

the deflection¹ due to a current c in one is mc , and in the other nc , where m and n are the "constants" of the two coils, then the deflection for currents c_1 and c_2 is $mc_1 - nc_2$.

Fig. 21 gives a scheme of the arrangement for measuring resistances with this instrument. V is the battery inserted in the common branch ED of the two circuits, which convey currents dividing off at D, and going in opposite directions round the coils of G. If we wish to measure the resistance of a wire, it is inserted at AB by means of binding screws or mercury cups, and the resistance of the other circuit is varied until there is no deflection; then AB is replaced by a known resistance, which is made up until there is zero deflection as before.

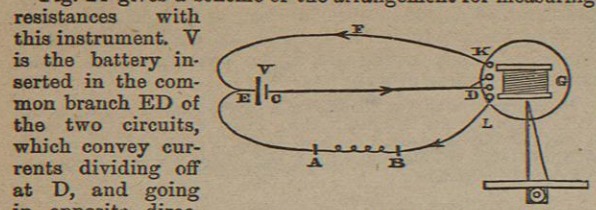


Fig. 21.

It is obvious that the only requisite here is that the resistances of EFK, EA, BL, and the galvanometer coils should remain constant. Variations in the electromotive force or internal resistance of the battery do not affect the result.

The method which we have thus sketched is the best way of using the differential galvanometer, and it does not matter even if the coils are not exactly symmetrical. Let the constants of the coils M and N be m and n , so that the deflection due to currents c_1 and c_2 in M and N is $mc_1 - nc_2$. Let the resistance from E to D in the single branch be B, and in the circuits EFK and EABL, which pass round M and N respectively, R and S + U, U being the resistance between A and B, which is such that the deflection is zero. Then

$$0 = mc_1 - nc_2 = \left\{ m(S+U) - nR \right\} \frac{E}{D} \dots (a),$$

where E is the electromotive force of the battery, and

$$D = (R + S + U)B + R(S + U).$$

Suppose we substitute U' for U, and arrange U' so that we have again zero deflection. Then

$$0 = \left\{ m(S + U') - nR \right\} \frac{E}{D} \dots (b).$$

From a and b we get $U = U'$.

For further details concerning this method, see Maxwell, vol. i. § 346, and Schwendler, *Phil. Mag.*, 1867.

The differential galvanometer method was much used by Becquerel and others, but it is now entirely superseded as a practical method in this country by the Wheatstone's bridge method. Suppose we have a circuit ABCD of four conductors. Insert a galvanometer G between B and C, and a battery between A and D. Adjust say the resistance AB until the galvanometer in BC indicates no current. The bridge is then said to be balanced, and the potentials at B and C must be equal. But the whole fall of potential from A to D along ABD is the same as that along ACD; hence if the fall from A to B is to be equal to that from A to C, we must have

$$\frac{R}{S} = \frac{T}{U},$$

where R, S, T, U are the resistances in AB, BC, CA, DC. This is the condition that BC and AD be conjugate. We might have deduced it as a particular case of the general theory given above. Hence if we know the resistances S, T, U, we

¹ The deflections are supposed small.

get in terms of these $R = \frac{ST}{U}$. S is often called the standard resistance, and T, U the arms of the bridge or balance. The sensibility of this arrangement may be found practically by increasing or decreasing R so as to derange the balance. The largest increase which we can introduce without producing an observable galvanometer deflection measures the sensibility of the bridge.

If we had a given set of four conductors, and a battery and galvanometer of given resistance, then it may be shown (see Maxwell, vol. i. § 348) that the best arrangement is that in which the battery or galvanometer connects the junction of the two greatest resistances with that of the two least, according as the former or the latter has the greater resistance. The practical problem might take another form. We might have given a resistance, and have at our disposal known resistances of any desired magnitude to form our bridge. We might also suppose further that we had given the total area of the plates of our battery, and the dimensions of the channel in which the galvanometer wire was to be wound. We may neglect the thickness of the silk coating, or assume that it is proportional to the thickness of the wire.

Then, B and G being the resistances of the battery and galvanometer, the electromotive force $E \propto \sqrt{B}$, and the number of turns in the galvanometer $\propto \sqrt{G}$.

Let us put $S = yR$, $T = zR$, and $U = yzR$. These resistances would balance; let us however put $(1+z)R$ in the branch AB instead of R, the others being unchanged, and calculate the effect on the galvanometer in G, which we put proportional to the current in BC, and to the number of turns on galvanometer. Then, from equation (7) (or Maxwell, vol. i. § 349), we find that the deflection δ varies as

$$\frac{yz\sqrt{BG}}{(1+y)(1+z)BG + y(1+z)^2BR + z(1+y)^2GR + yz(1+y)(1+z)R^2};$$

