Warth some fossils from the Salt-range of the Punjab. The fossils came from the upper part of a boulder-bed, the resemblance of which to the Talchir group at the base of the Gondwána system had long been recognized, but which had hitherto been classed with a stage immediately overlying, containing Upper Cretaceous fossils. The fossils now found by Dr. Warth included two forms of *Conularia* found in the Australian Carboniferous rocks, besides some other species evidently of Carboniferous age. Dr. Waagen consequently classed the boulder-bed together with other similar formations in other parts of the Salt-range as Carboniferous. There was one difficulty: the fossils just referred to were considered by Mr. Wynne to be contained in pebbles derivative from another bed. It was, however, shown that this did not affect the age of other boulder-beds in the Salt-range, and that the latter were connected with the Talchir beds in Central India by another discovery of Mr. R. Oldham's that a boulder-bed in the Indian deserts was also probably of Talchir age, and that the question as to whether the nodules containing the *Conulariæ*, &c. were concretions or pebbles might await further examination in the field.

Another contribution to the question had been made by Mr. Griesbach, who had recently found a boulder-bed which, from its character and fossils, he considered as Talchir, in the neighbourhood of Herat.

It was pointed out that the existence, over such extensive areas, of boulder-beds, all of which might, without any improbability, be of approximately the same age, rendered it highly probable that all were really contemporaneous and due to one Glacial period; that this period must have been towards the close of the Palæozoic era, which it may possibly have terminated by exterminating many of the principal forms of life. The peculiar flora of the Australian Newcastle beds and of the Indian Damudas, having nothing in common with the contemporaneous European Carboniferous flora, afforded an important proof of distinct botanical provinces in past times.

LXII. *Intelligence and Miscellaneous Articles.*

MAGNETIC INVESTIGATIONS. BY G. WIEDEMANN.

A PAPER on this subject appears in the March number of Wiedemann's *Annalen*, a translation of which will appear in an early number of this Journal.

The principal results of this research are as follows:—

1. The theory of magnetism put forth by Mr. Hughes as new is only a repetition of the author's far older theory.

2. The mutual relations between torsion and magnetism may, as has already been set forth by the author, be referred to a rotation of the magnetic molecules; but they cannot, as argued by Maxwell and by Chrystal, be explained solely by an extension and compression of the twisted wires.

3. The rotations of the molecules produced by torsion in nickel are exactly opposite to the rotations which they undergo in iron.

4. When temporarily magnetized wires have attained their stage of accommodation by being repeatedly twisted backwards and forwards on their fixed limits, the degree of magnetization is almost exactly the same at both limits; but the magnetization at the two limits of twisting differs in the case of temporary transverse circular magnetization, or permanent magnetization of either kind.

5. In all cases, by the torsion or detorsion of wires from one or the other limit, the magnetic moment changes in nearly the same way, and at first more quickly than by further twisting, so that the maximum or minimum, and accordingly the average magnetization, does not lie in the middle between the two limits.

6. The latter values, moreover, do not coincide with the permanent positions of equilibrium of the wires after removal of the twisting forces.

7. When a wire is twisted backwards and forwards by given forces between certain limits, after accommodation, the temporary torsion corresponding to a mean force is less with increasing than with decreasing forces.

8. According to Righi, Fromme, and Warburg an analogous behaviour is likewise exhibited as regards the temporary magnetization produced by increasing and decreasing magnetizing forces. This subsists also after the complete accommodation of the molecules.

9. The thermoelectric behaviour between alternately stretched and unstretched wires and unaltered wires, observed by Cohn, agrees generally with the results mentioned under 4 and 8; so also does the thermoelectric behaviour of alternately twisted and untwisted wires, as well as the corresponding changes in their conductivity.

10. By repeated temporary torsion up to a fixed limit the permanent torsion of a wire gradually rises to a maximum. In like manner, on repeated temporary magnetizations to the same degree, the permanent magnetic moment rises to a maximum.

11. Accordingly the molecules only attain their final positions of equilibrium after repeated turnings and shifting between certain limits, whether as the result of changes of figure, or as the result of magnetization. Hence they do not at once yield completely to the forces acting upon them at each instant. If a force opposite in direction to the first one afterwards acts, the same thing happens; the lagging of the molecules in respect of the position due to the original force can thus be always recognized. These further analogies between changes of form and magnetization are a further evidence for the mechanical theory of the latter.

12. The behaviour of mechanically deformed or magnetized bodies is different in changes of temperature, in which relations of this kind after accommodation of the molecules are no longer clearly apparent.

A LECTURE EXPERIMENT ON THE DIFFUSION OF GASES.

BY A. WINKELMANN.

On the occasion of experiments which were intended to determine the tension of elastic vapour in spaces filled with gas, I made the observation that the pressure of the vapour only became constant after the lapse of a very long time. If into a tube over mercury containing air under a pressure of about 0·300 millim. an excess of liquid be introduced, the vapour does not at once fill the space above the mercury. This only takes place slowly in accordance with the progress of the diffusion of vapours in the air above. As long as the density of the vapour is not everywhere the same, the pressure of the mixture of gas and vapour is not a maximum.

This method may be well used to show the difference between the velocity of diffusion in various gases, for instance air and hydrogen. With this view air and hydrogen are filled into two equally long barometer-tubes so that the mercury is at the same height. If then ether in excess is added to each tube, the mercury sinks more rapidly in the tube containing hydrogen, and after a few minutes the tubes show a marked difference in pressure, as is seen from the following numbers, which were obtained at a temperature of about 15°:—

Time, in minutes.	Height of the Mercury.		
	Air, millim.	Hydrogen, millim.	Difference. millim.
0 without the ether	449	449	0
2 with the ether	361	346	15
4 ,, ,, ...	359	332	27
8 ,, ,, ...	355	316	40
18 ,, ,, ...	332	280	52

Hence ether vapour diffuses far more rapidly in hydrogen than in air.

Ultimately the difference of pressure in the two tubes diminishes and becomes zero. This lasts some time, for after two hours the difference was still 30 mm.—Wiedemann's *Annalen*, No. 3, 1886.

ON VAPOUR AND MIST. BY ROBERT VON HELMHOLTZ.

The final results of the experiments and arguments on the formation of mist are stated by the author as follows:—

The formation of mist in moist air does not exactly coincide with the occurrence of normal saturation, but with one somewhat greater. This is partly due to the fact that there is greater tension over convex vesicles than over plane surfaces.

The formation of mist, at any rate after introducing a correction, is a sensitive and accurate criterion of saturation if care be taken that

First, the air contains approximately a normal quantity of solid particles of dust; it is sufficient for this that it is not filtered, and is renewed from time to time.

Secondly, the air must be free from any bodies which act chemically on aqueous vapour; solids and vapours of acids are most to be feared in this way.

If these conditions are fulfilled, adiabatic cooling furnishes a convenient way of determining the degree of saturation of air; for instance, of calculating the vapour-pressure of solutions.

This calculation gives at lower temperatures, that is below 30° C., values for the depression of tension, which are freer from errors of observation than direct measurements by means of mercurial columns.

In order, however, to anticipate a similar degree of accuracy at higher temperatures, the ratio of the specific heats of aqueous vapour should be determined with greater accuracy than it has hitherto been.—Wiedemann's *Annalen*, No. 4, 1886.

ON THE WEIGHT AND THE CAUSE OF THE LAYER OF WATER ON GLASS AND OTHER BODIES. BY E. WARBURG AND T. IHMORI, FROM JAPAN.

The results of this investigation are thus given :—

1. Above the dew-point no weighable deposit of water could be observed on bodies with smooth surfaces insoluble in water (platinum, glass with a coating of silicic acid, glass free from alkali); from the sensitiveness of the balance used, the thickness of any such layer could not exceed one or two millionths of a millimetre.

2. The film of water which forms above the dew-point on alkaline glass arises from a small quantity of free or loosely combined alkali on the surface of the glass. This must each time absorb water until the pressure of the vapour above the solution of alkali found is equal to the pressure in the place of experiment.

3. This deposit on alkaline glass, which can be weighed, is the cause of the electrical surface-conductivity which such glass shows in moist air when tried by the electroscope; any glass, which, with the balance in question, showed no weighable deposit of water, was found to be a good insulator when tested by the electroscope.

4. Rock-salt showed a deposit of moisture some millionths of a millimetre in thickness at temperatures for which the pressure of vapour was greater over a saturated solution of chloride of sodium than the pressure in the place of experiment. There was, however, in the rock-salt used a small quantity of magnesium chloride, which must attract moisture, until the pressure of vapour over the solution of magnesium chloride formed was equal to the pressure of vapour in the place of experiment.—Wiedemann's *Annalen*, No. 4, 1886.

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[FIFTH SERIES.]

JUNE 1886.

LXIII. *On the Conservation of Energy in the Earth's Atmosphere. By* WERNER SIEMENS *.

IN my communication to the Academy, "On the Admissibility of the Assumption of a Solar Electric Potential, and its Importance for the Explanation of Terrestrial Phenomena" †, I have endeavoured to refer certain still enigmatical meteorological phenomena to disturbances of the equilibrium of the atmosphere. Further consideration of these interesting questions has shown me that a consistent application of the fundamental law of conservation of energy in the atmosphere leads to a much more complete explanation of them than I had recognized.

The interdependence of meteorological phenomena has been minutely studied by meteorologists of late years.

There exists upon this subject an almost immeasurable mass of observations, upon which many ingenious theories have been founded. These are, however, for the most part concerned with secondary phenomena, and rest therefore upon a narrow foundation. It would even appear as if modern meteorology had somewhat neglected, for these special studies, the inquiry into the primary causes of the phenomena observed. Dove, in his theory of winds and storms, does, however, seek their cause altogether in the ascending currents of

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* Translated from the *Sitzungsberichte der Königlich preussischen Akademie der Wissenschaften zu Berlin,* March 4, 1886, vol. xiii.

† *Sitzungsberichte,* March 31, 1883; Phil. Mag. September 1883.

the torrid zone which form an expanded ring of air above it, which must flow over towards the poles, and he accounts for the constant change in direction and strength of the winds by the conflict between this equatorial current and the masses of air returning from the poles towards the equator. Even if there were no true ground to be found for this contest of opposed currents of air, and although it was not easy to understand why, with the great uniformity of the mean pressure of the whole atmosphere, the air should move with such great energy from the polar regions towards the equator, so distant in comparison with the height of the atmosphere, yet his explanation was at any rate more satisfactory than the usual almost exclusive reference of the motions in the atmosphere in high latitudes to maxima and minima of atmospheric pressure, of which one is absolutely unable to say whence they come and whither they go. These explanations of the direction and strength of winds can be regarded as having a scientific foundation only when it is shown where the forces act and are located which accumulate such enormous energy in maxima and minima, in a manner often not at all evident, and which then, in turn, produce storms and cyclones.

An attempt is made in the following pages to supply these gaps from the Theory of the Conservation of Energy.

It is universally admitted that all life and all motion on the earth originates in the sun's radiation. Without a supply of heat from the solar radiations the atmosphere would be without motion, or rather would follow the earth's rotation without any proper relative change of place and temperature, if we neglect the radiation of the stars and the earth's internal heat. The rotation of the earth would give to the atmosphere the form of an ellipsoid of revolution, assuming that at the temperature of space it was still gaseous and obeyed Mariotte's law, but could not produce any permanent circulation of air. Since the mean temperature and mean motion of the atmosphere change in any definite time just as little as the rotation of the earth itself, there must be stored up in the earth's atmosphere a constant quantity of solar energy in the form of sensible and latent heat, potential energy of masses of air in motion or local accumulations of pressure. Consequently the supply of heat from the radiation of the sun and stars must be equal to the loss of heat by radiation into space. The supply of heat is effected partly by the direct absorption by the atmosphere of the rays which traverse it, but chiefly by the heating of the earth's surface, and the heat thus absorbed is chiefly used up in warming the lower layers of air and in evaporating water. The loss of heat by radiation into space also takes place chiefly from the solid and liquid surface of the earth, and only to a very small extent directly from the mass of air. There are here two important considerations to be taken into account. Whilst the solar radiation, regarded as radiated from one point, falls chiefly upon low latitudes, the radiation from the earth into all parts of space is independent of latitude, and depends only on the differences between the temperature of the radiating portions of the earth's surface and that of space. Since the radiation of the stars, which apparently gives heat to space, is under precisely the same conditions for all parts of the earth's surface as its radiation, it may be neglected, and the temperature of space is to be taken as absolute zero. Of the radiation it is further to be observed that the direct loss by radiation of the higher and more rarefied layers of air must be greater than that of the lower layers, since radiation is greater in vacuo than in a space filled with air.

This having been premised, the following conditions for the equilibrium of the atmosphere may be stated :—

1. The condition of equilibrium of the atmosphere at rest is indifferent, the corresponding curve of temperature adiabatic. This amounts to saying that the transference of a mass of air from one height to another—disregarding any loss from friction—is accompanied neither by loss nor gain of work.

2. A disturbance of the indifferent equilibrium of the atmosphere, corresponding to a local accumulation of energy, is produced by the heating of the masses of air lying nearer the earth's surface by means of the sun's rays above the appropriate adiabatic temperature, as well as by the cooling of the higher layers of air through increased radiation. The heat employed in the evaporation of water increases this disturbance of equilibrium in the same direction and ratio, since aqueous vapour has a smaller specific heat than air, and since the latent heat of the vapour condensed by the adiabatic cooling of the air as it rises is used in the heating and expansion of air.

3. The energy accumulated in the disturbance of the neutral equilibrium of the atmosphere by excessive heating of the lower layers, and excessive cooling of the upper layers, must distribute itself by means of ascending and descending currents of air. In accordance with Clausius's second law of the mechanical theory of heat, the excess of heat of the expanding air is chiefly transformed into the *vis viva* of moving air; to a smaller extent it is distributed in larger and com-

paratively cooler masses of air. The current of air rising with increasing velocity must therefore retain a positive excess of heat up to the highest rarefaction, the descending stream a negative excess above the adiabatic temperature corresponding to the height.

4. The energy accumulated in the ascending and descending currents of air can only be destroyed again by being again transformed into heat by internal or external friction, or by local increase of pressure.

5. The mechanical energy accumulated in the rotation of the atmosphere round the earth's axis must be constant, and in the condition of relative rest must correspond to the velocity of rotation of that part of the earth's surface upon which it rests. Since, in consequence of polar and equatorial currents, a constant change in the geographical position of the air-masses takes place, the velocity of rotation of the whole atmosphere must lag behind the velocity of rotation of the earth's surface in low latitudes, and must gain upon it in higher latitudes. The magnitude of the friction with the earth, which diminishes these differences in velocity, must be as great in equatorial latitudes as in the polar latitudes, in order that the constancy of the mean velocity of rotation of the whole atmosphere may be preserved. The velocity lost by friction influences, therefore, only the local magnitude of the difference in velocity.

6. At the boundaries of currents of different velocities there takes place a constant mixing of neighbouring portions of air having different velocities. By this process, analogous to friction, there is caused a retardation of the more swiftly moving currents, and an acceleration of the slower ones proportional to the difference in velocity. There is thus produced in the boundaries an increase of pressure in the swifter, and a decrease of pressure in the slower, currents of air.

Of these fundamental statements only the last two require special explanation.

If we suppose the whole atmosphere in relative rest, and if we neglect its height as small in comparison with the radius of the earth, then its *vis viva* is

$$\mathrm{K}=\frac{4r^4\pi^3q}{\mathrm{T}^2}\int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}}\cos\alpha d\alpha=\frac{16}{3}\,\frac{r^4\pi^3q}{\mathrm{T}^2},$$

where K is the sum of the *vis viva*, q the weight of the air resting on the unit area, T the time of revolution of the earth in seconds, and α the angle of latitude. This gives for the mean velocity of the air, corresponding to this value of *vis viva*,

$$C=\sqrt{\frac{2}{3}}\cdot\frac{2r\pi}{T}=379 \text{ m. per second.}$$

This is the velocity corresponding to the 35th degree of latitude.

If we now imagine the whole atmosphere suddenly intimately mixed in such a way that each particle should have assumed the above mean velocity, then the air from the equator up to the 35th degree of latitude must rotate slower than the earth's surface, but in higher latitudes, on the contrary, faster; under the equator itself this difference in velocity would be 84 metres in the direction from east to west, at 45°, 59 metres, and under the 54th degree of latitude 107 metres in the direction from west to east. By friction with the earth's surface this difference of velocity would gradually be destroyed again if no currents of air in the direction from the equator to the poles, and in the opposite direction, were produced. Since these currents, however, always do occur, a condition of equilibrium must result, in which the mixture of the more rapidly rotating equatorial air with the more slowly rotating polar air is so far accomplished that the accelerating friction of the equatorial zone up to the 35th degree of north and south latitude is equal to the retarding friction of the rest of the earth's surface. Hence in the whole atmosphere of the equatorial zone east winds must prevail, and west winds in the regions lying north and south from 35°, and moreover the preponderance of the west winds must increase with the latitude*.

We will now consider the hypothetical case, that the earth is a smooth solid globe of homogeneous surface, and that the water contained in the atmosphere is vanishingly small. Then

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* I regret that the recently published Handbook of Dr. A. Sprung has only reached me a short time ago, from which I learn that Ferrel, from similar observations, has also designated the 35th degree of latitude as that above which the whole of the air-currents must have a meridional direction. I cannot, however, adopt his view, that in consequence of the retarding friction of the air on the surface of the earth the position of this zone must be displaced towards the equator. Friction at the earth's surface can, according to my view, only diminish the difference in velocity, that of the lower equatorially directed current of air, but not the place where this difference between the velocity of the earth and air is zero. It is evidently the endeavour of the author of this important work to furnish a mechanico-physical foundation for meteorological phenomena, and he has therefore frequently arrived at conclusions similar to those presented here. It is unfortunately not possible for me to examine further the, in some respects important, differences between us.

the neutral equilibrium and the adiabatic temperature of the strata at different heights of the atmosphere can be influenced only by the currents of air which are caused by the various heating of the air by the sun's rays and by the various cooling of the same by radiation. The heating of the air, and especially of the lower strata, is by far the greatest in the equatorial zone, and from there decreases approximately as the cosine of the latitude. Consequently, the transformation of solar energy into the kinetic energy of air in motion must be greatest at the equator, and decrease towards the poles. This transformation takes place in the ascending current. If, moreover, we disregard, for the present, the displacement of the hot zone, due to the change of seasons, we have present the conditions for a universal and continuous up-current of air. In fact, we have in the lower trade-winds a continuous flow of air from regions near the pole towards the equator. This current of air must have here a smaller velocity of rotation than the earth's surface situated under it, and must therefore have the direction from east to west, for the reason already mentioned, of the maintenance of the mean velocity of rotation of the atmosphere.

