

to a common temperature, were, for the  $H_2SO_4$ , 141.73, 141.64, 141.52, 141.53, 141.55, and, for the NaCl, —, 366.27, 366.23, 366.25, 366.21 Siemens units, with the driving weights 5, 7.5, 10, 15, 20 kgr. respectively. (2) The resistance of a solution of zinc sulphate was found, first, in Beetz's manner with constant current and amalgamated zinc electrodes; secondly, using alternating currents and the same electrodes as before; thirdly, with alternating currents and the platinized electrodes; the three results reduced to a common temperature gave 537.49, 537.41, 537.20. The greatest divergence from the mean might have been caused by an error of  $\frac{1}{20}$  degree in the temperature measurement. The agreement may therefore be pronounced complete. We think that it must be conceded that the experimental methods just described have solved in a satisfactory manner the problems involved in the determination of electrolytic resistance. We have dwelt on them so long partly because nearly all the information on the subject we possess has been obtained by their means, and partly because they present points of great theoretical interest.

Another method has been employed by Ewing and Macgregor.<sup>2</sup> The electrolyte was inclosed in a narrow tube with wide ends, in which were set platinum electrodes. This arrangement was inserted in a Wheatstone's bridge, and its resistance measured in the usual way. The precautions against polarization consisted in operating with currents of very short duration, sent through the bridge by means of a "rocker" worked by hand; the resistances in the arms of the bridge were also made large, in order to reduce the rate of polarization as much as possible; another essential feature of the method is the use of a "dead beat" galvanometer with a mirror of very small moment of inertia. The paper of Ewing and Macgregor has formed the subject of a somewhat bitter criticism by Beetz,<sup>3</sup> to which Macgregor has replied.<sup>4</sup>

Battery resistance.

**Battery Resistance.**—If the electromotive force and internal resistance of a battery in action were the same, whatever the external resistance, there would be no difficulty in finding the internal resistance by Ohm's method. We have simply to give two different values to the external resistance, and measure the current in the two cases. The electromotive force does not appear in the ratio of the two current measures; hence, knowing this ratio, we can find the internal resistance. Or we may use an electrometer, and measure the difference of potentials between the two poles of the battery, first, when the external resistance is infinite, secondly, when the external resistance is R. Then, if  $r$  be the internal resistance, the ratio of the first electrometer reading to the second is  $\frac{R+r}{R}$ , by Ohm's law; hence  $r$  can be found.

Difficulties in measuring.

Unfortunately, however, the electromotive force of a battery is *not* independent of the external resistance. In general, when a battery is circuited through a small resistance, its electromotive force is much smaller than when the external resistance is very great. This arises from the polarization set up by the passage through the battery of its own current, and possibly in some degree from other causes as well. There is also reason to believe that the internal resistance of the battery is a function of the current. This being so, it is clear that a theoretically satisfactory determination of battery resistance cannot be arrived at by such methods as we have described. Since, however, the increase of the electromotive force is very slow after the external resistance has reached a certain value, and since the alteration of the internal resistance takes some time, we can get in many cases measurements sufficiently accurate for practical purposes. A variety of methods have been devised with this object, and applied mostly to the so-called constant batteries. It must be remembered, however, that there is something indefinite in the term in-

<sup>1</sup> No observation made for NaCl in the first case.

<sup>2</sup> *Trans. R.S.E.*, 1873. <sup>3</sup> *Pogg. Ann.*, cliv. <sup>4</sup> *Proc. R.S.E.*, 1875.

ternal resistance, unless the circumstances be given under which it is found. In the method of Von Waltenhofen, the battery is "compensated" by another battery so arranged that no current passes through it; and then this arrangement is slightly altered, so that a very small current passes through the battery. This amounts to finding the internal resistance for very small currents. The method of Beetz also involves the principle of compensation; two batteries are used, but the one whose resistance is to be found is compensator and not compensated. The circuit of the compensator is joined for an instant, and then the compensated battery is thrown in. The assumption in the method is that the electromotive force is the same in the first instant whether the battery is closed through a resistance R or a resistance R'. The results seem to justify the assumption, and to establish the practical value of the method; but there are clearly limits to its application which it would not be very easy to define. Beetz himself shows that the electromotive force of a battery is greater when it is compensated than when it is compensating. A similar objection may be urged against the method of Siemens, which again gives good results when properly used. We refer the reader interested in this matter to the sources of information already quoted (see Historical Sketch), and content ourselves with an account of Mance's method, which, although subject to the same objection as all the others, is very convenient for rough purposes, and is much employed in this country.

Let A, B, C, D be four resistances arranged in circuit, B being the battery whose resistance is required. Insert a galvanometer between AB and CD, and a circuit which can be closed and opened by means of a key between AD and BC. We thus have an ordinary Wheatstone's bridge, with a key in place of a battery, and a battery in place of the ordinary resistance to be measured. Owing to the presence of the battery, there will be a current through the galvanometer, which will deflect the needle; this deflection is compensated by means of a magnet, and the needle brought back to zero. Then the resistances A, C, D are arranged so that the galvanometer is not affected when the key circuit is opened or closed; when this is so the key and galvanometer circuits are conjugate, and we have AC - BD = 0, from which we can find B, since A, C, D are known. In practice, however, it is impossible in the great majority of cases to fulfil the direction printed in italics. Suppose for a moment we had arranged the resistances so that AC - BD is very nearly but not quite zero, and suppose we close the key circuit, which had been formerly open, then, since this is not conjugate to the battery circuit, the external resistance opposing the battery is reduced; hence its electromotive force falls, the current through the galvanometer is altered, and the deflection of the needle alters. At the same time there is a current owing to the fact that AC - BD is not exactly zero. These two effects may either conspire or oppose each other. No data, so far as we know, have been obtained which would enable us to tell how quickly this fall in the electromotive force of any given battery comes on. In practice we see a sudden jerk of the galvanometer, and then a slow swing. The former is due to the deviation of the bridge from balance, and the latter to the alteration of the electromotive force. It is easy to decide which is which, for the direction of the former can be changed by making AC - BD positive or negative, while the direction of the latter is not affected in this way. This disturbing effect is very great with one-fluid batteries; it would, for instance, be a hopeless undertaking to measure in this way the resistance of a cell of Smee while sending a large current. The effect is not so great with a Daniell's cell, and can be reduced *ad libitum*, by introducing metallic resistance into the battery circuit. The effect having been thus reduced within reasonable limits, we operate thus:—Arrange the bridge until the deflection owing to deviation from balance is opposite to that due to the change in the electromotive force; then, by gradual adjustment, work down the initial jerk to nothing, so that the needle appears to start off on its slow swing without any perceptible struggle. When this state of matters is reached, there is a balance, and  $B = \frac{AC}{D}$ . Then subtracting from B

