

ELECTROLYSIS. A very slight acquaintance with the phenomena of conduction of electricity by different bodies shows us that conductors may be arranged in two very distinct classes. In one the passage of electricity produces no change in the chemical composition of the substance, unless indeed the electromotive force be so great that disruptive discharge occurs, or so large an amount of heat is generated that chemical effects ensue; the conductivity diminishes slowly as the temperature rises, and if the resistance of the rest of the circuit be small compared with that of the substance under consideration, an amount of heat is produced in the latter equivalent to the energy expended by the sources of electricity. To this class of conductors probably belong all solids, with the exception of hot glass, which conducts with decomposition at a temperature below the fusing point. The conductivity differs enormously in the different cases; those which conduct most readily are the metals, alloys, the chemical elements generally, and some few metallic oxides and sulphides (Faraday, *Exp. Res.*, 440, ser. iv.; Skey, *Chem. News*, xxiii.). Besides fused metals Faraday added one liquid, fused periodide of mercury, to the list, but subsequently gave reasons for considering that it was misplaced (*Exp. Res.*, 691, ser. vii.). The other class of conductors presents a remarkable contrast to the one just described. In these the passage of electricity results in the chemical decomposition¹ of the substance of the conductor at the points where the electric current² enters and leaves the body; a rise of temperature produces in such bodies a very considerable increase in the conductivity, but the specific resistance of even the best conducting among them is always very great compared with that of the metals. (For details see article ELECTRICITY, p. 46 sqq.) Only part of the energy of the circuit is spent in heating the conductor, as a transformation of energy takes place in the chemical and molecular actions at the points where the current enters and leaves the conductor.

It is the behaviour of the second class of bodies under the influence of the electric current that we have now to discuss. The physical side of the subject has already been considered in the article ELECTRICITY; so we shall principally confine our attention to the phenomena of electrolysis which bear on the laws and principles of chemistry. Before going further it will be necessary to introduce the technical terms which have now become familiar, and, in order to be definite, we will consider somewhat closely a particular instance of electrochemical decomposition of the simplest type.

The cell in which the action takes place consists of a wide tube of hard glass, bent into a V-shape; into this is introduced some silver chloride, which is kept fused during the experiment; into the liquid in one leg of the tube is dipped a platinum wire connected with the negative pole (zinc) of a battery³ of 3 or 4 Grove's cells, and into that in

¹ We have not space here to discuss whether or not conduction in electrolytes is always attended with decomposition, although the question has engaged the attention of many writers on the subject. The reader who wishes for information upon the point may consult Faraday, *Exp. Res.* 966-987, ser. viii.; Despretz, *Compt. Rend.*, t. xlii. p. 707; De la Rive, *Archives*, t. xxxii. p. 38; Logeman and Van Breda, *Phil. Mag.* [4], viii. 465; Buff, *Ann. d. Chem. u. Pharm.*, Bd. xciv. s. 15; Foucault, *Compt. Rend.*, t. xxxvii. p. 580; De la Rive, *Ann. de Chimie*, [3], t. xli. p. 41; Favre, *Compt. Rend.*, lxxiii. p. 1463; Helmholtz, *Berlin Monatsbericht*, 1873, Nachtrag zum Juliheft; and, for a summary of results, Wiedemann, *Galv.*, Bd. i. § 314-316, and Nachtrag, 36, § 334.

² The standard direction of the current is taken, as usual, to be from the copper through the wire to the zinc of an ordinary zinc-copper cell.