Since the northern and southern components of the two lower trade-currents, regarded as of equal strength, as they approach the equator rise from opposite sides, their *vis viva* increases the upward drift of the air. There must therefore take place an upward motion of the whole mass of air of the hot zone in spirals of opposite direction to the rotation of the earth. Only over the equator itself will there be left a ring of air which cannot take part in this upward motion, and whose northern and southern surfaces are grazed by the spirally-rising trade-winds. These, carrying with them the surface-layers of the relatively quiescent equatorial mass of air, must produce in it vortices which communicate to the centre of this mass of air an opposite velocity thus opposed to the rotation of the earth. This is the region of calms. The portions of the trade-winds lying next to the earth's surface, and thus more strongly heated, unite above the wedge-shaped ring of calms and form the central portion of the great equatorial upward-current. The velocity with which these masses of air ascend must increase in proportion with the rarefaction of the air brought about by decrease in pressure; since equal masses of air must pass through every horizontal section in unit time, and the *vis viva* thus obtained must drive the current high above the upper surface of the atmosphere until its weight, no longer balanced by the pressure of the surrounding strata of air, has destroyed the vertical component of its velocity. Hence we have formed above the centre of the hot zone the equatorial ring of air, as described by Dove, obviously similar to the solar prominences and flames which must continually flow over towards the poles.

This overflow is produced by the increasing pressure of the air-masses driven out by the velocity gained in the ascent over the pressure-equilibrium; the velocity which this pressure communicates to the poleward-flowing highly rarefied masses of air must therefore be equivalent to the maximum velocity gained in the ascent. It is, however, only the central strata, nearest to the equator, of the extensive region of the equatorial up-current which can preserve the vertical direction so as to destroy the vertical component of their motion by gravitation. This follows at once from the consideration that everywhere in the earth's atmosphere the masses of air which flow towards the poles and towards the equator must be equal for each latitude, unless local differences of pressure take place. The part of a mass of air rising with accelerated velocity in the hot zone must therefore be the sooner deflected polewards, the more distant it is from the equator. If we trace the paths of these different air-currents, we see that the strata of the masses of air streaming towards the equator which lie nearest the earth's surface—which also are the most heated by the sun's rays, in the neighbourhood of the equator—stream upwards vertically, up to the greatest height, and from thence are driven with the greatest velocity towards the poles; that the higher strata of the trade-winds do not reach the greatest heights of the atmosphere, and are driven so much the sooner polewards from the equator the greater their distance from it, and the greater at the same time their original height above the earth's surface.

The course of the air-currents in the hot zone will then be as follows:—The lower trade-wind, retarded at the earth's surface by friction with the earth, increases in velocity as its height above the earth's surface increases. Then at an unknown height we have a space between the upper and lower trade-winds filled with horizontal cyclones. Above that, the current towards the pole prevails up to the greatest height of the atmosphere, and moreover the velocity of this current increases in rapid proportion with the height.

It must here be observed that ascending and descending masses of air retain their local velocity of rotation, and that with increasing latitude the bed of the pole-directed current narrows whilst that of the equatorial current enlarges. Hence there results a constant increase of pressure in the pole-directed current, and a decrease in the equatorial current. In consequence of this combined action, a general return-flow, increasing with the cosine of the latitude of the upper pole-directed current, into the lower equatorial current must take place. The partial change of the upper current into the lower one will take place by means of the tract of horizontal cyclones separating the two regions without any important loss of *vis viva*. If there were no earth-rotation, this return-flow would take place up to the poles without disturbance. The loss of *vis viva* by internal friction can only be small in the higher strata of air, on account of their great dimensions. They will therefore flow into the polar regions from all sides with little loss of velocity, there produce a blockade and sink to the earth's surface, in order to return to the equator as a polar current. This process would take place partially in all latitudes, and the final result would be a system of cyclones taking place in meridional planes, embracing the whole atmosphere, in which the *vis viva* obtained by the impulse in lower latitudes is again destroyed by friction with the earth's surface and by internal friction communicating the same to the higher strata of air, or is converted into heat.

This representation of the circulation is, however, essentially altered by the rotation of the earth.

In consequence of the continual transference of air from lower latitudes to higher ones, and conversely, the atmosphere must assume a mean velocity of rotation, so that the kinetic energy accumulated in the whole rotation may remain unaltered. As already shown, this mean velocity of rotation corresponds to that of the 35th degree of latitude. Consequently, the courses of all air-currents must be displaced. Between the 35th degrees of north and south latitude, both the upper and under currents will lag behind the earth, and thus acquire a westerly direction; whilst between the 35th degrees and the poles a velocity increasing rapidly with the latitude, overtaking the earth's rotation, and thus eastward, must prevail in both currents. The return of the upper pole-directed current to the equator takes place therefore below the 35th degree in westerly paths as strengthening of the lower trade-wind, and the cyclonic motions separating the upper from the under current must also assume this figure of motion.

The motions of the air beyond the 35th degree assume a more complicated form; whilst the upper air-current, here wholly directed to the pole, will retain its eastward velocity of about 380 m. almost without alteration—since the retardation of the same by internal friction can only be very small in the higher regions of the air—the returning lower current will be very considerably retarded by friction with the earth's surface, and the more so the longer this lower course is.

The same holds good of the meridional velocity, which in the higher strata is very little diminished by friction, but in the lower strata very much diminished.

If, now, with increase of latitude the upper current-bed has become so contracted that a block takes place, the resulting local increase of pressure produces at the same time a disturbance in the curve of neutral equilibrium of the atmosphere. The excess of air flowing in must therefore at first compress the lower strata of air in such a way that the curve of equilibrium shall be reestablished down to the earth's surface. There results therefore a descending current of air, and an increase of pressure on the earth's surface depending upon the ratio of the increase of pressure in the higher regions of the air to its normal pressure—that is, a local maximum of atmospheric pressure. From this region of higher pressure currents will issue in radial directions along the earth's surface, which prevent the complete reestablishment of the neutral equilibrium corresponding to the increase of pressure in the higher rarefied strata of air.

Such a maximum of pressure may therefore persist for a long time; and, since it continuously supplies the excess of the inflowing equatorial air to the lower return-current, may even hinder for a long time the formation of a regular deflection of the upper current into the lower one. This must, however, finally take place, and with the cessation of the block in the upper strata of air ceases also the cause of the maximum.

The formation of the return-branch of the equatorial current is to be conceived as occurring in consequence of the continually increasing deflection towards the east of the current hemmed in, in consequence of the block in its progress towards the pole, so that it carries with it by internal friction the lower strata of air, relatively quiescent or moving in the opposite direction. It will therefore approach the earth's surface on a wide curve of gentle fall, until it finally unites with the polar current and enters upon its return journey to the equator. But by thus "carrying with it" the lower strata of air, it will produce a rarefaction of the bounding strata of air under it, and consequently one of the already-described opposite disturbances of the neutral equilibrium. There must therefore result an up-current of the lower strata of air to restore the neutral equilibrium, and a local minimum of atmospheric pressure on the surface of the earth results. The magnitude of the decrease of atmospheric pressure here observed is, just as with the maximum, not equal to the actual decrease of pressure caused by the carrying-power of the more rapidly-moving upper current of air, but to the ratio of this to the pressure corresponding to that height in the curve of neutral equilibrium. We have thus a complete explanation of the otherwise enigmatical magnitude of the observed variations in the barometer in medium and high latitudes.

On the earth's surface the local minimum so produced will draw in air from all sides, which ascends in cyclonic movement and is finally carried away with the equatorial current. It is thus here also the *vis viva* of the equatorial current which produces and maintains the minimum, and thus also puts the air into motion which streams in along the surface of the ground towards the minimum ; since the maximum of pressure is thus, in consequence of the geographical compression of the upper current, the cause of a resulting partial return-current of the equatorial current, and the path which this return-current describes in the upper regions gradually sinking is marked by a division of low pressure on the earth's surface. Maxima and minima thus stand in a causal connection, and therefore, as a rule, are produced simultaneously and in geographical neighbourhood.

The air-currents caused by these two in the lower strata of air must therefore combine into currents which pass essentially from maximum to minimum, but the direction of which is altered in known manner by the earth's rotation. This system of local winds must, however, finally yield to the equatorial current itself when it reaches the earth's surface in its gradual descent. As a rule (*i. e.* with insignificant blocking in the upper current-bed) this will in fact not occur. The return-stream which has been begun is completed by accumulation upon the higher strata of the polar return-current, and maxima and minima disappear after constant current-conditions have been again established in the higher strata of the atmosphere. If, however, any considerable block takes place, it brings about powerful maxima of pressure and a more rapid descent of the equatorial return-current. Over a tract of low pressure this will fall to the ground with a velocity but little diminished by carrying with it relatively tranquil air, and will here produce storms, which in the northern hemisphere begin as south-west, in accordance with Dove's law of rotation, through west and north-west, gradually becoming weaker by friction with the ground and carrying on with it relatively quiescent air, finally are absorbed in the prevailing return-current to the equator. These storm-winds must now, by convection of neighbouring strata of air, produce cyclonic aerial movement far beyond their own limits, which make it very much more difficult to trace the regular course of the atmospheric disturbance.

That the barometer, as a rule, still stands low when the equatorial current itself has already reached the ground is explained for the most part by the fact that, in consequence of convective power of the moving air, all the quiescent masses of air in the neighbourhood of the current suffer rarefaction. But the barometer shows the pressure of the surrounding quiescent air, and not the true pressure of the air entangled in the movement. A barometer in the car of a balloon moving rapidly with a storm must therefore indicate a perceptibly higher pressure than a stationary one*.

The *vis viva* active in winds and storms has thus its origin essentially in the acceleration which the air rising in the tropics attains in consequence of superheating at the earth's surface. The *vis viva* equivalent to this is transferred especially to the upper highly rarefied strata of air. In consequence of their momentum these are driven, with small loss of velocity by internal friction, to the polar regions of the earth. They retain the mean velocity of rotation which they possessed when raised in the equatorial latitudes. They must therefore, when they pass to higher latitudes, move more rapidly than the more slowly rotating earth, and hence, as seen from the earth, must approach the poles in spirals of decreasing inclination. If on this course they turn still earlier towards the earth's surface, in consequence of the narrowing of the upper current-bed, and so return to the equator united with the returning masses of air from higher latitudes, they strike these, and with more rapid descent the earth's surface itself, with a velocity combined of their own proper velocity and the difference between their velocity of rotation and that of the earth's surface at the point of contact. The source from which the storms of high latitude really draw their destructive energy is therefore the momentum of the earth itself. In order that its rotation may remain unchanged, the law must hold good that the acceleration which the earth receives from the difference in velocity in high latitudes is compensated by the retardation which it suffers in low latitudes, in which the mean rotation of the air is smaller than that of the earth's surface.

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* Experiments that I have made, and of which I reserve a fuller account, have shown that a current of air, which passes by the mouth of a narrow tube placed at right angles to its direction, produces in this tube a rarefaction proportional to the velocity of the air, which corresponds, within wide limits of velocity, to the pressure of a mercury-column of 0·025 millim. for each metre of air-velocity. I have constructed an anemometer upon this principle, which shows the velocity of the air very simply and without complicated apparatus. It consists essentially of a narrow vertical tube, which is carried as high as possible above the roof of the house. Any simple arrangement for measuring pressure placed in the room then gives directly the velocity of the air in metres.

It follows at once from these considerations that with increasing geographical latitude the frequency and strength of the air-currents in the direction of the earth's rotation—that is, in our hemisphere, the west winds—must increase rapidly. In the arctic regions themselves, the highest strata of the equatorial current, which alone can reach so far without having been compelled to return, must flow downwards to the earth's surface in north-easterly spirals. Hence, and from the rush on all sides towards the pole, they must produce an arctic maximum, and after sinking with preservation of their velocity must commence their return to the equator as a lower north-west wind. It is therefore again the *vis viva* obtained in the equatorial impulse which also drives back the air from the polar regions to the equator, and not the action of doubtful gradients of air-pressure, which are by no means sufficient for the explanation of the phenomena. By friction with the earth's surface the south-east velocity which this return-branch of the equatorial current everywhere possesses is soon considerably diminished, and at the surface of the earth itself would soon be altogether destroyed if the higher strata of air of the return-current did not maintain it. In consequence of the expansion of the lower current-bed, which takes place rapidly in the higher latitudes, a rarefaction is produced in the mean strata of air, advancing more rapidly towards the equator, which brings about an inflow of the relatively quiet lower strata of air into the higher ones rarefied beyond the condition of neutral equilibrium. This inflow must take place from lower latitudes, because in them the difference of pressure causing the impulse, in consequence of expansion of the current-bed, is a smaller one. Hence the current on the earth's surface, even in the northern hemisphere, must acquire a southerly component. This explains why, as experience shows is the case, the south-west, and not the north-west, has here the mastery, as must be the case in the higher strata of the return-current.

Also in the hypothetical case so far discussed, of a homogeneous smooth and dry earth's surface, the motions of the air in mean and high latitudes must be altogether irregular, and by no means to be determined beforehand, since the maxima and minima commenced and maintained by blocking, and the carrying on of relatively quiescent air by that in more rapid motion, serve as accumulators of the kinetic energy of the upper air-current, the charging and discharging of which must always cause new disturbances of the equilibrium of the atmosphere, and must produce air-currents circling up and down in it. In fact, the very unequal distribution of land

and sea, together with the unequal moisture of the air produced by it, the orographic conditions of the earth's surface, and the diverse qualities of the soil of extensive connected tracts of the same, form a chain of further disturbances in the equilibrium of the temperature, pressure, moisture, and local disturbances of motion of strata of air accumulated upon or beside each other as currents, which will no doubt always render any reliable weather-prophecies impossible.

If, moreover, the aqueous vapour contained in the ascending air exerts no important influence on the magnitude of the kinetic energy of the air in motion into which the energy of the solar radiations, for the most part, is converted, it at any rate produces this effect, that the atmosphere ceases to be homogeneous, since alternate strata of warm moist air and of colder drier air are formed. I must refrain from entering upon the local influence of these varying conditions, since they belong to the domain of observational meteorology. The same holds good of the large subject of local cyclones, produced, on the one hand, by local maxima and minima on the earth's surface; on the other hand, directly by local disturbances of the neutral equilibrium. I will make only a few remarks on the dynamics of the latter class: ascending cyclones with a vertical axis of rotation.

I have already shown that the violent motions of the air which occur in local cyclones cannot be well explained as the result of simple acceleration of the ascending air by overheating of the lower strata and by the aqueous vapour they contain. It appears altogether inadmissible to take account of the rarefaction produced at the centre of a cyclone by the centrifugal force of the masses of air circulating round it as an accelerating force acting upon it.

The comparative vacuum formed can produce suction only in the direction of the axis of the cyclone, thus either raising the water upon the surface over which it rotates, or drawing down air from the higher regions of the atmosphere. The existence of such a descending current of air within a tornado is confirmed by the clear sky and quiet air often observed at its centre. We must assume that the *vis viva* of the air hastening with enormous velocity into the cyclone, and ascending in it, is accumulated in repeated accelerating impulses, and that it results from the greater velocity of the air in the higher strata. We must then imagine a local cyclone as produced by an impulse of superheated air, due to some local cause or other, given at the boundaries of an upper and lower tract of disturbance of the neutral equilibrium of an atmosphere at rest, which reaches the boundary of the upper cooled strata of air, which have acquired a tendency to descend. We must thus have an outer descending current formed around the ascending one, by means of which as much air descends as has been carried up by the ascending current. If the disturbance of equilibrium embraces extended upper and lower strata of air, the descending masses will produce an increase of pressure in the neighbourhood of the cyclone, gradually extending to the surface of the earth, and on the other hand into the highest regions of the air, and transfer its *vis viva* continually to new superheated masses of air which ascend in the cyclone, whilst a part of the descending external cyclone circulating in the same direction ascends again with the inner, and transfers to it a part of the *vis viva* gained in the higher regions of the air. The course of the centre of the cyclone is then determined by the direction of the mean velocity of all the air-masses forming the cyclone, and its duration is that of the disturbance of the neutral equilibrium of the atmosphere which called it forth and maintains it.

In conclusion I will only mention that the suspicion which I have previously expressed that aqueous vapour can be cooled beyond its usual condensing-point without condensation taking place, in the same way as water can be cooled below its freezing-point without solidifying, has been confirmed by recent investigations of Robert von Helmholtz. We have thus the explanation of the remarkable fact that the ascent of air containing so much aqueous vapour from the tropical seas is not followed by ceaseless rain. We may now assume that the aqueous vapour in the absence of dust and particles of water reaches the higher regions of the air without condensing.

It follows, further, that a local ascent, like a solar prominence, which must reach the higher regions and carry with it dust and particles of water, may, by condensation of the aqueous vapour of these strata of air, bring about the tremendous rainfall which we observe. Further, we have the explanation of the quantity of water which the equatorial current conveys to the temperate zones.

LXIV. *Notes, chiefly Historical, on some Fundamental Propositions in Optics.* *By* Lord Rayleigh, *Sec. R.S., DC.L.*[*]

IT is little to the credit of English science that the fundamental optical theorems of Cotes and Smith should have passed almost into oblivion, until rediscovered in a somewhat

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[*] Communicated by the Author.

different form by Lagrange, Kirchhoff, and von Helmholtz. Even now the general law governing apparent brightness seems to be very little understood, although it has acquired additional importance in connection with the theory of exchanges and the second law of Thermodynamics. In seeking the most natural basis for the law of magnifying, usually attributed to Lagrange, I was struck with the utility of Smith's phrase "apparent distance," which has never been quite forgotten, and was thus induced to read his ch. v. book ii.*, founded upon Cotes's "noble and beautiful theorem." I think that it may be of service to present a re-statement, as nearly as may be in his own words, of the more important of the laws deduced by Smith, accompanied by some remarks upon the subject regarded from a more modern point of view.

The general problem is thus stated :—

"To determine the apparent distance, magnitude, situation, degree of distinctness and brightness, the greatest angle of vision and visible area, of an object seen by rays successively reflected from any number of plane or spherical surfaces, or successively refracted through any number of lenses of any sort, or through any number of different mediums whose surfaces are plane or spherical. With an application to Telescopes and Microscopes."

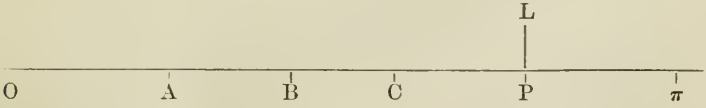
It is divided into three propositions, of which the first is:—

"Having the focal distances and apertures of any number of lenses of any sort, placed at any given distances from one another and from the eye and object, it is required to find the apparent distance, magnitude, situation, degree of distinctness and brightness of the object seen through all the lenses; together with the greatest angle of vision and visible area of the object, and the particular aperture which limits them both."

Apparent distance means the distance at which the object would have to be placed so as to appear by direct vision of the same apparent magnitude as through the lenses.

Let PL (fig. 1) be an object viewed by the eye at O through

Fig. 1.



any number of lenses placed at A, B, C, ... whose focal

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* Smith's 'Compleat System of Opticks,' Cambridge, 1738. French translations were published by P. Perzenas, Avignon, 1767, and by Duval Leroy, Brest, 1767.

distances are the lines a, b, c, ... and whose common axis is the line O A B C P. In the standard case the lenses are supposed to be concaves. Then if $O\pi$ be the apparent distance,

$$O\pi = OP + \frac{OA\,.\,AP}{a} + \frac{OB\,.\,BP}{b} + \frac{OC\,.\,CP}{c} + \frac{OA\,.\,AB\,.\,BP}{ab} + \frac{OA\,.\,AC\,.\,CP}{ac} + \frac{OB.BC.CP}{bc} + \frac{OA.AB.BC.CP}{abc}.$$

The statement is for three lenses, but the law of formation of the terms is general. If a, b, c are infinite, we fall back on direct vision, and $O\pi = OP$. If any of the lenses are convex, the focal distances of such lenses must be looked upon as negative.