the resistance put into the battery circuit, we get the resistance of the battery. Of course this does not solve the problem of finding the resistance of any battery sending any current; but we believe that as much can be done in this way as in any other. Various modifications of Mance's method have lately been proposed, but their practical advantages over the original method have scarcely as yet been established.

Mance's method.

#### On Resistance in General.

We have drawn no distinction between statical and dynamical electricity in our application of Ohm's law, and no such essential distinction has ever been proved to exist. In proportion as a body is a good conductor for galvanic electricity, it is a bad insulator for statical electricity. In general, however, bodies which are good enough insulators to retain a charge of statical electricity are so bad conductors that it is with difficulty that we can compare their conductivities by means of the voltaic current. On the other hand, it is difficult by means of statical electricity to compare satisfactorily the conductivities of very good conductors. Determinations of the last-mentioned kind have, however, been made by Riess (*vide infra*,—Heating Effects), and the results agree with those obtained by other methods. The insulating power of a substance depends practically to a great extent on the nature of its surface. The dissipation of statical electricity by insulating supports is due, in most cases, almost entirely to the conducting power of a thin surface layer of moisture condensed from the atmosphere, or of some product of chemical decomposition caused by exposure to the air, or of dust or other foreign matter accidentally deposited. As far as high specific resistance is concerned, paraffin, shellac, ebonite, and glass at ordinary temperatures would all be about equally good insulators; but in practice they stand in the order in which we have named them. Paraffin and shellac surpass the other two in their power of preserving for a long time a clean dry surface; ebonite is very good for a time, but ultimately its surface becomes covered with a layer of sulphuric acid, arising from the decomposition of the material; glass, again, is very hygroscopic, although white flint glass, when kept dry by artificial means, is said to be one of the best insulators known.

Metals.

Highest in the order of conductivity stand the metals and their alloys. In this class of bodies the passage of the electric current is unattended by chemical decomposition, and the conductivity decreases as the temperature increases. Along with the metals may be ranked a few other bodies, which have anomalous conductivity, but are not decomposed; such as graphite, red phosphorus, chloride and oxide of lead under the melting-point, various sulphides and selenides, tellurium, and selenium. In the great majority of the bodies included in this supplementary class the conductivity increases with the temperature; the last two present several anomalies, to which we shall refer farther on.

Electrolytes.

A second class of bodies is formed by those which are decomposed by the electric current. The specific conductivity of these is much lower than that of the metals, and it increases when the temperature is raised. To this class belong, when in solution or in the melted state, most simple binary compounds composed of equal equivalents of two elements, and compounds derived from these by "double decomposition" (see, however, art. ELECTROLYSIS); also some sulphides which have an anomalous conductivity, and glass and some bodies like it, which in the melted state, and in the soft state preceding fusion conduct as electrolytes.

Non-conductors, on the other hand, are:—All gases and vapours, whether at ordinary pressures or in what is called a vacuum, diamond, sulphur, amorphous phosphorus, amorphous selenium, fluid chlorine, bromine, solid and melted iodine, bichloride and biniodide of tin, sulphuric anhydride, solid silicic acid, oxide of iron, oxide of tin; most compounds that are not binary, that is, do not consist of an equal number of equivalents of two components, e.g., many organic compounds—etheric oils, resins, wood fibre, caoutchouc; also "binary compounds" in the solid state. To these may be added pure water, pure hydro-

chloric acid, &c., which are very bad conductors, if not absolute non-conductors.

Before leaving this part of our subject, it will be interesting to throw together a few of the general principles that have been arrived at, and to give a few numerical results, which will convey to the reader an idea of the position of the different classes of bodies in the scale of conducting power. For farther details we refer to Wiedemann's *Galvanismus*.

**Metals.**—(1.) It was remarked by Forbes that the order of conductivity is the same for electricity as for heat. The measurements of Wiedemann and Franz have established that the ratio of the conductivities for heat and for electricity is very nearly constant, not only for pure metals, but also for alloys. (See Wiedemann's *Galvanismus*, *bd. i.* § 194.)

(2.) The conductivity of the pure metals decreases as the temperature rises from 0° to 100° C., the rate of decrease becoming smaller towards the upper limit. Matthiessen expresses the conductivity by the formula  $k = k_0(1 - \alpha\theta + \beta\theta^2)$ , where  $k_0$  denotes the conductivity at 0° C.,  $\theta$  the temperature, and  $\alpha$  and  $\beta$  constants. He found that  $\alpha$  and  $\beta$  had nearly the same value for all pure metals in the solid state, with the exception of thallium and iron, and gives as the mean values for pure metals  $\alpha = 0.00376470$ ,  $\beta = 0.0000083402$ . The values for iron are  $\alpha = 0.0051182$ ,  $\beta = 0.000012915$ ; for mercury,  $\alpha = 0.007443$ ,  $\beta = 0.0000008263$ . Although there can be no doubt about the general agreement in the formulae for the different pure metals, yet the actual formulae arrived at is purely empirical and must be used only between 0° and 100° C. If we carried its application beyond, it would give a minimum conductivity for pure metals about 300° C. The direct experiments of Müller and Siemens give no indication of such a minimum. The latter represents the results of his experiments (extending in some cases as far as 1000° C.) by means of the formula  $r = \alpha\sqrt{T} + \beta T - \gamma$ , where  $r$  is the specific resistance, T the absolute temperature,  $\alpha, \beta, \gamma$  constants. Relying on a formula of this kind for platinum, Siemens has constructed a pyrometer for determining the temperature of furnaces by means of resistance measurements.

