XVII. *On the Electro-chemical Equivalent of Silver, and on the Absolute Electromotive Force of* Clark *Cells.*

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[Plate 17.]

§ 1. In former communications* to the Royal Society we have investigated the absolute unit of electrical resistance, and have expressed it in terms of the B.A. unit and of a column of mercury at 0° of known dimensions. The complete solution of the problem of absolute electrical measurement involves, however, a second determination, similar in kind, but quite independent of the first. In addition to resistance, we require to know some other electrical quantity, such as current or electromotive force. So far as we are aware, all the methods employed for this purpose define, in the first instance, an electrical current; but as a current cannot, like a resistance, be embodied in any material standard for future use, the result of the measurement must be recorded in terms of some effect. Thus, several observers have determined the quantity of silver deposited, or the quantity of water decomposed, by the passage of a known current for a known time. In this case the definition relates not so much to electric current as to electric quantity. A more direct definition of the unit current, and one which may perhaps be of practical service for the measurement of strong currents of 50 ampères or more, would be in terms of the rotation of the plane of polarisation of sodium light, which traverses a long column of bisulphide of carbon enveloped by the current a given number of times.†

Other observers have expressed their results as a measurement of the electromotive force of a standard galvanic cell. In this case it is necessary to assume a knowledge of resistances. The known current in passing a known resistance gives rise to a known electromotive force, which is compared with that of the cell.

In the present communication are detailed the experiments that we have made to determine the electro-chemical equivalent of silver, and the electromotive force of standard Clark cells. As regards the choice of *silver* there is not much room for a difference of opinion. The difficulties to be overcome in the use of a water voltameter are much greater. *Copper* is, indeed, employed in ordinary laboratory practice

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* Proc., Ap. 12, 1881; Phil. Trans., 1882, Part II.; and 1883, Part I.

† See Camb. Phil. Proc., Nov. 26, 1883.

and for commercial purposes; but it is decidedly inferior to silver, both on account of its tendency to oxidise when heated in the air, and also because it changes weight in contact with copper sulphate solution without the passage of an electric current. Dr. GORE[*] has made observations upon this subject, and our own experience has shown that no constancy of weight is to be found under these circumstances. Silver, on the other hand, seems to be entirely unaffected by contact with neutral solution of the nitrate.

§ 2. The readiest method of measuring currents is, perhaps, that followed by KOHLRAUSCH, both in his earlier[†] and in his recent[‡] work upon this subject, viz., to refer the current to the earth's horizontal magnetic intensity (H) with an absolute galvanometer. The constant of the galvanometer is readily found from the data of construction with the necessary accuracy, and there is no doubt that in a well-equipped magnetic observatory the method is satisfactory. But the determination of H is no such easy matter, and its continual fluctuations must be registered by an auxiliary instrument. Many of the results obtained in past years do not appear to be very trustworthy, though KOHLRAUSCH and WILD, who has discussed the sources of error in an elaborate manner, are of opinion that a high degree of accuracy is attainable. When, however, a current determination is the only object, the exclusion of this element seems to be desirable, except for rough purposes, when a sufficiently accurate value of H can be assigned without special experiment.

§ 3. Of the arrangements which may be adopted for measuring the mechanical action between a fixed and a mobile conductor conveying the same current, the one that is best known is WEBER's electro-dynamometer.[§] Two fixed coils may be arranged on HELMHOLTZ's principle, so as to give at the centre a very uniform field of force, in which the movable coil is suspended bifilarly. In the equilibrium position the planes of the coils are perpendicular, but under the influence of the current they tend to become parallel, and the deflection produced may be taken as a measure of the square of the current. The constant of the instrument, so far as dependent upon the dimensions of the large coils, can be readily determined; the difficulty is to measure with sufficient accuracy the dimensions of the small coil, and to determine the force of restitution corresponding to a given rotation. The latter element is usually obtained indirectly from the moment of inertia of the suspended parts and from the time of vibration. If the small coil contain a large number of turns in several layers, its constant is very difficult to determine by direct measurement. If, indeed, we could trust to the inextensibility of the wire, as some experimenters have thought themselves able to do, the mean radius could be accurately deduced from the total length of wire, and from the number of turns; but actual trial has convinced us that fine

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[*] 'Nature,' Feb. 1, 1883, Feb. 15, 1883.

[†] POGG. Ann., Bd. cxlix., S. 170, 1873.

[‡] Ber. der Phys.—Med. Ges. zu Würzburg, 1884.

[§] MAXWELL's 'Electricity,' § 725.

wire stretches very appreciably under the tension necessary for winding a coil satisfactorily. It is possible that the difficulty might be satisfactorily met by an electrical determination of the area of the windings after the method given by MAXWELL,[*] or that employed in the present investigation.

§ 4. In the researches of JOULE and CAZIN the electromagnetic action is a simple attraction or repulsion, and can be evaluated directly by balancing it against known weights. This method has been followed by MASCART in his recent important work upon this subject.[†] A long solenoid is suspended vertically in the balance, and is acted upon by a flat coaxal coil of much larger radius, whose mean plane coincides with that of the lower extremity of the solenoid. If the solenoid is uniformly wound, it is equivalent to a simple magnet, whose poles are condensed at the terminal faces. The electromagnetic action then depends upon $(M-M_0)$, where M is the coefficient of mutual induction between the fixed coil and the lowest winding of the solenoid, and M_0 the corresponding, much smaller, quantity for the uppermost winding.

This arrangement, though simple in conception, does not appear to us to be the one best adapted to secure precise results. It is evident that a large part of the solenoid is really ineffective; those turns which lie nearly in the plane of the flat coil being but little attracted, as well as those which lie towards the further extremity. The result calculated from the total length of wire (even if this could be trusted), the length of the solenoid, and the number of turns, has an appearance of accuracy which is illusory, unless it can be assumed that the distribution of the wire over the length is strictly uniform. In order to save weight, it would appear that all the turns of the suspended coil should operate as much as possible, that is, that the suspended coil should be compact and should be placed in the position of maximum effect.[‡]

§ 5. Neglecting for the time the small corrections of the second order rendered necessary by the sensible dimensions of the sections, let us consider the attraction between two coaxal coils of mean radii A and a, situated at distance x. If M be the coefficient of mutual induction for the central turns, n, n', the number of windings in the two coils, i the current which passes through both, the attraction is

$$nn'i^2\frac{dM}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this expression i^2 is already of the dimensions of a force, and M is linear. Accordingly dM/dx, though a function of A, a, and x, is itself a pure number, and independent of the absolute dimensions of the system. Its value is a question only of the *ratios* a/A, x/A. If we write $dM/dx=\pi f(A, a, x)$, and consider the variation of f as a function of the three linear quantities, the coefficients in the equation

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[*] 'Electricity,' § 754. MCKICHAN, Phil. Trans., 1873, p. 425. See also KOHLRAUSCH, Wied. Ann., Bd. xviii., 1883.

[†] 'Journal de Physique,' March, 1882.

[‡] B.A. Report, 1882, p. 445.

$$\frac{df}{f}=\lambda\frac{dA}{A}+\mu\frac{da}{a}+\nu\frac{dx}{x}\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\qquad(2)$$

are subject to the relation

$$\lambda+\mu+\nu=0\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\qquad(3)$$

If the coils are placed at such a distance apart that the attraction is a maximum, $\nu=0$, and the calculation is independent of small errors in the value of x. Under these circumstances $\lambda+\mu=0$, so that proportional errors in A and a affect the result in the same degree and in opposite directions. In other words, the attraction becomes practically a function of the ratio a/A only.

To this feature we attach great importance. The ratio of galvanometer constants can be accurately determined by the purely electrical process of BOSSCHA without linear measurement of either, and from this ratio we can pass to that of the mean radii by the introduction of certain small corrections of the second order.

In this way all that is necessary for the absolute determination of currents can be obtained without measurements of length, or of moments of inertia, or even of absolute angles of deflection. The forces are, however, evaluated in gravitation measure, so that the final result requires a knowledge of gravity at the place of observation; but except through this quantity there is no reference to the units of space or time.

§ 6. The final calculation of the attraction is best made with the use of elliptic functions; but useful information, sufficient for a general idea of the conditions and for the design of the apparatus, may be derived from the series developed in MAXWELL'S 'Electricity,' § 304. If B, b be the distances of two coaxal coils of radii A and a from a point on the axis taken as origin, and $C^2=A^2+B^2$, we have

$$\frac{dM}{db}=\pi^2\frac{A^2a^2}{C^4}\left\{1.2.3\,\frac{B}{C}+2.3.4\,\frac{B^2-\frac{1}{4}A^2}{C^3}b+3.4.5\,\frac{B(B^2-\frac{3}{4}A^2)}{C^5}(b^2-\tfrac{1}{4}a^2)+\ldots\right\}\;.\;.\qquad(4)$$

in which a, b are supposed to be small relatively to A, B. If we limit ourselves to the first term, which we may do when a/A is small, we see that so far as it depends upon the small coil the effect is proportional to the area. The position of maximum effect for given coils is found by making B/C^5 a maximum, which leads to $B=\frac{1}{2}A$; so that to obtain the greatest attraction the distance of the coils must be equal to half the radius of the larger.

In the present measurements there were *two* equal fixed coils, one on either side of the small coil. If we take the origin midway between, the terms of odd order in b ultimately disappear in virtue of the symmetry, and we may write

$$\frac{dM}{db}=\pi^2\frac{A^2a^2}{C^4}\left\{1.2.3\,\frac{B}{C}+3.4.5\,\frac{B(B^2-\frac{3}{4}A^2)}{C^5}(b^2-\tfrac{1}{4}a^2)+\ldots\right\}\;.\;.\;.\;.\;.\;.\qquad(5)$$

There would be some advantage in a disposition of the coils such that $B^2-\frac{3}{4}A^2=0$, for then the attraction would be in a high degree independent of the position of the suspended coil. In this case

$$\frac{dM}{db}=6\pi^2\frac{a^2}{A^2}\times\cdot 2138 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{6}$$

If, on the other hand, we take $B^2=\frac{1}{4}A^2$, we find from the first term

$$\frac{dM}{db}=6\pi^2\frac{a^2}{A^2}\times\cdot 2862 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{7}$$

showing a not unimportant increase of effect. To the second order of approximation the distance between the fixed coils (2B), corresponding to the maximum effect upon a small coil suspended at their centre, is given by

$$B=\frac{1}{2}A\left(1-\frac{9}{10}\frac{a^2}{A^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{8}$$

so that when a^2/A^2 is sensible the fixed coils should be somewhat closer than when a^2/A^2 is negligible. For the actual apparatus used a^2/A^2 is very sensible, and the ideal state of things was only imperfectly approached. The coils of the dynamometer used for the "fixed coils" conform to the relation $B^2=\frac{1}{4}A^2$, and are not adjustable. It will be seen later that but little is practically lost by the slight imperfection of the arrangements in this respect.

Formula (7) is sufficient for the preliminary estimate of the attraction to be expected, and from (5) we can form an idea of the exactitude necessary in the adjustment of the suspended coil. Thus if b be not zero, the correcting factor is, when $B=\frac{1}{2}A$,

$$1-3\cdot 2\,\frac{b^2}{A^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{9}$$

With the actual apparatus an error in b of one millimetre alters the attraction by only $\frac{1}{20,000}$.

§ 7. It may be convenient to carry through the rough theory so as to show the dependence of the current upon the quantities actually measured. Thus

$$\text{Force of attraction }=hnn'i^2a^2/A^2,$$

where h is written for $6\pi^2\times\cdot 2862$. If the ratio of the galvanometer constants of the coils be β, we have

$$a^2/A^2=\beta^2n'^2/n^2,$$

whence

$$\text{Force }=h\beta^2i^2n'^3/n,$$

and

$$i=\beta^{-1}h^{-\frac{1}{2}}n^{\frac{1}{2}}n'^{-\frac{3}{2}}(\text{Force})^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{10}$$

We may observe that an error in the number of windings, or, which comes to the same thing, a defect of insulation, produces a more serious effect in the case of the suspended than in the case of the fixed coils. The error in the ratio of the galvanometer constants enters proportionately, but the error in the weighings is halved.

Full details of the coils are given later. It will be sufficient here to say that the radius of the large coils is about 25 centims., and that of the suspended coil about 10 centims. The total number of windings on the fixed coils is 450, and on the suspended coil 242. The current usually employed was about $\frac{1}{3}$ ampère, and the double attraction was about the weight of one gram.*

§ 8. The double attraction is spoken of, inasmuch as the readings were always taken by *reversal* of the current in the fixed coils, for which purpose (Plate 17, fig. 1, E) a suitable key was provided. The difference of the weights required to balance the suspended parts in the two cases gives twice the force of attraction between the suspended coil and the fixed coils, independently of the action upon the former of any other part of the circuit, and of terrestrial or other permanent magnetism. The current was supplied from about 10 either GROVE or secondary cells A, and traversed in succession a rough tangent galvanometer D (convenient for a preliminary test of the strength and direction of the current), two or more silver voltameters in series C, the suspended coil G, and then (of course, in opposite directions) the two fixed coils F. The weights necessary for balance (in the same position of the key) alter somewhat, both on account of variation in the electric current and also from the formation of air currents, due to a slight progressive warming of the suspended coil. By recording the times of each weighing we can plot two curves (§ 24), from which we can find what would have been at any moment the weighing in either position of the key. The difference of ordinates gives us what we should have observed, were it possible to make both measurements simultaneously. The whole duration of an experiment was from three-quarters of an hour to two hours, measured by a chronometer, and as a weighing could be taken about every five minutes there was ample material for the construction of the curves. What we require for comparison with the deposited silver is the mean current, whereas what we should obtain directly from the curves represents the *square* of the current. The whole interval is divided into periods (usually of fifteen minutes), and the difference of ordinates corresponding to the middle of the periods is taken from the curves.

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* The actual apparatus was not adapted to the measurement of currents much exceeding $\frac{1}{2}$ ampère. The flexible copper connexions of the suspended coil would take an ampère, but the suspended coil itself is unduly heated by the passage of an ampère for more than a few minutes. Had it been desirable to use stronger currents, it would, of course, have been possible to do so by increasing the gauge of the wire. The grooves in which the wire is wound being given, it is evident that a proportional increase of the current and of the section of the wire leave both the heating and the electromagnetic effects unaltered. In this way the apparatus might easily be modified, so as to take currents of 3 or 4 ampères, the only other changes that would be required being a multiplication of the flexible leading wires, several of which might be arranged in parallel. But for the determination of the electro-chemical equivalent of silver, the currents actually used were quite strong enough.

The mean square root of the numbers thus obtained gives us a result to which the rate of silver deposit should be proportional.

§ 9. The use of a balance for the measurement of electromagnetic attraction involves some special arrangements. The suspended coil must in every case be brought to rest in its proper position, corresponding to the zero of the pointer of the balance. It was found desirable to give the balance a shorter period of vibration than usual, and to obtain control over the arc of vibration an auxiliary coil was introduced, through which, with the aid of a key, the current from a LECLANCHÉ cell could be made to pass. By this means a force tending to raise or to lower the suspended parts could be brought into play at the will of the operator, who, after a little practice, is able to stop the vibrations with very little delay.* The weighings were recorded to milligrams only; but the accuracy really obtained was greater than might appear, since by anticipating somewhat the change in progress it was possible to note the *time* at which the balance demanded an integral number of milligrams.