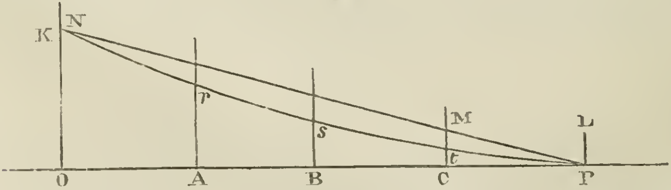
"§ 262. Corol. 1. While the glasses are fixt, if the eye and object be supposed to change places, the apparent distance, magnitude, and situation of the object will be the same as before. For the interval OP being the same, and being divided by the same glasses into the same parts, will give the same theorem for the apparent distance as before." This is a proposition of the utmost importance, from which follows without much difficulty :—

"§ 263. Corol. 2. When an object PL is seen through any number of glasses, the breadth of the principal pencil where it falls on the eye at O, is to its breadth at the object-glass C, as the apparent distance of the object to its real distance from the object-glass ; and consequently in Telescopes, as the true magnitude of the object to the apparent."

True magnitude here means apparent magnitude as seen directly, and the theorem is identical with that enunciated more than half a century later by Lagrange *.

In the investigation of apparent brightness the extreme ray P t s r K from the central point P of the image is considered (fig. 2):—

Fig. 2.



"If O K be not less than O N, the area of the pupil will be totally inlightened by the pencil which flows from P. Let P t s r N be a ray of that pencil, cutting the object-glass C t

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* "Sur une loi générale d'Optique," *Mémoires de l'Académie de Berlin*, 1803.

in t; and supposing the glasses were removed, let an unrefracted ray P M N cut the line C t in M. Then the quantity of refracted rays which fall upon the line N O is to the quantity of unrefracted rays which would fall upon it as the angle C P t to the angle C P M, that is as the apparent magnitude of the line N O seen from P, to the true. And therefore, by turning the figure round the axis O P, the quantity of refracted rays which fill the pupil is to the quantity of unrefracted rays which would fill it (as the apparent magnitude of any surface at O seen from P, to the true; or as the apparent magnitude of any surface at P seen from O to the true; and consequently) as the apparent magnitude of the least surface, or physical point P, to the true; that is as the picture of the point P formed upon the retina by those refracted rays, to its picture formed by the unrefracted rays. These pictures of the point P are therefore equally bright and cause the appearance of P to be equally bright in both cases. Now let the pupil be larger than the greatest area inlightened at O by the pencil that flows from P; and supposing a smaller pupil equal to this area, we have shown that the pictures of P made upon the retina by refracted and unrefracted rays would be equally bright; and consequently each of them would be less bright than when the larger pupil is filled with unrefracted rays, in the same proportion as the smaller pupil, or area inlightened by the refracted rays, is less than the larger pupil, inlightened by unrefracted rays."

"§ 267. Corol. 6. It is evident that an object seen through glasses may appear as bright as to the naked eye; but never brighter, even though all the incident light be transmitted through the glasses."

Smith's splendid work was evidently unknown to Helmholtz, when, after establishing the law of apparent brightness, he remarks *:—

"Diese Folgerung ist schon von Lagrange gezogen worden. Leider hat er den zweiten Fall, der gerade bei starken Vergrösserungen der gewöhnliche ist, nicht besprochen, nämlich den, wo das in die Pupille eindringende Strahlenbündel diese nicht ganz ausfüllt. Das mag nicht wenig zu der Vergessenheit beigetragen haben, in welche seine wichtige Abhandlung gefallen ist." It is indeed astonishing that a theorem of such obvious importance should need to be discovered three times†.

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* Pogg. *Ann.*, Jubelband, 1874, p. 566.

† In his biography of Lagrange (*Suppl. Enc. Brit.*; Young's Works, vol. ii. p. 575) Young, with some want of appreciation, thus refers to the memoir 'On a General Law of Optics, 1803':—"A demonstration of

The first advance upon the position attained by Smith is to be found in Kirchhoff's celebrated (but perhaps little read) memoir, "Ueber das Verhältniss zwischen dem Emissionsvermögen und dem Absorptionsvermögen der Körper für Wärme und Licht."* The Theory of Exchanges renders it evident that the law of apparent brightness must have an even higher generality than Smith had claimed for it. No limitation can be admitted to systems of optical surfaces centred upon an axis, to which the rays are supposed to be but slightly inclined. Kirchhoff's investigation is founded upon Hamilton's characteristic function T, which we may here take to represent the reduced optical distance ($\int \mu\, ds$) along a ray between any two points. At the extremities O, O′, of the central ray of a pencil undergoing any number of reflections and refractions, planes are drawn perpendicular to the final directions of the ray, and in these planes rectangular coordinate axes x_1, y_1, x_2, y_2 are taken. T expresses the reduced distance between a point x_1, y_1, in the first plane and a point x_2, y_2 in the second plane, as a function of these four variables. In Smith's terminology Kirchhoff's result may be thus stated :—The inverse square of the apparent distance between O and O′ is

$$\frac{d^2\mathrm{T}}{dx_1\,dx_2}\,\frac{d^2\mathrm{T}}{dy_1\,dy_2}-\frac{d^2\mathrm{T}}{dx_1\,dy_2}\,\frac{d^2\mathrm{T}}{dx_2\,dy_1};$$

the apparent distance being the same whether O′ be seen from O, or O be seen from O′.

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the foundation of the method long since used by English opticians for determining the magnifying powers of telescopes of all kinds, which form an image of the object-glass beyond the eye-glass, by measuring the diameter of that image. The author hazards, in this paper, the very singular assertion, that the illumination of the object must be the same in all telescopes whatever, notwithstanding the common opinion that it depends upon the magnitude of the object-glass; and his reasoning would be correct, if the pupil of the eye were always less than the image of the object-glass in question; since, as he observes, the density of the light in this image is always inversely as the magnifying power; but he forgets to consider that the illumination on the retina, when the whole pencil is taken in, is in the joint ratio of the density and the extent; a consideration which justifies the common opinion on this subject, and shows that a most profound mathematician may be egregiously mistaken in his conclusions, if he proceeds to calculate upon erroneous grounds. It deserves, however, to be remembered that the brightness of any given angular portion of a magnified image must always be somewhat less than that of an equal portion of the object seen by the naked eye, because it can be no greater if the pencil fills the pupil, and will be less in proportion as the pencil is smaller than the pupil, besides the unavoidable loss of light at the refracting surfaces."

In his *Theorie des Lunettes*, Berlin, 1778, Lagrange himself refers to Smith's Optics, Ch. v. Book ii.

* Pogg. *Ann.* t. cix. p. 275 (1860).

A nearly similar investigation in terms of the corpuscular theory is to be found in Thomson and Tait's 'Natural Philosophy' (1867), §§ 326, 327, where the authors emphasize strongly the optical importance of their conclusions. "The most obvious optical application of this remarkable result is, that in the use of any optical apparatus whatever, if the eye and the object be interchanged without altering the position of the instrument, the magnifying power is unaltered." And again, "Let the points O, O′ be the optic centres of the eyes of two persons looking at each other through any set of lenses, prisms, or transparent media arranged in any way between them. If their pupils are of equal sizes in reality, they will be seen as similar ellipses of equal apparent dimensions by the two observers."

It will be remarked that in general the "magnifying power" varies in different directions, a circle being seen as an ellipse. This phrase and that of "apparent distance" may be understood in an extended sense. Thus the apparent distance may be taken to mean the distance at which the object, if seen direct, would present the same angular *area* as when seen through the lenses &c.

The demonstration of the law of apparent distance upon the basis of Hamilton's characteristic function, is of course satisfactory, and perhaps indispensable to a complete investigation; but it is not unimportant to remark that the essential part of the law is really included in the vastly more general reciprocal theorem, established in the first instance by v. Helmholtz for vibrations in a uniform gaseous medium[*], and capable of extension to all vibrating systems, even though subject to dissipative forces[†].

Let Ψ denote the intensity of a radiant source at O, ψ the corresponding amplitude of luminous vibration at O′. By the doctrine of rays, the energy transmitted across any section of a pencil is the same, and thus if σ_1 be the area of the cross sections at O′ of a thin pencil of rays from O whose angular magnitude is there ω_1, we have

$$\sigma_1\psi^2 = \mathrm{H}\omega_1\Psi^2,$$

where H is an absolute constant.

In like manner if σ_2 be the area at O of a pencil starting from O′ with angular opening ω_2,

$$\sigma_2\psi'^2 = \mathrm{H}\omega_2\Psi'^2,$$

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[*] *Theorie der Luftschwingungen in Röhren mit offenen Enden.* Crelle, Bd. lvii., 1860.

[†] Proc. Math. Soc. June 1873; 'Theory of Sound,' vol. i. §§ 107, 108, 109.

where Ψ' now measures the source at O′, and ψ' the luminous amplitude at O. But by the reciprocal theorem

$$\psi' : \Psi' = \psi : \Psi,$$

and thus

$$\frac{\omega_1}{\sigma_1} = \frac{\omega_2}{\sigma_2};$$

or the "apparent distance" of O′ from O is the same as of O from O′.

If we now assume the reciprocal character of apparent distance, there is no difficulty in deducing the law of apparent brightness in a perfectly general manner. For consider the whole light received over a small area σ_1 at O′ (perpendicular to the ray) from a small luminous area σ_2 at O (also perpendicular to the ray). If, as before, ω_1 denote the angular opening at O of the pencil which corresponds to σ_1, this light is proportional to $\omega_1\sigma_2$. But $\omega_1\sigma_2 = \omega_2\sigma_1$, if ω_2 be the apparent magnitude of σ_2 seen from O′. Hence the whole quantity of light received by σ_1 is proportional to $\omega_2\sigma_1$; so that if σ_1 be given, representing, for example, the area of the pupil, the whole light received at O′ from a small area σ_2 at O is proportional to the apparent magnitude of that area. In other words the apparent brightness is constant.

In this way of regarding the matter the law of apparent brightness becomes a deduction from the general reciprocal theorem. The argument may, of course, be reversed, so as to exhibit the reciprocal character of apparent distance as a consequence of the law respecting brightness. And this view of the subject may perhaps commend itself to those who appreciate the independent evidence for the law of brightness derived from the theory of enclosures as based upon the second law of thermodynamics.

In any case the law connecting magnifying power with the section of the pencil follows as an immediate consequence. If σ_2 be given, its apparent magnitude, as seen from O′, is given by

$$\omega_2 = \sigma_2 \frac{\omega_1}{\sigma_1};$$

and is, therefore, inversely proportional to the section at O′ of a pencil of given angular magnitude issuing from O. This principle is of great use in the design of optical instruments. The application to the telescope is fully stated by Smith. By means of it the one-dimensional magnifying power of prisms, so placed that the emergence is more nearly grazing than the incidence, is readily traced[*].

There is, of course, no limit, either in telescopes or in microscopes, to the magnifying which may be obtained by sufficiently diminishing the section of the emergent pencil; but, as is now well known, the resolving power cannot thus be indefinitely augmented. It is interesting to note that Smith was aware of the fact, though he could have no knowledge of the reasons for it. He points out that in examining objects of great intrinsic brightness, there would appear to be advantage in diminishing the aperture of the object-glass. For by this means the disturbing influence of aberration, both spherical and chromatic, would be mitigated. "But[†] in reality it is quite otherwise; and that for two reasons. First because the minute parts . . . may be better discerned when all the light remains in the telescope than when it is reduced to $\frac{1}{100}$ part, though not in the same proportion. The other reason is that when the aperture is too much contracted the outlines that circumscribe the pictures in the eye become confused, which is carefully to be minded, and also what are the limits of this confusion. This is certain, that as the aperture is contracted the slender pencils or cylinders of rays that emerge from the eye-glass into the eye are also contracted in the same proportion. Now if the breadth of one of these pencils be less . . . than $\frac{1}{60}$ or $\frac{1}{72}$ part of an inch, the outlines of the pictures are spoiled, for some unknown reason in the make of the eye . . . For by looking through a hole in a thin plate, narrower than $\frac{1}{5}$ or $\frac{1}{6}$ of a line, the edges of objects begin to appear confused, and so much the more as the hole is made narrower." If we assume that a given apparent definition requires a given diameter of emergent pencil, it follows that the resolving power of telescopes is proportional to aperture.

The theory of the microscopic limit has been much discussed in recent years, and has been placed upon a satisfactory basis by Abbe, and by v. Helmholtz, who treats the subject in his usual masterly style. But I think that due credit has not been given to Frauenhofer, whose argument appears substantially correct. In his discussion on gratings Frauenhofer[‡] remarks:—"Es ist nicht wohl denkbar, das die Politur, welche wir durch Kunst auf Glas etc. hervorbringen können, mathematisch vollkommen sey. Besteht diese Politur aus

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[*] See "Investigations in Optics," Phil. Mag. January 1880.

[†] Book 2, Ch. 7, p. 144. Smith is here expounding the views of Huyghens (*Dioptrica*).

[‡] Gilbert, *Ann.* 1823, p. 337.

Unebenheiten, welche, in Hinsicht ihren Entfernung von einander, kleiner als ω sind [ω denotes the wave-length], so sind sie sowohl für durchfahrendes als zurückgeworfenes Licht ohne Nachtheil, und es können dadurch keine Farben irgend einer Art entstehen; auch wäre es durch kein Mittel möglich diese Unebenheiten sichtbar zu machen." And here he appends the very pregnant note:—"Man kann daraus schliessen, was möglicher Weise durch Mikroskope noch zu sehen ist. Ein mikroskopischer Gegenstand z. B., dessen Durchmesser = ω ist, und der aus zwei Theilen besteht, kann nicht mehr als aus zwei Theilen bestehend erkannt werden. Dieses zeigt uns eine Gränze des Sehevermögens durch Mikroskope."

Frauenhofer's views did not commend themselves to Herschel *, who regarded the "alleged limit to the powers of microscopes" as not "following from the premises." It so happens that I can give an independent opinion upon the persuasiveness of Frauenhofer's reasoning, for I had occasion in 1870, in connection with my own work upon the reproduction of gratings, and before the publication of the investigations of Abbe and v. Helmholtz, to consult his writings, when the note above quoted attracted my attention and fully convinced me of the general truth of the doctrine of the microscopic limit. It seemed evident, at any rate, that two radiant points, separated by only a small fraction of the wave-length, could not be optically distinguished.

It is worthy of notice that while Frauenhofer speaks of the whole wave-length, modern investigation fixes the half wave-length rather, as the limit of microscopic vision. It seems, however, that, on his own principles, Frauenhofer should have arrived at the latter result; for a grating whose period is equal to the wave-length can show colours when sufficiently inclined †. It is easy to see that when the angular aperture of a microscope is nearly 180°, a displacement of the radiant point amounting to half a wave-length, perpendicularly to the line of vision, will entail on one side of the pencil an acceleration and on the other a retardation of that amount, so that at the original focal point upon the retina the phases will now range just over a complete period. The displacement of half a wave-length corresponds therefore to something rather less than the half width of the best possible image of a mathematical point.

A definite limit to an operation such as visual resolution

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[*] *Enc. Met.*, 'Light,' § 758, 1830.

[†] Frauenhofer seems to have gone wrong in his formula for the case of oblique incidence.

(involving in some degree a mental judgment) is, of course, not to be expected. For the microscope, the purely physical question of the distribution of light in the ultimate image of a mathematical point cannot be definitely solved without some assumption as to the manner in which the light is radiated in different directions. Even if the radiation were uniformly distributed, it does not follow that the light emerging from the eye-piece consists of ordinary plane waves, equally intense over the area of section. It would seem, indeed, that such a uniform distribution of rays is inconsistent with good definition, except at the very centre of the field of the microscope. For, in accordance with principles already discussed, it implies at all points an equal magnifying power, which however is to be reckoned always in relation to an object supposed to be perpendicular to the initial direction of the ray. But inasmuch as the extreme rays of the pencil start in a direction oblique to the axis, it is evident that in relation to a given external object different parts of the system have different magnifying powers. In order that the efficient magnifying power (in the radial direction) may be alike for the whole of the emergent pencil, the rays must be concentrated towards the outer parts according to a law which will be obvious. In this way the resolving power might perhaps come to be a little greater than that estimated by v. Helmholtz, the concentration of rays towards the circumference playing somewhat the same part as a central stop.

Much more might be said upon this subject, but probably without results of practical importance. My main purpose has been to emphasize fundamental optical principles which have met with strange neglect, and to show how much excellent work had been done in this direction by some early writers.

April 18.

P.S. Reference should have been made above to an interesting paper of Clausius*, in which the author develops very fully the analytical theory of radiation, as based upon Hamilton's function. One general theorem, previously established with rather less generality by v. Helmholtz, may here be noticed. The angles of the cones formed by the pencil of rays at an object and at its image (supposed to be astigmatic) stand simply in the inverse ratio of the areas of the corresponding elements of object and image.

In terms of apparent distance the argument may be put thus. Consider a cross section of the pencil at any interme-

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* Pogg. *Ann.* t. cxxi. p. 1 (1864).

diate point P. Then the squares of the apparent distances of P from the object and image are as the solid angles of the cones. Again, consider a pencil of rays passing through P, which must mark out corresponding portions of object and image, and it is evident that these areas are also in the ratio of the squares of the same apparent distances. Hence the proposition, which is thus seen to be intimately connected with the notion of apparent distance.

Terling Place, Witham,
May 7.

LXV. *Notes on some New Polarizing Prisms.*

By Professor SILVANUS P. THOMPSON[*].

[Plate VI.]

I. *On a New Polarizer devised by Mr. Ahrens.*

THE new Polarizer constructed by Mr. Ahrens is a rectangular parallelopipedon of calc spar having square end-faces, and having its long sides in the proportion of about 1·6 : 1 relatively to the short sides. The actual dimensions of the prism which, at the request of Mr. Ahrens, I exhibited to Section A of the British Association, are :—

Side of nearly square end-face . 17·5 millim. (nearly) ;
Long side of prism . . . . . 27 millim.

The square end-faces are principal planes of section of the crystal.

Two oblique sections are cut in the prism, and run from the highest and lowest edges, *a b* and *c d* of fig. 1 (Pl. VI.), to the middle of the other face, where they meet in the line S S′. The dihedral angle between these planes of section is nearly 32°; the angle between either of them and the principal axis of vision through the prism being therefore nearly 16°. Mr. Ahrens also uses a dihedral angle as small as 30° in some of his prisms. The faces of these sections are polished and united with balsam in the usual manner.

It will thus be seen that the new prism consists of three wedge-shaped pieces of spar, and that one face of the prism is traversed by a line of junction.

On looking through the prism, the polarized field formed by extraordinary rays is observed to be bounded perfectly symmetrically by two regions into which the ordinary ray intrudes, the edges of both these regions being marked by

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[*] Communicated by the Author.

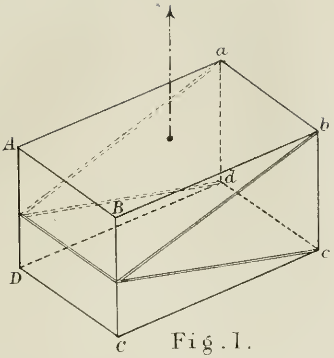

Fig. 1.