in order that δ may be a maximum, we must have

$$G\{(1+y)(1+z)B + z(1+y)^2R\} = y(1+z)^2BR + yz(1+y)(1+z)R^2 \quad (a),$$

$$B\{(1+y)(1+z)G + y(1+z)^2R\} = z(1+y)^2GR + yz(1+y)(1+z)R^2 \quad (b),$$

$$BG = zR^2 \quad (c),$$

$$BG = yR^2 \quad (d).$$

a and b give at once by addition and subtraction

$$\frac{B}{G} = \frac{z(1+y)^2}{y(1+z)^2} \text{ and } BG = yzR^2,$$

or

$$B = z \frac{1+y}{1+z} R \quad (e),$$

$$G = y \frac{1+z}{1+y} R \quad (f).$$

Combining the four equations (c), (d), (e), (f), we get

$$y = z - 1 \text{ and } B = G = R = S = T = U.$$

It appears, therefore, that when all the resistances on the bridge are at our disposal, we ought to make them all equal to the resistance to be measured, or come as near this as we can; e.g., if we had a very small resistance to measure, we should make the arms of the bridge small, and take a small-resistance in preference to a high-resistance galvanometer.

In order to carry out measurements of resistance with ease we must possess a series of graduated resistances, with which we can compare any unknown resistance, and of which we can make the arms of our balance, &c. Again, if the measurements of one electrician are to be of any use to another, there must be a common standard. It would be most convenient to have only one standard for all nations, and this standard might be either arbitrary, like the standard of length, or absolute in some sense such as we have defined above. Arbitrary standards have at different times been proposed by Jacobi and others. The mercury standard of Siemens, to which we alluded in the historical sketch, has obtained great prevalence on the Continent. The British Association unit or ohm is an absolute unit,

inasmuch as it professes to represent in electromagnetic measure a velocity of 10^9 centimetres per second, or, taking the original definition of a metre, an earth quadrant per second. It happens, by a curious accident, that the mercury unit and the ohm are very nearly equal, the latter being expressed in terms of the former (according to Döhms and Hermann Siemens; see Wiedemann, Bd. ii. 2, § 1074) by the number 1.0493.

One of the earliest instruments for furnishing a graduated resistance was the rheostat, brought into use by Wheatstone, but also invented independently by Jacobs at St Petersburg about 1840.

It consisted of two cylinders of equal diameter, one of wood and one of brass. A wire, whose extremities were in connection with the metallic axes of the cylinders, was wound in opposite directions round the cylinders. The axes of the cylinders were connected with two binding screws by means of sliding contacts. The part of the wire which does not lie on the metal cylinder is the only part that produces resistance between the binding screws; and, by winding and unwinding, we can increase or diminish the resistance continuously to a known extent, means being provided for measuring the angular rotation of the metal cylinder.

Resist-
ance
boxes.

We shall not stop to consider the defects of this instrument, which is now never used for delicate work. Its place is taken by resistance boxes, containing coils of wire whose resistances are different multiples of the unit of resistance (in this country always the ohm). The reader will find a full account of the methods by which the standards are reproduced in the collected reports of the Committee on Electrical Standards. The usual material for the wire of resistance coils is German silver. Most of the copies of the ohm issued by the British Association were made of an alloy of two parts of silver to one of platinum. The great advantage of alloys is that the variation of resistance with temperature is small for them; in the PtAg alloy, for instance, it is less than a tenth of the value for an average pure metal. To secure insulation the wires are carefully coated with silk, and after winding the coil is immersed in melted paraffin. To get rid of electromagnetic and inductive effects, the wire on resistance-coils is doubled on itself before being wound, so that, when a current passes through the coil, there are always two equal and opposite currents at each point. The terminals are formed by stout pieces of copper rod, whose resistance is either included in the coil, or is so small that it may be neglected. The connections for small resistances are managed by means of mercury cups, with pieces of amalgamated copper at the bottom, on which the copper electrodes are made to press.

For ordinary purposes the coils are arranged in a box (fig. 23), the terminals being stout pieces of brass fixed on the opposite lid;

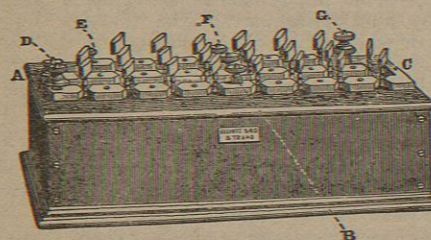


Fig. 23.

conical brass plugs inserted between these pieces serve to throw the coils in and out of circuit. The box represented in fig. 23 is specially arranged for use in Wheatstone's bridge. In E, F, G we have a series of coils, 1000, 100, 10, 10, 100, 1000; these are used for the arms of the bridge. In A, C, D there are sixteen coils, 1, 2, 2.5, 10, 20, 20, 50, &c., which give us any resistance of a whole number of ohms from 1 up to 10,000. In actual use the resistance to be measured is inserted between A and G, D and E are connected by a stout piece of copper, the galvanometer is inserted between F and

A, and the battery between E and G. The resistances of the arms of the bridge are taken equal, and as near the resistance to be measured as possible. In this way the resistance of any conductor may be very quickly found to an ohm. If it is desired to go farther, we may proceed thus. Suppose that we have found that a resistance lies between 5 and 6, put in the arm FE 100, and in FG 10, let the resistance in DCA, when there is a balance, be 57, then the resistance of the conductor is $\frac{100}{57} \times 57$, or 5.7. Similarly we might go to a second place of decimals by putting 1000 in FE and 10 in FG. There is a limit, however, to this process, because the increase in the resistance of the arm decreases the "sensibility" of the bridge. Another method is to balance as nearly as possible, and then interpolate by taking the deflection of the galvanometer. Suppose, for instance, in the above case, that, with 5 ohms in DCA, the deflection was 21 in one direction, and, with 6 ohms, 9 in the other direction, then, taking the deflection proportional to the deviation from balance (see formula for δ above), we have resistance = $5 + \frac{21}{30} \cdot 1 = 5.7$.