(3.) As we have seen, the specific resistance of pure metals goes on increasing continuously as the temperature rises. At the melting-point there is a sudden rise in the resistance, and after that the resistance goes on increasing with a smaller temperature coefficient than before. This is in accordance with the fact, that both the specific conductivity and temperature coefficient of mercury are smaller than those of the other metals in the solid state. Bismuth and antimony are exceptions to this rule, in that there is a sudden decrease of resistance at the melting-point. According to the results of L. de la Rive, the resistance of metals in general is about doubled in passing the melting-point. We should therefore expect the specific conductivity of frozen mercury to be about 3.31, that of silver being 100.

**Alloys.**—(1.) Matthiessen found that the metals could be divided into two classes, according to the conducting properties of their alloys

- Lead, Tin, Cadmium, and Zinc.
- Most of the other metals—Bismuth, Antimony, Platinum, Palladium, Iron, Aluminium, Sodium, Gold, Copper, Silver.

Let  $v, v'$  be the volumes,  $s, s'$  the specific gravities,  $k, k'$  the conductivities of the two components of any alloy; and let  $\bar{s} = \frac{vs + v's'}{v + v'}$ ,

and  $\bar{k} = \frac{vk + v'k'}{v + v'}$ , be called the mean specific gravity, and mean conductivity of the alloy. Then alloys of any one metal of class a, with any other of the same class, have very nearly the mean specific gravity and conductivity calculated by the above formulae.

Alloys of a metal  $\alpha$  with a metal  $\beta$  have specific gravity and conductivity always less than the mean. If a metal  $\alpha$  is alloyed with a considerable percentage of  $\beta$ , the conductivity is not much altered, but if a metal  $\beta$  be alloyed with even a very small quantity of  $\alpha$ , the conductivity is greatly reduced.

Alloys of the metals  $\beta$  among themselves have in general a conductivity much inferior to that of either component. The conductivity remains constant through a considerable range of percentage, but rises very quickly as the percentage of either metal approaches 100. This property is very marked in an alloy of gold and silver. Matthiessen recommended an alloy of two parts by weight of gold to one of silver for the reproduction of the standard of resistance. The resistance of such an alloy would be very slightly affected by small variations in its composition.

Mercury, and melted metals generally, are not subject to the foregoing laws. A very small percentage of another even worse conducting metal raises the conductivity of mercury, but the



addition of larger quantities of the foreign metal lowers the conductivity.

(2.) The formulae for the temperature variation for alloys of the metals  $\alpha$  among themselves agree very closely with the mean formulae calculated from the volume percentages.

If  $P$  denotes the fraction of itself by which the conductivity at  $0^\circ$  exceeds that at  $100^\circ$  for an average pure metal ( $P=0.29307$ ), and  $P$  be same fraction, observed in the case of any alloy for which the observed and mean or calculated conductivities at  $0^\circ$  and  $100^\circ$  are  $k_0$ ,  $k_{100}$ , and  $\bar{k}_0$ ,  $\bar{k}_{100}$ —then, according to Matthiessen, the following relation holds for alloys of metals  $\alpha$  among themselves, and metals  $\beta$  among themselves:—

$$P : \bar{P} :: k_{100} : \bar{k}_{100}$$

or, which is the same thing,  $R_0$ , &c., denoting resistances,  $R_{100} - R_0 - \bar{R}_{100} - \bar{R}_0$ .

For alloys of  $\alpha$  with  $\beta$ , the observed value of  $P$  is in general greater than that calculated by this formulae.

Other Physical Conditions affecting the Resistance of Solid Bodies.

Besides temperature, a variety of other circumstances affect the specific resistance of metals. As a general rule, metals are worse conductors in the hard than in the soft state. Tempering steel increases its resistance considerably, but subsequent heating and gradual cooling reduces the resistance again. The resistance of a wire stretched by a weight is increased more than can be accounted for by the mere decrease of the section.<sup>1</sup> Winding on a bobbin has the same effect. The finer a metal is drawn into wire, the greater is its specific resistance in the case of iron, the smaller in the case of copper. Magnetization has also in certain cases been found to affect the resistance. These effects were studied by Sir William Thomson; the results of his researches are given in his Bakerian Lecture, *Phil. Trans.*, 1856. The experiments are very instructive, and many of them well worth repeating now that we have more delicate apparatus. The most curious case of alteration of resistance is that of tellurium and selenium. We have already mentioned that selenium in the amorphous state is a non-conductor. After continued heating it passes into the crystalline state and conducts. Sale found<sup>2</sup> that the conductivity of this crystalline form of selenium is greatly affected by light, and that, too, differently by light of different colours. Prof. W. G. Adams<sup>3</sup> has lately made a series of experiments on the subject, and concludes that there is an action of light, which varies as the square root of the illuminating