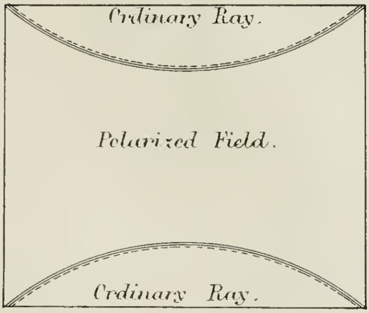

Fig. 2.

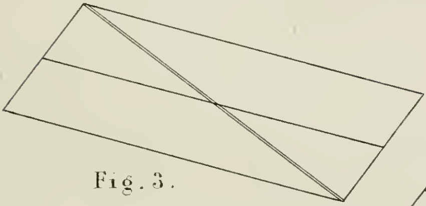

Fig. 3.

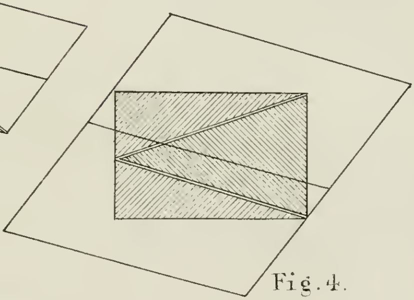

Fig. 4.

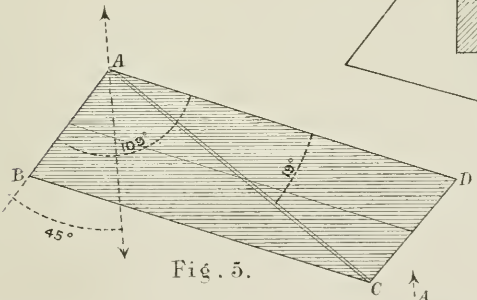

Fig. 5.

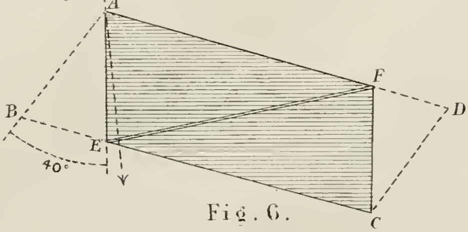

Fig. 6.

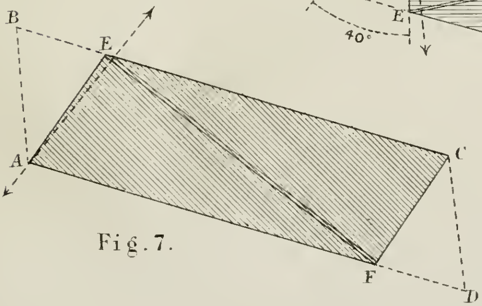

Fig. 7.

Mintern Bros. lith.

the usual faint red iris of interference-bands (fig. 2). The breadth of the available polarized field at its narrowest part is about 28°. Right and left there is no intrusion of ordinary rays, the field extending to an angular breadth exceeding 100°. The *blue* iris, which in the ordinary Nicol prism is so annoying at the limit of the field where the extraordinary ray vanishes by total reflection, is entirely absent in this prism. There is very little distortion, as might be expected from the tetragonal form of the prism.

The one disadvantage of the new prism is the presence of the line of section S S′ right across the face. This prevents its being used, in some cases, as an analyzer, for which purpose indeed other more suitable prisms exist, and for which this prism was not designed. But it serves admirably as a polarizer, the end A B C D, which is crossed by the section-line, being turned towards the source of light. For use as a polarizer with the optical lantern, or with the microscope, it is preferable to the prisms of Nicol, Foucault, or Glan, as it has a wider angle than any of these, and does not lose light by oblique reflection at its end-faces as the Nicol and Foucault do. Its angle is not so wide as that of the prism described* by the author of this note; but it uses less spar than either that prism or Hartnack's prism. Figs. 3 and 4 show Nicol and Ahrens prisms of equal area of aperture-section.

Since the limitation of the available field is due to the intrusion of the ordinary ray, and does not depend on the vanishing by total reflection of the extraordinary ray, there is nothing to be gained by substituting in this prism any cement such as linseed oil having a higher refractive index. On the contrary, since the critical angle of total reflection for ordinary rays increases as the index of refraction of the cement-film decreases, it would be a gain to use, instead of balsam, a cement of lower index.

On suggesting to Mr. Ahrens that the prism might be cut so that the section-line S S′ bisected the face A B C D vertically instead of horizontally (so making the section-planes principal planes of section, as in the plan suggested by the writer for polarizing prisms in 1881, at the York meeting of the British Association), Mr. Ahrens replied that he had already tried the plan and that the result was the same. This should be so, and should be so for any position of the line S S′ across the face, provided the dihedral angle between the section-planes is constant, because the effective field depends only on the ordinary rays whose properties are symmetrical in all directions. Nevertheless there is some advantage in making the films lie

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* Phil. Mag. November 1881.

in principal planes of section, for then, using a cement of given index, the dihedral angle may be made wider (and the prism correspondingly shorter) without risk of having the centre of the field spoiled by total reflection of the extraordinary ray.

To sum up, the advantages of the new prism are :—

(1) Decrease in length.
(2) Increase in angular aperture.
(3) Saving of light consequent on non-obliquity of end-faces.
(4) Minimum of distortion.
(5) Requires less spar than Hartnack, Glan, or Thompson prism of same section.

Against this are the slight disadvantages—

(1) Line of section across end face.
(2) Uses more spar than Nicol of equal section.

Mr. Ahrens has recently added a thin covering-glass at the end-face crossed by the line S S′, thereby making this line almost imperceptible, as well as affording protection against scratches. Mr. Ahrens has also succeeded in finding a new method of cutting the prism in which there is extremely little waste of spar.

II. *On a Simple Modification of the Nicol Prism, giving wider angle of field.*

As remarked above, in the ordinary Nicol prism the available polarized field is limited, on the one side by the intrusion of the ordinary ray, on the other by the vanishing of the extraordinary ray by total reflection. Of the various methods suggested from time to time for widening the available angular aperture, some have affected one side of the field, some the other, some both. For example, the suggestion made by the writer in 1881 (and by Mr. Glazebrook in 1882) to alter the prism in such a way as to make the balsam-film a principal plane of section, has the effect (irrespective of the external shape of the prism, which we may suppose given) of throwing back to its furthest possible limit (for any given cement) the point at which the extraordinary ray vanishes by total reflection. The obliquity of the end face (other things being given) affects the limit of intrusion of the ordinary ray to a much greater degree than it affects the extraordinary ray : hence by increasing the slope of the end-faces we may add to the available width of field, but this involves increased distortion of the field as well as loss of light. The use of a more highly refringent cement than Canada balsam causes a gain on the side of the extraordinary ray—it thrusts the blue iris further back—but causes a slight loss on the side of the ordinary ray, which intrudes a little more than before.

Now, taking the Nicol prism as it is ordinarily made, there would be a real gain, if it could, without additional labour or cost, be so cut as either to widen the field (using the same length of prism as before) or to shorten the length of the prism (if obtaining the same angular aperture as before). The method of cutting adopted by Hartnack, and that suggested in 1881 by the present writer, both add to the cost of spar and to the labour of cutting. In Hartnack's construction the width of field is gained partly by employing linseed oil, partly by the device of making the plane of the film lie at right angles to the crystallographic axis of the spar. In the writer's own construction of 1881 the balsam-film was made to lie in a principal plane of section, whilst the principal axis of vision through the prism was made to lie at right angles to the crystallographic axis. A gain of about 9° in the width of the field over that of a Nicol of the same external form was the result; being a little less for flat-ended prisms, a little more for oblique-ended prisms.

The author has now devised a simple modification of the mode of cutting the Nicol prism, which possesses several of the advantages of these costlier methods of construction, but without adding appreciably to the cost.

Fig. 5 shows the ordinary Nicol prism as usually cut, the end-faces A B and C D being natural faces of the crystal polished up. The books assert that makers of Nicol prisms cut down these faces, making them still more oblique by 3°. I have not found any constructor who does this. Mr. Ahrens does not; Messrs. Steeg and Reuter do not; M. Lütz does not. The natural angle between the face A B and the arrête A D is about 109°. The crystallographic axis makes about 45° with the end-face A B. The balsam-section is at about 90° (it is exactly 90° in all Mr. Ahren's prisms; it is a little less in some of Dr. Steeg's) to the plane of the end-face. The consequence of this is that there are about 45° between the plane of the balsam-film and the crystallographic axis. This limits the field: those rays which traverse the prism at small angles to the film, and which would traverse the film if the crystallographic axis were at right angles to it (as in the Hartnack prism) are totally reflected out, because the crystallographic axis slopes at 45°.

To remedy this I cut the crystal in the manner shown in fig. 6 or fig. 7. Fig. 6 represents a piece of spar of the same size as fig. 5. The end-faces are first cut away about 40°

each, making the ends of the prism A E and F C reversed in position, but inclined at about 69° instead of 71° to the long edges. The prism is then cut across E F, which makes about 89° with the end-faces. The result is a shortened and "reversed" Nicol, in which the crystallographic axis lies very nearly in the plane of the end-face, and in which the balsam-film is very nearly at right angles to the crystallographic axis. Or, comparing the two :—

	Ordinary Nicol.	Reversed Shortened Nicol.
Obliquity of end-face . . .	71°	69°
Angle between end-face and crystallographic axis . . .	45	5
Angle between balsam-film and crystallographic axis . . .	45	94

The result is that the blue-iris limit is thrown right back, and a shorter prism is obtained, having an equally wide field or wider.

Fig. 7 shows the same method applied to a slightly longer piece of spar, producing a "reversed" prism of precisely the same external form as the ordinary Nicol, and having indeed everything the same save the direction of the crystallographic axis, as a comparison of figs. 5 and 7 will show.

The method of "reversing" the section is of course equally applicable to flat-ended Nicols. If a piece of spar is first cut so that the terminators are orthogonal to the long edges of the prism, it is obviously just as easy to slice the prism with a section that is very nearly perpendicular to the crystallographic axis as to slice it with one that makes only 45° with it.

This new method of construction may be regarded as a compromise, for the sake of cheapness, between the method of Hartnack and the older method of Nicol.

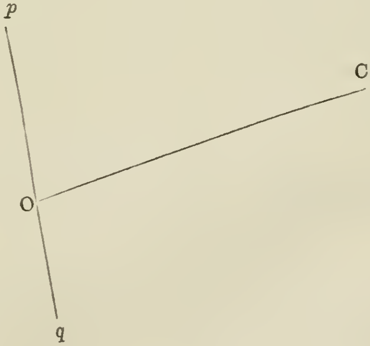
The prisms exhibited by the author at the British Association Meeting at Aberdeen consisted of a "reversed" and of a "reversed-shortened" prism; both of them cut for the author by Messrs. Steeg and Reuter, of Homburg.

LXVI. *The Foundations of the Kinetic Theory of Gases. Note on* Professor Tait's *paper* (No. 131, p. 343). *By* S. H. Burbury[*].

I THINK Professor Tait (p. 345, A, B, and C) has postulated rather more than is necessary. There may, as it appears to me, be a set of spheres which never collide with each other, and one other sphere which collides with the first set, and it will be found that this single sphere will knock the others into "the special state." I prove it as follows:—

Let there be a number of elastic spheres moving in any space, each of mass P, but of infinitely small radius, so that they never collide with each other. Into this system introduce one elastic sphere of mass Q, and of considerable radius, so that collisions will occur between it and the P spheres.

Assume Maxwell's distribution to exist; that is, that the number of P spheres whose component velocity in given direction lies between x and $x+dx$ is proportional to $\epsilon^{-h\mathrm{P}x^2}dx$, and the time during which, on the average of any long time, the sphere Q has component velocity between x and $x+dx$ is proportional to $\epsilon^{-h\mathrm{Q}x^2}dx$. When the sphere Q collides with one of the P spheres, let V, represented by $p\mathrm{O}q$ in the figure, be the relative velocity of the two spheres, and V′, represented in the figure by O C, be the velocity of their common centre of gravity.



Let $\dfrac{p\mathrm{O}}{q\mathrm{O}}=\dfrac{\mathrm{Q}}{\mathrm{P}}$.

Consider all the collisions which take place in unit time in which V and V′ have these values before collision. The

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[*] Communicated by the Author

actual velocity of the P sphere before collision is represented by pC and that of Q by qC. Then I propose to prove

(1) If Maxwell's distribution prevail, for any given direction of pOq, OC is on average of all the collisions in question as likely to have any direction in space as any other.

(2) Therefore on average of all these collisions the difference between the kinetic energies of the spheres before collision is

$$\tfrac{1}{2}\mathrm{P}\{\mathrm{O}p^2+\mathrm{OC}^2\}-\tfrac{1}{2}\mathrm{Q}\{\mathrm{O}q^2+\mathrm{OC}^2\}.$$

(3) After collision V′ remains unaltered in magnitude and direction. V remains unaltered in magnitude, but by the law of impacts between elastic spheres is as likely to have any direction in space as any other. Therefore after collision the difference of energies on the average of all the collisions in question is

$$\tfrac{1}{2}\mathrm{P}\{\mathrm{O}p^2+\mathrm{OC}^2\}-\tfrac{1}{2}\mathrm{Q}\{\mathrm{O}q^2+\mathrm{OC}^2\},$$

or the same as before collision. Therefore the difference of energies is on average unaffected by collisions. It follows that Maxwell's distribution, if existing, is not affected by collisions.

It remains to give a proof of (1). About O as centre describe two concentric spheres, of radii OC and $\mathrm{OC}+d\mathrm{V}'$. Between them at C form an element of volume

$$\mathrm{OC}^2 d\mathrm{V}'.\sin\phi\, d\phi\, d\alpha,$$

where ϕ is the angle $\mathrm{CO}p$, and α the angle between the plane of $\mathrm{CO}p$ and a fixed plane through $p\mathrm{O}q$. Then, according to Maxwell's law (which we assume to prevail), the chance that the velocity of P shall be represented by a line drawn from p to some point or other within that element of volume is proportional to

$$\epsilon^{-h\mathrm{P}.\mathrm{C}p^2}\mathrm{OC}^2 d\mathrm{V}'\sin\phi\, d\phi\, d\alpha.$$

And the chance that the velocity of Q shall be represented by a line drawn from q to *some point or other* within that element of volume is proportional to

$$\epsilon^{-h\mathrm{Q}.\mathrm{C}q^2}\mathrm{OC}^2 d\mathrm{V}'\sin\phi\, d\phi\, d\alpha.$$

And therefore the chance that the velocities of P and Q shall be represented by lines drawn from p and q *both to the same point* within the element of volume is proportional to

$$\epsilon^{-h(\mathrm{P}.\mathrm{C}p^2+\mathrm{Q}.\mathrm{C}q^2)}\mathrm{OC}^2 d\mathrm{V}\sin\phi\, d\phi\, d\alpha.$$

And this measures the chance that the angle $\mathrm{CO}p$ shall lie between ϕ and $\phi+d\phi$.

Now since $\frac{\mathrm{O}p}{\mathrm{O}q}=\frac{\mathrm{Q}}{\mathrm{P}}$, $\mathrm{P}.\mathrm{C}p^2+\mathrm{Q}.\mathrm{C}q^2$ is independent of ϕ.

Therefore the chance that the angle COp shall lie between ϕ and $\phi+d\phi$ is proportional to $\sin\phi\, d\phi$. And therefore, as stated in (1), for any given direction of pOq all directions of OC are in Maxwell's distribution equally probable.

If Maxwell's distribution does not exist, then for any direction of pOq some directions of OC are more probable than others before collision. After collision all are equally probable; I think it follows that collisions tend to bring about Maxwell's distribution.

LXVII. *Remarks on a new Theory of Dew.*

By CHARLES TOMLINSON, *F.R.S.*[*]

MR. AITKEN read before the Royal Society of Edinburgh, on the 21st of December last, a paper in which a new theory of Dew is promulgated in opposition to that of Dr. Wells, "who," he says, "has justly been considered the great master of this subject." An abstract of the paper, presumably by the author himself, was given in the number of 'Nature' for the 14th of January last, preparatory to the publication of the memoir in the 'Edinburgh Transactions.'

Many years ago I showed that the chief points which Dr. Wells is said to have established had already been demonstrated by his predecessors; and in noticing his essay in the 'Quarterly Review' for 1814, Dr. Thomas Young enters a protest against "the total novelty of the opinions which Dr. Wells's laborious series of experiments had so amply illustrated and confirmed; for while the author affords us complete information respecting the sentiments of Aristotle and Theophrastus as to the nature and causes of dew, some of the works of the most distinguished philosophers of modern times have most unaccountably escaped his attention."

The fact is there is a considerable difference between a scientific worker and a scientific writer. The worker is generally too intent on his own share in discovery to do more than accept the conditions of the question in hand from some writer who may have compiled from earlier books and not taken the trouble to consult original memoirs. There are not many writers who work at scientific literature with the same zeal with which literary men pursue their labours; and the reason is to be found in the marked difference between literature and science. A literary work bears the impress of *mind*, scientific work bears the stamp of *nature*.

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[*] Communicated by the Author.

The one is individual and proper to the man; the other is general and has no individuality. A work by Shakspere remains for all time untouched, unchanged (except to make the text more correct, and thus augment the author's individuality); a work by Davy may be taken up by Faraday, and Faraday's work may be carried forward by his contemporaries or successors. And this is probably what Lord Bacon meant when he said that his inductive method of philosophizing tended rather "to level wit and intellect."

The interest that is felt in literary history, contrasted with the comparative indifference to scientific history, rests on the fact that a Chaucer, a Shakspere, a Dryden, a Gibbon is each an intellect rounded, complete, fixed, and final. But, without meaning the slightest disrespect to such great men as Newton, Davy, and Faraday, it must be admitted that they are but parts of a great whole, and that whole is Nature. We care more about the laws of Nature than about their discoverers; but every one feels an interest in a great writer because he and his works are inseparably connected. An unpublished poem or letter by one of the great writers of the past would excite the ardour of the literary world; a new fact in the history of oxygen or of the composition of water would fail to receive more than a passing glance from scientific men. They consider that all the main known facts are embodied in text-books, while that which is not so embodied is of no consequence. They consider that we have the names of the discoverers and the dates of all important facts in the main correct. They want to pursue discovery, not its history; and hence they feel but little interest in the light thrown by old memoirs on the progress of the past.

Sir John Herschel, writing a scientific treatise, refers to Wells's Essay as "one of the most beautiful specimens of inductive experimental inquiry," and earnestly recommends it to the student "as a model with which he will do well to become familiar." Dr. Whewell, writing scientific history, is more cautious: he refers to Wells's Essay as "one of those books which most drew attention to the true doctrine."

Wells, in his essay, writes with an air of authority. His tone is everywhere that of a man announcing his own discoveries. For example, he says:—"I have frequently seen, during nights that were generally clear, a thermometer lying on the grass-plat rise several degrees upon the zenith being occupied only a few minutes by a cloud." Most of the important steps in the theory are thus stated as if for the first time, and we find only a loose and general reference to authorities, and a very scant acknowledgment of other men's labours. Nevertheless, most of Wells's results had been published long before the author commenced his labours, and the theory for which he has obtained so much credit was also similarly indicated, in brief but unmistakable terms *.