³ It is not necessary to use a voltaic battery,—any source of electricity serves,—but either a voltaic or a thermoelectric battery is usually employed, since these so conveniently supply a large quantity of electricity, with an electromotive force sufficient for the purpose.

the other a piece of graphite or gas carbon connected with the positive pole of the same battery. We will suppose a galvanometer introduced into the circuit, and that the current strength as indicated thereby is, roughly speaking, constant, so that the quantity of electricity which passes can be measured roughly by the time occupied in passing. After the circuit has been closed a short time, bubbles of chlorine will begin to come off from the carbon, while pure silver is deposited upon the platinum wire, but *except at these points no alteration will take place at any part of the fluid.* If the platinum wire with the attached silver be weighed at intervals, it will be found that the amount deposited after the current has become constant is proportional to the time, i.e., to the amount of electricity which has passed through the liquid. The same will be true of the chlorine if collected in the other leg of the tube, due allowance being made for the small bubbles retained by the carbon, &c. And the amount of chlorine will be chemically equivalent to the amount of silver; thus for every 108 grammes of silver on the platinum there will be 35.5 grammes of chlorine set free in the other leg of the tube. Moreover if the current be varied by varying the number of battery cells, it will be found that the amount of decomposition in a given time is proportional to the current, that is, again, to the quantity of electricity which traverses the substance.

Faraday, who was the first to define the laws which hold in electrochemical decomposition, introduced, for the sake of precision, a system of nomenclature which has since been generally employed. Wishing to regard the terminals corresponding, in any similar case, to the carbon and platinum in the above experiment merely as the "doors" by which the electricity enters and leaves the liquid, he denominated them *electrodes*, and, comparing the "path" of the current to those of the currents which may produce terrestrial magnetism, and hence to the course of the sun, he called the homologue of the carbon (where the current, so to speak, "rose," or entered) the *anode*, that of the platinum (where the current "set," or left) the *cathode*. The component parts, no matter how complex, into which the liquid was decomposed, corresponding to the Ag and Cl of the above, received the name of "ions"—that component which went down with the current to the cathode, and there either was set free or combined with the cathode or the surrounding liquid, being the *cation*, and that which went up against the current, and appeared or promoted some chemical action at the anode, the *anion*. Moreover, the substance decomposed was called an *electrolyte*, and the process itself *electrolysis*. (Faraday, *Exp. Res.*, 662 sqq.)

The phenomena which occur at the electrodes when the ions there set free react upon the electrode or the surrounding fluid, so that the resulting products of electrolysis are not the ions themselves, are called *secondary actions*.

The anion and the cation are frequently called the negative and positive ion respectively. Similarly the cathode and anode are termed the negative and positive electrodes; Daniell denoted them the platinode and the zincode, but these terms have fallen into disuse.

Of the bodies which are capable of electrolytic conduction nearly all, if not all, are liquids. Faraday (*Exp. Res.*, 433, 1340) apparently obtained some chemical decomposition in sulphuret of silver and a few other salts when solid, but this did not alter his opinion that the mobility secured in the fluid state, either by fusion or by solution, was necessary to the phenomena of electrolysis; and his view, which he supported by experiments on ice and other solids that conduct when fused (*Exp. Res.*, 380-397, 419-428), still obtains. Electrolytic action doubtless sometimes takes place in gases, but accurate investigation of the subject is difficult on account of the extreme mobility of the particles

and the danger of confusing electrolytic effects with effects due to disruptive discharge by convection. Gases have, however, been decomposed by the silent discharge, as CO₂ into CO + O.

From Faraday's time attempts have continually been made to classify strictly, according to their chemical composition or constitution, the liquids capable of electrolytic conduction, but hitherto without very much success. It must be remembered that, as the resistance of a liquid increases, the tests of electrolytic conduction become less and less sensitive. We can consider a body an electrolyte if we can (1) collect the products of decomposition, or (2) demonstrate their presence on the electrodes by means of the return current due to polarization. If the resistance be very great the former method becomes evidently very difficult, and in the latter complications are introduced which cannot here be discussed (see ELECTRICITY). On the other hand, we might easily be misled into considering a body an electrolyte from the presence of mere traces of a foreign substance. Thus at one time water was regarded as the only electrolyte, but it is found that the purer the water is the less does it conduct electricity, and now Kohlrausch and Nippoldt have shown that the presence of one 10-millionth of H₂SO₄ would be sufficient to account for its observed conducting power, so that the weight of evidence goes to show that water itself is not an electrolyte at all.