The current was led into the suspended coil by means of fine flexible copper wires. To diminish the force conveyed by these to the suspended parts, they were bent so as to place themselves naturally in the required positions before the final solderings were made. It is important, however, to observe that no assumption is made as to the equality of these forces before and during the passage of the current. Under its influence the fine wires are no doubt sensibly warmed, but this effect and any consequent alterations in the mechanical properties are the same in both sets of readings, the *only* change relating to the direction of the current in the fixed coils.

This point is the more important since the balance is not used in these experiments in quite the normal manner. In ordinary weighings there is no force in operation upon the pans but gravity, and this vertical force is transferred to the beam. In the present application the "pan" is not quite free and is subjected to forces which may have a small horizontal component. In virtue of the freedom of rotation about the knife-edge suspending the pan, these forces are transferred without change to the beam. The horizontal component would, however, produce little effect in any case, since in the horizontal position of the beam its direction would pass very nearly through the knife-edge supporting the beam. The weights in the other scale-pan give rise to a strictly vertical force. We shall thus be doubly secured against error if we provide that the force to be measured (due to the reversal of the current in the fixed coils) is strictly vertical, and that the horizontal force, if sensible, remains unaltered in passing from one direction of the current to the other. These objects are attained when the coils are carefully levelled, and when the readings are always taken for a definite position of the suspended coil conveying a constant current.

§ 10. The suspended coil is wound upon an ebonite ring (§ 13), and is supported by

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* See "Suggestions for Facilitating the Use of a Delicate Balance." B. A. Report, 1883.

three screws upon a light brass triangle hanging in the balance by a stout copper wire. The fixed coils are those of the dynamometer, described in MAXWELL'S 'Electricity,' § 725, and in LATIMER CLARK'S paper (Phil. Trans., 1874, Part I). In setting up the apparatus the ebonite coil is first suspended, and the dynamometer coils are levelled, and adjusted laterally until concentric with it. This is tested by carrying round a metal piece making five contacts with the upper ring of the dynamometer, and provided with a pointer just reaching inwards to the circumference of the ebonite coil. The piece in question may be described as a sort of three-legged stool, standing upon the upper horizontal face of the dynamometer ring and carrying below two studs which are pressed outwards into contact with the inner cylindrical face of the ring. As the piece is carried round the pointer describes a circle coaxal with the dynamometer rings. To level the ebonite ring, the distance is calculated by which its upper surface should be below the upper surface of the (upper) dynamometer ring, and a pointer attached to a straight rule is so adjusted that when the rule is laid upon its edge along the upper face of the dynamometer ring the pointer should just scrape the upper face of the ebonite ring. By applying this test at three points the ebonite ring is brought to occupy the desired position. These adjustments were made in the first instance by our assistant, Mr. G. GORDON, and subsequently examined by ourselves. With a little care the necessary accuracy is attained without difficulty, for, it is scarcely necessary to say, all the errors due to maladjustment are of the second order. When in use the suspended parts are protected from currents of air by a suitable paper casing.

Examination showed that the insulation of the various parts was satisfactory. Twenty-five cells of a DE LA RUE'S battery failed to show any appreciable leakage between the wire and the rings of the dynamometer coils, though the capacity of the *condenser* thus formed was very noticeable.

§ 11. The test for leakage from winding to winding of a coil is a more difficult matter. The ebonite ring was first wound on August 9, 1882, and its galvanometer constant was compared with that of one coil of the dynamometer by Mr. J. M. DODDS. The result agreed very ill with the measurements taken during the winding, and led to the suspicion that several turns were short-circuited by a false contact. The matter was put to a further test in two ways. A second coil of the same dimensions was wound with the same number of turns; and the two coils were placed co-axally close together, and so connected in series that a current would circulate opposite ways. The circuit was completed by a galvanometer of long period. Under these circumstances when one pole of a very long steel magnet is thrust suddenly through the opening, there should be no effect observable if the insulation is good; but if any of the turns of one of the coils are short circuited the other coil will of course have the advantage, and the galvanometer will indicate a current in the corresponding direction. It was found in fact that the second coil preponderated, and that 13 extra turns had to be put upon the first coil to obtain the balance. With proper precautions this method of testing seems satisfactory, being approximately independent of the equality of mean radii of the coils compared.

A second test was suggested and executed by Mr. GLAZEBROOK. The two coils retaining a fixed position, the ratios of the self-inductions of each to the mutual induction of the pair were determined by MAXWELL'S method.* These ratios, which should have been nearly equal, were found to differ considerably in the direction which showed a deficiency in the self-induction of the ebonite coil.

After this it was no longer doubtful that the coil was defective. In unwinding it more than one bad place was detected, although the original winding had been carefully done under our own eyes. The ring was rewound with fresh wire on Nov. 30, 1882; and we were so much impressed with the necessity of a thorough check upon the insulation that we devised a delicate test similar, as we afterwards found, to one that had already been successfully used by GRAHAM BELL.† Four similar coils of fine wire, wound upon wood, and of the same mean diameter as the ebonite coil, were arranged so as to form a HUGHES induction balance. The lower coils form a primary circuit, and are connected with a microphone clock or other source of variable current. The upper coils and associated telephone form a secondary current. The distance between the upper and lower coils is such as to allow the insertion of the ebonite coil between them, suitable support being provided for it to guard against displacement of the principal coils. If the distances of the four coils are adjusted by screw-motions to an exact balance, so that no sound is audible in the telephone (held at some distance away), the introduction of a tertiary circuit between one primary and secondary causes a revival of sound whose intensity depends upon the conductivity, &c., of the tertiary circuit. If the tertiary circuit consists of a single turn of wire, such as that on the ebonite ring, the sound heard is quite loud, and remains audible when a resistance of about 1 ohm is included. A single circlet of copper wire ·004 inch diameter gives a very distinct sound. When the ebonite coil, with ends unconnected, is introduced, the sound is audible, but much less than that from the fine copper circlet. Part of this effect may be attributed to its finite capacity as a condenser, in virtue of which sound might be heard in any case; but it is probable that the insulation is in reality somewhat imperfect. The closing of the circuit through a megohm gives a distinct augmentation of sound; and thus it is evident that the insulation, if not perfect, is at any rate abundantly sufficient for the purposes of the present investigation.

The current weighing apparatus was set up in February, 1883, and worked satisfactorily from the first. Apart from errors in the constant of the instrument, the

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* 'Electricity,' § 756.

† "Upon the Electrical Experiments to Determine the Location of the Bullet in the Body of the late President GARFIELD," &c. A paper read before the American Association for the Advancement of Science, August, 1882.

determination of the mean value of a current of (say) half an hour's duration should easily be correct to $\frac{1}{10,000}$.

The fixed coils.

§ 12. These are the coils of the dynamometer constructed by the Electrical Committee of the British Association (see § 10). The mean radii of the two coils and the dimensions of the sections are very nearly identical, and for our purpose it is unnecessary to note anything but the mean. The following are derived from the dimensions recorded in Professor MAXWELL's handwriting in the laboratory notebook:—

A=mean radius=24·81016
$2B$=distance of mean planes =25·00
$2h$=radial dimension of section =1·29
$2k$=axial . . . . =1·50

the unit in each case being the centimetre.

The number of turns of wire on each coil is 225.

The above values are those employed in the calculations of the present investigation, and they can be only partially verified without unwinding the wire. Owing, however, to the final result being comparatively independent of A and B, even a rough verification is not without value. The distance parallel to the axis from outside to outside of the grooves in which the wire is wound can be found pretty accurately with callipers, and was determined to be 10·433 inches. From inside to inside of the grooves the corresponding distance was 9·252 inches. The mean of these is the distance of mean planes, which is thus 9·8425 inches, or 25·000 centims. exactly. This element is, therefore, verified with abundant accuracy. The half difference of the two numbers above given represents the axial dimension of the section, and comes out 1·5024 centims., practically identical with 1·50 centims. The mean radius and the radial dimension of the section are not now accessible to measurement, but the outside circumference agrees sufficiently well with that calculated from the recorded dimensions to serve as a verification.

The number of turns has to be taken entirely upon trust; but the use of the method given in MAXWELL's 'Electricity,' § 708, makes a mistake in this respect very unlikely. Moreover, the electrical comparisons to be detailed later (§ 14) verify the *equality* of the number of windings on the two coils.

The resistance of each coil is about 14½ B.A. units, and both coils are well insulated from the frame on which they are wound.

The suspended coil.

§ 13. This consisted of 242 turns of copper wire insulated with silk saturated with paraffin wax, and was wound upon an ebonite ring supplied by Messrs. ELLIOTTS. The weight of the ring was 135 grms., and its section is shown full size in the adjoining figure (Plate 17, fig. 2). The weight of the wire was 440 grms., so that the total weight to be carried in the balance was about 575 grms. The mean diameter of the coil of wire, as determined from the inside and outside circumferences, was 8·090 inches; but it cannot be so determined with sufficient accuracy, and the result is not used in the calculation. It agrees perhaps about as well as could be expected with that deduced electrically by comparison with the large coil.

The radial dimension of the section $(2h')=$ ·9690 centim.
The axial . . . . $(2k')=1·3843$ centims.

The difficulties experienced in respect of the insulation, and the tests applied, have already been related (§ 11).

The electrical comparison of radii (§ 14) gave for the ratio of the dynamometer radius A to that of the suspended coil a

$$2·42113,$$

whence

$$a=10·2473 \text{ centims.}$$

The mean radius thus determined is not necessarily that corresponding to the geometrical centre of the section, as it allows for any inequality in the distribution of the windings.

The resistance of the coil is about $10\frac{1}{2}$ ohms.

Determination of mean radius of suspended coil.

§ 14. This quantity cannot be determined advantageously by direct measurement, but its ratio to that of the large coils can be deduced from the ratio of the galvanometer constants of the coils, and this ratio can be accurately determined by the electrical method introduced by BOSSCHA.*

It may be shown† that for all purposes we may take the mean radius and mean plane of a coil to correspond with the circle passing through the *centre of density* of the windings. If the windings are distributed with absolute uniformity, this point coincides with the geometrical centre of the section; otherwise there may be an appreciable distinction. The corrections of the second order, which in consequence of the finiteness of the section must be introduced in calculating the effects of the coil, have the same values as if the density of the windings were absolutely, instead of merely approximately, uniform.

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* POGG. Ann., 93, p. 402, 1854.

† Camb. Phil. Proc., Feb. 12, 1883.

For example, the galvanometer constant G_1 is related to the mean radius A (as above defined) and to the radial and axial dimensions of the section, $2h$, $2k$, according to*

$$G_1=\frac{2\pi}{A}\left(1+\frac{1}{3}\frac{h^2}{A^2}-\frac{1}{2}\frac{k^2}{A^2}\right)$$

If, therefore, we can determine for two coils the ratio of galvanometer constants, it is a simple matter to infer therefrom the ratio of mean radii.

In BOSSCHA's method the two coils to be compared are arranged approximately in the plane of the magnetic meridian, so that their axes and mean planes coincide, and a very small magnet with attached mirror is delicately suspended at the common centre. If the current from a battery be divided between the coils, connected in such a manner that the magnetic effects are opposed, it is possible by adding resistances to one or other of the branches in multiple arc to annul the magnetic force at the centre, so that the same reading is obtained whichever way the battery current may circulate. The ratio of the galvanometer constants is then simply the ratio of the resistances in multiple arc.

To obtain this ratio in an accurate manner, the two branches already spoken of are combined with two standard resistances so as to form a WHEATSTONE's balance. Of these resistances both must be accurately known, and one at least must be adjustable. The electromagnetic balance is first secured by variation of the resistance associated with one of the given coils, which resistance does not require to be known. During this operation the galvanometer of the WHEATSTONE's bridge is short-circuited. Afterwards the galvanometer is brought into action, and the resistance balance is adjusted. The ratio of the galvanometer constants is thus equal to the ratio of the known resistances. The two adjustments may be so rapidly alternated as to eliminate any error due to changes of temperature in the copper wires.

The above comparison was carried out for each of the two coils of the dynamometer, and the coil wound on the ebonite ring, called for shortness the ebonite coil. On account of the smallness of the latter some care is necessary in the adjustments, which, however, do not require to be described in detail. It will be sufficient to refer to the description of the adjustments when the ebonite coil was suspended, and to mention that the errors arising from maladjustment (all of course of the second order) could hardly affect the final ratio by more than $\frac{1}{10,000}$. The length of the magnet was $\frac{1}{10}$ inch, and the error due to neglecting it could not exceed $\frac{1}{10,000}$. To the magnet was attached a light silvered glass mirror, such as are employed in THOMSON's galvanometers, and it was protected from air currents by a glass cell. The readings were taken by observing the motion of a spot of light thrown upon a scale in the usual way.

The electrical connexions are shown in the adjoining figure (Plate 17, fig. 3). The current from a large DANIELL cell A, after passing the reversing key B, divides itself

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* See MAXWELL's 'Electricity,' § 700.

at C between the brass coil of the dynamometer D and the ebonite coil E. The remaining terminals of these coils are led into mercury cups F and H, into which also dip the terminals of the bridge galvanometer *g*. With the ebonite coil is associated a resistance box N. The other branches of the balance were (in one arrangement) composed of a coil of 10 units in multiple arc with which was placed a high resistance box K, and three coils combined in series whose values were about 24, 1, 1 units, making together 26. All these coils were of the standard pattern, and their values had been already carefully determined. From the cup L the current passed back to the key B. The high resistance box K gives a fine adjustment by which the ratio of resistances can be brought to the required value. The smallest resistance actually used here was 4000 units. While the electromagnetic balance was under observation a horse-shoe piece of stout copper rod P, connected with the key as shown in the figure, was inserted in the cups F, H. By this means these cups are brought accurately to the same potential, and nearly all the current is diverted from the standard resistance coils.

The determination of the electromagnetic balance is rendered more troublesome by the fact that the first motion of the magnet on the reversal of the current is influenced by induction, and cannot be used as a test. No attempt was made actually to complete the adjustment, but by preliminary trials resistances from N differing by about $\frac{1}{20}$ unit were found, such that the effects observed were reversed in passing from one to the other. From the magnitude of these effects the required result is obtained by interpolation. At the beginning and end of a series the *two* ratios of resistances were determined by use of K, the horse-shoe P being of course withdrawn; and the mean of the initial and final values (which usually differed extremely little) was employed in the reduction.

As an example, we may take some observations on Sept. 5, 1883, with the coil of the dynamometer marked B. The difference of readings on reversal of the battery in a given manner was taken alternately with certain resistances from N, which we may call *a* and *b*. The results were

with *a* $+\cdot 7, +\cdot 3, +1\cdot 3, +1\cdot 0$ mean $+\cdot 8$;
with *b* $-8\cdot 4, -8\cdot 4, -8\cdot 5, -9\cdot 5$ mean $-8\cdot 7$.

Now with *a* the resistance from K, associated with the [10], and necessary for the resistance balance, had to be such that (at a standard temperature) the resultant resistance of this branch was 9·97772; while with *b* the resultant resistance had to be 9·99182. The resistance that would have been required here, if N had been accurately adjusted for the electromagnetic balance, is thus

$$9\cdot 97772+\frac{\cdot 8}{9\cdot 5}\times\cdot 01410=9\cdot 97890.$$

The resistance in the other branch was 25·95648, so that the ratio of galvanometer constants is determined to be

$$25{\cdot}95648/9{\cdot}97890=2{\cdot}60113.$$

It will be seen that even with a single cell the sensitiveness was such that the errors of reading could scarcely exceed $\frac{1}{10,000}$; indeed, the weakest part of the arrangement is in the standard resistances.