The chief points which Dr. Wells is said to have established may be thus stated :—

I. That on clear and serene nights the surface of the earth is colder than the air some feet above it.

II. That on such nights dew or hoar-frost is formed.

III. That in cloudy weather the temperature of the ground approaches, and is often identical with, that of the air ; and under such circumstances little or no dew is formed.

IV. That screens, even of the lightest material, interposed between the ground and the clear sky, and, in general, whatever interrupts the view of the sky, prevents that portion of the ground thus protected from cooling below the temperature of the air.

V. That different bodies exposed to the clear sky become colder than the air ; the times and amounts of cooling being, in general, different in different bodies.

VI. That all these varied phenomena are to be accounted for on the principles of radiation and condensation, by the first of which the surface of the earth after sunset, provided the sky be clear, cools down below the temperature of the air ; and by the second of which, the vapour suspended in the air is reduced to the liquid state by contact with a body cooler than itself. But should the sky be clouded or the ground be protected by means of screens, the heat radiated from the earth is reflected back again, and thus maintains the surface at or about the same temperature as that of the air.

Mr. Aitken, in his theory of dew, states :—

I. That the ground below the surface is always hotter than the air over it, and that, so long as this excess keeps the surface above the dew-point of the air, it will, if moist, give off vapour, which will condense on the grass and form dew, and not the vapour that was previously present in the air.

II. That vapours rising from the ground during dewy nights are thus trapped by the herbage, or within tin trays inverted on the ground.

III. That on weighing a small area of the exposed surface

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* The details are given in my essay, "On the Claim of Dr. Wells to be regarded as the Author of the Theory of Dew," published in the 'Edinburgh New Philosophical Journal,' for January 1861 ; and in a somewhat enlarged form in 'Experimental Essays,' published in 1863, in Weale's Series. See also a notice from my pen in the 'Chemical News' of the 12th April, 1867, of a reprint of Wells's Essay.

of the ground, such as a turf six inches square that had been exposed for some hours while dew was forming, it was always found to have lost weight.

IV. That bare soil loses nearly as much in weight as grass-land.

V. That pieces of blackened glass placed on the ground remain clear of vapour, thereby showing the soil to be always giving off vapour because the surface is above the dew-point.

VI. That even where radiation is strong and vapour is condensed on the soil, such vapour is supposed to proceed from below, and to be trapped by the cold surface-soil. Thus the under surface of clods are often covered with hoar-frost, while there is little on the upper surface; and in roads the under surface of stones may be wet as well as the under sides of slates placed on gravelly roads.

VII. That the leaves of plants apparently wet with dew are not really so, but the moisture is an exudation from the plants themselves *.

VIII. That the radiating powers of different bodies have hitherto been erroneously stated. Black and white cloths were found to radiate equally well; soil and grass were also almost exactly equal to each other; lampblack was equal to whitening; sulphur was about two thirds that of black paint; snow in the shade on a bright day was at mid-day 7° colder than the air, while a black surface at the same time was only 4° colder; but at night both radiated almost equally well.

Such is the new theory of dew, which, if accepted, must go far to render nugatory the results obtained by some of the most celebrated observers. It would occupy too much time and space to examine the above eight propositions minutely, and to compare their statements with already received results. It will, perhaps, be sufficient for our purpose to give a few details from those researches upon which we have hitherto most relied, and leave the reader to contrast them with Mr. Aitken's ingenious speculations.

That "the ground at a short distance below the surface is always hotter than the air over it," is not a new observation. In 1779 Pictet † found that a thermometer suspended 5 feet from the ground marked a lower temperature on clear nights than one suspended at the height of 75 feet; he also placed a thermometer with its bulb buried in the earth, and found it to

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* Muschenbroeck regarded dew as a real perspiration of plants.

† *Lettres Physiques &c.* of M. de Luc, La Haye and Paris, 1779; also *Essais de Physique*, by M. Pictet, Geneva, 1790.

indicate a higher temperature than the air above it. He had supposed the cold of evening to descend from above, and could scarcely believe his eyes when he found the thermometer at the height of 75 feet to read more than 2° R. above one at 5 feet. "It is then from the ground that this coldness proceeds, for the thermometer at 4 lines from the ground generally read lower than the one at 5 feet." All this is correctly observed; but the buried thermometer led him astray; for this naturally indicating a higher temperature than any of the other instruments, he supposed that the earth retained a considerable portion of the heat it had acquired during the day, that a layer of air cooled by evaporation from the surface produced the cold to the height of four lines, while at higher elevations the warmer air escaped this chilling influence.

In January 1781 Professor Patrick Wilson noticed at the Glasgow Observatory, between 1 and 3 A.M., the temperature of the air 24 feet from the ground to be 7° F., while the snow in the Park at the depth of 6 inches was 24°. He also noticed the effect of clouds and screens in raising the temperature, and Dr. Black suggested a screen of gauze, which was tried, with a like effect.

That dew rose out of the ground is a very old notion. Mr. Aitken refers it to Gersten; but his Treatise appeared so lately as 1748, under the title *Exercitationes recentiores circa Roris meteora.* In a volume in my library, entitled *De Rore disquisitio physica D. Joannis Nardii* (Florentiæ, 1642), it is stated:—"*Rorem obseruant hi fieri exhalitu è terra eleuato, silente vento, celo sereno, anni tempore, loco, et regione temperatis.*"

The Florentine Academicians were the first to show that the moisture which supplied dew already existed in the air. The Hon. Robert Boyle, in his 'Experimental History of Cold' (1665), showed that the beautiful exhibition of frost on the window-pane is condensed from the vapour of the air in the room, and he attempted to estimate, by weighing, the amount of vapour condensed within a given time upon a phial containing a mixture of salt and snow. Boyle distinctly recognized the fact that dew and hoar-frost are formed by the precipitation of the vapour of the air upon a colder body.

In 1752 M. le Roi, of Montpellier, doubting the received notion that dew rose from the ground, sealed up a bottle of white glass containing air at 20° R. (77° F.), and he noticed that as the temperature cooled down there was a considerable deposit of dew within the bottle, which again disappeared as the temperature became higher. Le Roi made a number of admirable observations, among others the method of determining the dew-point, which has generally been assigned to Dalton under the date 1801.

But probably among all the researches into the phenomena of dew those of M. Melloni are best adapted to furnish an answer to Mr. Aitken. His observations were made in the autumn of 1846 in the valley of La Lava, situate between Naples and Salerno. It is curious to note that the Austrian and Bourbon Governments, in their dread of novelty, would not allow a new text-book on Physics to be introduced into colleges and schools: so that the old theory was taught, namely, that dew rose from the earth. Melloni, in order to show that the laws of radiation are the same in Italy as in other countries, where there is more political liberty, undertook these researches *.

The early experimentalists seemed to pride themselves on the great differences between the thermometers on the grass and other substances, and the thermometer suspended in the air above them, as when Wells assumes a kind of injured tone in noticing that Six had obtained a greater difference than he had done, viz. 16° F. †; whereas Melloni rather prides himself on the smallness of this difference, and maintains that the great depression of temperature, as observed by Wells and others, arose quite as much from the radiation of the glass and other materials of the thermometers, as from that of the substance under examination ‡. Nor does he find it necessary, in the economy of nature, that vegetation should cool down so much below the temperature of the air as had hitherto been supposed; since a difference of one or two degrees C. would, in most cases, suffice to condense the moisture of the air upon grass and the tender surfaces of leaves. He answers the theory which supposes that, as the cold varies from 1° to 10° C. with the amount of shelter or exposure, so certain plants are bedewed while others are quite dry, by denying the fact; for we have either the entire absence of

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* "On the Nocturnal Cooling of Bodies exposed to a Free Atmosphere in Calm and Serene Weather, and on the resulting Phenomena near the Earth's Surface," read to the Royal Academy of Naples on the 23rd February, and 9th and 16th March, 1847. A French translation of these Memoirs was made under the Author's superintendence for the *Annales de Chimie et de Physique* for February and April 1848. An excellent English translation appeared in Taylor's 'Scientific Memoirs,' vol. v. 1852.

† Mr. Aitken also notices a difference on dewy nights of from 10° to 18° F. between two thermometers, one placed on the grass and the other under the surface among the stems, but on the top of the soil.

‡ Melloni took extraordinary pains to prevent his thermometers from sharing in the radiation of the bodies, the amount of whose cooling they had to measure.

dew, or its diffusion in quantities sensibly equal on all low-growing plants, whatever their position with respect to the sky. He also insists that dew is never formed except when the air is nearly saturated: also that radiation under a clear sky is always a fixed quantity, whatever the temperature may be; so that in nights equally serene the same substance always cools to the same extent, whatever the temperature of the air at the time.

The nocturnal differences in heat, moisture, and aqueous condensation do not proceed, as hitherto supposed, from the direct action of the cold due to the radiation of plants and of exposed portions of the soil, but most of the phenomena which precede and accompany the formation of dew result from the more or less prolonged sojourn of the air around the radiating surfaces. In a meadow while dew is forming under a clear sky and a calm air, let us divide the lower region of the atmosphere into two strata—the *lower*, which scarcely rises above the grass; the *higher*, which extends upwards from it 30 or 40 metres; and suppose the cold due to the nocturnal radiation of the herbage to be only 1°; this degree of cold will always remain the same whatever the temperature of the atmosphere. If the air be at 20°, the higher portions of the grass will descend to 19° a few minutes after sunset; the air in contact with them will be cooled, will descend into the interior of the meadow, and reach the ground. This movement of descent along the leaves and stems will necessarily restore to the air a portion of the lost heat, and will force it to reascend towards the higher part of the meadow, where it will undergo a fresh cooling which will cause a second descent, and so on; so that the air of the meadow or of the lower stratum, impelled by two opposite influences, will soon take a circulating or convective motion. The cold produced at the surface of the meadow will be gradually transmitted by this aerial circulation to the lower parts, which will also be cooled; and, on the other hand, both by radiation and by their contact with the superior portion of the stems, the temperature of the whole mass of air which is put in motion will fall. If it be at 19°·5, the grass will sink to 18°·5. By repeating the process the air will fall to 19°, and the grass to 18°; the air to 18°·5, the grass to 17°·5, and so on; so that by the action of the grass on the air and the reaction of the air on the grass, the temperature of the lower stratum will be gradually diminished by several degrees, and the space occupied by the herbage retaining its vapour will approach the state of saturation. A thermometer introduced into this space will mark a temperature much lower than that of the higher stratum; the hygrometer will there be kept near its maximum of humidity; and the slightest degree of cold will suffice to precipitate the aqueous vapour on the bodies which are immersed therein.

In the same way may be explained the large amount of cooling which takes place when a thermometer loosely enveloped in wool, or cotton-wool, is exposed to the clear nocturnal sky. The air cooled by coming in contact with these envelopes penetrates into them, and tends to fall by virtue of its greater density; but the mechanical resistance and the attraction offered by the innumerable tangled fibres retain it for some time in the midst of those parts which are radiating towards the sky. A series of actions and reactions similar to those just described then takes place, and the mixture of air and of wool cools much more than a simple layer of varnish or of lampblack applied to the thermometer. In the same way plants with velvety leaves acquire a somewhat lower temperature than plants with smooth ones, and consequently become covered with a greater quantity of dew. Now in studying the phenomena of cooling in the meadow, if the greatest cold be produced at the top of the grass, the cooler air would, by its superior density, soon sink to a lower level. We may imagine three layers of air—one in contact with the points of the grass; the second immediately below it, where the blades are more numerous, and more or less exposed to the zenith; and the third entangled in the matted portion, which is entirely sheltered from the sky. The points of the grass are in a condition most favourable for free radiation, but the blades are there fewer in number, and the air is exposed to slight disturbances which diminish the radiating effect; but the middle portion, where the blades are most numerous and the disturbance less, radiates most powerfully and produces the greatest cooling. The lowest layer of air being sheltered, will at first have a higher temperature than the other two; but these, being cooler and denser, will descend and react on the radiating portions of the grass, and the more so in proportion as the movement is slow. In time the middle portion will contract the greatest cold, and in descending will displace the somewhat warmer air, and in the end the lower stratum will be colder than the first, so that the blades and stems which are least exposed to the aspect of the sky will be colder than the points of the blades, and the thermometer buried in the grass will mark a lower temperature than one in contact with the surface. And here, too, the formation of dew will be most abundant, not on the surface, but just below it. But as the cooling goes on, the lower layer of air will be again displaced, and radiation continuing from the soil, a certain amount of dryness will be produced, evaporation will take place, and the vapour thus formed will be again precipitated on the upper parts of the blade. But in order to effect this, the ground must be comparatively dry. *This appearance of dew on the upper parts of plants led to the idea that dew rose out of the earth.*

The process above described will of course be disturbed or destroyed by wind. On the other hand, what is called "a perfectly calm night" does not exist in nature. Air is so very mobile a fluid, that the least difference in temperature sets it in motion in the form of imperceptible currents ; and there are always numerous inequalities of temperature depending on the nature of the soil, the greater or less amount of vegetation, the degree of cultivation, the presence of houses, all of which prevent equilibrium from being attained in the air. But supposing the air to be tranquil so far as our perceptions are concerned, then the processes of radiation, convection, and condensation sufficiently account for the presence of dew, whether on the herbage or on the inner surface of Mr. Aitken's thin metal trays.

But let us hear Melloni. He says:—"Some have pretended to discover proofs of the existence of *a current of warm vapour exhaled by the earth,* and an objection against the principle of nocturnal radiation in the different proportions of water deposited during calm and clear nights on the two surfaces of a bell-glass inverted on the ground; for it often happens that the dew is more copiously formed on the inside than on the outside of the vessel. But this fact by no means justifies the conclusion; for the phenomena of circulation and aqueous precipitation just described with reference to the air and grass of a meadow are also produced in the interior of the vessel, the sides of which are cooled by radiation. These actions become even more intense in this case, because the imprisoned air is sheltered from the least atmospheric disturbance; and we have just seen that the quantity of water condensed on the outside depends, on the contrary, on the degree of calm in the atmosphere. Hence the slightest degree of wind will suffice to render more abundant the precipitation on the interior of the bell-glass, without leading to the conclusion of an increase favouring the pretence of an exhalation of vapour from the earth, and contrary to the theory of dew founded on the cold produced by nocturnal radiation.

"Nothing, then, is simpler now than to comprehend why a radiating body such as a piece of wood or stone, placed on a moist soil towards sunset, is abundantly covered with dew on its lower side before a single drop of liquid appears on the upper surface. The body submitted to the frigorific action of the sky is in contact with two masses of air—the one at rest and humid, because it is sheltered and situated close to the earth's surface; the other less humid and exposed to the changes of the atmosphere. The former then will be more disposed than the latter for the precipitation of vapour, and the dew ought to show itself first on the side turned towards the soil; it may even exist only on this surface, if the air has but little moisture, or is agitated by wind. Hence the experiment of a plate covered with waxed cloth, which being placed on the grass was found sometimes to be moistened only on its lower surface, by no means proves that the dew is exhaled from the ground like those clouds of vapour which are seen to arise from a vessel full of hot water."

Melloni, in two letters to Arago, describes some experiments with thin tin plates in which the surface looking towards the ground is covered with dew while the upper portions remain dry.

While Melloni insists on the influence of radiation in the formation of dew, whereby bodies become colder than the air and so condense its vapour, he claims to have first pointed out the great influence exerted by the reaction of the air on the radiating body; and he defines dew, not as an immediate effect of the cooling produced by nocturnal radiation, but as a consequence of a series of actions and reactions between the cold due to the radiation of plants &c. and the cold transmitted to the surrounding air. The grass becomes slightly cooled below the temperature of the air, but it soon imparts to it a portion of the cold thus acquired; and as the difference in temperature between the radiating body and the air is independent of the absolute temperature at the time, grass surrounded by the colder air becomes lower in temperature and imparts a fresh amount of cold to the air, which in its turn reacts on the grass and gives to it a still lower temperature, and so on. In the mean time the air acquires a kind of vertical circulatory movement, the upper portions condensed by cold descending and those at the surface ascending. As this gradual cooling goes on, the surface air gradually becomes saturated with moisture and the slight amount of cold produced by the direct action of radiation is sufficient to condense the vapour contained in the air.

If in the above statement we read a thin metal tray instead of grass, the process and its result remain the same.

If we now turn from the grass meadow to grander natural objects, abundant proof will be found that dew is condensed from the air and does not rise out of the ground. The interior of Persia is characterized by the absence of dew. In this region there are no rivers of any magnitude, and no rain falls from May to the end of November. But on approaching the Persian Gulf nocturnal dews are heavy and the coverings of beds on the house roofs become saturated with wet. In the African desert of Sahara, the traveller Denham suffered from the dryness of the air until within a certain distance of Lake Tchad, where, though there was no appearance of water at any part of the horizon, the dews were so abundant as to wet the clothes of people outside the tent. When Dr. J. D. Hooker was in East Nepal he noticed that the sun in many places did not reach the bottom of the valleys until 10 A.M., and was off again by 3 P.M., while the radiation towards a clear sky was so powerful that dew frequently formed in the shade throughout the day. Such, too, was the clearness of the sky that at night our traveller found the upper blanket of his bed coated with moisture from the rapid abstraction of heat by the tarpaulin of his tent, which had become frozen by its own radiation.

In equatorial regions, where the nights are long, dews are so abundant that Humboldt compares their effects to those of rain, and they become more and more abundant in approaching the equator; whereas in the great assemblage of islands known as Polynesia, the dew is feeble or absent, in consequence of the trade and other warm winds from the sea preserving a nearly uniform temperature.

There is such a vast consensus of scientific opinion in favour of the received theory of dew, that any attempt to set it aside in favour of another must be supported by the strongest experimental evidence. And yet some of Mr. Aitken's proofs seem to bear testimony to the received theory rather than to the one now advocated. For example, when Mr. Aitken exposes a turf six inches square to the air in a scale-pan and finds it to have lost weight, he does not touch the question whether the vapour that forms dew is not already in the air before it is condensed and deposited. He only proves that a moist soil is constantly giving off vapour under a clear sky. Snow and ice behave in like manner: 100 grains of light snow have been known to lose 60 grains in weight during one night when the temperature was below 25°; and Patrick Wilson, exposing various objects on a balanced board (named by him a "snow-scale"), noticed that as they cooled down by radiation, they became covered with hoar-frost and increased in weight, and the vapour which supplied the rime was derived from the air, seeing that the scale-board was elevated 24 feet above the ground.

When Mr. Aitken places his shallow trays of thin metal "over the ground to be tested," are we to understand that the edges of the trays are in contact with the ground? If so, the results are not in harmony with another set of observations, in which two slates or two iron weights are placed one on the ground and the other elevated a few inches above it. That on the ground, "and in heat communication with it," is said to have remained dry, while the elevated one was bedewed all over. Surely this result is in favour of the received theory.

Perhaps the most startling portion of the new theory is that which relates to plants, whose very existence would seem in many cases to depend on the formation of dew. If the moisture on plants were "the excretion of liquid" by the plants themselves, and not dew, for what purpose are plants endowed with such high radiating powers, in some cases superior to that of lampblack? Taking this at 100, Melloni, by his careful method. found the radiating power of different herbs with flexible leaves to be 103, the leaves of the elm and poplar to be 101, that of vegetable mould 92.