We might also construct small graduated resistances; and this would enable us to use smaller arms in the bridge, and thus increase the "sensibility" when used to measure small resistances. Owing to the multiplication of connections, there is a limit to the ordinary resistance box arrangement. The difficulty may be evaded to a certain extent by using conductivity boxes, according to Sir W. Thomson's suggestion, where the resistances are arranged abreast, so that a small alteration of the resistance is brought about by adding on a very great resistance to the multiple arc. The rheostat principle has been used by Poggendorff in his rheocord for producing small resistances. He stretches two platinum wires side by side; on these is strung a hollow box filled with mercury, whose longitudinal motion is read off on a scale. If this arrangement be thrown into any circuit by means of two binding screws connected with adjacent terminals of the wires, the parts of the two wires up to the bridge give a small resistance, which may be adjusted at pleasure.

In the quicksilver agometer of Müller (Wiedemann, i. § 160), the resistance is formed by a column of mercury of variable length. We may remark here that difficulties equally arise in constructing very large resistances. To get such within reasonable compass the wire must be exceedingly thin and the insulation very good. Messrs Warden and Muirhead have wound coils of fine wire, giving a resistance of 100,000, and have constructed in compact form resistance boxes up to 1,000,000, or a megohm, and beyond. They have also given practical form to a suggestion of Phillips to utilize the resistance of carbon, by drawing fine pencil lines on ebonite or glass; they mix plumbago with the pulp in the ordinary process of paper manufacture, and thus produce a species of carbon paper. A strip of this about 21 in. long and .5 in. broad gives a resistance of about 50,000. This seems a valuable invention; but we are not aware how far it has stood the test of practical use.

Selenium and tellurium have been proposed as material for high resistances, but owing to the variability of their resistance under the action of light, &c., they are unfit for the purpose.

The best method for comparing resistances with great

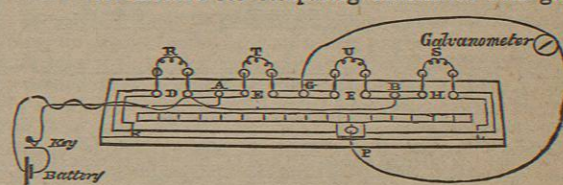


Fig. 24.

accuracy is the modification of Wheatstone's bridge introduced by Kirchhoff (fig. 24).

KL is a platinum-iridium wire, DK and HL are stout copper terminals to which it is soldered, DAE, EGF, FBH are stout copper pieces with binding screws and terminals for mercury cups, by means of which resistances R, T, U, S can be inserted at D, E, F, H, A, B, and G are binding screws for the battery wires and one end of the galvanometer wire. The other end of the galvanometer wire is screwed to a spring contact piece fixed to a sliding block at P; when the button of this block is depressed, contact is made with KL, at a spot which is definite to an eighth or tenth of a millimetre. Platinum-iridium is chosen for KL, because it is hard and tough, not liable to be scratched or abraded by the contact piece, does not oxidize or amalgamate with mercury, and changes very slightly in resistance when the temperature alters. The wire must be calibrated to find what correction, if any, must be applied for variation of resistance per unit of length at different parts; for methods of doing this see Matthiessen and Hockin; *Brit. Assoc. Reports on Electrical Standards*, p. 117; or Foster, *Journ. of Society of Telegraphic Engineers*, 1874.

Kirchhoff's arrangement may be used in the ordinary way after we have made special experiments to determine the resistance of the connections, &c. Professor Foster (*l.c.*) has given a very useful method, by which the difference of two resistances can be got independently of the resistances of the connections. Suppose we wish to find the difference between R and S, which we suppose so near each other that, with the arms T and U approximately equal, there will be a balance when P is somewhere on KL. Let the reading for the position of the block be x , taken from left to right. Interchange R and S, balance again, and let the new reading be x' (we suppose the difference between R and S so small that P is still on KL); then, if μ be the resistance of unit length of KL, $R - S = \mu(x' - x)$.

For, if α represent the resistance of the connections in DK, β the same for the other end of the wire, and if T and U include the resistance of the invariable connections, then we have

$$\frac{R + \alpha + \mu x}{S + \beta + \mu(l - x)} = \frac{T}{U},$$

where l = length of KL. Hence

$$\frac{R + \alpha + \mu x}{R + S + \alpha + \beta + \mu l} = \frac{T}{T + U}.$$

Similarly

$$\frac{S + \alpha + \mu x'}{R + S + \alpha + \beta + \mu l} = \frac{T}{T + U},$$

therefore

$$R - S = \mu(x' - x).$$

Methods of Matthiessen and Hockin and of Sir W. Thomson.