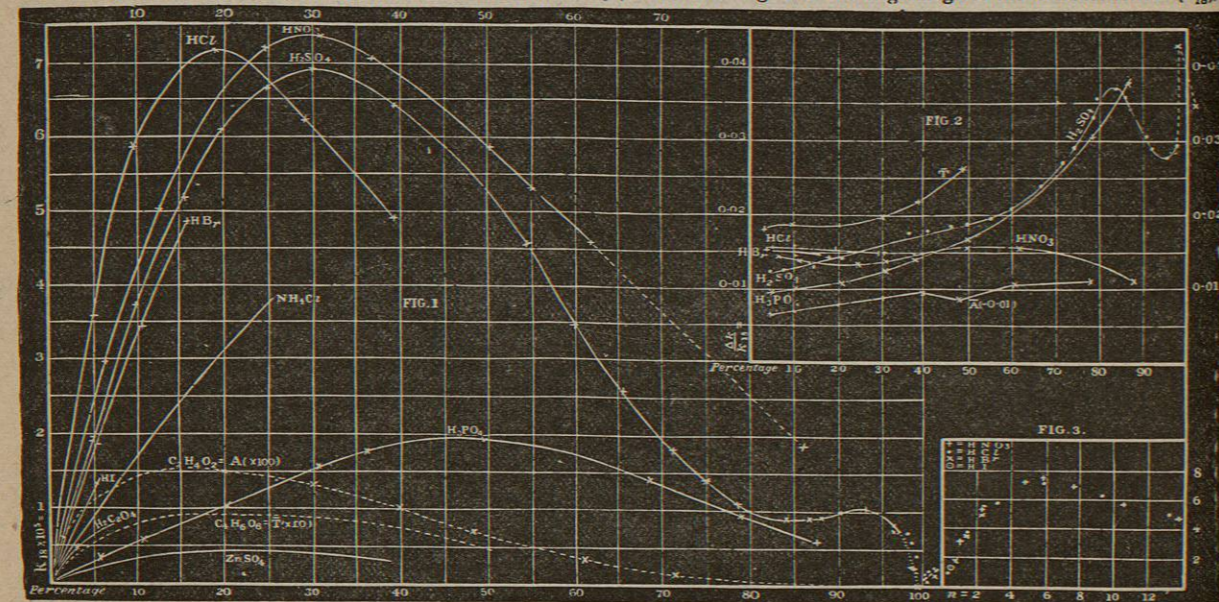


Diagram illustrating Electrical Conductivity.

$48^\circ\text{C}$ .; the ordinates represent  $k_{18} \times 10^5$ , except for acetic and tartaric acid, where they represent  $k_{18} \times 10^7$  and  $k_{18} \times 10^6$  respectively, the abscissae represent percentages by weight in the solution of HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ , &c. In fig. 2 the values of the temperature

<sup>1</sup> For recent experiments on this subject see *Proc. R. S.*, Dec. 1876, and June 1877. Authorities for some of the other facts stated will be found in Wiedemann, i. § 207.

<sup>2</sup> *Proc. R. S.* 1873. <sup>3</sup> *Proc. R. S.*, vols. xxiii. xxiv. xxv.

power, and is distinct from any heating effect. He found the resistance of selenium in one case diminished by a fifth when it was exposed to the light of a certain paraffin lamp; the change in tellurium under similar circumstances was  $\frac{1}{3}$ th. He found that the passage of a strong current through selenium sets up a kind of polarization, which opposes a current in the same direction as that which produced it, and aids a current in the opposite direction. This led him to suspect that the action of light might of itself start a current in the selenium, and he found that under certain circumstances this is the case.

Fluids.—The verification by the experiments of Kohlrausch and Nippoldt of Ohm's law for electrolytes, through a wide range of electromotive force, has greatly increased the interest of all data relating to the resistance of this class of conductors. We have no difficulty in working with electrolytes whose composition and physical state is perfectly definite, a thing next to impossible in the case of solids. Hence the resistance of an electrolyte has, far beyond the resistance of a solid metal, a value as datum for physical speculations concerning the ultimate properties of matter, which underlie Ohm's law. We refer the reader to Wiedemann's *Galvanismus* for an account of the earlier results in this department of Pouillet, Hankel, Becquerel, Horsford, Wiedemann, Becker, Lenz, and Saweljew. We recommend to his notice particularly the careful experiments of Beetz on zinc sulphate (his temperature determinations are the most extensive of the kind), also the researches of Paalzow, who examined the conductivity of various mixtures of two solutions, the conductivities of which had been separately determined. He finds that if  $R$  and  $R'$  be the resistances of the components, the resistance of the

mixture is not  $\frac{RR'}{R+R'}$ ; so that the current is not divided between the liquids as if they were metals in multiple arc; nor is it the mean of  $R$  and  $R'$ , but it lies nearer the smaller of the two. A similar result was arrived at by Ewing and Macgregor.<sup>4</sup>

Kohlrausch and Grotrian<sup>5</sup> have made the most recent as well as the most extensive investigations; and we shall best describe the present state of scientific knowledge on this subject by giving an analysis of their results and conclusions. Their experiments deal with the chlorides of the metals of the alkalies and alkaline earths. Kohlrausch has also examined a number of the commoner acids. For convenience we have transcribed the diagram given by Kohlrausch, which embodies certain of the results obtained by himself and Grotrian. Fig 1 of the diagram gives the conductivities ( $k_{18}$ ) at

continuously with the concentration, an approach to zero for infinitely weak solutions being indicated in all cases. The chlorides may be divided into two classes. (1.)  $\text{CaCl}_2$  and  $\text{MgCl}_2$  reach maximum conductivities  $1968 \times 10^{-8}$ ,  $1310 \times 10^{-8}$ , at  $18^\circ\text{C}$ . for percentages 24 and 19.8 respectively, in each case short of saturation.  $\text{LiCl}$  probably does the same, and  $\text{NaCl}$  appears to reach a maximum between 23.9 p.c. and its saturation percentage 26.5. (2.)  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{SrCl}_2$ , and  $\text{BaCl}_2$  increase in conducting power up to the point of saturation.