Enough, however, has been said on this subject; but we cannot conclude without offering an apology to the readers of the 'Philosophical Magazine' for the very elementary details of this article.

LXVIII.—*On the Efflux of Air as modified by the Form of the Discharging Orifice.* By Henry Wilde, *Esq.*[*]

In my former paper on the Efflux of Air, the hydraulic coefficient ·62, as commonly applied to the discharge of elastic fluids through an orifice in a thin plate, was taken as the value of the contraction of such orifice, and from this coefficient the highest velocities shown in the several tables were deduced. A review of the results of my experiments by Prof. Osborne Reynolds [†] led me to doubt the value of this coefficient, and to make further experiments with the object of determining the maximum rate of discharge from an orifice of the best form.

Five disks of brass had each a hole drilled through its centre two hundredths of an inch in diameter. Equality in the size of the holes was accurately determined by means of a standard cylindrical gauge. These disks I shall designate A, B, C, D, E.

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[*] Communicated by the Author, having been read at a Meeting of the Manchester Literary and Philosophical Society, March 23rd, 1886.

[†] Proceedings Manchester Lit. and Phil. Society, vol. xxv. p. 55; Phil. Mag. March 1886, p. 185.

The disk A was three diameters of the orifice in thickness, and was equal to a plain cylindrical tube three diameters in length.

Disk B was the same thickness as A, but the hole was coned out on one side to a depth of one diameter and a half.

C was six diameters in thickness, and was coned out on one side to a depth of three diameters.

D had a thickness of twelve diameters of the orifice, and was coned out on one side to a depth of six diameters.

E was eighteen diameters of the hole in thickness, and was coned out on both sides to a depth of six diameters, which left a plain tube in the centre of the disk six diameters in length.

The wide sides of the coned orifices were equal to two diameters, and their outer edges were rounded off to a conoidal form.

The thin iron disk O was ·007 of an inch in thickness, or nearly one third the diameter of the orifice, which was two hundredths of an inch. One side of the orifice was chamfered to reduce the cylindrical part of the hole as much as possible to a sharp edge. The chamfering had, however, so small an effect in diminishing the rate of discharge, that the determinations might have been taken from the cylindrical orifice without interfering with the general accuracy of the results.

The mode of experimenting was similar to that already described. Air of an initial absolute pressure of 135 lb. was discharged into the atmosphere through the orifice in the thin plate O, and through the orifices in A, B, C, D, E successively, and the times were recorded for the reduction of 10 lb. from each of the atmospheres of pressure, as shown in the following table :—

Table I.—Discharge into the Atmosphere.

Lb. per square inch absolute pressure.	Orifice in thin plate. O	Plain tube orifice. A	Conoidal orifice inside. B	Conoidal orifice inside. C	Conoidal orifice inside. D	Double conoidal orifice. E	Coefficient for orifice. O
	sec.	sec.	sec.	sec.	sec.	sec.	
135	15·5	14·5	14·5	14·5	15·0	15·5	·935
120	17·5	16·5	16·5	16·5	17·0	17·5	·943
105	20·5	19·0	19·0	19·0	20·0	20·5	·927
90	25·0	23·5	23·5	23·5	24·5	25·0	·940
75	31·5	29·5	29·5	29·5	30·5	31·5	·936
60	42·0	39·5	39·5	39·5	41·0	42·0	·940
45	58·0	54·5	54·5	54·5	56·5	58·0	·940

Mean coefficient for orifice in thin plate, ·937.

An examination of this table will show that the form of the orifice has very little influence on the rate of discharge of elastic fluids compared with what it has on those which are inelastic.

No difference was observable in these experiments in the rates of discharge through the orifices A, B, and C, notwithstanding that A was a plain cylinder, and B and C were coned to a depth of half their thickness and formed tubes from three to six diameters in length. Moreover, although the results shown in the tables were obtained with the coned sides of the orifices inside the vessel, yet, when the sides were reversed, the rate of discharge through A, B, and C was only diminished by one thirtieth part, and there was no difference in the rate of discharge through D whether the coned side of the orifice was inside or outside the vessel.

Taking A, B, and C as the orifices producing the maximum rate of discharge, we have ·935 as the value of the coefficient of discharge from an orifice in a thin plate for the highest pressure of 135 lb. This value, as will be seen, is the same for all the pressures in the table within errors of observation and experiment, and the mean value of the coefficient for all the pressures is ·937.

Applying this coefficient to the velocity deduced in Table I. of my former paper for an orifice in a thin plate, we have for the maximum velocity with which air of 135 lb. pressure rushes into a vacuum, before expansion, $V=\frac{750}{\cdot 937}=800$ feet per second.

Some anomalous rates of efflux from the same orifice, which were obtained when air of less than 15 lb. effective pressure was discharged into the atmosphere, induced me to make a series of experiments on the discharge of air of an initial pressure of 15 lb. through the same orifices as in the last experiments, and the times were recorded for each reduction of 2 lb. of pressure.

All the discharges were made with the conoidal orifices inside the vessel, but they were also made through C and D with these orifices outside the vessel. The results are shown in the following table (II.).

On comparing the times of discharge through the several orifices among themselves, and with those in Table I., a marked difference is observable in them. Thus the ratio of discharge through the tube-orifice A and the orifice in a thin plate is greater than that for the same orifices in Table I.,

TABLE II.

Discharge into the Atmosphere.

Lb. per square inch effective pressure.	Orifice in thin plate. O	Plain tube-orifice. A	Conoidal orifice inside. B	Conoidal orifice inside. C	Conoidal orifice outside. C	Conoidal orifice inside. D	Conoidal orifice outside. D	Double conoidal orifice. E	Coefficients for orifice. O
	sec.	sec.	sec.	sec.	sec.	sec.	sec.	sec.	
15	16·0	13·5	14·0	14·0	14·0	14·5	14·5	15·0	·829
13	17·5	14·5	15·0	15·0	15·0	16·5	16·0	16·0	·829
11	19·5	16·0	16·5	16·5	16·5	18·5	18·0	17·5	·820
9	22·5	18·0	18·5	18·5	18·5	20·5	19·5	19·0	·818
7	26·0	21·0	21·5	22·0	21·5	24·0	21·5	22·0	·808
5	33·0	26·0	26·5	27·5	26·5	30·0	25·5	27·0	·788
3	51·0	39·0	40·5	42·5	40·5	47·0	38·5	42·5	·765

the coefficients for the highest and lowest pressures in this table being ·935 and ·940 respectively; whereas the coefficients for the same orifices in Table II. are ·829 and ·765 respectively. Again, while there is little difference in the times of discharge from the tubular orifices among themselves, a remarkable change occurs during the fall of pressure from 15 lb. to 1 lb. when the discharge is made through C and D with the conoidal orifices outside the vessel.

The discharge through D from 15 lb. to 13 lb. is the same whether the conoidal orifice is inside or outside; but in the latter position, as the pressure diminishes, the rate of discharge increases, till at the lowest pressure this increase amounts to 8·5 seconds, and exceeds the maximum discharge from the tube-orifice A. A similar change is also noticeable in the rate of discharge through reversing the orifice C; but as the change does not come on before the pressure is below 7 lb., it is less marked than when the discharge is made through D.

Suspecting that the phenomenal change in the rate of discharge for the same orifice was due to the varying resistances of the discharging and receiving atmospheres of pressure described in my former paper, the discharges from the orifices O, A, and D were made into a vacuum of 1·5 inch of mercury instead of into the atmosphere, and the times of discharge were recorded for each reduction of 1 lb. of pressure. The results are shown in the table.

Table III.

Discharge into a Vacuum 1·5 inch Mercury.

Lb. per square inch absolute pressure.	Hole in thin plate. O	Plain tube-orifice. A	Conoidal orifice inside. D	Conoidal orifice outside. D	Coefficient for orifice. O
15	16·0	15·0	16·0	16·0	·937
14	17·5	16·5	18·0	18·0	·943
13	19·0	17·5	20·0	20·0	·921
12	21·0	19·5	22·5	22·0	·928
11	23·0	21·5	24·5	24·0	·935
10	25·5	24·0	27·5	27·0	·941
9	28·5	27·0	31·0	30·5	·947
8	32·5	31·0	35·5	35·0	·954
7	37·5	35·5	41·0	40·0	·947
6	45·0	42·5	49·5	48·5	·944
5	55·0	52·5	63·0	61·5	·955
4	70·0	67·0	81·0	79·0	mean
3	102·0	101·0	125·0	120·0	coefficient
2	180·0	192·0	241·0	224·0	·941

A comparison of the times of discharge through D with the conoidal orifice in both positions will show that they approach nearly to a ratio of equality. The phenomenal change in the rate of discharge from the same orifice was consequently due to the diminished resistance of the external atmosphere, the conoidal form of the orifice increasing the amount of rarefaction above that obtained with a plain tube-orifice. This conclusion is further evident on comparing the times of discharge from D in reversed position from a pressure of 3 lb. to 1 lb.; for as the rarefaction in the vacuum-chamber was only reduced to 1·5 inch of mercury, the phenomenal change in the rate of discharge again presents itself, making a difference of 17 seconds in the times of discharge between the reversed position of the orifice for the lowest pressure.

Comparing the times of discharge through the tube-orifice A and the orifice O in the thin plate, it will be seen that there is much less difference between them than for the same orifices in Table II., the ratio agreeing very closely with those shown in Table I. for similar times of discharge. The approaching equality in the times of discharge through the tube-orifice A and the orifice in the thin plate for the lower pressures is no doubt due to the friction of the issuing stream of air against the sides of the tube-orifice. The effect of this friction for the lowest pressure, as will be seen, reduces the rate of discharge from the orifice A below that from the orifice in the thin plate.

From the results of my previous experiments on the discharge of atmospheres of higher into atmospheres of lower density, the times and coefficients in Table I. and Table III. for the higher pressure may well be considered as having been obtained for discharges into a perfect vacuum, the difference in the coefficients for pressures below 10 lb. in Table III. being entirely due to friction of the issuing stream of air against the sides of the orifices.

From the results shown in Tables I. and II. the maximum rate of efflux is obtained from the orifices A, B, and C, and taking the efflux from these orifices as unity, the value of the coefficient for the efflux of air into a vacuum through an orifice in a thin plate is ·937.

These experiments also prove conclusively that the coefficients which have hitherto been applied to the efflux of air below 15 lb. effective pressure derive nearly the whole of their value from the phenomenal changes of resistance between the discharging and receiving atmospheres, and not from the forms of the orifice and length of the adjutages, as in the discharge of inelastic fluids.

Applying the coefficient ·937 to the velocity with which the atmosphere of 15 lb. absolute pressure rushes into a vacuum before expansion, as deduced in table ii. in my former paper, we have $V = \frac{633}{\cdot 937} = 677$ feet per second, or approximately one half the velocity due to the height of the homogeneous atmosphere.

The following approximate velocities with which atmospheres of several gases of 15 lb. absolute pressure rush into a vacuum through an orifice of the best form, before expansion, have been calculated on the basis of Graham's law of the velocities of efflux for equal pressures being inversely as the square roots of the specific gravities.

Air	1·000 × 677 =	677	feet per second.
Oxygen	0·950 × 677 =	643	„ „
Nitrogen	1·015 × 677 =	687	„ „
Hydrogen . . .	3·800 × 677 =	2572	„ „
Saturated steam .	1·445 × 677 =	978	„ „

LXIX. *On the Determination of the Modulus of Errors.*

By F. Y. EDGEWORTH, *M.A., Lecturer on Logic, King's College, London*[*].

FOR most of the applications of the Law of Errors[†] there is required the determination of a constant which may be described as the mean-square-of-error upon the supposition that the centre-of-gravity is the point of null error—in short the radius of gyration—for a certain plane curve. This curve is the facility-curve under which a given observation ranges[‡]: the curve which would be generated if we registered an indefinite number of observations made under unaltered conditions. Take, for example, Laplace's proof[§] that the difference between the mean of 400 barometrical observations taken at 4 P.M. and the mean of observations[||] taken at 9 A.M. is not accidental, but indicative of a cause. The reasoning turns upon the incident that the mean of 400 observations may be regarded as ranging under a *probability-curve*, whatever the curve under which the individual observations range. In Laplace's example it is supposed to be given that an observation is as likely to occur at one point as another of a line measuring 8 millimetres, but cannot occur outside that range. The facility-curve then for each of the individual observations is a rectangle of base 8 and of height $\frac{1}{8}$ inch. The mean-square-of-error for this facility-locus being $\frac{16}{3}$, we know that the *modulus*-squared of the probability-curve under which the mean of 400 observations ranges is $2\times\frac{16}{3}\div 400=\frac{1}{37\cdot 5}$. Whence it is deducible that the observed difference, namely one millimetre, being about six times the modulus, is very unlikely to have occurred by mere chance.

The object of this paper is to soften the difficulty which the calculation of this constant is apt to present. The cases which it is proposed to treat are intermediate between the least and the most perfect data: between those which admit, and those

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[*] Communicated by the Author.

[†] For some account of these see the references given at the beginning of my paper in the April Number of this Journal.

[‡] Mr. Todhunter's $y=f(z)$. (Hist. of Prob. art. 1001.)

[§] *Théorie Analytique*, Book II. ch. v.

[||] It will be found, I think, that Laplace's reasoning assumes the morning mean (which also rests upon 400 observations) as a *fixed point*. It might have appeared more natural to find the modulus for the difference between the two means on the supposition that neither was perfectly determined by 400 observations.

which require, no remedy. On the one hand are the problems in which it is required to determine the constant in question, not from an ample registry of observations*, but from a few samples. On the other hand are problems which follow the analogy of games-of-chance; where the constant is predetermined, and does not require to be elicited from a register of observations. The intermediate case, where the modulus is to be determined empirically and the material for determining it is copious, is the most frequent in practical statistics. Suppose, for instance, it has been observed that the death-rate in a certain occupation exceeds by a certain amount the rate in other occupations. To determine whether or not that excess is accidental, we require to know the modulus of the probability-curve under which such death-rates range. Or, if it is observed that the mean height of a certain class†, the Royal Society for instance, exceeds the general mean, to complete the argument based on that excess it may be requisite to know what degree of excess would be likely or unlikely to be presented by the mean height of a batch of men taken at random from the general population. The latter example may be contrasted with the former in this respect, that the quantity with which it deals—linear dimension—is continuous, not discrete. It follows that, in examples of the latter type, the data for the calculation of our constant are apt not to possess the perfection of which they are theoretically susceptible. We are usually given the number of men corresponding to each *degree* of height; but the scale is not finely graduated. For example, in the statistics just referred to the unit is *an inch*. In the copious statistics given by Dr. Baxter in the Report of the Sanitary Commission of the United States, the unit is *two inches*. To treat such *finite differences* as *differentials* may introduce error.

The cases which present this difficulty may be divided, according as we have, or have not, preliminary knowledge of the form or family of the curve whose radius of gyration is required. In the former case we may proceed by first reducing our imperfect data to the known form, and then calculating for the curve thus determined the radius of gyration. The second part of the operation is particularly easy in the case of most frequent occurrence, namely where the presumed

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* In this case the required constant must be elicited by Inverse Probability, as explained in my paper on Observations and Statistics (Cambridge Philosophical Journal) under the heading $\overline{f}$.

† *Cf.* Report of the Anthropometrical Commission of the British Association.

form is that of the *probability-curve.* For, in determining what member of this family our facility-curve is, we at the same time find its mean-square-of-error. Anthropometrical statistics exemplify this case. It is known by a copious induction that the height-measurements of a homogeneous population correspond to a probability-curve, or at least a Binomial (to use Mr. Galton's phrase) not materially different from that form. Take, for instance, Dr. Baxter's statistics referred to above and cited in full below. Prof. Unwin, to whom I submitted these figures, has by an elegant method found for the reduced curve,

$$y = 4770\ (1{\cdot}074)^{-x^2}.$$

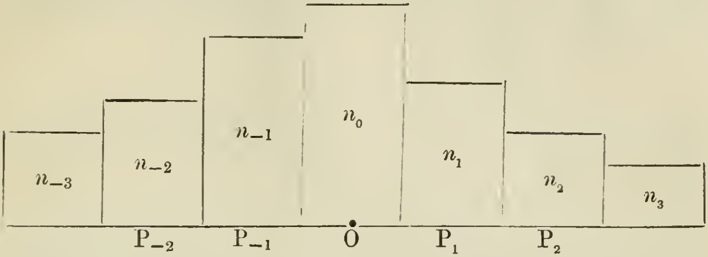
Identifying the right-hand member with the expression

$$\mathrm{N}\frac{1}{\sqrt{\pi}c}\,e^{-\frac{x^2}{c^2}},$$

where N is the total number of observations, namely 315,620, and c is the sought modulus, we find $c = 3{\cdot}7$ (inches), the same value which Signor Perozzo found for the ten Italian provinces, and which I have found for many other groups. Similarly, if we were given the mortality of a stationary population, not for each year of age but for periods of five years, as in the example given below, we might first construct a continuous curve from these imperfect data according to the hypothesis of Gompertz, and then find the radius of gyration for that curve.

When we have no previous knowledge of the form of the curve, the operation of quadrature becomes indeterminate. In this case it is proposed to proceed as follows:—What is required for the purpose in hand—the use of the Theory of Errors as an aid to Induction by the Elimination of Chance—is not so much an exact determination of the modulus, as a superior, but not very wide, limit. For, by using a modulus larger than the real one, we shall be on the safe side; we shall be underrating the evidence in favour of what is usually the *demonstrandum,* the proposition that some observed *écart* (as in the example cited from Laplace at the beginning of this paper) is due to law rather than chance. And, on the other hand, if our assumed constant is not very much larger than the real one, we shall not require a materially larger number of observations to get up to the same degree of evidence. In short, we do not want to conduct our reasoning along the very edge of fallacy, but rather to keep at a safe distance, without, however, having to make a laborious détour.