With use of the above resistance coils the values obtained for coil B on three occasions were

2·60087, 2·60098, 2·60113, mean 2·60099.

As a further check, the experiment was repeated with a different combination of resistance coils. The 26 was replaced by 13, made up of three singles and of the same [10], while the [10] was replaced by a [5]. Two experiments gave

2·60046, 2·60026, mean 2·60036.

The mean result of the two arrangements is thus 2·60067. The difference is about $\frac{1}{4000}$, and would be explained by an error of $\frac{1}{8000}$ in the value of the [10].*

For coil A of the dynamometer the ratio of galvanometer constants was found in like manner to be 2·60072, the close agreement of which with 2·60067 is a verification of the winding and insulation of the coils. For the further calculations we require only the mean, and we therefore take as the ratio of galvanometer constants for the ebonite coil and a coil of the dynamometer

2·60070.

The accuracy obtained in the above determinations is doubtless quite sufficient for the purposes of the present investigation, but if it were desired to push the power of the method to its limit it would be necessary to design the coils so that the ratio should be (approximately) expressible by very simple numbers. If in the present case, for example, we were content to sacrifice one-fifth of the number of turns on the ebonite coil, the ratio could be made to approach that of 2 : 1. The standard resistances might then be composed of three equal resistance coils, which could be more accurately combined and tested than the more complicated combinations that we were obliged to use. In such a case the limit of accuracy could probably depend upon the difficulty of adjusting the coils under comparison and the suspended magnet to their proper places. It is scarcely necessary to say that care must be exercised in the disposition of the leading wires, and that the direct action of the current in the principal coils upon the needle of the bridge galvanometer must be tested, and, if necessary, allowed for.

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* For the methods used to find the values of the [24], &c., reference must be made to former papers.

We have now to deduce the ratio of mean radii. For the ebonite coil the correcting factor is

$$1+\tfrac{1}{3}\frac{h'^2}{a^2}-\tfrac{1}{2}\frac{k'^2}{a^2}=1+\cdot000741-\cdot002269.$$

For the dynamometer coil

$$1+\tfrac{1}{3}\frac{h^2}{\mathrm{A}^2}-\tfrac{1}{2}\frac{k^2}{\mathrm{A}^2}=1+\cdot000225-\cdot000457.$$

Thus

$$\frac{\mathrm{A}}{a}=\tfrac{225}{242}\times 2\cdot60070\times 1\cdot001296=2\cdot42113\,;$$

and from this when A is known the value of a can be deduced (§ 13).

Calculation of attraction.

§ 15. The attraction between two coaxal circular currents of strength unity, of which the radii are A, a, and distance of planes is B, is (MAXWELL, § 701)

$$\frac{\pi \mathrm{B}\sin\gamma}{\sqrt{(\mathrm{A}a)}}\{2\mathrm{F}_\gamma-(1+\sec^2\gamma)\mathrm{E}_\gamma\}\quad .\ .\ .\ .\ .\ .\ .\ .\ .\quad (1),$$

where F_γ and E_γ denote the complete elliptic integrals of the first and second kind whose modulus is $\sin\gamma$. The value of $\sin\gamma$ itself is

$$\sin\gamma=\frac{2\sqrt{(\mathrm{A}a)}}{\sqrt{\{(\mathrm{A}+a)^2+\mathrm{B}^2\}}}\quad .\ .\ .\ .\ .\ .\ .\ .\ .\ .\quad (2).$$

The functions F_γ and E_γ were tabulated by LEGENDRE. In an Appendix (p. 455) will be found a table of

$$\sin\gamma\ \{2\mathrm{F}_\gamma-(1+\sec^2\gamma)\mathrm{E}_\gamma\}\quad .\ .\ .\ .\ .\ .\ .\ .\quad (3),$$

calculated with seven figure logarithms from those of LEGENDRE for the purpose of the present and similar investigations. It has been carefully checked, and it is hoped is free from error, except of course in the last place.

The value of (1), with omission of the factor π, is denoted by $f(\mathrm{A}, a, \mathrm{B})$, and, as has already been explained, it is a function of no dimensions. To calculate it for the central windings of the fixed and suspended coils, we have first to find γ from (2). With the data already given $\gamma=58^\circ\ 57\tfrac{446}{760}'$ whence with use of the table

$$f(\mathrm{A}, a, \mathrm{B})=1\cdot044576.$$

This multiplied by π, by the product of the numbers of terms in the two coils, and by the square of the strength of the current, gives very nearly the force of attraction, but a correction is required for the finite dimensions of the sections. The quadruple integration over the two areas may be effected by suitably combining various values of f corresponding to the central turn of one section and to the middle of one of the linear boundaries of the other. (See MAXWELL's 'Electricity,' 2nd edition, § 706, Appendix II.) We find

$$\left.\begin{aligned} f(A+h, a, B) &= \cdot 992719 \\ f(A-h, a, B) &= 1\cdot 098740 \end{aligned}\right\} \text{sum } 2\cdot 091459$$

$$\left.\begin{aligned} f(A, a+h', B) &= 1\cdot 158576 \\ f(A, a-h', B) &= \cdot 937866 \end{aligned}\right\} \text{sum } 2\cdot 096442$$

$$\left.\begin{aligned} f(A, a, B+k) &= 1\cdot 024612 \\ f(A, a, B-k) &= 1\cdot 059526 \end{aligned}\right\} \text{sum } 2\cdot 084138$$

$$\left.\begin{aligned} f(A, a, B+k') &= 1\cdot 026306 \\ f(A, a, B-k') &= 1\cdot 058569 \end{aligned}\right\} \text{sum } 2\cdot 084875$$

The sum of the eight values is 8·356914. From this we subtract $2 \times f(A, a, B)$, viz., 2·089152, and divide by 6; whence for the mean value of f applicable to the sections as a whole

$$f = 1\cdot 044627,$$

differing, as it turns out, extremely little from $f(A, a, B)$.

From the values given we see that f increases very sensibly as B diminishes, so that, as was expected, the distance between the fixed and the suspended coil, or between the two fixed coils, is too great to realise fully the advantageous condition of things described as the ideal, in which f would be approximately independent of variations in B.

To express the actual variations of f as a function of A, a, B, we write

$$\frac{df}{f} = \lambda \frac{dA}{A} + \mu \frac{da}{a} + \nu \frac{dB}{B};$$

and we obtain sufficiently accurate values of λ, μ, ν from those of f already given. Thus

$$\lambda = \frac{f(A+h, a, B) - f(A-h, a, B)}{f(A, a, B)} \div \frac{2h}{A} = -1\cdot 95.$$

In like manner $\mu = +2\cdot 23$, $\nu = -\cdot 28$; so that

$$\frac{df}{f} = -1\cdot 95 \frac{dA}{A} + 2\cdot 23 \frac{da}{a} - \cdot 28 \frac{dB}{B}.$$

In the present investigation, however, a is not measured directly, but by comparison with A. If we write $a/\mathrm{A}=\alpha$, so that

$$\frac{d\alpha}{\alpha}=\frac{da}{a}-\frac{d\mathrm{A}}{\mathrm{A}},$$

and eliminate da/a, we have

$$\frac{df}{f}=2\cdot23\,\frac{d\alpha}{\alpha}+\cdot28\,\frac{d\mathrm{A}}{\mathrm{A}}-\cdot28\,\frac{d\mathrm{B}}{\mathrm{B}},$$

which is the equation by which the suitability of the proportions is to be judged. It will be seen that the stress is thrown upon the measurement of α, and that the errors of A and B enter to the extent of only about one quarter. If the proportions had been those described as ideal, the coefficients of $d\mathrm{A}/\mathrm{A}$ and $d\mathrm{B}/\mathrm{B}$ would have been zero.

It must not be forgotten that the error of f itself is halved in the final result, which thus involves the errors of A and B only after division by 8.

If the current be i, and the number of turns in the fixed and suspended coils n, n', the attraction or repulsion is measured by

$$\pi nn'i^2f.$$

This is expressed in absolute units. To find the value in gravitation units we must divide by g. If m be the observed difference of weights in air necessary to counterpoise the suspended coil when the current is reversed in the fixed coils,

$$\pi nn'i^2f=\tfrac{1}{2}\,mg\times\cdot99986,$$

the last factor representing the "correction to vacuum" rendered necessary by the finite density of the brass weights.

The value of g at Cambridge is taken to be 981·2282. Introducing this and the numerical values of n, n', f, already given, we find

$$i=\mu\sqrt{m},$$

when

$$\mu=\cdot0370484.$$

The silver voltameters.

§ 16. The arrangement adopted for the voltameters is similar to that recommended originally by POGGENDORFF. The deposits are formed upon metallic basins (usually of platinum) charged with a neutral 15 per cent. solution of pure silver nitrate. They are prepared by careful cleaning with nitric acid and distilled water with subsequent ignition. After complete cooling in a desiccator, they are weighed to $\frac{1}{10}$ milligrm. in a delicate balance with trustworthy weights. The anode, by which the current enters the voltameter, is formed of fine silver sheet, suspended by platinum wire in a horizontal position near the top of the solution. In order to protect the kathode from disintegrated silver, which in our experience is invariably formed upon the anode, the latter is wrapped round with pure filter paper, secured at the back with a little sealing-wax. This arrangement appears to us for several reasons preferable to the vertical suspension of the electrodes in the form of flat plates. In the latter arrangement the deposited metal usually aggregates itself upon the edges and corners of the kathode with a tendency to looseness. Again the solution rapidly loses its uniformity. At the kathode the solution becomes impoverished and at the anode it becomes concentrated. With vertical plates the strong solution soon collects itself at the bottom, and the weak solution at the top, so as to give rise to considerable variation of density. It is true that the horizontal position of the electrodes necessitates the use of a porous wrapping, which would increase the difficulty of determining the loss of weight at the anode. M. MASCART appears to have succeeded in determining this loss, but the disintegration which we have always met with rendered the attempt on our parts hopeless. It is possible that something may depend upon the mechanical condition of the metal, but as to this we cannot speak with confidence. The blackish powder left upon the anode has at first the appearance of being due to chemical impurity, but it occurs with anodes of the highest quality of silver, and is completely soluble in nitric acid.

In our earlier trials, dating from October, 1882, we were much impressed with the importance of obtaining sufficient coherence in the deposit to guard against risk of loss in the washing and subsequent manipulations. The addition of a very small proportion of *acetate* of silver was found to be in this respect a great improvement, affording a deposit less crystalline in appearance and of much closer texture; and in consequence nearly all our experiments during the first year were conducted with solutions containing sensible quantities of acetate. In order to detect whether anything depended upon the "density" of the current, two platinum basins of different sizes were employed, the area of deposit being in about the proportion of 2 : 1, but no distinct systematic difference was observed. When the deposits were completed the basins were rinsed several times with distilled water, and then allowed to soak over night. The next day after more rinsings they were dried in a hot air closet at about 160° C, and after standing over another night in a desiccator were carefully weighed. Repetition of these weighings after intervals of standing in the desiccators showed that they were correct to $\frac{1}{10}$ milligrm., so that as the total weights of deposit amounted to 2 or 3 grms., a high degree of accuracy in the final evaluation of the ratio of deposit to current was expected. Discrepancies, however, presented themselves of an amount much greater than we had been prepared for, and they were of such a character as to show that the disturbing causes were to be sought in the behaviour of the voltameters and not in the current weighing apparatus. Thus it was found that the numbers obtained on the same occasion from the two voltameters in series, through which exactly the same quantity of electricity had passed, were liable to as great a disagreement as the numbers derived from experiments on different days.

§ 17. At this stage the question presented itself as to whether the deposits were really pure silver. Two or three gravimetric analyses by conversion into chloride, conducted both by ourselves and by Mr. SCOTT, to whose advice and assistance we have been constantly indebted throughout these investigations, having favoured the idea that the deposits were not quite pure, we arranged for a systematic volumetric analysis of all the deposits. The bulk of the metal after solution in pure nitric acid having been thrown down with a known quantity of chloride of sodium in strong solution, the titration was completed with weak ($\frac{1}{1000}$) salt solution from a burette in the usual manner. The bottle containing the solution was enclosed in a dark box and lighted in the manner recommended by STAS, with a convergent beam of yellow light which had passed through a flask containing chromate of potash. Towards the close of the operation the effect of the addition of two drops of solution (containing $\frac{1}{10}$ milligrm. of salt) becomes difficult of observation unless the liquid be very thoroughly cleared. At this stage we found it convenient to filter off about half the liquid into another bottle, through a funnel plugged with (purified) cotton wool. As soon as the pores are penetrated by the chloride of silver the filtration is effective, and yet so rapid that but little time is lost by the adoption of this procedure. The two drops of chloride solution are added to the liquid thus filtered, and *shaken up* so as to effect a complete mixture, and the bottle is then placed so that the cone of light traverses the *body* of the liquid. After an interval varying from a few seconds to several minutes the cloudiness develops itself, and the delay gives an indication of how nearly the point is approached. Before each test the filtrate is of course returned to the stock bottle and thoroughly shaken up. The operation is complete when the last addition of two drops gives no effect after a quarter of an hour. There is no difficulty in determining in this way the necessary quantity of salt to $\frac{1}{10}$ milligrm., and the point may be recovered any number of times after addition of small known quantities of silver.

In the interpretation of the results we placed no trust in the purity of the NaCl, nor depended upon any assumption as to the ratio of NaCl to Ag, but made comparison with the numbers obtained from precisely similar determinations with substitution for the electro-deposits of equal weights of silver of the highest quality, supplied by Messrs. JOHNSON and MATTHEY. A large number of such comparisons showed that there was no difference that could be depended upon between the two kinds of silver; there was, indeed, a slight indication of inferiority in the deposits, to the extent of perhaps $\frac{1}{6000}$, but not more than might plausibly be attributed to the greater risk of loss in dissolving the deposits from off the platinum basins. The standard silver was dissolved without transference in the bottle used for the subsequent analysis, and thus under more advantageous conditions than were possible in the manipulation of the deposits.

§ 18. Table I. (p. 437) gives the results of a laborious series of determinations made with solutions containing more or less acetate. It will be seen that up to August 16 the numbers in the final column are fairly concordant, and they rather narrowly escaped being accepted as satisfactory. In the month of November, however, the experiments were continued with a fresh stock of depositing solution (probably containing less acetate), when a systematic change became apparent in the direction of smaller deposits. From the first we had taken, as we thought, full precautions to secure adequate washing out of the silver salt, and special experiments had proved that the weights were not appreciably changed by further washing with pure water, or by resoaking in the depositing solution with a second washing and drying conducted like the first. Nevertheless the appearance of the deposits under the microscope was such as to suggest a doubt whether a complete elimination of the salt from its pores was possible with any amount of washing, and the evidence of the analyses was felt not to be decisive, inasmuch as the deficiency to be found in this way would correspond to only about one-third of the weight of salt actually present. According to this view the diminution in the weight of the deposits after August 16 was due to a more complete washing out of the salt, rendered possible by the more open texture of the deposits, and we proceeded to test the behaviour of pure nitrate solutions. The result was a further small, but distinct, diminution in the weights, as shown in Table II., and we were now convinced that the use of acetate had been a great mistake, costing us six months' almost fruitless labour. When the deposits are taken upon the concave surface of a bowl they are coherent enough for convenient manipulation without the aid of acetate. The danger of retention of salt or other impurity is far greater than of loss of metal, and this danger is aggravated by the acetate. Indeed it would be scarcely too much to say that the danger is converted into a certainty, for from the fine pores of these deposits it seems almost impossible to remove the salt effectually.