Taking the best conducting solutions, the order of conductivities is  $\text{NH}_4\text{Cl}$ ,  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{LiCl}$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{MgCl}_2$ , the alkaline chlorides heading the list. A 25 p.c. solution of  $\text{NH}_4\text{Cl}$  is in fact half as good a conductor as the best acid solution known.

It was found that, if the conductivity for small percentages be represented by  $k = \kappa p - \kappa' p^2$ , so that  $\kappa$  may be called the specific conductivity in watery solutions, then  $\kappa$  varies inversely as the specific gravity, that is, directly as the "specific volume."

The temperature coefficients for the chlorides are very nearly independent of the temperature. There is a slight increase for higher temperatures, which is most marked in the case of highly concentrated and viscous solutions of  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ .

For weak solutions the coefficients are all very nearly equal; at  $18^\circ\text{C}$ . the extreme value for 5 p.c. solutions lies between  $\frac{1}{2}$  (for  $\text{LiCl}$ ) and  $\frac{1}{3}$  (for  $\text{NH}_4\text{Cl}$ ). There is a tendency, as seen by the curves, to a value  $\frac{1}{2}$ , or  $\cdot 022$  for very weak solutions. It will be noticed (see table below) that this coefficient is much larger than  $\cdot 0039$ , which is about the corresponding number for a pure metal.

When the percentage is increased from five upwards, the temperature coefficient for  $18^\circ\text{C}$ . decreases at first for all the chlorides; it reaches a minimum for  $\text{NaCl}$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , which belong to class (1); but there is no minimum for  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{BaCl}_2$ , which belong to class (2), and have no maximum conductivity.

The acids investigated were nitric, hydrochloric, sulphuric, phosphoric, oxalic, tartaric, and acetic. In every case, except that of oxalic acid, a maximum conductivity was obtained. The order in which we have named the acids is that of the conductivity of the best conducting solutions at  $18^\circ\text{C}$ .; for the first three we have respectively  $k_{18} 10^8 = 7330, 7174, 6914$ , the corresponding percentages being 29.7, 18.3, 30.4, so that the maxima are very nearly equal, and the maximum percentages not far apart. The curve for sulphuric acid is exceedingly remarkable. Between 0 and 100 p.c. of  $\text{H}_2\text{SO}_4$  it shows two maxima. The first minimum occurs at the percentage corresponding to the hydrate  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ . The conductivity corresponding to  $\text{H}_2\text{SO}_4$  is also a minimum; for when  $\text{SO}_2$  is added, causing supersaturation, the conductivity again increases, there must therefore be at least one more maximum, since melted  $\text{SO}_2$  is a non-conductor. There is no peculiarity in the curve corresponding to the hydrate  $2\text{H}_2\text{O} + \text{H}_2\text{SO}_4$ , which is distinguished from  $\text{H}_2\text{O} + \text{H}_2\text{SO}_4$  in not being crystallizable. A striking similarity in the case of sulphuric and acetic acid is remarked between the curves of resistance and of solidification temperature; wherever the latter is high, the former is so also; there is a maximum in both cases for  $\text{H}_2\text{O} + \text{H}_2\text{SO}_4$  and for  $\text{H}_2\text{SO}_4$ , and a minimum in both cases near 92.5 p.c.; the other minima do not agree so well.

A remarkable relation is given, which appears to connect the resistance of the monobasic acids  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ , and  $\text{HNO}_3$ . If any percentage be multiplied by the specific gravity of the solution, and divided by the molecular weight of the acid, the result is the number of molecules ( $n$ ) in unit of volume of the solution. On forming a table of resistances with  $n$  for argument, it was found that for solutions with the same  $n$ , whether of  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ , or  $\text{HNO}_3$ , the conductivity is the same. This appears very clearly from the dotted curve in fig. 3 of the diagram, calculated from the different acids, the regularity of the curve, and in parts the coincidences, are very marked. This result may be stated thus:—In solutions containing an equal number of molecules, whether of  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HBr}$ , or  $\text{HI}$ , the components of electrolysis under equal electromotive forces pass in opposite directions with equal relative velocities.<sup>6</sup>

The temperature coefficients for the four monobasic acids are nearly equal, and nearly independent of the concentration. The same increase of temperature coefficient with increase of concentration as was noticed in the case of viscous chloride solutions appears also in the viscous acid solutions of phosphoric, tartaric, and sulphuric acid. It is also found that where the conductivity is a minimum, the temperature coefficient is correspondingly great; so that, with increasing temperature the maxima and minima tend to get smoothed out. It appears also that the proximity of the maxima for  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ , becomes more marked as the temperature rises.

The existence of the maxima in most cases, and of the minima in the sulphuric acid curve, led Kohlrausch to suggest the principle that no stable chemical compound in a pure state is a conductor, and that mixture of at least two such compounds is necessary for conduction. He mentions many instances of this principle, e.g., water, sulphurous acid, carbonic acid, acetic acid, melted boric

<sup>1</sup> A similar law might be stated for the chlorides, but it holds only for very weak solutions.

acid, chromic acid, anhydrous  $\text{SO}_3$ , &c. In a recent paper<sup>7</sup> he gives some very interesting results concerning the conductivity of pure water and other bad conductors. The lowest conductivity he got for water was 71 ( $\text{Hg} = 10^{12}$ ). This was after careful purification and repeated distillation in glass, and finally in platinum vessels. After standing under a glass bell jar for 4.3, 20, 78, and 1060 hours, the water rose in conductivity from 78 to 133, 350, 850, and 3000 respectively. He calculates that, if pure water were a non-conductor, the presence of 0.1 mgr. per litre of  $\text{HCl}$  would be sufficient to account for the observed conductivity. He also found conductivities for  $\text{SnCl}_4$  ( $< 200$ , alcohol (commercial distilled) 30, acetic acid (glacial melted) 4, ether ( $< 8$ ). Among recent researches of interest may be mentioned Braun's attempt<sup>8</sup> to measure the conductivity of melted salts, and Grotrian's<sup>9</sup> on the relation between the viscosity and the electric conductivity of electrolytes. For the speculations of Kohlrausch, Hankel, Beetz, Wiedemann, and Quinceke on the ultimate nature of electrolytic resistance, see the papers, of the first-mentioned, or Wiedemann's *Galvanismus*, Bd. i. § 434 sqq.