If we have to find the resistance of a thick cylindrical body, what is really wanted is the ratio of the current strength to the difference of potential between the two ends, when the current flows parallel to the axis at every point. The last condition is not generally fulfilled. It is obviously not so in the case where the cylinder is joined up with a thin wire. In cases where we wish to compare the specific resistance of two metals which we possess in cylindrical pieces, we get over the difficulty by observing the potential at a point at some distance from the end of the piece, where the flux is parallel to the axis at all points of the section.

Matthiessen and Hockin used the following method for this purpose (fig. 25). The two pieces XZ, YZ are soldered together and connected in circuit with two resistance coils A and C, and a graduated wire PR as before. S, S' are two sharp edges, at a measured distance apart, fixed in a piece of ebonite or hard dry wood, and connected with mercury cups. T, T' is a similar arrangement for YZ. The galvanometer is inserted between S and Q, and the position of Q is found for balance; then the terminal is shifted to S', and if necessary the resistances A and C altered, so as to keep their sum constant, until balance is again found. The same is done for T and T'. Then, XS denoting the resistance between X and S, and A, C, the values of A and C in the first case, and so on, we have

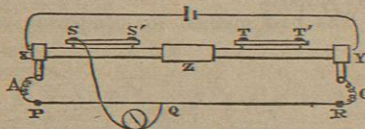


Fig. 25.

$$\frac{XS}{XY} = \frac{A_1 + PQ_1}{R}, \quad \frac{XS'}{XY} = \frac{A_2 + PQ_2}{R},$$

where

$$R = A_1 + C_1 + PR = A_2 + C_2 + PR$$

Hence

$$\frac{SS'}{XY} = \frac{A_2 - A_1 + Q_1 Q_2}{R}$$

Similarly

$$\frac{TT'}{XY} = \frac{A_4 - A_3 + Q_3 Q_4}{R}$$

Therefore

$$\frac{SS'}{TT'} = \frac{A_2 - A_1 + Q_1 Q_2}{A_4 - A_3 + Q_3 Q_4}.$$

This gives us the ratio of the resistances between SS' and TT'. The method does not depend for its success on the goodness of the contacts at SS', &c. Another ingenious arrangement for effecting a similar purpose is due to Thomson, and will be found described in Maxwell, vol. i. § 351.

In measuring very large resistances, such as the insulation resistance of a telegraph cable, it is convenient to use the quadrant electrometer. One end of the cable is connected with one electrode of a condenser, the other end of the cable is insulated, and the other electrode of the condenser put to earth. The condenser is charged, and the difference of potential between its electrodes measured by means of the electrometer. If E_1, E_2 be the value of the difference at the beginning and end of an interval of t seconds, and if S be the capacity of the condenser in electromagnetic measure, then the resistance of the cable is

$$\frac{t}{S(\log_e E_1 - \log_e E_2)}$$

in electromagnetic measure. If the condenser itself leaks, we must determine its resistance by insulating the electrodes and operating as before. Then, regarding the circuit in the first experiment as a multiple arc, composed of the insulation of cable and the dielectric of condenser, the true conductivity of the cable envelope is the difference of the conductivities obtained in the two cases. Several other methods might be used to compare metallic resistance but they are of small importance compared with those we have now been describing.

The reader who desires information concerning the application of Ohm's law to conductors other than linear will find the sources sufficiently indicated in Wiedemann's *Galvanismus*; some of them have been alluded to in the Historical Sketch.

Application of Ohm's Law to Electrolytes.

In our discussion of Ohm's law, we have hitherto had in view principally the metallic part of the voltaic circuit. We now turn our attention more particularly to the fluid parts. It is of no importance in the present connection whether the fluid forms part of the "battery" or "electromotor," or whether it is inserted outside the battery; the only difference in these two cases is, as we shall hereafter see, that in the former case energy is being absorbed by the current, and in the latter it is being evolved. In many respects the properties of the metallic and fluid parts of the circuit are alike: the electromagnetic action is the same for both; heat is also developed in the body of the conductor, whether metallic or fluid, according to the same law. But there is one peculiarity about a large class of fluids which has no analogue in purely metallic conduction, viz., that in them the passage of a steady current of electricity is invariably accompanied by chemical decomposition, definite in kind and quantity. To such fluid substances Faraday gave the name of electrolytes.

For example, suppose we fill a small beaker with a solution of zinc chloride ($ZnCl_2$), and suspend in the liquid two strips of platinum foil (called electrodes), at a moderate distance apart. Let a current enter at one of these strips, which we shall call the anode, and leave at the other, which we shall call the cathode. It will be

Resistance measurement with electro-meters.

His law of electro-chemical equivalents.

Polarization and transition resistance.

Electrolytic conduction.

found that the solution continues to decompose so long as the current passes, zinc appearing at the cathode, and chlorine at the anode. The metallic zinc precipitates, and the chlorine combines with the platinum of the anode to form platonic chloride.