It is evident that, in spite of the retention of a small quantity of salt, a satisfactory conclusion might be reached were there any means of estimating its amount. Theoretically the analysis for silver, as many times effected, is adequate to this purpose, since the difference of the total weight of the (impure) deposit, and of the metal found on analysis, would represent the NO_3 of the salt. But the circumstances are so disadvantageous that no satisfactory result could be looked for without an extraordinary, and perhaps impossible, perfection of manipulation. A direct test for nitric acid is not applicable; but at a sufficiently high temperature the silver nitrate would be decomposed, so that the loss of weight incurred on heating to redness (after previous thorough drying at, say, 160° C.) would represent the NO_3. Unfortunately this method is difficult to carry out thoroughly without injury to the platinum basins, inasmuch as silver and platinum begin to alloy at a red heat. But an exposure for five minutes to a heat just short of redness does not seriously damage the basins, and appears to be nearly, if not quite, sufficient to drive off the last traces of NO_3. With a pure nitrate depositing solution, and with the treatment for elimination of the salt presently to be described, there was sometimes no loss on heating (Table II.), but perhaps more often the balance indicated a loss of one or two-tenths of a milligram. With respect to the interpretation of this, it is difficult to say whether or not it ought to be regarded as due to traces of salt retained in spite of all the washings. If so, the true weight of deposit is smaller still by nearly twice the apparent loss; but it is very possible that there may be traces of grease liable to be burnt off at a red heat, so that the loss in question cannot with confidence be attributed to nitrate. On this account the real amount of the deposit remains somewhat uncertain to nearly half a milligram.

With respect to the procedure best adapted to eliminate the salt from the pores of the deposit, it is evident that the difficulty is to cause any displacement of the liquid in the interior. It was thought that this object might to some extent be attained by rapid alternations of temperature, and for this purpose the basins were (after thorough rinsing) passed backwards and forwards between cold and boiling distilled water. Recourse was had also to soaking in alcohol, somewhat diluted. Still wet with the alcohol, the basins were plunged into boiling water with the idea of promoting disturbance inside the cavities of the deposit. After a course of treatment of this kind the basins were filled and allowed to stand over night so as to give free play to diffusion. They were then rinsed a few times, and placed in the air closet to be dried at 160° C.

§ 19. In order to meet the difficulty of the alloying of silver and platinum at a temperature high enough to decompose with certainty the last traces of silver nitrate, we made, at the suggestion of Professor DEWAR, several attempts to replace platinum by silver bowls. One evident objection to the silver is the impossibility of removing the deposit with nitric acid, so as to restore the original condition of the bowl. But a more serious difficulty arises from the want of constancy in the weight of a silver bowl (without deposit) when strongly heated. On more than one decision a *gain* of a milligram or two was observed after heating in a porcelain basin over an alcohol flame. We have reason to believe that this effect depends upon the presence of traces of copper. In order to test the question we carefully cleaned and dried at 160° a piece of the highest quality of silver, such as was used latterly for the anodes. The weight was now 28·1628, and after heating to redness for a quarter of an hour over a naked alcohol flame *fell* to 28·1619. On another occasion a loss of 2 milligrms. was observed under similar circumstances. On the other hand, a parallel experiment with a less pure sample of silver, known to contain a small quantity of copper, gave after the first heating to redness a *gain* of 3 milligrms., followed by a further gain of 2 milligrms. after a second heating.

These changes are, however, insignificant compared to that observed by Mr. SCOTT, who heated one of our large silver basins in a porcelain bowl for a long time over a BUNSEN gas flame. After two nights treatment the weight had risen from 57·3008 to 57·4521. Mr. SCOTT traced the increase in his case to the formation of silver sulphate, but it does not appear possible that this can be the explanation of the changes observed by us. The matter appears worthy of the further attention of chemists; but for our purposes the conclusion is that, for the present at any rate, platinum is preferable to silver. With suitable precautions, the platinum basins may be heated to redness without changing more than $\frac{1}{10}$ milligrm.

§ 20. In some of our later experiments (*e.g.*, those on January 30, April 2) we included a voltameter, charged with a higher proportion of acetate, in order to exaggerate the errors that we had met with, in the hope of better detecting their origin. When the nitrate solution is nearly saturated with acetate, the deposit is of a beautiful snow-white appearance, and almost always 5 or 7 milligrms. too heavy. On the second weighing, after heating to the verge of redness, a loss revealed itself, whose amount usually agreed fairly well with the view that the original excess of weight was due to nitrate, reduced to metal by the second heating.

§ 21. In the hope of obtaining better evidence as to the cause of the anomalous weights, and also with the view of confirming our results by the substitution for nitrate of some other salt of silver, we have made several observations on deposits from *chlorate* of silver. The salt was prepared for us by Mr. SCOTT from chlorate of barium, and was found to give as good deposits as the nitrate. The chlorate was used in a nearly saturated 10 per cent. solution,* and also in a 5 per cent. solution. Voltameters charged with nitrate were included in the same circuit, so that the comparison was made under the most favourable condition. The results (Table II.) show an exceedingly good agreement, and constitute perhaps the most accurate verification which FARADAY'S law of electrolysis has as yet received.

But the second object which we had in view in using the chlorate has not been attained. The idea was to get a too heavy deposit by addition of acetate, and then after washing and weighing as usual, to dissolve up the metal with nitric acid and test for chlorine. If chlorate were present, and were the cause of the excessive weight, it should on strong heating be resolved into chloride, whose presence might be detected. Preliminary experiments showed that as little as $\frac{1}{10}$ milligrm. of silver chloride could be rendered evident. The deposits were dissolved in nitric acid, and strongly supersaturated with pure ammonia. After standing for some time with frequent stirring, the solution was diluted, and again rendered acid with nitric acid. The deposits from chlorate, which we had reason to regard as pure, stood the test almost perfectly, the amount of chloride of silver present being less than $\frac{1}{20}$ milligrm. If one drop of the dilute NaCl ($\frac{1}{20}$ milligrm.) were added to the solution in its alkaline condition, the cloud formed on acidification was perfectly evident after a minute or two when examined in STAS' box. When a piece of fused silver chloride weighing 3 milligrms. was added to the alkaline solution, it dissolved after about half an hour, and gave a dense milkiness on addition of nitric acid.

The application of this method to deposits from chlorate and acetate, which the

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* The tendency to crystallise upon the anode is an objection to the use of the strong solutions, and probably makes itself the more felt in consequence of the paper wrapping, which impedes the free circulation of the liquid.

balance showed to be several milligrams too heavy, has given the unlooked for result that no corresponding quantity of chloride was present. Something more than a mere trace was indeed detected, but of amount probably not exceeding $\frac{1}{2}$ milligrm. The deposit from chlorate and acetate of April 2, and another which does not appear in the table as the current weighings were not taken successfully, in which the excess was about 7 milligrms. were both treated in this way with similar results. The loss of weight on strong heating appears to exclude the supposition that though chlorate was present it escaped decomposition, and thus we seem almost driven to the conclusion that the redundant matter is principally acetate, although the proportion of acetate to chlorate in the solution is a small one.

§ 22. We have had occasion to examine another point relating to the chemistry of electrolysis, of which the result may here be recorded. In our earlier experiments we used anodes containing an appreciable quantity of copper. The copper evidently tended to accumulate in the solution, becoming after a time apparent by its colour even when neutral; on addition of ammonia a distinct blue was struck. We were desirous of ascertaining whether under these circumstances there is danger of the deposits becoming contaminated. A distinctly blue solution was prepared, in which the proportion of copper to silver was considerable, and a deposit made. The texture was very much modified by the action of the copper, and the appearance was such that it was difficult to believe that the weight could be more than a small fraction of that of the simultaneous deposit from a pure silver solution. Some of the metal, which adhered very loosely, was lost in the washing, but the weights agreed to within a few milligrams. On dissolution in nitric acid and supersaturation with ammonia the solution showed no trace of colour, although about $\frac{1}{10,000}$ of copper can thus be detected.

§ 23. In the absolute measurements the determination of the interval (never less than three-quarters of an hour) between the first passage of the current through the voltameters and its final cessation could readily be effected with sufficient accuracy (probably to $\frac{1}{10,000}$), but a slight correction is called for in order to take account of the loss of time incurred at each operation of the reversing key, which controlled the direction of the current in the fixed coils (§ 8). To obtain the necessary data for this correction the main current was led through a few turns of wire surrounding a reflecting galvanometer. The resulting deflection is independent of the position of the key, but at the moment of reversal the current is interrupted, and the spot of light falls back towards zero. From a comparison of the amount of this falling back with that of the steady deflection, in conjunction with observations of the period of vibration, it is easy to deduce the time of interruption. It proved to be less than $\frac{1}{10}$ second, and was so nearly constant that after sufficient experience had been gained further observations were judged to be unnecessary. The connexions for this purpose are accordingly not shown in the diagram (Plate 17, fig. 1).

§ 24. In order more fully to explain the procedure in taking a deposit it will be advisable to give the details of one experiment. Thus on March 10, 1884, the current, roughly regulated to the desired value with the aid of the tangent galvanometer, was allowed to pass through the coils of the current-weighing apparatus for about half an hour. The electromotive force of the storage cells (when in good order) remains almost perfectly constant during an experiment, but the gradual warming of the copper conductors causes a slight falling off of current. On the present occasion the preparatory current was a little stronger than that ultimately used, so as to produce a slight overheating. During this time the three platinum voltameters, previously cleaned and weighed, were charged with solution of silver nitrate; and the pure silver anodes, wrapped in filter paper, were adjusted to their places at the top of the liquid. As will be seen from Table II., two of the bowls were charged with solution of normal strength (15 per cent.), and the other with solution of double this strength. When all was ready, the current, previously running along a shunt, was caused to pass through the voltameters at 4^h 17^m by the chronometer. The weights required to bring the pointer of the current-weighing balance to zero, with the corresponding times, are given in Table III. In the second column the first number means that at the moment in question the weight required to balance the suspended coil, as acted upon electromagnetically, was 7·694 grms., or rather 577·694 grms., but the 570 grms. being never moved need not be recorded. In this position of the reversing key the electromagnetic force increased the apparent weight of the suspended coil. The other set of readings, in which the magnetic force tended to lift the coil, are given in the fourth column. At 5^h 2^m the circuit was interrupted.

TABLE III.

Time.	Weight.	Time.	Weight.
h. m. s.		h. m. s.	
4 19 30	7·694	4 25 0	6·795
4 32 15	7·698	4 40 20	6·791
4 42 50	7·699	4 50 30	6·790
4 53 10	7·699	4 56 30	6·789
		5 1 15	6·789

From the numbers above given two curves are constructed (Plate 17, fig. 4), representing what would have been observed in either position of the key during the whole course of the experiment. To effect the integration of the current, the whole time, 45^m, is divided into nine periods of 5^m each, and the magnitude of the current at the middle of each period is taken to represent its value throughout the period. A more elaborate evaluation could easily have been applied, but was superfluous. The difference of ordinates at the middles of the periods gives the difference of weights in the second column of Table IV., and the mean of the square roots of these differences, viz. ·95171, is the square root of the difference of weights corresponding to the *mean current.*

TABLE IV.

Time.			Difference of weight.	Square root of Difference.
h.	m.	s.		
4	19	30	·897	·9471
4	24	30	·900	·9487
4	29	30	·904	·9508
4	34	30	·906	·9518
4	39	30	·908	·9529
4	44	30	·908	·9529
4	49	30	·909	·9534
4	54	30	·910	·9539
4	59	30	·910	·9539
Mean			. .	·95171

The whole time of deposit was 2700 seconds, but from this a deduction has to be made for the time lost in operating the reversing key. The loss of time at each operation was found (by a process already described) to be ·083 second. Thus the actual time of passage of the current through the voltameters is to be taken at

$$2700-7\times{\cdot}083=2699{\cdot}4 \text{ seconds.}$$

After the deposits had been formed they were washed in the manner already described with alcohol and hot and cold water, soaked over night, then rinsed and set to dry at 160° C. In the first row of Table V. will be found the weights of the bowls without deposits; in the second the weights after the deposits had been dried at 160° C.; in the third the differences representing the weights of the deposits; in the fourth the weights of the bowls after heating for about five minutes nearly to redness over an alcohol flame; and in the fifth the weights of the deposits as determined from the previous row.

TABLE V.—Deposits of March 10, 1884.

	Large bowl I. Pure nitrate. Normal strength.	Small bowl II. Pure nitrate. Double strength.	Small bowl III. Pure nitrate. Normal strength.
Before deposit	80·4490	17·2985	21·8789
After deposit, first weighing	81·5138	18·3628	22·9434
Gain	1·0648	1·0643	1·0645
After strong heating . . .	81·5135	18·3627	22·9433
Gain	1·0645	1·0642	1·0644

Mean 1·0644 grms.

To obtain numbers which, though of no absolute significance, allow of the comparison of experiments made on different occasions, we may divide ·95171 (the square root of the difference of the current weighings) by the amount of silver deposited per second. Thus for March 10 we have

$$\cdot95171 \div \frac{1\cdot0644}{2699\cdot4} = 2413\cdot7$$

The magnitude of the current was about ·4 ampère, and the areas of deposit about 37 sq. centims. for the small bowls, and about 75 sq. centims. for the large bowl.

The whole resistance of the current-weighing apparatus and of the voltameters is about 42 ohms, so that sufficient current can be obtained from 10 small GROVE cells, or from a rather less number of cells of a secondary battery.

§ 25. The tables in which are embodied the results of these protracted experiments will not now require much explanation. Those of Table I. are certainly erroneous on account of the presence of acetate (§ 18), and no weight is given to them in calculating a final result. For the same reason those deposits in Table II. which were prepared from solutions to which acetate had been added for the purpose of investigating the nature of the disturbance thereby produced, are of course excluded. The weights adopted for the silver deposits are those found after strong heating (nearly to redness) for about five minutes, no distinction being made between the deposits from chlorate and from nitrate of silver. The final mean 2414·45 expresses the square root of the difference of current weighings in grams divided by the rate of silver deposit in grams per second.

If we consider separately the deposits from chlorate of silver (without addition of acetate), we get as the mean number corresponding to the above 2414·3, in almost perfect agreement.

The deposits made on March 25 were *twice* strongly heated with intermediate weighing. Similar tests have been applied in other cases not recorded in the tables.

It should be stated that every determination since November, 1883, in which the manipulations were successfully conducted, is included in the table, and that nothing is excluded except in consequence of a decision made before the result was known. In one or two cases the current was too irregular to give good weighings of the suspended coil, and then the observations were not reduced with the view of obtaining absolute results, although the comparison of the silver deposits in different bowls might still be of interest. This happened on an occasion already alluded to when acetate and chlorate of silver were used in combination.

The results of Table II. agree together about as well as could be expected, the extreme difference from the mean being $\frac{1}{2500}$. It must be remembered that apart from the difficulties of manipulating the silver deposits errors may arise in the determination of the current, whose mean value has to be deduced from observations relating to only a part of the whole time involved. A small fluctuation in the strength of the current, lasting for a short time only, may thus escape detection. There is also an error involved in the determination of the time of electrolysis, which may altogether

TABLE I.