Gases.—We are not aware that any experiments have hitherto established that any gas or vapour at ordinary temperature and pressure is a conductor. Boltzmann<sup>10</sup> has arrived at the negative result that air at ordinary temperature and pressure must have a specific resistance at least  $10^{20}$  times that of copper. Sir William Thomson has, we believe, arrived at a similar result for steam; and recent experiments by Prof. Maxwell<sup>11</sup> on air, steam, mercury, and sodium vapour (at high temperatures) have led him to a similar negative conclusion. It was found, however, that the heated air from a Bunsen's burner conducts remarkably well.<sup>12</sup> The so-called unipolar conductivity of flames presents many anomalies, which have been examined by various experimenters. For the literature see F. Braun, *Pogg. Ann.*, 1875.

It would appear, therefore, that the loss of electricity from insulated conductors at moderate potentials, observed by Coulomb and Riess, cannot be due to conduction or convection by the air, but must arise almost wholly from the insulating supports. Warburg, who has experimented much on this subject, appears to be of the same opinion (*vide* Boltzmann, l.c. p. 415). Varley has lately investigated the passage of the current of a large number of Daniell's cells through a Geissler's (hydrogen?) tube. He found that it required 323 cells to start the current, but that once it was started it could be maintained by 308 cells; the current which flowed was proportional to the excess of the number of cells over 304. Thus, for  $317 = 304 + 13$  the current was proportional to 25, for  $330 = 304 + 26$  it was proportional to 51. Accordingly, if  $E_0$  be a constant, and  $R$  another constant (the resistance of the gas?) we get for the electromotive force  $E$ , required to send a current  $I$ ,  $E = E_0 + RI$ .  $E_0$  is analogous to the electromotive force of polarization. For further details about the resistance of dielectrics we refer the reader to Maxwell's *Electricity and Magnetism*, vol. i. § 366 sqq.

The following table will give an idea of the conducting power of General different bodies;  $r$  denotes the specific resistance in C.G.S. units (to reduce to ohms divide by  $10^9$ );  $\alpha$  is the percentage of itself that  $r$  increases in the case of metals and decreases in the case of electrolytes per deg. C.;  $t$  is the temperature at which  $r$  is given.

	$t$	$r$	$\alpha$
Silver (annealed).....	20°	1521	·37
Copper (annealed).....	20	1615	·38
(hard drawn).....	20	1652	—
Platinum (annealed).....	20	9158	—
Iron (annealed).....	20	9827	—
Lead (pressed).....	20	19850	·38
Mercury (liquid).....	20	21170	·04
German silver.....	20	96190	·07
$\text{H}_2\text{SO}_4$ (max. soln.).....	18	$1.39 \times 10^9$	1.5
$\text{NH}_4\text{Cl}$ (sat.).....	18	$2.55 \times 10^9$	1.5
$\text{ZnSO}_4$ (max. soln.).....	10	$26.60 \times 10^9$	2.3
$\text{H}_2\text{SO}_4$ (pure).....	18	$120.20 \times 10^9$	4.2
$\text{H}_2\text{O}$ (pure).....	18	$135 \times 10^{13}$	—
Glass.....	200	$227 \times 10^{14}$	—
".....	400	$735 \times 10^{11}$	—
Gutta percha.....	24	$353 \times 10^{21}$	—
".....	0	$7 \times 10^{24}$	—

<sup>7</sup> The residual conductivity he would attribute to residual impurities, or, as in the case of  $\text{H}_2\text{SO}_4$  and melted salts, to dissociation, whereby the solution becomes in reality a mixture of different compounds. — *Pogg. Ann.*, clviii. 1876. <sup>8</sup> *Pogg. Ann.*, cliv., 1875.

<sup>9</sup> *Pogg. Ann.*, clvii., 1876; clx., 1877. <sup>10</sup> Unpublished results. <sup>11</sup> *Pogg. Ann.*, clv., 1875.

<sup>12</sup> Herwig (*Pogg. Ann.*, 1874) has recently concluded from some experiments that  $\text{Hg}$  vapour does conduct in a certain anomalous way. His experiments were complicated by the conductivity of the glass tubes containing the heated vapour; steps were taken, however, to eliminate this. Considerable doubt hangs over the whole subject.

coefficient ( $\frac{\Delta k}{k_{18}}$ ) for  $18^\circ\text{C}$ . are given by the ordinates, the abscissae being percentages as before. For convenience of drawing the coefficient of acetic acid is decreased by 0.01.

The curves which appear in the diagram include all the distinct varieties; and it will be seen that in all cases the conductivity varies

<sup>4</sup> *Trans. R.S.E.*, 1873. <sup>5</sup> *Pogg. Ann.*, cliv., 1875, and cliv., 1876. <sup>6</sup> Mercury is the standard.



On the Passage of Electricity through Insulators.

Hitherto we have divided bodies into *conductors*, through which electricity passes under the influence of any electromotive force, however small, and *non-conductors* or *insulators*, through which electricity will not pass, no matter how great the urging force. In practice, however, when the value of the electromotive force reaches a certain limit, electricity does pass through a non-conductor. A discharge of electricity taking place suddenly in this way through a non-conductor is called a "*disruptive discharge*." The power of a non-conductor to resist up to a certain limit the passage of electricity through it has been called its *dielectric strength*. The dielectric strength of any medium is greater the greater the electromotive force it will stand, when placed say between two parallel metal plates arranged in a given way, before it is broken through by the disruptive discharge. We shall by and by attach a definite quantitative signification to the term, but the general notion will be sufficient for the present.