Such being our *quæsitum*, let us represent our imperfectly graduated data by the accompanying figure. The divisions



of the horizontal line correspond to the degrees employed in the given statistics—*e. g.* two inches in the case of Dr. Baxter's statistics—degrees usually, but not necessarily, equal. They are here at first supposed equal, each of length $2i$. The symbols n_0, n_1, n_{-1}, &c. represent the number of observations corresponding to each degree, *e. g.* the number of men between two heights differing by two inches. Let h_0, h_1, h_{-1} be the heights of the corresponding columns, so that $n = 2i \times h$. Take a point O at the middle (or, if it seem better, at one of the extremities) of the base of the highest compartment. The sum of the squares of errors measured from the real centre of gravity is less than the sum of squares of errors measured from any other point, in particular O. The latter quantity is less than what it becomes, if we suppose the observations in each of the compartments outside the central one to be disposed, not as, doubtless in fact, under a descending curve, but in a rectangle as represented in the figure. This quantity

$$= n_1 \, \mathrm{O\,P}_1^2 + n_2 \, \mathrm{O\,P}_2^2 + \text{ \&c.}, \; + n_{-1} \, \mathrm{O\,P}_{-1}^2 + \text{ \&c.},$$

(where P_1, P_2, P_{-1}, &c. bisect the bases of the corresponding compartments) $+ S\frac{2}{3}i^3h$ (exclusive of h_0) + the contribution of the central compartment. It remains to find a superior limit for the last term of this expression. Assuming, as we have done all along, that the curve with which we are concerned has only one maximum, we may be sure that the points at which the curve strikes the upright boundaries of the highest compartment are higher than h_1, the height of that one of its immediate neighbours which is lowest. The contents of the highest compartment then consist of a rectangle at least as high as h_1, surmounted by a figure which terminates in a cap (much like, but not in general so regular as, the vertical section of a conical rifle-ball. The contribution to the errors about O which the solid rectangle of height h_1 makes is $\frac{2}{3}i^3h_1$. The contribution of the remaining contents is a maximum, when they are all massed at a point as remote as possible from O, that is at one of the corners. The maximum contribution of the residue is then

$$i^2 \times \text{area of residue} = 2i^3(h_0 - h_1).$$

Hence, as a superior limit for the whole compartment, we have $2i^3(h_0 - \frac{2}{3}h_1)$. And as a superior limit of the sum of squares of error for the whole curve,

$$\mathrm{S\,OP}^2 \times h + \mathrm{S}\,\tfrac{2}{3}i^3h \text{ (inclusive of } h_0) + \tfrac{4}{3}i^3(h_0 - h_1).$$

This quantity must be divided by Sn, and multiplied by 2, in order to obtain a superior limit for the square of modulus-constant.

But what we require is not merely a superior limit, but one which is not very much superior. The value which we have found will possess this additional property, provided that the highest of the given compartments (h_0) is in the neighbourhood of the Greatest Ordinate of the real facility-curve with which we are concerned, and that the real Greatest Ordinate is in the neighbourhood of the real Centre of Gravity. For then the assumed centre of gravity will be in the neighbourhood of the real one. The first condition may be taken for granted. And there is reason to think that the second is very generally fulfilled. It is true of facility-curves which are of the *Probability* form, and that form is always tending to arise *in rerum naturâ*. It is true* of symmetrical Binomials, which, according to Mr. Galton, are very prevalent. It is true* also of unsymmetrical Binomials—a form which there is some reason for attributing to many of the unsymmetrical facility-curves which occur. For the hypotheses made by Mr. Galton with regard to symmetrical Binomials, *mutatis mutandis*, may, I think, be applied to the unsymmetrical species. Again, the simple hypothesis by which Quetelet and others have explained the rise of the Probability-curve, or infinite symmetrical Binomial, slightly † modified, will explain the rise of unsymmetrical Binomials.

So far, then, as Binomials, infinite or finite, symmetrical or unsymmetrical, prevail, our method is serviceable. For example, it is applicable to anthropometrical statistics; I have applied it to Dr. Baxter's statistics of human stature, above

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* See note to p. 320 of my paper "On the Law of Error" &c. in the last No. of this Journal.

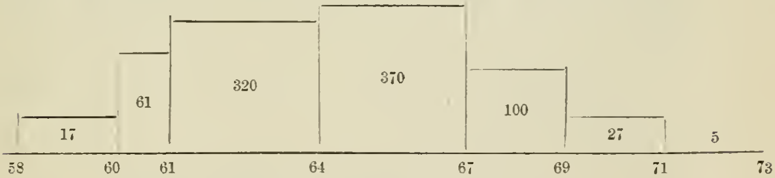
† A form of the modified hypothesis will be found at p. 317 of my paper on the Law of Error.

alluded to. Here the interval represented by our $2i$ is two inches, and the remaining data are :—

$n_1 = 64591,$ $n_{-1} = 76157,$
$n_2 = 25500,$ $n_{-2} = 36989,$
$n_3 = 6358,$ $n_{-3} = 9871,$
$n_{-4} = 1674,$
$n_0 = 94450,$
$Sn = 315620.$

Taking O as the centre of the highest compartment, I find, as a superior limit of the mean-square-of-error, 7·6. This is a very serviceable approximation, considering that the real value of this quantity (as given directly by Prof. Unwin's reduction, and indirectly from a copious anthropometrical experience) is 6·9. Instead of the real modulus 3·7, we have the assumed modulus 3·9. In employing the latter constant to investigate whether certain classes, *e. g.* savants or artizans, are materially taller or shorter than the general population, we shall neither overrate nor seriously underrate the evidence in favour of a significant distinction.

As an example of i variable, I have taken the following summary of anthropometrical observations, cited from M. Bodio by Dr. Baxter :—



Here the figures below the horizontal line represent inches of height*; the figures above the corresponding numbers of men. There are, for instance, 370 men whose height is between 64 and 67 inches. The total number of men is 1000. An inspection of the data suggests the advisability of taking O at the extreme left corner of the highest compartment. Employing the formula, *mutatis mutandis*, I find, as a superior limit for the assumed modulus, 4·2.

Our method requires modification when the Centre of Gravity and Greatest Ordinate are far from coinciding, as when the data assume the accompanying form. In this case it is

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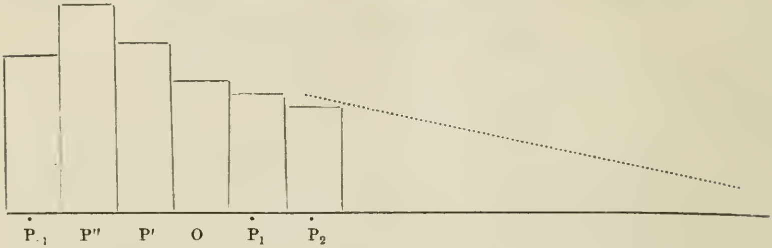
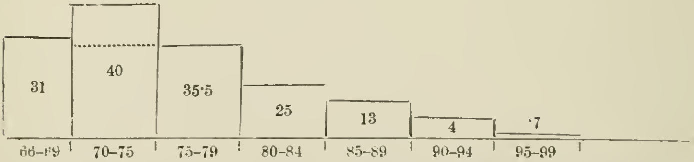
* It should be observed that in this and the preceding example the *bases* of the outmost compartments have not been given. I have assumed that they may be regarded as each equal to 2 inches.

best to take O in the neighbourhood of the apparent centre of gravity, that which is obtained from the unreduced discontinuous data. Between O and the highest compartment inclusive we must calculate superior limits for the contribution of each compartment upon the principle above employed for the highest compartment; and for the rest, proceed as before.



Suppose, for instance, we are given the number of deaths in each quinquennium after the age of 65 of a certain number of persons who have attained that age, the population being supposed stationary—in short, part of a very imperfect column d_x of a life-table. We want to know the constant which governs investigations like the following *:—The mean age-at-death of a certain number of total abstainers being less than the general mean, is the difference accidental or significant?



The accompanying figure represents an imperfectly graduated column d_x. Each of the divisions of the base-line corresponds to a quinquennium, except the one on the extreme left, which is limited to four years in order that the result may be compared with what I have elsewhere given, obtained by a more accurate calculation. The apparent centre of gravity occurs in the third compartment, corresponding to the period 75–79. I take for O the left corner of that compartment, and for the unit of length one of the equal divisions of the abscissa. Here $h_1 = 35·5$; $h_2 = \frac{5}{4}\,31$, is a little larger. Hence the maximum distribution is afforded by supposing the highest com-

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* See my paper on "Methods of Determining Rates," Journal of Statistical Society, Jan. 1866.

partment full up to the height of the next compartment, as shown by the dotted line in the figure; and the rest of the contents of the highest compartment massed at its left corner. The quantity SOP^2n is

$$\tfrac{1}{4}(2\times 35{\cdot}5)+\tfrac{9}{4}(31+25)+\tfrac{25}{4}\times 13+\tfrac{49}{4}\times 4+\tfrac{81}{4}\times {\cdot}7=288.$$

To this is to be added $S\,\frac{2}{3}\,\frac{1}{8}h$ (35·5 being substituted for h_0)

$$=\tfrac{1}{12}(Sn-4{\cdot}5)=\tfrac{1}{12}\,145=12.$$

Lastly, there is to be added the contribution of the upper layer of the highest compartment on the most unfavourable supposition; $=4{\cdot}5$. Thus the limit of the sum of the squares of error is 305. This is to be divided by Sn for the modulus-constant. The result is 2·04. This must be multiplied by 5^2 for the mean-square-of-error in terms of a *single year*; and again by 2 for the modulus-constant. The result is 102. By a more accurate calculation, founded upon the discrete column d_x, from which the above data were compressed, I found for the corresponding constant 90. We have therefore a very serviceable approximation. The method may be extended to cases where the facility-curve has more than one maximum.

In conclusion, it may be observed that the procedure which has been indicated is appropriate also to cases where a more exact determination of the constant is theoretically possible. The rough-and-ready method is sufficiently accurate for the purposes of statistical induction. It is therefore the most serviceable method whenever it is the most convenient.

LXX. *Notices respecting New Books.*

Select Methods in Chemical Analysis (chiefly Inorganic). By WILLIAM CROOKES, *F.R.S.*, *V.P.C.S.* Second Edition. London: Longmans, 1886. Demy 8vo; pp. xxii and 725.

IF it were allowable for a science to be provided with a motto, "*Crescit eundo*" might well be that of Chemistry. In the early years of this century, a single treatise of somewhat modest dimensions was sufficiently large to "carry all we knew"; but modern chemistry has as many departments, and is as varied in its applications, as modern mathematics. Two journals, indeed, are devoted exclusively to analysis,—a department which also occupies a prominent place in many others.

The 'Chemical News,' of which Mr. Crookes is Editor, has for many years past reserved a portion of its pages for abstracts of papers in foreign chemical periodicals. These abstracts refer in many cases to new or modified analytical methods; and it fortunately occurred to Mr. Crookes that a selection of the best of these—proved to be the best by actual trial in his own laboratory—would be of service to chemists generally. The first edition, accordingly, of 'Select Methods' appeared in 1871; and, after an interval of fifteen years, we are now presented with its much enlarged successor. It need hardly be said that this, the second edition, has been to a great extent rewritten; and the distinguished compiler of the work still continues to vouch personally for the value of the processes he describes. Few chemists, probably, would be disposed to undertake such a laborious task of literary filtration; and Mr. Crookes undoubtedly deserves the thanks of all his confrères for a sustained effort, unique in the history of this science. On the other hand, the scheme is, from its very nature, tinctured with some disadvantage. Some methods, not less efficient than those here selected, must have been passed over from sheer lack of opportunity to try them; others,—omitted as "universally known," "untrustworthy," or "doubtful,"—might (legitimately perhaps) have been inserted by a second author, also possessed of competent ability. And so deeply is this stamp of a personal judgment impressed upon the work, that it lies almost without the province of logical review. When an able analyst has, after experiment, stated his opinion of a given process, the attitude of others must long continue to be one of simple receptivity.

The general features of the first edition will be found to characterize the second. There is the same perfectly just stress laid on the inclusion of "rare" elements (after all, not rare); the same range through the various departments of gravimetric and volumetric analysis (including that of gases) and what is known as "technical" analysis. Volumetric processes no longer (excepting for gases) occupy a separate chapter; this is a distinct systematic improvement. There is a separate section devoted to "New Processes and General Methods of Manipulation"; and the "Useful Tables" are naturally more numerous than previously.

The special aspects of Mr. Crookes's work would require more space than we have at our disposal for their complete summary; a few comments will, however, suffice. The order mainly observed is:—(1) lighter metals, (2) heavier metals, (3) metalloids. Take *Potassium*. Under this heading, ten or eleven new methods or modifications are adduced as meeting various conditions. Much stress is laid on the platino-chloride process and the limits of its accuracy, an abstract being given of the Report of the British Association's Committee upon this subject. It would have been an advantage here to have given some simple plan for obtaining a platinum solution free from iridium. To the chapter on *Sodium* little has been added; indeed, there has been little to add. A good direct gravimetric method for estimating sodium is still a desideratum. There is a good deal of new matter under *Magnesium*. The intricate topic of the *Cerium Metals* receives very ample treatment, as might have been expected from the Author's special acquaintance with the subject. Here the reader will find the process of fractional precipitation duly in prominence, and may form a fair estimate of the work that lies before him if he essays their separation. Since this chapter was written, much doubt has been thrown upon the homogeneousness of Didymium. Samarium is, of course, a new feature here; and Thorium is an additional entry. Under *Glucinum* we wish it could have been possible to say something of Mr. Greville Williams's experiments. The detailed exposition of Mr. Crookes's own researches on the detection and wide distribution of *Yttrium* is extremely interesting, and constitutes an admirable guide for a young investigator. Other rare earth-metals are referred to in considerable detail, none in fact being omitted. One can hardly read the account of *Titanium* and *Zirconium* without seeing that pure compounds of the former metal can hardly have been yet prepared. The results of Pierre and Thorpe as to the combining weight of the former element are hopelessly discordant, and yet, on the face of them, equally trustworthy. The volumetric estimation of *Chromic Acid* by adding an iodide and hydric chloride is liable to considerable error if allowed to consume "a few hours," as stated in the text. The reviewer uses strong hydrochloric acid diluted with an equal bulk of water and heated to 50°: titration can then be proceeded with at once. Manganese ores can be valued in the same way, after a contact seldom exceeding 15 minutes. The whole section on *Iron* (nearly 90 pages) is admirably written, the requirements of technologists being evidently borne well in mind. Here the Author appears to us to have been adding and selecting at his best. The entire chapter deserves the most careful perusal. As regards Eggertz's method, we have always considered its weak point to be the dilution, which necessarily affects the constitution of all liquids, and may be the source of grave error. The best colorimeter to employ in this case is one of the forms for which dilution is not necessarily required. Clark's method of analyzing chrome-iron ore is certainly the best. Many of the failures in analyzing this ore are not the fault of any particular method, but of overheating. In the separation of *Cobalt* from *Nickel*, it would have been an advantage if Gibbs's simple and perfectly accurate plan of boiling the aqueous sulphates with plumbic peroxide could have been inserted. As regards *Copper*, we could wish the volumetric cyanide process were a thing of the past. *Sulphur* in pyrites has been the *béte noire* of many analysts. Mr. Crookes commends Pearson's method, which is doubtless the best; the reviewer, however, prefers to carry out the early stages of the attack at 30°–40°, not at 100°. It is curious that Nakamura's method should fail for pyrites. We are glad to see Gibbs's elegant phosphate process given for *Manganese*. Few analysts practise it; but we hope Mr. Crookes's description may induce many to use it habitually. We have nothing but praise for the section on *Gas Analysis*, which is quite full enough, though succinctly written. In the *Tables*, we could have wished that Captain Clarke's figures had been employed as the basis of metric equivalence.

Some omissions ought perhaps to be noticed. In our opinion, a future edition might advantageously contain more copious reference to colorimetric methods. These (though it is true they have a probable error of about 2 per cent. per single determination) are nevertheless quite accurate enough in numerous cases, and particularly for small quantities. The subject also of probable error is a vital one in connection with accurate measurement. It would be a great advantage to state the principal formulæ required in quantitative investigation. Though given in Merriman's and Airy's special treatises and in Clarke's Recalculation of the Atomic Weights, they are not yet easily accessible to chemical inquirers. Occasionally, also, the reader is desirous of forming an independent judgment, and referring to an original memoir on a particular process. It is much to be desired that in a future edition full references be given.

Any one who, like ourselves, has made a careful perusal of Mr. Crookes's 'Select Methods,' has before him the necessary data for answering the question, What are the general characteristics of a good analytical process? If, however, he should be inclined to ask, "What is the general method of analytical discovery?" the answer must be sought elsewhere. Laboratory work, laboratory tradition, chemical environment, and a native chemical mind are the necessary factors of a reply. But the idea of the 'Select Methods' will be always at hand; and the volume itself will remain, as we have said, unique in the history of chemical science.

Fourth Annual Report of the United States Geological Survey, for 1882–83. *By* J. W. Powell, *Director*. 4to. Pages i–xxxii and 1–473, with 48 maps and plates. Washington, 1884.

The Director's Report and the Reports from the Heads of Departments give general and in some respects special information as to work and progress in the topographical, geological, palæontological, chemical, and statistical branches of this extensive and well-conducted Geological Survey. Plate I. indicates the extent of work already done. The "Accompanying Papers" in this fine volume are of great interest in many aspects,—the geographer, miner, palæontologist, and geologist finding useful matter to hand, Capt. C. E. Dutton gives a full and richly illustrated account of the Hawaiian Volcanoes (pp. 81–219, with 29 maps and plates). Chapter XI., on "the Volcanic Problem," carefully thought out, is very suggestive. An "Abstract of a Report on the Mining Geology of the Eureka District, Nevada," by Mr. J. S. Curtis (pages 225–251, with 3 plates of sections), comes next. The ores and their position in Prospect Mountain and its spurs (Ruby Hill in particular) are treated of practically as to their occurrence and hypothetically as to their sources and origin, whether as sulphurets, oxides, carbonates, &c., or in a metallic state—the various ores of lead, zinc, and iron, with silver and gold, being the subjects of remark.

Mr. Albert Williams, Jun., supplies a concise article on "Popular

Fallacies regarding Precious-metal Ore-deposits" (pages 257–271). This controverts some of the many prejudices held by "the practical miner," such as "against certain formations and in favour of others," arising from unfavourable results in some local workings, or *vice versâ*, unchecked by subsequent experience. Also against mines having unusually rich ores, in some instances,—for or against veins with certain strikes, and other circumstances, particularly as to the "appearance of ores." A hopeful view of advance in mining knowledge with both miners and geologists is held in this Report.

The next memoir is "a Review of the Fossil Ostreidæ of North America; and a Comparison of the fossil with the living forms; by C. A. White, M.D., with Appendices by Prof. A. Heilprin and Mr. J. A. Ryder" (pages 273–430, including 39 plates of the fossil and 10 of the recent Oysters of North America). Dr. White treats of the group generally, and of the successional forms of *Ostrea* and its immediate allies, from the Carboniferous to the Cretaceous, inclusive. Prof. Heilprin notices the Tertiary species; and Mr. Ryder supplies an account of the life-history of the Oyster as known in the living state in North America. "A Geological Reconnaissance in Southern Oregon," by Mr. I. C. Russell (pp. 431–464, with 3 plates and 10 woodcuts of maps, sections, &c.), is more particularly interesting as showing the extent and changes of the great lake-system of that country, and the immediate relationship of the faults and displacements of strata to the water-areas of the several valleys at successive periods, and of the climatic oscillations during their history.

A good Index enhances the value of this useful volume.

"*Photo-relief*" *Maps*, published by the Society for Promoting Christian Knowledge: London.

We have received specimens of a series of the Relief-maps to be issued as "photo-lithograph." This new adaptation of relief-maps, photographed from models, to education, as an aid in realizing the surface-configuration of a country, will, we think, be largely appreciated by both teachers and students, especially as the maps are published at a low cost. Looking at the specimens before us,—those of a map of Scotland, which has the slight defect of too even a shore-line for the West Coast,—we are forcibly impressed by the valley-systems as a leading feature, and are reminded of the immense denudation which, during terrestrial history, has carved out the surface, and left us the hills as vestiges of the old land. The relative positions of watersheds, and of the tracks of roads and canals, and the sites of battles, as well as of early occupation, are hereby readily recognized and their reasons understood. These maps are to be issued in three forms:—(1) Plain, with the physical configuration only, besides parellels of latitude and longitude and sites of some chief towns. (2) In addition, the names of the chief mountains, rivers, towns, &c., and the divisions of counties. (3) In addition, the counties marked out with colours. The vertical scale, being six times that of the horizontal, exaggerates the heights; but the relative altitudes of the mountains are preserved. The further issue of this series will be a great aid to both geographer and geologist; and to the meteorologist these maps will facilitate the study of rainfall and other phenomena.

LXXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 449.]

April 7, 1886.—Prof. J. W. Judd, F.R.S., President, in the Chair.

THE following communications were read:—

1. "On Glacial Shell-beds in British Columbia." By G. W. Lamplugh, Esq.

This paper was divided into two parts, relating respectively to Vancouver Island and the Fraser Valley. Having to spend nearly a month at the city of Victoria in 1884, the author had leisure for the investigation of the geological features of the district, but he expressed his regret that, at the time, he was unacquainted with the publications of Mr. Bauerman and Dr. Dawson on the subject.

The most important shell-beds were disclosed in an excavation for a dry dock at Esquimault, V.I. Here a fissure in an igneous rock had been filled in by glacial beds. Shells were most numerous on the north side of the dock in Boulder-clay, associated with irregular sandy seams, the whole being softer than the general mass. The containing rock was not glaciated at this point. *Leda*, *Nucula*, *Cardium*, *Tellina*, *Mya*, and *Saxicava* are the principal genera.

There was great difference in the state of preservation according to position; the shells below the waterline being remarkably fresh, while acidulous waters, engendered by vegetable decay, had attacked the upper portions.

The author concludes that the whole mass of drift, including the shells, had been pushed up by ice in its passage southwards. The general mode of occurrence was very similar to that at Bridlington. He further observed that the rocks were not striated in the first instance by these shelly clays, but he believed the glaciation to have taken place through the action of harder substances, and that afterwards a milder term set in, when an arctic fauna established itself in the neighbourhood, after which fresh ice pushed the sea-bottom along with other accumulations into its present position.

The shell-beds in the Fraser Valley are about 100 feet above sea-level. Three sections of glacial beds were given. The stratified clay in which the shells were found contains no pebbles, and, though somewhat disturbed, has evidently been deposited where it now occurs.

2. "On a Lower Jaw of *Machærodus* from the 'Forest-Bed,' Kessingland." By James Backhouse, Esq., F.G.S.

3. "A contribution to the History of the Cetacea of the Norfolk 'Forest-Bed.'" By E. Tulley Newton, Esq., F.G.S.

April 21.—Prof. J. W. Judd, F.R.S., President, in the Chair.

The following communications were read:—

1. "On a certain Fossiliferous Pebble-band in the 'Olive group' of the Eastern Salt Range, Punjab." By A. B. Wynne, Esq., F.G.S.

The principal object of this paper was to oppose the views recently published by Dr. Waagen as to the age of certain boulder-beds in the Salt Range of the Punjab. By that author these beds had been considered contemporaneous with each other, and assigned to the epoch of the Coal-measures, in consequence of the discovery by Dr. H. Warth of carboniferous fossils, especially Australian forms of *Conularia*, in nodules restricted to a particular layer in the upper part of a boulder-bed in the eastern Salt Range. Mr. Wynne adduced evidence to show that the fossils in question occur, not in concretions, as supposed by Dr. Waagen, but in pebbles evidently derived from an older series; and consequently there was no proof that the boulder-bed in question was older than the Cretaceous Olive beds with which it had hitherto been associated.

The principal boulder-beds in the Salt Range were then briefly noticed; those beneath the Carboniferous Limestone west of the Indus, those near Amb and Sakesir peak, associated with the "purple sandstone," "*Obolus*-beds," and "speckled sandstone," and those in the eastern portion of the Salt Range, amongst the beds of the "Salt pseudomorph zone" and "Olive group," being successively passed in review, and their relations to overlying and underlying strata explained. It was shown that boulder-beds and conglomerates containing pebbles and boulders of the same crystalline rocks are not confined to one horizon.

In conclusion, the resemblance of the rock, of which the pebbles containing *Conulariæ* &c. were formed, to that forming some of the "magnesian sandstone" and "*Obolus*-beds" was pointed out, and it was suggested that the pebbles in question may have been derived from representatives of those beds formerly existing to the southward.

2. "On the Phosphatic Beds in the neighbourhood of Mons." By M. F. L. Cornet, For. Corr. G.S.

These beds are situate in the province of Hainault, near the town of Mons (Belgium); the workings have increased of late years, and in 1884 yielded 85,000 tons of phosphate.

They occur in the Upper Cretaceous, which is exceptionally well developed in the district, filling a trough in the Carboniferous rocks, and itself denuded for the reception of Tertiary and Quaternary beds.

Omitting all Cretaceous groups below the middle of the fifth stage, the following is the sequence of the Cretaceous beds which contain the phosphatic series :—

C. Tufaceous Chalk of Ciply, with the Poudingue de la Malogne at its base.
D. *Brown Phosphatic Chalk of Ciply.*
E. Coarse Chalk of Spiennes.
F′. White Chalk of Nouvelles.

F is a pure white chalk with some flints and containing *Belemnitella mucronata*, *Rhynchonella octoplicata*, *Terebratula carnea*, *Ananchytes ovatus*, &c.—an horizon well known throughout North-western Europe. Series F and F′ represent one geological horizon characterized by *Ostrææ*, Brachiopoda, &c. in great numbers, but also containing *Belemnitella mucronata*, and lying between two distinct planes of erosion.

The Lower Phosphatic Chalk (D), which forms the upper division of the series, is about 70 feet thick, and may be described as consisting of three parts; the upper is tolerably pure carbonate of lime, but in its lower portion becomes charged with brown granules mainly consisting of phosphate of lime; these continue to increase towards the central or main phosphatic mass, which is also highly fossiliferous in places. This central portion constitutes the main phosphatic beds, but the amount of phosphoric acid (dry) is not more than 12 per cent.

Hence, it is necessary to increase the richness in phosphate of the deposit in order that it may be available for conversion into a superphosphate. This may be done by mechanical means.

But nature has already partially anticipated this process, and the result has been a deposit known as "rich phosphate," containing about 25 per cent. of phosphoric acid. This occurs in wide cracks and holes in the ordinary phosphatic chalk. It usually occurs as a fine sand-like powder, and is evidently the result of the action of carbonated waters upon the phosphatic chalk, whereby the amount of carbonate of lime is reduced. This is especially the case where the phosphatic chalk is not protected by the tufaceous chalk of Ciply, but is only covered by Tertiary or Quaternary beds.

The author calculates that each square foot of the phosphatic basin, which he estimates approximately at 5 miles by 3, contains 355 lb. of tribasic phosphate of lime. Finally he intimates how the phosphatization of the chalk may have been brought about.

LXXII. *Intelligence and Miscellaneous Articles.*

ON MAGNETIZATION. BY M. MASCART.

WHEN an isotropic and feebly magnetic substance is placed in a uniform field, it acquires a magnetization parallel to the field, and its coefficient of magnetization is the ratio of the magnetic moment for unit volume, or intensity of magnetization, to the intensity of the field.

With highly magnetic substances, on the contrary, such as iron, nickel, cobalt, the reaction due to the induced magnetism must be allowed for, and the preceding definition is only applicable for infinitely long cylinders magnetized longitudinally or for closed rings.

The calculation of the magnetizing force as a function of the external field is very simple in the case of the sphere or the ellipsoid, or of an infinitely long cylinder magnetized transversely; but except in the case of very elongated ellipsoids, the coefficient of magnetization may vary within very extensive limits without the magnetic moment of the body being sensibly modified. The slightest want of homogeneity has in that case a considerable influence.

The coefficient of magnetization is often determined by using cylinders arranged parallel to the field, and which are assimilated to infinite cylinders, or to ellipsoids of the same length and the same median section; the magnetic moment is then measured, or the discharge, induced in a coil surrounding the central section, when the magnetization is reversed. With rings, induced charges can alone be used, and the coefficients of magnetization are generally found too high. It may then be asked if one of the methods is at fault; and if, for instance, a special phenomenon is produced in the case of closed rings which exaggerates the effects of induction. In order to solve this question, I used with the same metal closed rings, and a series of cylinders in which the ratio of the length to the diameter varied within very wide limits.

The cylinders were placed in the axis of a cylindrical coil of 1·20 metre in length, and 0·03 metre in diameter, so that the internal field of the current may be considered as sensibly uniform over a length of more than 0·80 metre. This coil was at right angles to the magnetic meridian, and its action on an adjacent declinometer was compensated by that of an external coil. The magnetic moment of the cylinder is deduced from the deflection produced in the declinometer. Further, a coil of several turns, wound on the mean portion of the magnetized cylinder, was connected with a ballistic galvanometer, and the induced charge produced by the inversion of the magnetization, eliminating the effect produced by the field itself.

The measurement of the magnetic moment by the deflection of the declinometer requires in strictness that the position of the poles be known, or at any rate that the experiments be made at two different distances so as to eliminate the factor of correction; but with very narrow cylinders, Coulomb's rules furnish a sufficient approximation for the degree of exactitude I had in view. Finally, the field F of the magnetizing coil is determined by the intensity I of the current, and the number n of turns of the wire for unit length,

$$F=4\pi n_1 I.$$

The quotient of the magnetic moment M of the cylinder by its volume V gives the mean intensity of magnetization A, and we may denote as the mean coefficient of magnetization,

$$f=\frac{A}{F}=\frac{M}{4\pi n_1 IV}.$$

On the other hand, if S is the section of the cylinder, A the intensity of magnetization in the median region, F the action of the magnetism induced in this region, p the number of turns of the small coil, R the resistance of the circuit of which it forms part, and Q the discharge induced by the reversal of the magnetization, we have

$$QR=2pS(4\pi A_1-F_1)=8p\pi S\left(A-\frac{F_1}{4\pi}\right).$$

Putting

$$f_1=\frac{1}{F}\left(A_1-\frac{F_1}{4\pi}\right),$$

we shall obtain by experiment two mean coefficients f and f_1 which have slightly different significations.

Experiment shows in the first place that we have always $f^1>f$. These two quantities, which are very different for short cylinders, approximate more and more, and this ratio tends to unity as the length of the cylinder increases. At the same time, the greatest values of the coefficients f and f_1 correspond to fields which are gradually weaker. Lastly, the values of f and of f_1 furnished by very long cylinders are equal to the coefficient k given by closed rings.

With the iron which I used, when the ratio of the length to the diameter varied from 40 to 500 or 600, the maximum value of the coefficients f or f_1 varied from 25 to 190, or from 40 to 220, while the corresponding fields diminished from 20 to 25 C.G.S. units to 3 units; the same wires used as rings gave for the maximum of the coefficient k, a value of about 200 with a field of 3 units. The agreement of these results is sufficient, if we allow for the difficulty of obtaining specimens which are identical.

The method of cylinders, provided their length is at least 500 times the diameter, is then equivalent to that of the rings; it has this advantage, that we can ascertain at any moment the real magnetic condition of the metal, and demagnetize it so as to subject it to fresh tests.

The mean coefficient of magnetization diminishes very rapidly with the ratio λ of the length of the cylinder to its diameter, and soon becomes of the same order as the coefficient f_1, relative to the transverse magnetization. Further, the magnetization is proportional to the intensity of the external field, within much more extended limits.

By forming short cylinders with packets of the same iron wire as before, we have obtained as mean values in fields of 1 to 10 units:

λ.	f.	f_1
12·3	3·40	0·13
7·5	1·90	0·14
5·0	1·20	0·14
3·3	0·73	0·14

Rectangular bars of soft iron gave in like manner for the mean coefficients of magnetization f, f_1, f_2, parallel to the three edges:—

Dimensions.					
c.	c.	c.	f.	f_1.	f_2.
9	1	1	2·0	0·15	..
9	2	1	1·34	0·22	0·10
9	2	2	0·88	0·15	..
9	3	2	0·72	0·20	0·13

Theory shows that in the case of infinitely long cylinders the coefficient f for transverse magnetization is expressed by

$$\frac{k}{1+2\pi k}=\frac{1}{2\pi\left(1+\frac{1}{2\pi k}\right)}=\frac{0{\cdot}159}{1+\frac{1}{2\pi k}},$$

and should be below 0·159; it will be seen that experiment gives values near this limit, even with very short cylinders.

A knowledge of these coefficients of magnetization is of particular interest, as furnishing a correct means of calculating the effect of the magnetization induced by the Earth in a magnetized bar, in observations relative to the absolute measurement of the terrestrial field.

More generally, when a body is isotropic and of any given form, there are three rectangular directions for which the magnetization is parallel to the external field, with different coefficients f, f_1, and f_2; these coefficients have the same properties as the coefficients of magnetization of a feebly magnetic anisotropic substance.

Suppose, for instance, that $f>f_1$ and that the body is movable about an axis parallel to the direction f_2 in a field whose component perpendicular to this axis is H. If V is the volume of the body and the angle of the field with the direction f, the moment of the couple due to the action of the field is

$$C=V\,(f-f_1)\,H^2 \sin \alpha \cos \alpha.$$

It is readily seen that magnetization may be regarded as the superposition of two other magnetizations—the one constant, $f_1 H_1$, parallel to the field and producing no couple; the other, $(f-f_1)$ H cos α, connected with the body, and parallel to the direction of greatest magnetization. This latter is sensibly constant for feeble deflections.

This is the case of a magnet which oscillates under the influence of the Earth. If we take into account the induced magnetization, we should strictly add to the rigid magnetization a magnetization in the same direction $(f-f_1)$ H proportional to the difference of the longitudinal and transverse coefficients.

We may add that for steel the mean coefficient of longitudinal magnetization is much weaker than for soft iron, which greatly tends to increase the importance of transverse magnetization.—*Comptes Rendus*, May 5, 1886.

ON AN INSTRUMENT FOR REPRODUCING AN INVARIABLE QUANTITY OF ELECTRICITY. BY M. MARCEL DEPREZ.

The object of this instrument is to reproduce readily and under any given conditions of temperature and pressure the unit quantity of electricity which is known as a *Coulomb.*

It consists of a U-tube the two limbs of which end in glass bulbs the volume of which is far greater than that of the cylindrical parts, the whole being hermetically sealed. One of the bulbs and the corresponding limb is completely filled with water acidulated by phosphoric acid; in the other limb it is filled with air at a definite pressure as well as the bulb in which it ends. In the branch filled with liquid are four platinum wires facing each other in pairs, two at the top of the bulb and two others in the cylindrical part a little below the lowest point of the bulb. If an electrical current is passed through these latter, water is decomposed, and the detonating gas arising from this decomposition accumulates in the upper bulb, while the liquid driven into the second limb ascends in this, compressing the air in the second bulb. If we take care to note the point of departure of the column of liquid in the second limb, which is divided into parts of equal capacity, as well as the point at which it stops when the current is suppressed, we have all the elements necessary for knowing the quantity of electricity expended in producing the detonating mixture. It is readily seen that, if the volume of this liquid measured by the rise of the liquid in the second limb is constantly the same, the quantity of electricity necessary to produce it will be always the same, and that also whatever be the temperature of the instrument, provided it is the same in both limbs—a condition which is easily realized. The barometric pressure and the hygrometric state of the air clearly do not affect the results, for the apparatus is hermetically sealed. Finally, as the liquid is always the same, we can reproduce by this instrument at any time a quantity of gas corresponding to an invariable quantity of electricity taken as standard, the whole operation resolving itself into reading a volume which is always the same, without *the necessity of any correction,* while with the ordinary voltameter the corrections for temperature, pressure, and the tension of vapour are far from being negligible.

In order that the instrument may be used over and over again, the water decomposed must be re-formed at each operation; this is the object of the platinum wires at the top of the bulb where the detonating gas accumulates. When a spark is passed, the gases reunite, the acidulated water again fills the bulb, and the instrument is ready for a new operation. The apparatus may be made more or less sensitive by filling it before sealing with air below the atmospheric pressure.—*Comptes Rendus*, March 22, 1886.

EXPERIMENTS IN THERMOELECTRICITY.

BY MM. PILLEUR AND E. JANNETAZ.

We have endeavoured to ascertain if, when we heat a given point of a conductor having a schistous texture, thermoelectric currents are produced in it.

Our experiments extended to zinc, tin, iron, and copper. The schistous or long-grain texture was imparted to them by carefully drawing them out, an operation performed under our superintendence in the workshops of M. Pirot.

A point A at the centre of the plate is heated and one contact is made on the other side of the plate, at the end of the line which connects this point with A *across the long grain*, the other taken at a point C on the end of the line joining the point A *along the long grain.*

In all cases a current was obtained from B to C. The strength of the current for the same metal appeared connected with the development of the *long grain.* Thus, that zinc which had passed four times through the draw-plate gave a feebler current than zinc which had been drawn out six times. But copper with a good deal of long grain, that is much more fragile in one direction than another, gave a feebler current than tin, which seemed to have no appreciable grain. It must moreover be observed that this tin had passed six times through the plate; hence the thermoelectric action shows the action of the draw-plate, even when the fracture does not show it.

The strongest currents were shown by zinc, and the feeblest by copper.

The currents are, however, difficult to observe, doubtless owing to the facility with which they unite across the plates themselves; more powerful effects may be obtained by cutting a knee-piece in the metal plate, in one branch of which the long grain is across and in the other in the direction of the length, and then joining the two ends of the knee-piece to the external circuit.—*Journal de Physique*, April 1886.

ON THE ORIGIN AND THE LAWS OF ATMOSPHERIC ELECTRICITY.

BY PROF. FRANZ EXNER.

After a critical historical discussion of previous theories, the author communicates the results of his experiments on this subject, which have extended over several years. They refer chiefly to an examination of the electrical field of the earth under *normal* atmospheric conditions. It has appeared that the equipotential surfaces are continually as if the Earth had a negative charge. Over a plane the fall of potential is always linear, and its absolute value is constant if the condition of the atmosphere does not change. Such changes are due to the greater or less quantity of aqueous vapour in the air, for this leaves the Earth charged with negative electricity.

The greatest fall of potential amounts to 600 volts per metre in the complete absence of aqueous vapour, and sinks to below 100 volts in the height of summer. These numbers hold, however, only for continuous fine weather. A measurement of the fall of potential in summer at great heights, by means of air-balloons, has proved that this increases considerably with the height; that is, that aqueous vapour in air is really negative.

All the phenomena of negative electricity are completely explained on the assumption already made by Peltier that the Earth contains a negative charge. Starting from Franklin's theory, this charge appears as a necessary consequence of the gradual formation of the Earth, and would correspond to an excess of electricity above the normal amount. Bodies which are in the condition last named would thus appear negatively electrified. From the magnitude of the fall of potential at the surface of the Earth, the absolute potential of the Earth may be determined. This is found to be $= -4 \cdot 10^9$ volt; that is to say, a point in space which is infinitely distant from all electrical masses has a potential which is $4 \cdot 10^9$ volts higher than that of the Earth. The repulsive force which is exerted by the charge of the Earth on a square centimetre of surface is equal to $16 \cdot 10^{-9}$ grams, and is thus extremely small.— *Sitzungsberichte der kaiserlichen Akademie der Wissenschaften in Wien*, February 1886.

INDEX TO VOL. XXI.

END OF THE TWENTY-FIRST VOLUME.

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