Date, 1883.	Solution.	Bowl.	Weight of deposits in grams.	Weight adopted as that of the silver deposited.	Duration of observation.	Duration in seconds, corrected.	Mean square root of double attraction in grams.	$\frac{\sqrt{m}}{\text{deposit per sec.}}$
					h. m.			
May 1 . . .	15 parts of nitrate of silver dissolved in 100 parts of water and filtered through acetate of silver.	Large platinum . Small platinum .	2·6338 2·6340	2·6339	2 0	7198·5	·88142	2408·9
,, 4 . . .		Large platinum . Small platinum .	2·9162 2·9154	2·9158	2 0	7198·4	·97580	2409·0
,, 8 . . .		Large platinum . Small platinum .	2·6887 2·6878	2·6882	1 45	6298·6	1·02889	2410·7
,, 12 . . .		Large platinum .	2·7218	2·7218	2 0	7198·9	·91147	2410·7
August 16 . .		Large platinum . Small platinum .	2·1441 2·1420	2·1430	1 15	4499·02	1·14765	2409·4
November 5 .	A new one similar to the last.	Large platinum . Small platinum .	2·3675 2·3659	2·3667	1 25	5099·08	1·11947	2411·9
,, 13 .		Large platinum . Small platinum .	4·0251 4·0233	4·0242	2 18	8278·67	1·17268	2412·5
,, 19 .		Large platinum . Small platinum .	3·0237 3·0233	3·0235	1 45	6298·83	1·15773	2411·9

TABLE II.

Date, 1883 and 1884.	Bowl.	Solution.	Weight of deposits in grams.		Weight adopted as that of the silver deposited.	Duration of observation.	Duration in seconds, corrected.	Mean square root of double attraction in grams.	√m / deposit per sec.	From chlorate alone.
			After drying at about 160°.	After heating to verge of redness.		h. m. s.				
November 29	Large platinum	Nitrate 15 to water 100	3·0166	..	3·01655	1 45 0	6298·67	1·15608	2413·9	
	Small „	„ „	3·0165							
December 4	Large „	„ „	2·9907	2·9901	2·9898	1 40 0	5998·67	1·20321	2414·1	
	Small „	„ „	2·9902	2·9895						
December 7	Large „	„ „	2·3731	..	2·3731	1 25 0	5098·75	1·12371	2414·4	
January 30	„ „	Nitrate 15 to water 100, but filtered several times through acetate	2·3316	2·3287						
	Small „	Nitrate 15 to water 100	2·3230	2·3229	2·3229	1 15 0	4499·08	1·24716	2415·5	
	„ silver	„ „	2·3229	..						
February 18	Large platinum	„ „	2·3484	2·3483	2·3482	1 25 0	5099·08	1·11213	2415·0	
	Small „	Nitrate 7½ to water 100	2·3482	2·3481						
	„ „	Nitrate 15 to water 100	2·3483	2·3481						
„ 22	Large „	„ „	3·2977	3·2975	3·2972	2 1 0	7258·75	1·09667	2414·4	
	Small „	„ „	3·2966	3·2965						
	„ „	Nitrate 30 to water 100	3·2979	3·2975						
„ 29	Large „	Nitrate 15 to water 100	2·2698	2·2696	2·2695	1 30 0	5399·17	1·01497	2414·6	
	Small „	„ „	2·2693	2·2691						
	„ „	Nitrate 30 to water 100	2·2701	2·2699						
March 5	Large „	Nitrate 15 to water 100	1·2247	1·2245	1·2245	0 45 0	2699·33	1·09544	2414·8	
	Small „	„ „	1·2247	1·2246						
	„ „	Nitrate 7½ to water 100	1·2248	1·2245						
„ 10	Large „	Nitrate 15 to water 100	1·0648	1·0645	1·0644	0 45 0	2699·42	·95172	2413·7	
	Small „	Nitrate 30 to water 100	1·0643	1·0642						
	„ „	Nitrate 15 to water 100	1·0645	1·0644						
„ 14	Large „	„ „	1·2897	1·2896	1·2894	0 45 0	2699·50	1·15311	2414·2	
	Small „	„ „	1·2892	1·2892						
	„ „	Nitrate 15 to water 100 with nitric acid added	1·2893	1·2893						
„ 25	Large „	Chlorate 10 to water 100	1·5306	1·5305 1·5303	1·52985	1 0 0	3599·08	1·02629	2414·4	2414·1
	Small „	Nitrate 15 to water 100	1·5298	1·5295 1·5295						
	„ „	Chlorate 10 to water 100	1·5302	1·5297 1·5297						
„ 29	Large „	Chlorate 5 to water 100	1·4530	1·4529	1·4531	1 0 0	3599·00	·97489	2414·6	2414·6
	Small „	Nitrate 15 to water 100	1·4532	1·4530						
	„ „	Chlorate 5 to water 100	1·4533	1·4533						
April 2	Large „	Chlorate 5 to water 100, filtered several times through acetate	1·7300	1·7287						
	Small „	Nitrate 15 to water 100	1·7232	1·7232	1·72325	1 12 59½	4378·58	·95018	2414·3	2414·2
	„ „	Chlorate 5 to water 100	1·7234	1·7233						
								Mean . .	2414·45	2414·3

amount to nearly half a second on a total in some cases as low as 2700 seconds. When so many experiments are made we must expect the cases to arise in which the small errors, due to various causes, are accumulated in the result.

§ 26. We may now calculate the results of our experiments in absolute measure. In the notation of § 15 we have, as the relation between the current i and the difference of weighings observed in air m,

$$i=\mu\sqrt{m},$$

where

$$\mu=\cdot037048.$$

If w be the electro-chemical equivalent of silver in C.G.S. measure, viz., the quantity of silver in grams deposited per second by the unit C.G.S. current, then the rate of deposit by current i is $w.i$, or $w.\mu.\sqrt{m}$. Now, by the table this rate of deposit is $\sqrt{m}./2414{\cdot}45$; so that

$$w=\frac{1}{2414{\cdot}45\times\cdot037048}=\mathbf{\cdot0111794.}$$

In terms of practical units we have as the quantity of silver in grams deposited per ampère per hour

$$1{\cdot}11794\times10^{-3}\times3600=\mathbf{4{\cdot}0246.}$$

The number found by KOHLRAUSCH in his recent experiments is

$$w=\cdot011183,$$

while that found by MASCART * is

$$w=\cdot01124.$$

The agreement between KOHLRAUSCH and ourselves is perhaps as good as could be expected, and would be diminished almost to nothing were we to take in our experiments the weights as found after drying at 160° C., viz., before the strong heating. The account hitherto published by KOHLRAUSCH is only an abstract, and does not explain how the deposits were treated.†

§ 27. Considering that the silver voltameter may now be used satisfactorily for the standardising of current-measuring instruments, we have made some experiments in order to ascertain the limits within which the method is applicable. With regard to the strength of the nitrate solution there is considerable latitude when the currents are weak, *e.g.*, not exceeding $\frac{1}{4}$ ampère. In such cases a 4 per cent. solution may be used satisfactorily in our voltameters. However, for practical purposes at the present time the object will usually be to measure stronger currents, and then it is advisable to keep the solution up to 15 or 30 per cent. If the solution is too weak in relation to the density of current, the deposit has a tendency to looseness, and is

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* 'Journal de Physique,' March, 1882.

† See Notes.

liable to grow up in an irregular manner, so as to meet the anode. In a 3-inch platinum bowl such a solution will allow of a current of about 1 ampère for a period of an hour. The strongest current which we have been able to use with a single voltameter is about 2 ampères, and for this purpose we employed a solution containing one part of salt to two parts of water. It is probable that the deposit would have deteriorated if the current had been allowed to flow for much longer than a quarter of an hour, but in that time an ample amount (about 2 grms.) is obtained. The practical conclusion is that currents not exceeding $1\frac{1}{2}$ ampère may be conveniently measured in a 3-inch voltameter by using a strong solution, and by stopping the operation after about a quarter of an hour. A shorter time than this would hardly allow of sufficiently precise measurement when a high degree of accuracy is aimed at. For purposes where an error of $\frac{1}{3}$ per cent. is admissible, a duration of five minutes (300 seconds) would be sufficient, and under these circumstances a stronger current would be unobjectionable.

It will be seen that the application of this method to the measurement of such currents as are usually passed through incandescent lamps presents no difficulty, and we hope that it may be generally adopted as a control upon the indications of instruments depending for their trustworthiness upon the constancy of springs or of steel magnets. The anodes should be composed of fine silver sheet (about $\frac{1}{8}$ inch thick), such as is sold for five shillings per ounce, and should not approach the sides of the bowl too closely. As there need be no waste of metal, the expense of silver as compared with copper should not be allowed to stand in the way of its use. For practical purposes it will be unnecessary to take some of the precautions which we thought incumbent upon us. After rinsing a few times with distilled water the deposit may be left to soak for an hour or so, and then after another rinsing dried over a spirit lamp. After the lapse of another hour it may be weighed, with a risk of error not exceeding a few tenths of a milligram.

When still stronger currents have to be dealt with, the silver voltameter is less convenient. Platinum bowls of large size are not usually met with, but two or three may be combined in parallel without much trouble. In one of our experiments the same current was passed successively through a single voltameter, and through two arranged in parallel. The deposit in the single bowl, thrown down in 13 minutes, was 2·2327 grms. Those in the other bowls were 1·0114 and 1·2215, altogether 2·2329, agreeing almost precisely. In this way with three bowls, such as we have used, in parallel, there would be no difficulty in measuring currents up to 5 ampères.

§ 28. The second branch of our subject is the evaluation of the electromotive force of standard galvanic cells. Enough has been said as to the means employed for measuring electric currents in absolute measure. If a current, after passing the current weighing apparatus, is made to traverse a known resistance, it will generate at the extremities of that resistance a known electromotive force. By suitably accommodating to one another the magnitude of the resistance and the strength of the current, the electromotive force may be made to balance that of a standard cell, whose force is thus determined. The difficulty of the matter relates principally to the preparation and definition of the standard cells, and in order to test the constancy of the cells it is desirable to extend both the absolute determinations and the comparisons of various cells over a considerable range of time.

Before describing further the arrangements adopted for the absolute measurements, it will be convenient to consider the comparisons of E.M.F., which were always made by the method of compensation, in order to diminish as far as possible the currents actually passed through the cells under examination. The main circuit consisted of two LECLANCHÉ cells M, and two resistance boxes N, O (joined by a short stout wire) of 10,000 ohms each (Plate 17, fig. 1). Of this resistance a variable and adjustable proportion was included between the points of derivation, and (by use of the second box) the total was in all cases made up to 10,000. Thus, in compensating a single CLARK cell the resistance from the first box might be 4900, and from the second 5100. By this means the constancy of the main current is secured. The derived branch includes the cell or cells to be tested (P), a mercury reversing key (Q), and a galvanometer (T), with which is associated a resistance (S) of 10,000 ohms. The galvanometer itself was of the THOMSON pattern, and had a resistance of about 200 ohms. By the substitution of an instrument with a longer wire and of resistance up to 10,000, a greater degree of sensitiveness might have been obtained, but with careful reading of the galvanometer scale the arrangements were sufficient for the purpose, and would indicate the E.M.F. to about $\frac{1}{10,000}$. In the preliminary trials a simple contact key with platinum studs was used in the galvanometer branch with the idea that shorter contacts would thus suffice. But, probably from thermoelectric disturbance, the readings thus obtained were not so consistent as with the mercury reversing key, and the smallness of the currents actually allowed to pass rendered the longer contacts unobjectionable. From the data already given it will be seen that a current of 10^{-8} ampères was sensible, and no disturbance could be expected from currents 100 times, or more, greater than this. In order to test whether the connexions were rightly made, the first observation was usually taken with a still higher resistance in the galvanometer branch, which could easily be effected by causing the current to pass through the body of one of the observers from hand to hand. If by accident too large a current was allowed to pass through a cell, no further use was made of that cell until the next day.* It must be mentioned that great care was taken, and was necessary, in respect of the insulation of the various parts. For instance, no correct results were obtainable when the LECLANCHÉ's stood upon the (tiled) floor, if at the same time other parts of the combination were touched with the hand. A sheet of paraffined paper interposed proved a remedy. In this matter we have had several disagreeable lessons, and we

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* Experiments detailed later (§ 31) show that the precautions observed in this respect were more stringent than was really necessary.

cannot too strongly emphasise our advice to take too many rather than too few precautions.

When two cells under comparison differ by a considerable fraction, they may be compared separately with the LECLANCHÉ'S, or rather expressed in terms of the current afforded by the LECLANCHÉ'S through 10,000 ohms. Thus, on Dec. 3, 1883, in order to balance CLARK No. 1 (see below) 4926 were required between the points of derivation. When a standard DANIELL of RAOULT'S pattern was substituted for the CLARK, the number required was 3798. In terms of No. 1 CLARK the E.M.F. of the DANIELL is thus 3798/4926, or ·7710. At the end of a series of comparisons it is proper to repeat the observation of the first standard cell, in order to check the constancy of the current supplied by the LECLANCHÉ'S. In our experience there was usually no appreciable variation.

When the cells to be compared are nearly alike, it is better in the second observation to express the *difference* of forces by setting the second cell to act against the first. Thus, the force of CLARK No. 1 being expressed as before by 4926, the corresponding resistance for the excess of the force of CLARK 1 over CLARK 3 was 2 ohms. Hence, in terms of CLARK 1 the force of CLARK 3 is ·9996, and the result is less liable to error than if the comparisons of each with the LECLANCHÉ'S were effected separately.

§ 29. Of the first batch of CLARK'S which were compared together from November, 1883, onwards, No. 1 was set up near the beginning, and Nos. 2, 3, 4, 5, towards the end of October. They were prepared generally according to the directions given by Dr. ALDER WRIGHT,[*] to whom we have been indebted for advice and for samples of some of the materials. The saturated solution of zinc sulphate was nearly neutral. The metallic zinc was bought as pure from Messrs. HOPKIN and WILLIAMS. The mercurous sulphate was from the same source, and the metallic mercury was redistilled in the laboratory. We did not consider it desirable to take precautions against the presence of air, thinking that it was sure to find an entrance sooner or later.

Four new cells, Nos. 6, 7, 8, 9, were set up from the same materials on January 10, 1884. It will be seen from the table that when a fortnight old they differed but little from the first batch.

In preparing these cells the most troublesome part of the process was found to be the casting of the zincs. The metal, melted in a porcelain crucible, was sucked up into a previously heated tube of hard glass, but the operation required some address, and there was considerable waste of zinc from oxidation and otherwise. It occurred to us to try whether equally, or perhaps still more, satisfactory results might not be obtained by substitution for the solid metal of an amalgam of zinc. For this purpose a form of cell, called for brevity the H-cell, was contrived, and is shown full size (Plate 17, fig. 5). One of the legs is charged with the amalgam of zinc (B), the other with pure mercury (C), covered with a layer of mercurous sulphate (D). The whole is then

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[*] Phil. Mag., July, 1883.

filled up above the level of the cross tube with saturated zinc sulphate (E), and a few crystals are added. Evaporation is prevented by corks (F), closing the upper ends of the tubes. Electrical contact with the amalgam and with the pure mercury is made by platinum wires (A), sealed into the glass.