It is obviously essential in an electrolyte that it should be a compound in some sense or other. It is not, however, true that all compound bodies are electrolytes. Fluidity is also a necessary condition, whether attained by heating to the melting-point, or by dissolving in water or other solvent. Faraday established as a law, to which there appear to be few, if indeed any, exceptions,—that all substances which in the solid state are very bad conductors, but conduct on being heated to the melting-point, are electrolytes, i.e., are decomposed by the passage of the electric current. Faraday thought that periodide of mercury, fluoride of lead, and some other bodies were exceptions to this law; but later researches seem to have established that this is not so. (Cf. *Experimental Researches*, 414, 439, 1340, &c., and Wiedemann's *Galvanismus*, i. § 191, &c.) The conductivity of electrolytes in solution also increases rather quickly with increase of temperature, while the conductivity of metallic conductors, on the other hand, diminishes, but more slowly, as the temperature rises.

In considering the passage of the current through electrolytes, it is convenient to distinguish two cases. First, let there be a steady, or at least permanent current, and a continuous evolution of the products of electrolytic decomposition (these are called the "ions," anion and cation at the anode and cathode respectively). The amount of ion that appears at an electrode in a second is equal to the strength of the current (supposed constant during a second) multiplied by a constant called the electrochemical equivalent of the ion. The electrochemical equivalent is proportional to the chemical equivalent, account being taken of the "valency" of the ion. (See art. ELECTROLYSIS.)

For instance, if C be the strength of the current in the illustrative case above, then the amount of zinc deposited at the cathode in time t will be zCt , and the amount of chlorine liberated at the anode cCt , where z and c the electrochemical equivalents of zinc and chlorine, and $z : c :: 65 : 35.5$, zinc being divalent. If a cell containing lead chloride ($PbCl_2$) were also inserted into the circuit, the same amount of chlorine would be liberated at the anode, and the amount of lead precipitated at the cathode would be pCt , where $p : z : c :: \frac{207}{2} : \frac{65}{2} : 35.5$, i.e. $:: 103.5 : 32.5 : 35.5$

As the electrochemical decomposition ("electrolysis") goes on, the surface of the electrodes is altered. In some cases the ion is merely deposited on the electrode, in other cases it combines more or less intimately therewith; but in general there is an alteration of the nature of the contact, and a consequent alteration of the electromotive force at the surface of the electrode. Experiment shows that this electromotive force, in a great many cases, tends to oppose the passage of the current. So that if we insert an electrolyte into any circuit, the current starts with a certain value, and falls more or less quickly, until it reaches a limit at which it remains steady. The opposing electromotive force of "polarization," as it is called, has then reached its maximum, and the deposition of the ions goes on without further alteration of the contact surfaces. It is obvious that this limit may be reached under a variety of different circumstances (*vide infra*, p. 86). There is also another phenomenon, the possibility of which we must not overlook, viz., an alteration of resistance, owing to the presence of the ions at the electrodes. This resistance, due to the ions, has been called the "transition resistance." The enfeebling of the current by the electromotive force of polarization might, as far as the observed result is concerned, be due entirely to an increase of resistance, or to a transition resistance, and such was the explanation given by the earlier physicists. It is easy, however, to show that there is an

actual electromotive force of polarization; for, if we disengage our electrolytic cell from the battery, and connect its electrodes with a galvanometer, a current is indicated, which passes through the cell in the opposite direction to the original current. This could not be due to any transition resistance, but must arise from an opposing electromotive force generated by the passage of the battery current. This point can be illustrated by a hydrodynamical analogy. If we attempt to force water through a narrow capillary tube, or through a wide vertical tube against gravity, there is an opposing force in both cases. But, when we remove the pressure, the water has a tendency to return in the latter case, but none in the former. The former case represents a transition resistance, the latter an electromotive force of polarization.¹

Without denying the existence of a transition resistance, we see that an electromotive force of polarization actually exists. In some cases, e.g., amalgamated zinc in zinc sulphate, it is very small; in other cases, e.g., platinum electrodes in dilute sulphuric acid, it may considerably exceed the electromotive force of a Daniell's element.

We have, up to this point, been treating the case where a permanent current finally flows through the electrolyte; but there are cases where the existence of such a current would violate the principle of the conservation of energy.

Suppose that a single Daniell's cell is the electromotor, then (see below, p. 90) if a current C is sent for a time t , an amount of energy dCt is absorbed in the cell, d being constant. Suppose, farther, that the excess of the intrinsic energy of the ions, in the state in which they are being delivered in the electrolytic cell, over that which they possess when in combination is w , then if a current C pass for a time t , an amount of energy wCt will be evolved. But if $w > d$, this cannot go on for any time however short, no matter how feeble the current may be, otherwise more energy would be evolved in the cell than is absorbed in the battery.