Although it may be found when both phenomena have been more fully analysed, that conductive and disruptive discharge are really two different aspects of one and the same phenomenon, yet for the experimenter they are two distinct things, which must not be confounded.

This would be the place to set forth the quantitative relations which regulate the electromotive force required to produce disruptive discharge, the quantity of electricity that passes under given circumstances, and the dielectric strength of different media; in fact, to lay down for disruptive discharge a law corresponding to the law of Ohm for metallic and electrolytic conduction. The present state of electrical science, however, does not permit us to do this in a satisfactory manner. Experiment has not as yet led to a single dominant principle, like Ohm's law, which will account for all the phenomena of disruptive discharge. The best theory of the subject is Faraday's, which will be gone into under "*disruptive discharge in gases*." Observation and experiment, on the other hand, have been occupied for the most part with the various transformations of energy which accompany the disruptive discharge. We prefer, therefore, to discuss the whole matter under the single head "*disruptive discharge*."

TRANSFORMATIONS OF ENERGY ACCOMPANYING THE ELECTRIC CURRENT.

Under this head we propose to discuss (to use a word of Rankine's) the energetics of electricity. It may be objected that this heading might have been put over a good deal of what has gone before, and we shall, for convenience, treat certain matters under it which, in a strictly logical division, would have found a place elsewhere. If we had formed a definite conception of what we call electricity—had, for instance, assumed that it is a material fluid, having inertia like other fluids, then no doubt the energetics of the subject could have been much extended. As it is, we think that advantage is to be gained by associating in our minds the experimental laws which we are now to arrange under the above heading.

We shall consider (1) the heat developed in metallic and electrolytic conduction, and at the junctions in heterogeneous circuits; (2) the mechanical, sound, heat, and particularly light effects accompanying disruptive discharge; (3) the energy of magnetized iron and steel, and of electric currents in the neighbourhood of the electric current (electromagnetism); (4) the energy of the electrotonic state, or electrokinetic energy (magneto-electric induction). In this list ought to be included the potential energy of chemical separation, which would come under the head of electrolysis. At present, however, electrolysis is quite as much a chemi-

cal as an electrical subject, and it has been found convenient to treat it in a separate article (see ELECTROLYSIS). Some points in connection with it have already been touched upon, and a few more will come up in (5), which treats of sources of electromotive force, and deals with the question, whence comes the energy which is evolved in the voltaic circuit? a question the answer to which is for the most part experimental and practical—the only one, in fact, that the state of electrical science permits us to give.

Heating Effects.

It is easy to show, by a variety of simple experiments, that a current of electricity heats a conductor through which it passes. In the case of moderately strong currents the heat developed is perceptible to the touch; the wire may, in the case of very strong currents, be raised to a white heat; it may melt, and even be volatilized. In the case of very weak currents, the heating effect may be demonstrated by passing the current through the spiral of a delicate Breguet's thermometer. We find, when we examine the experimental data on the subject, that heating effects may be conveniently divided into two distinct classes. In the first of these the fundamental law is that the development of heat in any part of a linear circuit varies as the resistance of that part multiplied by the square of the current. In the second class the development of heat varies as the first power of the current. The heating effects of the first class are obviously independent of the direction of the current, and are irreversible; and the more we examine them the more they appear to correspond to the loss of energy by the frictional generation of heat in ordinary machines. In the language of the dynamical theory of heat, the part of the energy of the electric current which disappears in this way is said to be dissipated. The effects of the second class change their sign when the direction of the current is changed; so that, if anywhere there was evolution of heat when the current flows in one direction, then, when the current is reversed, there will be absorption of heat to an equal extent. We shall find that we have great reason to believe that such effects are strictly reversible.<sup>1</sup> In order to get a satisfactory foundation for the simple theoretical views which we have thus indicated, it is essential to be able to separate the two classes of effects. Now, this is possible to a very great extent even in practice. The effects of the first class increase much more rapidly with the strength of the current than those of the second, so that, by sufficiently increasing the current, we can make the effects of the second class as small a fraction of the whole heating effect as we please; while, on the other hand, by sufficiently decreasing the current, the preponderance of the second class may be increased to any desired extent. We shall in what follows suppose the two classes of effects separated in this way.

*Discharge of Static Electricity.*—One of the earliest attempts to study the heating effects of the electric discharge was made by Kinnersley. He constructed an thermoelectrometer, which consisted of a closed glass vessel, in which were fixed two metal balls communicating with electrodes outside the vessel. The bottom of the vessel was filled with a little coloured fluid, which communicated with a tube having a vertical arm rising outside the vessel. When a spark passed between the balls, the heat developed caused the air to expand and force the liquid into the vertical tube, the rise of level in which indicated the degree of expansion, and, by inference, the amount of heat developed in the spark.

Sir Wm. Snow Harris<sup>2</sup> revived this instrument of Kinnersley's, and improved it by stretching a fine wire between

Development of heat in circuit.

Heating effects of discharge.

<sup>1</sup> That is, in the thermodynamic sense. <sup>2</sup> *Phil. Trans.*, 1827.

the terminals inside the vessel, so that the heat measured was now that evolved in a metallic conductor.