A preliminary experiment in which both legs of a cell were charged with amalgam (the mercurous sulphate being dispensed with) having shown that the E.M.F. was independent of the excess of undissolved zinc, two cells, H_1, H_2, were set up on February 12, 1884, and submitted to various tests, such as stirring up the amalgam with a glass rod. The amalgam was prepared from pure mercury and the same zinc as before. Subsequently, on March 6, six more cells were charged with a somewhat different treatment. The sulphate of zinc was from another sample and contained appreciable quantities of iron. Moreover, the amalgam was differently prepared. The mercury and zinc were shaken up together in a bottle with a little acid, after which the acid was washed out by shaking with several changes of water, until litmus paper was no longer reddened. Into each cell, in addition to the fluid amalgam, there was dropped a piece of solid zinc from the bottle. The same mercurous sulphate as before was employed, but the washing with distilled water was dispensed with. The three remaining cells of this pattern H_9, H_{10}, H_{11}, were charged on March 12, 1884, with a third sample of zinc sulphate.

The agreement among themselves and the constancy of the H-cells has been all that could be wished; but some modification in preparation will be desirable, for it has been found that the amalgam tends to harden into compact lumps, the expansion of which is liable to burst the cells. From this cause H_3, H_4, H_7, succumbed at a comparatively early stage. It is probable that the addition of solid zinc to the fluid amalgam had better be omitted, but on this and other points we hope to make further investigation. The H pattern lends itself conveniently to experiment, as it is possible by withdrawing the corks to make any desired addition to the contents. On more than one occasion the contents of each leg have been vigorously stirred, without the slightest change in the E.M.F.

Since the first draft of this memoir was written two new batches of cells of the ordinary pattern have been prepared with different materials. In this case the zincs were used as supplied, without re-casting,* and the mercurous sulphate, though distinctly acid, was not washed. The first batch (10, 11, 12, 13) were set up on May 7, and the second batch (14, 15, 16, 17, 18, 19) on May 26.

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* The surface of the metal was brightened with file and sand paper.

TABLE VI.

	Nov. 6, 1883.	Nov. 9, 1883.	Nov. 12, 1883.	Nov. 14, 1883.	Nov. 20, 1883.	Nov. 22, 1883.	Nov. 30, 1883.	Dec. 3, 1883.	Dec. 5, 1883.	Dec. 11, 1883.	Dec. 12, 1883.
CLARK 1 . . .	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
" 2 . . .	1·0015	1·0016	1·0006	1·0002	1·0006	1·0008	1·0014	1·0010	1·0010	1·0006	1·0008
" 3 . . .	1·0001	1·0000	·9988	·9990	·9990	·9996	1·0000	·9996	·9996	·9994	·9996
" 4 . . .	1·0008	1·0008	·9996	·9996	·9994	1·0000	1·0004	1·0000	1·0000	·9994	·9998
" 5 . . .	1·0012	1·0016	1·0002	1·0002	1·0004	1·0008	1·0010	1·0000	1·0004	1·0000	1·0002

TABLE VII.

	Jan. 25, 1884.	Jan. 28, 1884.	Feb. 16, 1884.	Feb. 20, 1884.	Feb. 23, 1884.	March 7, 1884.	March 11, 1884.	March 18, 1884.	March 27, 1884.	April 3, 1884.	April 25, 1884.	May 8, 1884.	May 27, 29, 30, 1884.	June 11, 1884.
CLARK 1 . .	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
" 2 . .	1·0005	1·0000	·9996	..	1·0000	·9998	..	1·0004						
" 4 . .	·9999	·9997	·9994	..	·9998	1·0000	..	·9998	·9996	1·0000	·9998	1·0000	·9998	1·0000
" 5 . .	·9998	..	·9998	..	·9992	·9990	..	·9994	·9988	·9998	·9980	·9994	·9996	·9990
" 6 . .	1·0005	..	1·0008	..	1·0002	1·0008	..	1·0008	1·0008	..	1·0006	1·0006	In ice.	1·0009
" 7 . .	·9997	..	·9998	..	·9996	·9996	..	·9998	·9996	..	·9994	·9996		
" 8 . .	1·0001	..	1·0000	..	..	·9998	..	1·0000	·9998	..	·9998	·9999	1·0000	1·0000
" 9 . .	1·0003	..	·9998	..	..	1·0002	..	1·0002	1·0000	..	1·0000	1·0000	1·0001	1·0001
H_1	..	..	·9988	·9993	1·0000	·9998	..	·9996	·9996	·9996	·9994	·9994		
H_2	..	..	1·0006	1·0003	1·0003	1·0002	..	1·0000	1·0000	1·0001	·9998			
H_3	..	..	..	..	..	1·0010	1·0010	1·0008	1·0006					
H_4	..	..	..	..	..	1·0008	1·0008	1·0007	1·0008					
H_5	..	..	..	..	..	1·0008	1·0008	1·0007	1·0008	..	1·0006	1·0006	1·0006	1·0004
H_6	..	..	..	..	..	1·0008	1·0008	1·0007	1·0006	..	1·0006	1·0006	1·0006	1·0006
H_7	..	..	..	..	..	1·0008	..	1·0007	1·0008					
H_8	..	..	..	..	..	1·0008	..	1·0006	1·0008	..	1·0006	1·0006	1·0008	
H_9	..	..	..	..	..	..	..	1·0003	1·0005	..	1·0002	1·0006	..	1·0003
H_{10}	..	..	..	..	..	..	..	1·0005	1·0006	..	1·0003	1·0005	1·0006	1·0006
H_{11}	..	..	..	..	..	..	..	1·0005	1·0005	..	1·0002	1·0005	1·0006	1·0006

TABLE VIII.

	1884.									
	May 8.	May 12.	May 14.	May 15.	May 16.	May 17.	May 19.	May 20.	May 21.	May 22.
CLARK 1 . . .	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
,, 10 . . .	1·0200	1·0150	1·0022*	1·0022*	1·0022	1·0016*	1·0010*	1·0006	1·0004	1·0002
,, 11 . . .	1·0132	1·0116	1·0104	1·0096	1·0010*	1·0010*	1·0010	1·0008	1·0008	1·0008
,, 12 . . .	1·0072	1·0124	. .	1·0118	1·0110	1·0104	1·0092	1·0080	1·0072	1·0050
,, 13 . . .	1·0030	uncertain	. .	1·0150						

	1884.									
	May 23.	May 24.	May 26.	May 27.	May 28.	May 29.	May 30.	June 2.	June 4.	June 11.
CLARK 1 . . .	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
,, 10 . . .	1·0003	1·0002	1·0002	1·0003	1·0002	1·0002*	1·0002	. .	1·0003	1·0003
,, 11 . . .	1·0006	1·0004	1·0004	1·0006	1·0004	1·0002*	1·0004	. .	1·0003	1·0003
,, 12 . . .	1·0026	1·0010	1·0006	1·0007	1·0004	1·0002*	1·0004	. .	1·0001	1·0004
,, 13 . . .	1·0090	. .	. .	. .	1·0080	1·0008*	1·0008	. .	1·0005	1·0003
,, 14 . . .	. .	. .	. .	1·0240	1·0214*	1·0158*	. .	1·0126	1·0132	1·0100
,, 15 . . .	. .	. .	. .	1·0240	1·0230	1·0220	. .	1·0195	1·0148	1·0092
,, 16 . . .	. .	. .	. .	1·0090	1·0144	1·0134	. .	1·0098	·9997	1·0109
,, 17 . . .	. .	. .	. .	broken						
,, 18 . . .	. .	. .	. .	1·0210	1·0194	1·0168	. .	1·0014	1·0006	1·0000
,, 19 . . .	. .	. .	. .	1·0230	1·0200	1·0168	. .	1·0032	1·0006	1·0006

* For continuations of these tables, see notes.

§ 30. Tables VI., VII., VIII. show the results of most of the comparisons, the value of every cell on each day being expressed in terms of CLARK No. 1. It will be seen that there are durable differences between cells of the same batch, but that these do not much exceed $\frac{1}{1000}$. There are also changes of small amount in the force of a given cell, part of which is perhaps attributable to a difference of temperature coefficient. Moreover the actual temperatures may possibly have differed a few tenths of a degree in the case of various cells, many of which stood some feet apart. CLARK No. 3 does not appear in Table VII., since on January 25 it was found to be short circuited. During the later comparisons, Nos. 6 and 7 were unavailable, having been diverted to another use.

The two last batches took a longer time than usual (about three weeks) to reach their normal values. It will be seen from Table VIII. that when first set up these cells were too strong by as much as 1 or 2 per cent. It was thought that the process of settling down might be quickened by closing the circuit occasionally for some minutes, through a resistance of 1000 ohms, and the asterisk in the table indicates that on the day previous to the comparison the cell in question had been so treated for about ten minutes. When once the settling down is completed, further short circuiting appear to be without effect.

TABLE IX.

Time.	Resistance between Poles.	E. M. F.
h. m.		
3 35	∞	4994
3 47	∞	4994
3 53	Changed from ∞ to 10,000	
3 56	10,000	4851
3 41	10,000	4853
4 59	Changed from 10,000 to ∞	
5 2	∞	4990
5 15	∞	4991
5 47	∞	4992
6 3	Changed from ∞ to 1000	
6 5	1,000	3990
6 11	1,000	3860
6 13	Changed from 1000 to ∞	
6 19	∞	4990
6 25	∞	4991
6 29	Changed from ∞ to 500	
6 34	Changed from 500 to ∞	
6 36	∞	4985
6 37	∞	4988
6 52	∞	4991

§ 31. Some observers having laid great stress upon the importance of guarding CLARK cells from the passage of sensible currents, we give a specimen of the results of some tests to which we have subjected a few of the cells, in order to find out how much care was really necessary in their use to avoid polarisation. The accompanying Table IX. shows the variations of E.M.F. of CLARK No. 6 on April 28, when very rudely treated. The other connexions remaining as usual, the poles of the cell were joined through a resistance-box, by means of which the cell could be short circuited with any external resistance from 0 to infinity. The numbers entered (such as 4994) are proportional to the difference of potential between the poles, being in fact the resistance between the points of derivation on the LECLANCHÉ circuit. It will be seen that in the course of a quarter of an hour the cell recovers, to within a few ten-thousandths of its value, from the effects of being short circuited for several minutes through such resistances as 1000 ohms. From the electromotive forces *during* the short circuiting it appears that the internal resistance is high, nearly as much as 300 ohms.

The manner in which the CLARK cells have borne the tests applied to them justifies the hope that they may be found generally available as standards of E.M.F. But further experience is necessary as to the effect of various modes of preparation, and it is to be hoped that this may soon be forthcoming. As used by us, the process is so simple that no one need be deterred from setting up cells for himself.

§ 32. Experiments on DANIELL cells gave only a moderately good result. RAOULT'S form was employed, in which the zinc and copper solutions are placed in separate beakers, the connexion being only through a Y-tube charged with zinc sulphate and tied over the ends with bladder. One electrode was of pure zinc amalgamated with pure mercury, and the other of copper freshly coated electrolytically. The zinc and copper solutions were both of sp. gr. 1·1.

TABLE X.

	November 30, 1883.	December 3, 1883.	December 5, 1883.	December 11, 1883.	December 12, 1883.
CLARK No. 1. . .	1·0000	1·0000	1·0000	1·0000	1·0000
DANIELL	·7702	·7710	·7705	·7698	·7702

The DANIELL cell has of course to be charged freshly on each occasion, and is thus far less convenient in use than the CLARK'S, which stand for months always ready for use. The temperature of the cells at the time of the comparisons tabulated was about 16° C.

Through the kindness of the inventor, we have had the opportunity of comparing some DE LA RUE cells with the CLARK'S. The cells are of a somewhat modified construction, the atmospheric oxygen being excluded by a layer of paraffine oil. They were set up some days before the comparisons, and short-circuited for five minutes in order to start the chemical action.

We found

No. 1 De La Rue = ·7510 Clark.
No. 2 „ = ·7512 „
No. 3 „ = ·7382 „
No. 4 „ = ·7458 „
Mean „ = ·7465 „

Mr. De La Rue (Phil. Trans., Vol. 169, Part I.) found a result decidedly smaller, the explanation of which is to be sought in the fact that in his experiments the cells were making a current of about $\frac{1}{1000}$ ampère, whereas in ours the electromotive force is measured when no current passes.

It may be useful to record also a comparison between our Clark's and a new form of Daniell, introduced by Sir W. Thomson. This cell is charged with zinc sulphate of sp. gr. 1·02, and with saturated solution of copper sulphate. The zinc is not amalgamated. According to Sir W. Thomson's directions, the circuit of the cell is closed through 250 ohms, and the E.M.F. measured is that between the poles under these conditions. After the current had been running for about an hour and a half, the E.M.F., which had been increasing, became fairly constant, and its value was then ·743 in terms of Clark No. 1. The comparison was made on April 8, 1884.*

§ 33. We now pass to the description of the method adopted for the absolute determinations. The current, after leaving the current-weighing apparatus, is caused to traverse a wire of known resistance R, whose stout copper terminals rest on the copper bottoms of suitable mercury cups H, K (Plate 17, fig. 1). To these cups are brought also the terminals of the derived branch, in which are included the galvanometer and the standard cell.

On account of the strength of the currents (about $\frac{1}{3}$ ampère) the resistance required to be of special construction in order to avoid too great heating.

Two ebonite rods were held in a parallel position by a frame of wood, and round these uncovered german silver wire was wrapped so as to be exposed to the air as much as possible. The rods are about a foot apart, and are grooved, the better to keep the wire in its place. The resistance is about 4 B.A., and was determined with the aid of a *five* and a *single*.† At 17°·6 its value is 4·00699 B.A.

Even this resistance-wire heats sensibly when the current of $\frac{1}{3}$ ampère is passed through it for more than a few seconds. The increment of resistance was determined by observations taken immediately after the passage for some minutes of a stronger current (about 1 ampère). In this way it was found that for the currents usually employed a correcting factor 1·00041 must be introduced to take account of the heating, independently of course of the correction necessary for the difference between 17°·6 and the temperature of the atmosphere at the time of an absolute determination.

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* See notes.

† For the methods used to ascertain the value of the *five* the reader is referred to former papers.

§ 34. In order to obtain the balance of electromotive forces two distinct methods have been followed. In the earlier determinations there was no electromotive force in the derived branch except that of the standard cell, and the adjustment was effected by variation of a comparatively high auxiliary resistance from a box, placed in multiple arc with the [4]. The readings were taken by reversal of the galvanometer connexions at a mercury commutator, and the small outstanding galvanometer displacement was allowed for with the aid of observations of the effect of a known change in the auxiliary resistance. In this way could be determined the auxiliary resistance, and from it (by addition of conductivities) the effective resistance between the points of derivation necessary for a balance with the actual current. The value of the current at the moment in question is deduced from the curves representing the two sets of current-weighings (§ 24). In the course of half an hour several almost independent determinations of the electromotive force could be completed.

This method is the simplest, and could usually be made to work satisfactorily. It is, however, open to the objection that if the current changes rapidly we must either allow for a considerable galvanometer displacement or else alter the auxiliary resistance. But the latter change reacts upon the principal current, and renders the current weighing curves discontinuous, thereby increasing the difficulty of specifying the value of the current at the moment of observation.