If we insert an electrolytic cell containing dilute sulphuric acid along with a galvanometer into a circuit in which there is a single cell of Daniell, we observe the galvanometer needle swing out vigorously, and then settle down to a small and gradually decreasing deflection. The current ultimately becomes zero;² but the time it takes to do so may be considerable, and varies with the nature of the electrodes. If we remove the battery after the current has stopped, and connect the polarized cell with the galvanometer, we observe an initial swing very nearly equal to the former but in the opposite direction, and a corresponding deflection, which after a time disappears entirely. Although, as a rule, a sensible time elapses before the polarization reaches its maximum, yet it is important to remark that it may rise to a very considerable fraction of the maximum in a very short time indeed. Edlund³ found that in a certain case the electromotive force of polarization reached 0.57 of a Daniell in about $\frac{1}{100}$ of a second. Bernstein has recently arrived at results of a similar kind. He found, for instance, that platinum plates, polarized to 1.85 of a Daniell, fell, when the resistance of the circuit was 7.46 Siemens units, to 1.57 in .00111 sec.⁴ This rapidity of the rise and fall of the polarization is of very great importance, and has, we think, been overlooked by some experimenters.

In cases where the polarization does not reach its maximum, no liberation of gas or other ion is observed, such as is seen with a permanent current, and it might of course be denied that chemical decomposition takes place at all. We shall, however, assume that Faraday's law holds for this case also, and assert that the current in the first instance actually passes through the liquid and produces chemical decomposition, according to the same law as a permanent current, and that this goes on until the accumu-

¹ Maxwell, *Electricity*, vol. i. § 266.

² For an exception to this statement see below, p. 87.

³ *Pogg. Ann.*, lxxxv., 1852.

⁴ *Pogg. Ann.*, clv., 1875.

lation of the ions has generated an opposing electromotive force, equal to that of the battery, when of course the current must stop. We cannot justify this position very easily by direct experiment; yet there are many facts to support it, and so long as it is tenable it seems to afford the most philosophical view of the matter.

Having explained the phenomena of polarization so far as is necessary for our immediate purpose, we now proceed to inquire how far experience justifies the application of Ohm's law to electrolytes, or, which is much the same thing, to examine how far the methods of different physicists for measuring electrolytic resistance have led to concordant results.

One of the earliest methods, in which polarization was eliminated, was that of Horsford.¹ He filled a rectangular trough with the electrolyte, and inserted in the trough two electrodes very nearly fitting the cross section. These electrodes could be set at different measured distances apart. They were coated on the further side with non-conducting substance, so that the current could flow between the opposed sides only. In this way he secured that the stream lines in the neighbourhood of the electrodes should depend as little as possible on the distance between them. This trough was inserted in the battery circuit along with a tangent galvanometer; then the distance between the plates was decreased, and a metallic resistance R inserted in the circuit, so as to bring the current to the same strength as before. The current being the same in both cases, it is assumed that the polarization in both is the same, in which case the resistance of a length of the electrolyte equal to the difference of the distances between the electrodes in the two cases is equal to R. Knowing the section of the trough, we might calculate from R the specific resistance of the electrolyte. If the values arrived at be the same when deduced from different lengths of the electrolyte, and for different strengths of current, it may be concluded that Ohm's law applies. The application of this method requires the passage of a permanent current, in consequence of which the ions appear at the electrodes, and the solution in the neighbourhood becomes altered; so that it is difficult to make certain that the polarization is exactly the same in the two cases, and that no resistance of transition is generated. Matters may be mended a little by passing the current for the same time in both cases; but this is scarcely a satisfactory remedy. Still valuable results were obtained with this method by Horsford and Wiedemann; the latter, in applying it to silver and copper solutions used electrodes of silver and copper respectively, whereby the polarization to be eliminated was very much reduced.

Taking advantage of the discovery of Matteucci and Du Bois Reymond,² that carefully amalgamated zinc electrodes in a neutral³ solution of zinc sulphate are not polarizable, Beetz⁴ determined, by means of Wheatstone's bridge, the resistance of various solutions of this electrolyte.

The liquid was inclosed in a cylindrical tube, 29.7 cm. long, with a mean section of 1.4061 sq. cm. Amalgamated zinc plates were applied to the ends of the tube, and fastened on by india-rubber collars. The ends were then inserted tightly into openings in the sides of two bottles which were filled with the solution (the same as that contained in the tube). The thick electrodes leading to the discs, and the backs of the zinc discs themselves, were lacquered, to insulate them from the liquid in the bottles. The whole apparatus was immersed in a trough of water, which could be heated to any desired temperature.

In the course of his experiments Beetz demonstrated the absence of polarization when amalgamated zinc electrodes are used, and eliminated the transition resistance by boiling the electrodes in zinc sulphate, and transferring them to the ends of the tube without exposure to the air.

Beetz further proposed to find the specific conductivity of other electrolytes in terms of that of zinc sulphate, by experimenting on

¹ Pogg. Ann., 1847. ² Monatsber. der Berl. Akad., 1850. ³ Patry, Pogg. Ann., cxxxvi., 1869. ⁴ Pogg. Ann., cxvii., 1862.

resistance.
Horsford.

closed circuits consisting entirely of the electrolyte to be examined. He tried damping experiments for this purpose, but the effects to be observed turned out too small for accurate observation.

Paalzw⁵ inclosed the electrolyte to be examined in a siphon, the two ends of which dipped into vessels of porous clay also filled with the electrolyte. The clay vessels were immersed in beakers filled with zinc sulphate, at the bottoms of which were placed large amalgamated zinc discs, which formed the electrodes. The only polarization or transition resistance to be feared is that at the boundary of the two liquids, and this is very small. What little remained was eliminated, as in Horsford's method, by taking differences.