With this improved instrument he made a number of valuable experiments on the heating of wires by the discharge of a Leyden battery, whose charge was measured by a Lane's electrometer. Assuming that the heat developed varies inversely as the conductivity of the wire (which is not the case), he arranged the metals in a series which agrees with that given later by Riess, although the numbers given do not properly represent the conductivities owing to the erroneous assumption on which they are deduced. Harris observed that the specific conductivity of alloys is often less than that of either metal, and that a very small admixture of another metal considerably reduces the conductivity of pure copper. He also arrived at the result that the amount of heat developed in a wire varies as the quantity of electricity which passes in the discharge, but seems to have concluded that the amount of battery surface used had no effect.<sup>1</sup>

Riess made two very important improvements on the thermoelectrometer by substituting spirals for the straight wire of Harris, and by inclining the tube containing the liquid so as to be nearly horizontal. The sensibility of the instrument was thus greatly increased. Riess took up the whole question of the heating of wires, and investigated it thoroughly.

The actual instrument which he used is represented in figure 27 (taken from his *Reibungselectricität*). It consists of a glass tube of

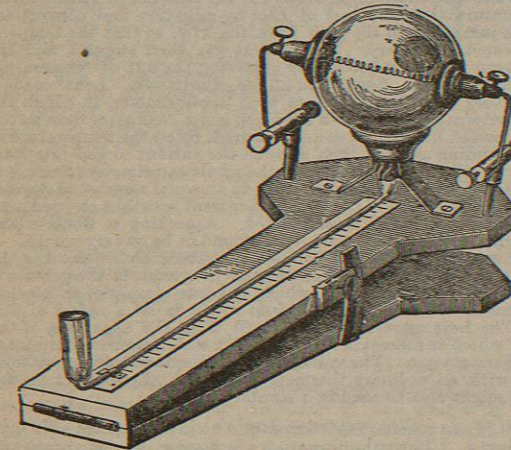


Fig. 27.

narrow bore, 16 to 17 inches long, to which is blown a glass globe 2 to 4 inches in diameter. This tube is partially filled with some coloured fluid which confines the air in the globe, a wide reservoir at the other end of the tube allows the fluid to accumulate without sensible change of level. The stand of the instrument consists of two pieces hinged together, so that the tube can be placed at a small inclination to the horizon. The rest of the instrument will be understood from the figure. Details concerning the manipulation will be found in the *Reibungselectricität*, Bd. i. § 410. When the fine wire is heated by a current of electricity, the heat developed is divided between the wire and the air; the expansion very quickly reaches a maximum, and the level of the liquid in the fine tube becomes stationary for a moment. If *m* be the number of scale divisions between its original and final positions, we have (see Riess, *l.c.*, or Mascart, t. i. § 325)

$$T = mA \left( 1 + \frac{B}{CW} \right), \text{ and } H = mA(CW + B) \dots (1),$$

where *T* denotes the amount by which the temperature of the wire would have risen had no heat left it, and *H* the whole amount of heat developed by the current. *C* and *W* are the mean specific heat and weight of the wire, and *A* and *B* constants, which depend on the make of the instrument, and on the initial temperature and pressure of the air.

A very convenient form of thermoelectrometer, called the *thermomètre inscripteur*, has been used by Mascart (*l.c.*).

<sup>1</sup> *Phil. Trans.*, 1834.

The alterations of pressure are registered automatically on a revolving drum, after the manner of the pulse-registering instrument of Marey. One advantage of this instrument is that it gives a representation of the course of the temperature in the apparatus.

In most of his experiments Riess used batteries of Leyden jars. The jars were all as nearly as possible alike, and the inner armatures were in general connected together. The quantity of electricity given to the battery was measured by means of a Lane's jar, the balls of which were placed at a distance of about a line apart. The battery was then discharged through the thermo-electrometer along with any external circuit connected with it.

It is of great importance in such experiments as we are now describing to examine what happens at the place where the circuit is closed. This closure is effected by bringing two metallic balls into contact. But before contact is reached, a spark passes in which sound, light, and heat are given forth,—in a word, energy evolved. When the resistance of the circuit is small, this spark passes at a considerable distance, and is very intense, no matter how quickly the conductors are brought together. The energy consumed in this case is a considerable fraction of the whole energy given out by the discharge. If, however, the resistance of the circuit through which the discharge takes place be considerable, the electricity takes longer to accumulate sufficiently to raise the electromotive force between the balls to the discharging limit. We may, therefore, by operating quickly, get the balls very nearly in contact before the spark passes. In this case the spark is much less intense, and the fraction of the whole energy which appears in it is very small. Riess made some very valuable experiments on this point. He arranged an air-break in the circuit of the thermoelectrometer, which he could widen or narrow at pleasure, and discharged his batteries through this circuit in the usual way. He found that as the gap is widened the amount of heating in the thermometer is at first increased, but after a certain length of break is attained it decreases again. It must be remembered that we have now two air breaks in our circuit of discharges, the discharging break and the inserted break. One effect of the inserted break is to diminish the intensity of the spark at the discharging break, and cause a decrease of the energy which appears there. On the other hand it makes the discharge of the battery *incomplete*, so that part of the potential energy is not exhausted. It is very likely to the opposition of these two effects that the peculiarity observed by Riess is due. Mascart has observed a similar phenomenon in disruptive discharge through oil of turpentine. At all events Riess showed that, when the inserted break was not longer than  $\frac{2}{10}$ ths of a line, the heating in the thermometer was the same as when there was no break at all. Hence, if we make the resistance of our circuit so great that the spark at the discharger is not longer than  $\frac{2}{10}$ ths of a line, the energy consumed there may be neglected.

The resistance of the connections belonging to the battery and the thermometer were always very small compared with that of the thermometer wire, and the wire, if any, inserted outside the thermometer; so that, if the resistances of these be *R* and *S*, the resistance of the whole circuit may be taken to be *R* + *S*. The law to which the experiments of Riess led can be expressed by means of the formula

$$H = \frac{S}{R + S} Q \dots (2),$$

where *Q* is the amount of electric potential energy which has disappeared, and *H* the amount of heat (measured by its dynamical equivalent) developed in the wire of the thermometer, whose resistance is *S*.

In the case of the complete discharge of a battery of *n*

General considerations.