§ 35. In the second method the resistance between the points of derivation is the [4] simply, and compensation is made in the galvanometer branch by the introduction of a graduated E.M.F. (Plate 17 fig. 1). The arrangement is in fact almost the same as in the comparison of two cells by the method of difference (§ 28), one of the cells being replaced by the resistance [4] traversed by the main current. As the apparatus for these comparisons was always ready for use, this method was, under the circumstances of the case, really more convenient than the other, and was employed in the later determinations. The procedure will be best understood from an example.

On March 29, 1884, determinations of silver and of electromotive force were made simultaneously, so that the same set of current weighings might serve for both purposes. Accordingly the main current traversed the three voltameters, the current weighing apparatus and the resistance [4]. In the derived branch (Plate 17, fig. 1) were the standard cell No. 4 CLARK, the galvanometer with its commutator, and coils from a resistance box, through which passed the current from the two LECLANCHÉ cells (§ 28). If the compensation between the CLARK and the difference of potentials at the terminals of the [4] were incomplete the balance could be restored by the introduction of a graduated part of the E.M.F. of the LECLANCHÉ'S, the value of which, in terms of the CLARK, is found by a subsequent experiment, in which the [4] is excluded. It will be understood that the LECLANCHÉ'S worked in a perfectly constant manner, the whole resistance in circuit being always made up to 10,000 ohms (in addition to that of the cells themselves). If E be the E.M.F. of the CLARK, ρ the resistance (traversed by the current of the LECLANCHÉ'S) which must be used to get a balance when the [4] is excluded, r the resistance actually required during a set of measurements when [4] is connected, then the electromotive force actually compensating the action of [4] is $E(1-r/\rho)$.

At the beginning of the proceedings on March 29 the main current was stronger than that required for the simple compensation of E, so that to get a balance at the galvanometer the LECLANCHÉ'S would have had to be reversed. At 18^m from the commencement the current had fallen to the point of compensation with $r=0$. At 28^m balance required $r=20$ B.A., at 34^m $r=37$, and at 48^m $r=90$. To take these observations, the easiest way is to overshoot the point somewhat, and then continually reversing the galvanometer to note the time of passing through the balance. From the curves representing the current weighings, the double force of attraction at the above times were found to be ·9645, ·956, ·9495, ·931, expressed in grams. This is what has been denoted by m (§ 26), and the corresponding current is

$$i=\cdot 037048\sqrt{m}.$$

§ 36. The resistance R between the points of derivation must be expressed in absolute measure, if we wish E to be so expressed. But for comparison with the results of other observers it will be convenient to keep this question apart and, in the first instance, to express our electromotive forces as if the B.A. unit were correct. Any factor (such as ·9867) which may be adopted to express the B.A. unit in terms of the ohm will enter also into the expression of E in true volts.

At the atmospheric temperature 13°·1 the value of the [4] is 3·9998 B.A., whence

$$R=4\cdot 00143 \text{ B.A.},$$

correction being made for the heating effect of the current.

The formula for E is

$$E=\cdot 037048R.\sqrt{m}.\frac{\rho}{\rho-r}$$

The value of ρ (on the occasion in question) was 4999 B.A., and this completes the data for the evaluation of E. The four values corresponding to the above observations are

$$1\cdot 4559, \quad 1\cdot 4553, \quad 1\cdot 4553, \quad 1\cdot 4566,$$

giving as mean

$$E=1\cdot 4558 \text{ B.A. volts.}$$

This result is for No. 4 at a temperature of 13°·1. The value of No. 4 in terms of No. 1 at the time in question was about ·9998, so that we should have found for No. 1

$$E=1\cdot 4561 \text{ B.A. volts.}$$

We have still to reduce to the standard temperature of 15°. The coefficient originally given by LATIMER CLARK is 1·0006 per degree centigrade. WRIGHT and

THOMSON[*] found a smaller number, viz., 1·00041, and with this our results were first reduced. Later, however, we found reason to suspect that the actual change was greater than this, and accordingly made some special observations to clear up the doubt. One cell (No. 6) was mounted in a large test tube, the gutta-percha-covered leading wires being brought through a tightly-fitting indiarubber cork, and was kept constantly at 0° centigrade by being surrounded with ice. With this No. 1 at the temperature of the room was compared from day to day, with the result that its temperature coefficient is about the double (1·00082) of that given by WRIGHT and THOMSON. A similar result was found by HELMHOLTZ,[†] who remarks that the effect of temperature may vary according to the preparation of the cell.

Using this number to reduce the result of March 29, we have to subtract ·0022, thus obtaining

$$E = 1{\cdot}4539 \text{ B.A. volts}$$

as the electromotive of No. 1 CLARK at 15°.

TABLE XI.

I. Date, 1883 and 1884.	II. Cell used.	III. Temperature.	IV. E.M.F. in B.A. volts.	V. E.M.F. relative to No. 1.	VI. E.M.F. of No. 1.	VII. Correction to 15°.	VIII. E.M.F. in B.A. volts, corrected to 15°.
October 23 . .	CLARK No. 1	15°·9	1·4542	1·0000	1·4542	+·0010	1·4552
November 20 .	,, No. 2	15·3	1·4549	1·0006	1·4540	+·0004	1·4544
,, 21 .	,, No. 1	14·9	1·4543	1·0000	1·4543	−·0002	1·4541
,, 22 .	,, No. 1	14·9	1·4533	1·0000	1·4533	−·0002	1·4531
December 4 .	,, No. 1	15·8	1·4524	1·0000	1·4524	+·0010	1·4534
,, 11 .	,, No. 1	17·2	1·4524	1·0000	1·4524	+·0026	1·4550
,, 12 .	,, No. 2	15·8	1·4549	1·0008	1·4537	+·0010	1·4547
January 28 . .	,, No. 2	15·0	1·4541	1·0000	1·4541	+·0000	1·4541
March 20 . . .	,, No. 4	15·8	1·4533	·9998	1·4536	+·0010	1·4546
,, 25 . . .	,, No. 1	13·5	1·4560	1·0000	1·4560	−·0018	1·4542
,, 29 . . .	,, No. 4	13·1	1·4558	·9998	1·4561	−·0022	1·4539
April 2 . . .	,, No. 1	16·1	1·4524	1·0000	1·4524	+·0014	1·4538
,, 7 . . .	,, No. 1	15·5	1·4535	1·0000	1·4535	+·0006	1·4541
Mean	. .	15·3	. .	. .	. .	. .	1·4542

§ 37. This determination and twelve others, made at intervals from Oct., 1883, to April, 1884, are exhibited in Table XI.[‡] They are all deduced from observations with the current-weighing apparatus. It will be seen that there is little or no evidence of any progressive change. The casual fluctuations are of course partly due to errors of observation, but it would seem are principally to be attributed to real variations of

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[*] Phil. Mag., July, 1883, p. 36.

[†] Sitzungsber. d. Kön. Akad. d. Wiss. zu Berlin, February, 1882.

[‡] For continuation of Table XI. see notes.

electromotive force of the same kind as appear in the Tables VI., VII., VIII., showing the relative values of the various cells. The mean temperature at the times of the determinations differs so little from 15°, that the final number for that temperature is almost independent of the temperature coefficient.

We may take as applicable with but little error to all the cells of this type that have been experimented upon

$$E = 1 \cdot 454 \text{ B.A. volts at } 15^\circ.$$

The value for the H-cells would be a little higher. (See Tables.)

The corresponding number found by Mr. LATIMER CLARK was

$$E = 1 \cdot 457 \text{ B.A. volts,}$$

so that the difference between us is small, and perhaps even dependent upon variations in the materials or construction of the cells.

To express our results in true volts we have only to introduce the factor expressive of the B.A. unit in terms of the ohm. If in accordance with our own determinations we take

$$1 \text{ B.A. unit} = \cdot 9867 \text{ ohm,}$$

we shall have as the value of a CLARK cell at 15°

$$E = \mathbf{1 \cdot 435} \text{ volt.}$$

§ 38. It has been mentioned that on March 29 silver deposits were made at the same time as the observations of E.M.F. One object of this was to exemplify the procedure which will probably be in future the most convenient for the determination of E.M.F. when the very highest accuracy is not required. It is evident that if we assume a knowledge of the electro-chemical equivalent of silver, the weights obtained in a given time on March 29 will lead to a determination of E.M.F., *independently of the current weighings.* We propose to exhibit the method of calculation, ignoring altogether the use of the current-weighing apparatus, whose only effect will be that of a resistance of about 40 ohms. If W be the weight of silver deposited in the time t, w the electro-chemical equivalent, we have as the relation between W and E,

$$W = \frac{wE}{R} \int \left(1 - \frac{r}{\rho}\right) dt$$

$$= \frac{wEt}{\rho R} \left(\rho - \int \frac{r dt}{t}\right)$$

On this occasion $W = 1 \cdot 4531$ grms., $t = 3599$ seconds, $R = 4 \cdot 0014$ B.A., $\rho = 4999$ B.A., as before. If w be assumed, the only other element required for the evaluation of E is

$$\int\frac{rdt}{t},$$

viz., the mean value of r necessary for a balance of E.M.F. during the time that the current ran through the voltameters. To get this the actual observations of r are plotted, the times being taken as abscissæ, and a curve constructed representing the value of r throughout the course of the experiment.* From this curve the ordinates are measured, which correspond to the middle of every five minutes' period. The values of r thus obtained are

TABLE XII.

Time.	r.	Time.	r.
m.		m.	
$2\frac{1}{2}$	-22	$32\frac{1}{2}$	$+32$
$7\frac{1}{2}$	-16	$37\frac{1}{2}$	$+48$
$12\frac{1}{2}$	-10	$42\frac{1}{2}$	$+66$
$17\frac{1}{2}$	-2	$47\frac{1}{2}$	$+86$
$22\frac{1}{2}$	$+8$	$52\frac{1}{2}$	$+112$
$27\frac{1}{2}$	$+18$	$57\frac{1}{2}$	$+140$

Mean $= +38{\cdot}3$.

The rapid falling-off of the current towards the end of the hour is believed to be due to the formation of crystals upon the anodes of the cells charged with silver chlorate. The value of

$$\rho-\int\frac{rdt}{t}$$

being thus found to be 4960·7, the calculation of E may be completed. Taking $w=1{\cdot}1180\times10^{-2}$, we get

$$E=1{\cdot}4562 \text{ B.A. volts},$$

as the electromotive force of No. 4 CLARK at 13°·1.

On April 2 an equally satisfactory result was found from the silver deposits without use of the current weighings. It will be seen that in this way anyone may determine the E.M.F. of his standard battery with a very moderate expenditure of trouble and without the need of any special apparatus. So large a resistance in the main circuit as in the above example, due to the idle coils of the current-measuring apparatus, is not necessary, but some resistance in addition to R and that of the battery and voltameters would probably be advisable. Otherwise the magnitude of the current would be too sensitive to the resistance of the voltameters, which cannot be included

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* In the formation of the curve use was made of observations in which the galvanometer balance was incomplete, the value of the scale divisions being approximately known.

in the circuit until the experiment actually begins. In the preliminary adjustments the resistance of the voltameters should be represented by an estimated equivalent of wire resistance, and this should not be too large a fraction of the whole. In our case the resistance of the three voltameters charged with nitrate solution of 15 per cent. was a little under two ohms, and the conditions under which we worked would be sufficiently imitated by a circuit containing, besides the [4] and the voltameters, an extra resistance of 10 ohms. A battery of three or four GROVE cells would then be sufficient for the generation of the current.

APPENDIX (see § 15).

TABLE of the values of $\sin\gamma\ \{2F_\gamma-(1+\sec^2\gamma)E_\gamma\}$ from $\gamma=55°$ to $\gamma=70°$.

° '		° '		° '	
55 0	$\bar{1}$·9198899	60 0	·1786408	65 0	·4433405
55 6	$\bar{1}$·9250674	60 6	·1838431	65 6	·4487720
55 12	$\bar{1}$·9302440	60 12	·1890478	65 12	·4542107
55 18	$\bar{1}$·9354198	60 18	·1942546	65 18	·4596565
55 24	$\bar{1}$·9405945	60 24	·1994636	65 24	·4651097
55 30	$\bar{1}$·9457677	60 30	·2046748	65 30	·4705707
55 36	$\bar{1}$·9509400	60 36	·2098887	65 36	·4760395
55 42	$\bar{1}$·9561123	60 42	·2151058	65 42	·4815165
55 48	$\bar{1}$·9612837	60 48	·2203260	65 48	·4870015
55 54	$\bar{1}$·9664536	60 54	·2255491	65 54	·4924944
56 0	$\bar{1}$·9716227	61 0	·2307753	66 0	·4979956
56 6	$\bar{1}$·9767918	61 6	·2360045	66 6	·5035052
56 12	$\bar{1}$·9819605	61 12	·2412367	66 12	·5090234
56 18	$\bar{1}$·9871288	61 18	·2464720	66 18	·5145504
56 24	$\bar{1}$·9922966	61 24	·2517106	66 24	·5200861
56 30	$\bar{1}$·9974637	61 30	·2569525	66 30	·5256304
56 36	·0026304	61 36	·2621981	66 36	·5311838
56 42	·0077970	61 42	·2674478	66 42	·5367469
56 48	·0129635	61 48	·2727014	66 48	·5423195
56 54	·0181298	61 54	·2779585	66 54	·5479017
57 0	·0232962	62 0	·2832194	67 0	·5534935
57 6	·0284628	62 6	·2884843	67 6	·5590948
57 12	·0336297	62 12	·2937533	67 12	·5647060
57 18	·0387966	62 18	·2990263	67 18	·5703278
57 24	·0439638	62 24	·3043035	67 24	·5759599
57 30	·0491317	62 30	·3095854	67 30	·5816022
57 36	·0542999	62 36	·3148717	67 36	·5872550
57 42	·0594684	62 42	·3201621	67 42	·5929188
57 48	·0646364	62 48	·3254571	67 48	·5985936
57 54	·0698062	62 54	·3307575	67 54	·6042795
58 0	·0749769	63 0	·3360628	68 0	·6099767
58 6	·0801480	63 6	·3413729	68 6	·6156851
58 12	·0853198	63 12	·3466879	68 12	·6214051
58 18	·0904926	63 18	·3520081	68 18	·6271370
58 24	·0956665	63 24	·3573335	68 24	·6328810
58 30	·1008414	63 30	·3626642	68 30	·6386371
58 36	·1060175	63 36	·3680004	68 36	·6444054
58 42	·1111950	63 42	·3733422	68 42	·6501859
58 48	·1163737	63 48	·3786896	68 48	·6559791
58 54	·1215535	63 54	·3840425	68 54	·6617852
59 0	·1267346	64 0	·3894014	69 0	·6676045
59 6	·1319170	64 6	·3947666	69 6	·6734371
59 12	·1371009	64 12	·4001380	69 12	·6792833
59 18	·1422865	64 18	·4055155	69 18	·6851433
59 24	·1474739	64 24	·4108993	69 24	·6910170
59 30	·1526636	64 30	·4162893	69 30	·6969043
59 36	·1578552	64 36	·4216858	69 36	·7028058
59 42	·1630486	64 42	·4270894	69 42	·7087220
59 48	·1682439	64 48	·4324998	69 48	·7146529
59 54	·1734412	64 54	·4379166	69 54	·7205985

EXPLANATION OF PLATE.

PLATE 17.