The resistance of the whole arrangement was measured by means of Wheatstone's bridge, and then the siphon was replaced by a shorter one filled with the same liquid. If R_1, R_2 be the resistances found in the two cases, $R_1 - R_2$ is obviously the resistance of a length of the electrolyte equal to the difference between the lengths of the siphons. If R_1, R_2 be similar values obtained when the electrolyte is replaced by mercury, then the specific resistance of the electrolyte is $\frac{R_1 - R_2}{R_1' - R_2'}$, that of mercury being taken as unity.

The most important of all the recent researches on the application of Ohm's law to electrolytes are those of F. Kohlrausch and Nippoldt. In order to avoid the effects of polarization, they used the alternating currents of an electromagnetic machine. These currents varied very nearly as the sine of the angle of rotation, and could be sent in rapid succession through the electrolyte. The whole quantity of electricity that passes in the first part of any alternation is exactly equal and opposite to that which passes in the second; hence equal quantities of the two ions (say H and O) will be separated at each electrode. If the H₂ and O combine to form water, it is obvious that, on the whole, there will be no resultant electromotive force of polarization either way; and if they coexist side by side without combining, there will still be no resultant electromotive force, provided the electrodes be exactly similar. There are two advantages in this method. There is no evolution of gas or other ion, and consequently no alteration of the solution and electrode, such as goes on with a constant current. We have, besides, another great advantage, which is denied⁶ us with constant currents, — viz., that by increasing the size of the electrode, we can diminish the effects of polarization.

The whole amount of electricity which passes in each induction current is the same, and consequently the whole amount of ion deposited on the electrode is the same; hence, if we increase the surface of the electrode, the density of the deposit is decreased in an inverse ratio. Now, the researches of Kohlrausch and Nippoldt have shown⁷ that, within certain limits, the electromotive force is proportional to the surface density of the deposit. Hence, by sufficiently increasing the surface of the electrodes, the polarization may be made as small as we please.

In the earlier experiments platinum electrodes, having a surface of 1.08 cm. were used, and it was found that each induction current of the magneto-electric machine deposited on each square millimetre of the positive electrode only $\frac{1}{18,500,000}$ c. cm. of oxygen. It was therefore expected that the polarization would be insensible, and that the electrolyte would behave like a metallic resistance. The magneto-electric machine and the electrolyte were connected up with an electro-dynamometer, and it was found that the deflection of the suspended coil of the electro-dynamometer was scarcely sensible when the machine made 10 revolutions per second, although it was 15 scale divisions when the electrolyte was replaced by 70 Siemens units. On the other hand, when the velocity reached 77 revolutions per second, the deflection was much greater with the electrolyte than with 70 Siemens units. It was found, however, that when the surface of the electrodes was increased to 29 cm. a metallic resistance could be found, which gave the same deflection (within errors of observation) as the electrolyte for speeds varying from 4.8 to 76.9 revolutions per second.

⁵ Pogg. Ann., cxxxvi., 1869. ⁶ The advantage gained even with constant currents by increasing the size of the electrodes is, however, appreciable (see below, p. 88). ⁷ Pogg. Ann., 1873, and "Jubelbd.," 1874.

The above results seem to compel us to one or other of two conclusions,—either that Ohm's law does not apply to rapidly alternating currents, where the maximum of polarization is not reached, or else that the electromotive force of exceedingly small deposits of the ions must be very considerable. The fact that, under certain conditions, the electrolyte is apparently a better, and under others, apparently a worse conductor than a certain metal wire, seems at first sight rather to point to the former conclusion. On the other hand, the result with the 29 cm. electrodes, is a direct verification of Ohm's law. Kohlrausch, therefore, adopted the latter conclusion, and justified his doing so by special researches on the electromotive force of small gas deposits. He showed that, with the currents he used, the electromotive force is proportional to the surface density of the deposit, and estimated that the products of decomposition of $\frac{1}{10}$ mg. of water per square metre would generate an electromotive force equal to that of a Daniell's cell. It is of the greatest importance to remark that the polarization effects, from which this result is deduced, must have arisen and disappeared in some cases in much less than $\frac{1}{10}$ of a second. The anomalous behaviour of the electrolyte with small electrodes is explained by Kohlrausch by taking into account the self-induction of the circuit.

A little consideration will show that the electromotive force due to this cause always opposes the electromotive force of polarization, when the current strength is a simple harmonic function of the time. Let i denote the current strength, reckoned positive in a given direction, then, according to Kohlrausch's law, the electromotive force of polarization at time t is $-p \int i dt$, where p is the

electromotive force generated by the passage of a unit of electricity; its value depends on the electrolyte and on the electrode being, *ceteris paribus*, nearly inversely proportional to the surface of the latter. Let n be the number of revolutions of the machine per second, and let $2\tau = \frac{1}{n}$; then we may represent the electromotive force of the machine at time t by $\frac{k}{\tau} \sin \frac{\pi}{\tau} t$, and the electromotive force of self-induction by $-q \frac{di}{dt}$, where k and q are constants, the latter being the coefficient of self-induction of the circuit (see Electromagnetism, p. 76). If w be the whole resistance of the circuit, we may write

$$wi = \frac{k}{\tau} \sin \frac{\pi}{\tau} t - q \frac{di}{dt} - p \int i dt,$$

or

$$q \frac{d^2 i}{dt^2} + w \frac{di}{dt} + pi = \frac{k\pi}{\tau} \cos \frac{\pi}{\tau} t.$$