Fig. 1. A. Principal battery of GROVE's or storage cells.
B. Resistance for adjustment of current.
C. Voltameters.
D. Rough tangent galvanometer.
E. Reversing key of current weighing apparatus.
F. Fixed coils.
G. Suspended coil.
H, K. Mercury cups, into which dip the terminals of resistance R.
L. Earth connexion.
M. LECLANCHÉ's of E.M.F. compensator.
N, O. Resistance-boxes of same.
P. Standard galvanic cell.
Q. Galvanometer commutator.
S. Associated resistance of 10,000 ohms.
T. Galvanometer.

Fig. 2. Section of ebonite ring (full size).

Fig. 3, § 14. Connexions for comparison of galvanometer constants.
A. DANIELL cell.
B. Mercury reversing key.
C. Point where current divides.
D. Coil of electro-dynamometer.
E. Ebonite coil.
F, H, L, M. Mercury cups.
G. Bridge galvanometer.
K. Resistance-box in multiple arc with [10].
P. Short circuiting piece to connect F and H.
N. Resistance added to E.

Fig. 4, § 24. Curves of current weighings. In the original drawing two divisions along the line of abscissæ represent one minute, and two divisions along the line of ordinates represent one milligram. Of these divisions every tenth only is shown in the Plate.

Fig. 5, § 29. H-pattern of CLARK cell.
- A. Platinum wires sealed through glass.
- B. Amalgam of zinc.
- C. Pure mercury.
- D. Mercurous sulphate.
- E. Saturated solution of zinc-sulphate.
- F. Corks.

NOTES.

(Added December, 1884.)

Note to § 25.

In order to investigate the effect (if any) of temperature upon the amount of silver deposits, we have made experiments in which voltameters maintained at different temperatures were exposed to the same current. The results, exhibited in the accompanying table, show a small but apparently real *increase* in the weight of the deposit as the temperature rises. Had the effect been in the other direction, we should have been disposed to attribute it to imperfections of manipulation, for the deposits from the warm solutions were always coarser and looser in texture than the corresponding deposits (upon the same area) from the cold solutions.

1884.	After usual washing and drying at 160°.			After heating to verge of redness.			Excess of hot over cold.
	Hot bowl (about 50°).	Bowl at temperature of room (15°).	Cold bowl (4°).	Hot bowl.	Bowl at temperature of room.	Cold bowl.	
May 27. . .	..	..	..	2·3915	..	2·3905	·0010
June 4. . .	2·0230	..	2·0220	2·0229	..	2·0221	·0008
July 22. . .	1·9050	..	1·9043	1·9049	..	1·9043	·0006
July 31. . .	1·9438	1·9432	1·9430	1·9440	1·9432	1·9431	·0009

The solution was a 15 per cent. solution of pure nitrate of silver, and the anodes were of pure metal. The current was about $\frac{1}{2}$ ampère, and passed for rather more than an hour.

The results here disclosed diminish, of course, the chemical significance of the number given as representing the electro-chemical equivalent of silver, but the variation is so small at ordinary laboratory temperatures that the use of the silver voltameter as a means of defining electric quantity is not practically interfered with.

Note to § 26.

M. MASCART (Journal de Physique, t. iii.; Juillet, 1884) has recently revised the calculation of the constant of his apparatus, by which revision the final number is altered from ·01124 to ·011156.

Note to § 27.

Although there can be no doubt that silver is greatly preferable to copper for the electrolytic measurement of currents, we have thought that it might be useful to make a few comparisons of the two metals, so as to allow copper to be referred to on an emergency with as much success as the nature of the case admits. The copper deposits were taken in the same way as the silver upon platinum bowls, the anodes being wrapped in filter paper and suspended at the top of the liquid. On account of the tendency to oxidation it is not advisable to allow the copper deposits to soak for a long time. They were washed in boiling water for about half an hour, and then dried off in the hot closet at 150°. The solutions were made from sulphate, bought as pure, no acid being added. Of the four bowls I., II. are large and somewhat deep, III., IV. are shallow saucers about 3 inches in diameter. In the large bowls the area of deposit was about 32 sq. centims., in the smaller about 25 sq. centims. The strength of current on the first two occasions was about $\frac{1}{3}$ ampère, on the last about $\frac{3}{4}$ ampère, thus representing the circumstances for the measurement of the current through an incandescent lamp.

Date, 1884.	Bowl.	Solution.	Weight of deposits.	Mean.	Ratio of copper to silver.	Equivalent of copper (silver = 108).
Nov. 20 ..	I.	Silver nitrate 15 per cent.	1·3874	1·3872	·2937	31·72
,, ..	III.	..	1·3870			
,, ..	II.	Copper sulph. sp. gr. 1·174	·4065	·4074		
,, ..	IV.	..	·4082			
Nov. 27 ..	II.	Silver nitrate 15 per cent.	1·0523	1·0522	·2934	31·69
,, ..	IV.	..	1·0522			
,, ..	III.	Copper sulph. sp. gr. 1·115	·3094	·3087		
,, ..	I.	..	·3081			
Dec. 11 ..	II.	Silver nitrate 15 per cent.	3·0489	3·0488	·2938	31·74
,, ..	IV.	..	3·0487			
,, ..	III.	Copper sulph. sp. gr. 1·115	·8956	·8959		
,, ..	I.	..	·8962			
Mean ..	..	..	..	..	·2936	31·72

Multiplying ·2936 by 4·0246 we get 1·182 grms. as the amount of copper deposited per ampère per hour.

Note to § 30.

Observations made at intervals since this paper was read may here be given in continuation of Tables VII. and VIII.

	June 26.	July 14.	July 21, 22.	Aug. 6.	Oct. 8.	Oct. 28.	Nov. 14.	Dec. 5.
CLARK 1 . .	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
,, 4 . .	·9998	1·0000	1·0000	1·0004	·9996	·9997	0·0000	0·0000
,, 5 . .	·9997	1·0007	·9998	1·0006	·9990	·9994	·9993	·9997
,, 8 . .	·9997	·9998	·9998	·9996	·9997	·9998	1·0000	·9996
,, 9 . .	1·0000	1·0000	1·0002	·9998	1·0000	1·0002	1·0002	·9999
,, 10 . .	1·0003	1·0003	1·0003	1·0003	1·0003	1·0003	1·0003	1·0003
,, 11 . .	1·0003	1·0004	1·0003	1·0007	1·0003	1·0003	1·0003	1·0004
,, 12 . .	1·0004	1·0004	1·0004	1·0007	1·0003	1·0003	1·0003	1·0003
,, 13 . .	1·0002	1·0002	1·0002	1·0000	1·0002	1·0002	1·0003	1·0001
,, 14 . .	1·0026	1·0003	1·0003	1·0002	1·0003	1·0003	1·0003	1·0003
,, 16 . .	1·0004	1·0003	1·0004	1·0002	1·0002	1·0003	1·0003	1·0003
,, 18 . .	·9974	·9920	·9900	·9860	·9800	·9810	·9760	unsteady
,, 19 . .	1·0004	1·0000	1·0000	·9997	1·0000	1·0002	1·0001	·9999
H_5	1·0005	1·0004	1·0005	1·0005	1·0003	1·0003	1·0004	1·0006
H_6	1·0007	1·0004	1·0005	1·0005	1·0004	1·0002	1·0003	. .
H_{10} . . .	1·0004	1·0005	1·0005	1·0003	1·0003	1·0003	1·0004	1·0004
H_{11} . . .	1·0004	1·0005	1·0005	1·0003	1·0002	1·0003	1·0003	1·0003
H_{12} . . .	. .	. .	1·0030	1·0004	1·0003	1·0003	1·0003	. .
H_{13} . . .	. .	. .	1·0009	1·0003	1·0002	1·0003	1·0003	1·0001

Some H-cells have been set up Mr. THRELFALL, with amalgams of known composition, varying from $\frac{1}{32}$ zinc to $\frac{1}{5}$ zinc by weight. The duration of the test has as yet been scarcely adequate, but it appears that the smaller quantity of zinc is sufficient.

Note to § 32.

Comparisons of standard DANIELL cells of the Post Office pattern sent me by Mr. PREECE have been made on several days, but did not give satisfactory results. The E.M.F. rises about 1 per cent. during the half hour following the placing of the zincs and porous cells in the working compartment, and the two specimens differed from another about $2\frac{1}{2}$ per cent. The mean values were about 1·081 and 1 056 true volts.

Note 1 *to* § 37.

An examination of the recent comparisons of cells of different ages will probably lead to the conclusion that no important absolute change of E.M.F. can have occurred during the thirteen months; but since the cells have been employed as standards for the determination of electric currents in various experiments, *e.g.*, for the determination of the constant of magnetic rotation (Proc., June, 1884), it seemed desirable to supplement Table XI. with observations of later date. Two further absolute determinations have accordingly been made on November 21 and November 27, 1884, by the method of § 38, with the following results :—

TABLE XI. (continued).

Date.	Cell used.	Temperature.	E.M.F. in B.A. volts.	Correction to 15°.	E.M.F. in B.A. volts corrected to 15°.
November 21 . .	CLARK No. 1 .	13°·7	1·4548	—·0016	1·4532
,, 27 . .	,, No. 1 .	13·4	1·4555	—·0019	1·4536
Mean . . .	..	..	..	.. .	1·4534

The difference between 1·4534 and the mean of Table XI., viz., 1·4542, would indicate a fall of about $\frac{1}{2000}$, but the determinations are hardly precise enough to warrant us in regarding this fall as an established fact.

Note 2 *to* § 37.

Two further determinations of the E.M.F. of CLARK cells have been published since this paper was communicated to the Royal Society. They both depend upon the evaluation of currents by means of silver, as in § 38.

A. v. ETTINGSHAUSEN (Zeitschrift für Elektrotechnik, 1884, xvi. Heft) finds at 15°·5 the value 1·433 volt, using KOHLRAUSCH'S (second) value of the electro-chemical equivalent.

Again (Amer. Journ. Sci., Nov., 1884) Mr. CARHART obtains 1·434 volt. This appears to correspond to a temperature of 18°.

These results are satisfactory as tending to show that CLARK cells may be set up in different places and by different hands so as to give nearly identical E.M.F.

Rayleigh & Sidgwick. *Phil. Trans.* 1884. *Plate* **17.**

Fig. 1.

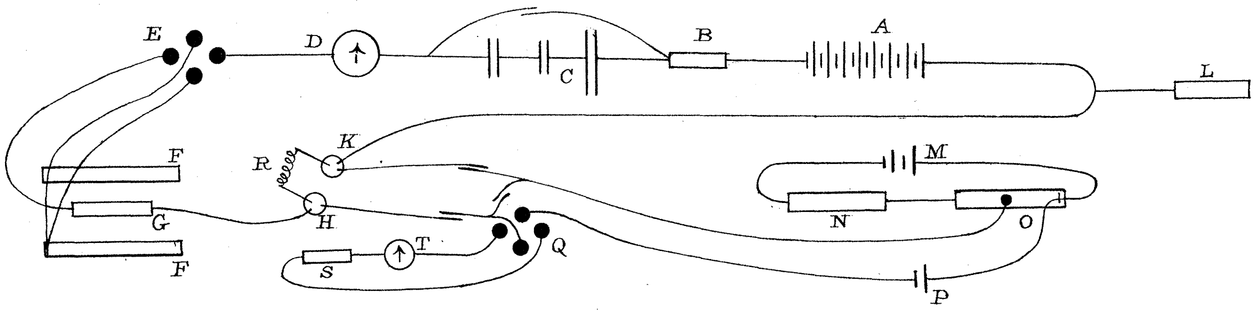


Fig. 2.

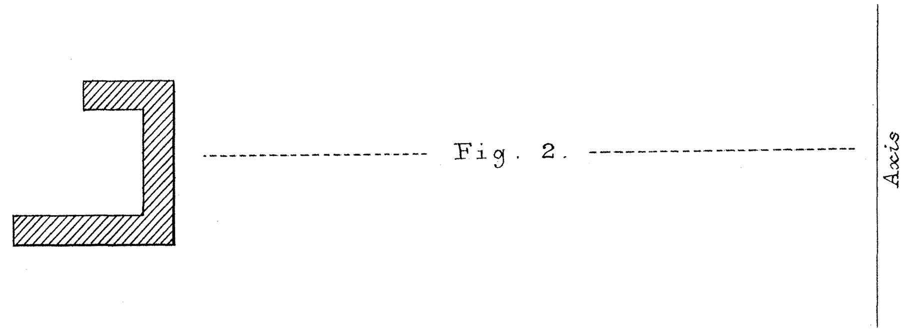


Fig. 3.

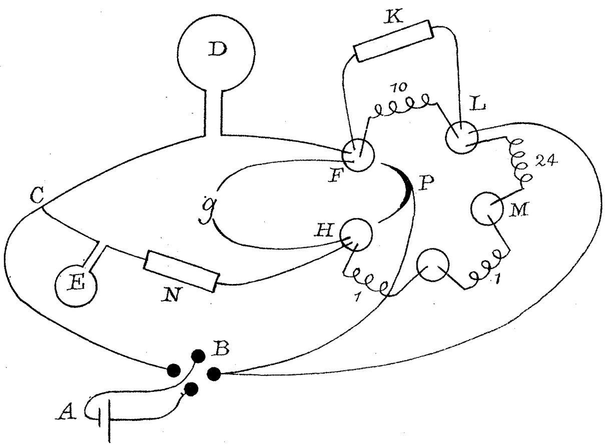


Fig. 5.

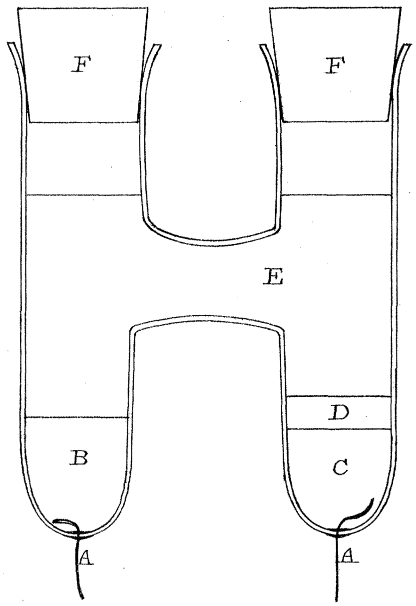
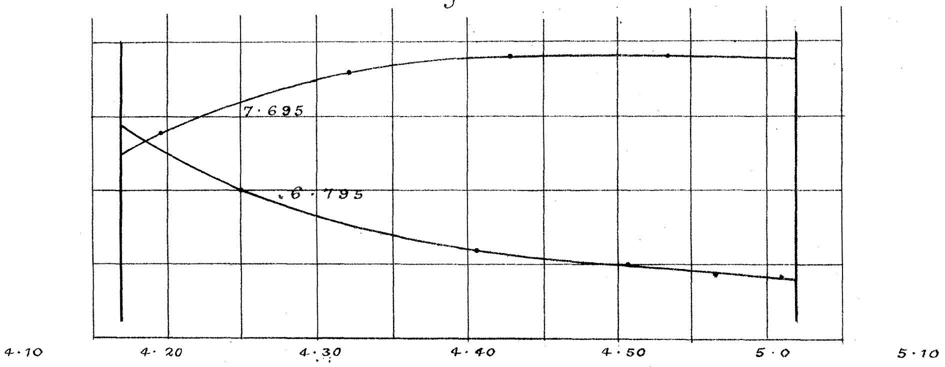


Fig. 4.



Two divisions to one milligram.
Two divisions to one minute.

West Newman & C° lith.