Neglecting disturbances that die away very soon after starting the machine, we get for the value of i ,

$$i = \frac{\frac{k}{\tau} \sin \frac{\pi}{\tau} t}{\sqrt{w^2 + \left(\frac{p}{\tau} - q\right)^2}},$$

where the origin of time has been thrown back by

$$\frac{\tau}{\pi} \tan^{-1} \frac{1}{w} \left(\frac{p}{\tau} - q \right).$$

The deflection α of the dynamometer is proportional to $\frac{1}{\tau} \int i^2 dt$, and may be written

$$\alpha = \frac{An^2}{w^2 + \left(\frac{p}{2\pi n} - 2\pi nq\right)^2}$$

Kohlrausch found that this formula completely accounted for all the peculiarities in the behaviour of the electrolyte (for the numerical verifications see the papers quoted). We see that the deflection is increased or diminished by the insertion of the electrolyte, according as n is greater or less than $\frac{1}{\pi} \sqrt{\frac{p}{8q}}$, and, if $n = \frac{1}{\pi} \sqrt{\frac{p}{8q}}$, the insertion of the electrolyte makes no difference. Again, if $n = \frac{1}{2\pi} \sqrt{\frac{p}{q}}$

the deflection will be the same as if there were no extra current and no polarization. So that, for any given electromagnetic machine, working at any given speed, a certain electrolytic arrangement can be found, which will exactly eliminate the effect of self-induction, and thereby render the efficiency of the machine a maximum. It is obvious too that, with a given electrolytic cell, the deflection reaches a maximum when

$$n = \frac{p}{2\pi \sqrt{pq - \frac{1}{2}w^2}};$$

this maximum was actually observed by Kohlrausch (*l.c.*).

Having due regard to these circumstances, Kohlrausch and Nippoldt found that Ohm's law was applicable to their alternating currents, for electromotive forces varying from over $\frac{1}{2}$ to under $\frac{1}{4}$ of a Grove's cell. By using the constant current of an iron-copper thermo-electric pair, they found Ohm's law applicable to zinc sulphate with amalgamated zinc electrodes, when the electromotive force was reduced to $\frac{1}{250000}$ of a Grove's cell.

It is important to remark that the fact that the electrolyte behaves like a metallic conductor through a considerable range of velocities of the sine inductor, is not a conclusive proof that the last trace of polarization has been eliminated.

In fact, let α be the resistance of the electrolyte, W that of the rest of the circuit, and w the metallic resistance that gives the same electro-dynamometer deflection for n revolutions of the inductor per second, then the above formula gives

$$\alpha - w = \frac{2}{2W + \alpha + w} \left(pq - \frac{p^2}{8\pi^2 n^2} \right) = \frac{1}{W + w} \left(pq - \frac{p^2}{8\pi^2 n^2} \right),$$

since we suppose α very nearly = w . If now p be reduced to a very small value, it may happen, especially for tolerably high speeds, that $\frac{p^2}{8\pi^2 n^2}$ is very small compared with pq , in which case $\alpha - w$ will be independent of n through a considerable range of speed, and the electrolyte will be replaceable by a wire whose resistance is less than the real resistance of the electrolyte by a small constant quantity.

The earlier results of Kohlrausch and Nippoldt for sulphuric acid, in which they used 29 cm. electrodes, were affected with an error due to this cause, amounting to about 4 per cent. In the later experiments of Kohlrausch and Grotrian,¹ this error was finally eliminated by "platinizing" the platinum electrodes. Kohlrausch had found that, with "platinized" electrodes of only 1 sq. cm. surface, the polarization of the currents of his sine-inductor was insensible; he therefore concluded that, with 25 sq. cm. platinized electrodes, the residual polarization would be finally eliminated. To make quite certain, he instituted three tests, which were carried out on the method used in all the later experiments on this subject.²

The Wheatstone's bridge arrangement was adopted. Fig. 26

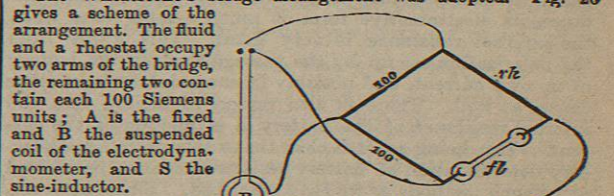


Fig. 26.

In this way, (1) the resistance of a receiver with 25 cm. platinized electrodes was found, when filled first with H₂SO₄ of maximum conductivity, and secondly, with NaCl, the driving weight of the inductor being varied, so as to give speeds of 10 to 100 revolutions. The results, reduced

¹ Pogg. Ann., cliv., 1875. ² Kohlrausch and Grotrian, Pogg. Ann., cliv., 1875; Kohlrausch, *Ibid.*, cliv., 1876.