It is not, then, surprising that views on the question of what constitutes an electrolyte have changed considerably. Davy and the older chemists, as mentioned above, considered water to be the only electrolyte; Faraday, by electrolysis fused chlorides, &c., dissipated these notions, but still regarded water as the electrolyte which was decomposed when acids were subjected to the electric current, and his general conclusion was that an electrolyte must be a compound consisting of an equal number of chemical equivalents of its elements, that is, in modern notation, must be of the type M^xR^y where x and y are the atomicities or valencies of the elements whose atomic weights are represented by M and R, and thus that two elements would be uniting form only one electrolyte (*Exp. Res.*, 679-701, 830). The oxygen salts for which Faraday assigned no law were included by Daniell in the same formula as binary compounds, of which the part R acting as anion was no longer an element but a compound; thus ZnSO₄ was shown to be split up by electrolysis into Zn and SO₄; in that case y would represent the basicity of the acid forming the salt.

This hypothesis lacks definiteness, on account of the variation of the atomicity of the elements, and falls through altogether in the case of copper and iron, which form each two chlorides, (CuCl₂, Cu₂Cl₂), (FeCl₂, Fe₂Cl₂), both electrolytes, and in consequence Wiedemann (*Galv.*, Bd. i. §§ 295, 346a, 418 (5)) modifies the statement of the hypothesis, and considers that for a body to be an electrolyte it must be capable of formation by double decomposition from one of the simple binary electrolytes, the exchanging atoms or groups of atoms forming the ions of the new compound. Thus silver acetate gives, by double decomposition with sodium chloride, silver chloride and sodium acetate. Sodium acetate and silver chloride are therefore electrolytes of which Ag, Cl, Na, C₂H₃O₂ are the respective ions. This hypothesis may be illustrated by a great number of instances:—the case of the decomposition of uranium compounds, as UOCl into UO and Cl, is a very good example. But Wiedemann's view would indicate that a body, in order to be an electrolyte, need but be one of a "series of salts," and we then see no reason for excluding the hydrogen salts from the class; thus H₂O and HCl can be easily formed by double decomposition, yet the former is, when pure, one of the worst liquid conductors, while the latter as liquefied

gas is apparently not decomposed even by 5640 cells of De la Rue's chloride of silver battery, but gives vibrations indicating very high resistance.¹ Bleekrode has also shown that, of all the pure liquefied hydrogen acids, only HCN is an electrolyte. On the other hand, liquefied NH₃, which is not formed, so far as we are aware, by double decomposition, is electrolysable by only a moderate battery of Bunsen's cells, giving a blue liquid at the cathode. Moreover, Buff (*Ann. d. Chem. und Pharm.*, Bd. cx.) has electrolysed molybdic and vanadic anhydrides after the manner MoO₃ = MoO₂ + O, but these bodies are not obtainable by double decomposition with a simple electrolyte.

Miller (*Elements Chem.*, i. § 282 (v)) considers that an electrolyte must be a combination of a conductor and a non-conductor, and so the majority of electrolytes are. But alloys behave to a certain extent as electrolytes when fused (see Wied., *Galv.*, Bd. i. § 328), and SnCl₄, though consisting of a conductor and a non-conductor, is not an electrolyte; so that this classification is not exclusive.

It would therefore appear that the condition does not lie in the chemical constitution of the body, but rather in its molecular state, and to this points the fact that two non-conductors, as H₂O and HCl, on being mixed form a very good conductor. In addition to this, quantitative measurements of the resistance of electrolytes show that, in the case of many salt and acid solutions, there is a point of concentration below saturation, for which the conductivity is a maximum. This would scarcely be the case if one alone of the bodies were the conductor.

The liquids which do not conduct are very various, including, besides oils and resins and other organic bodies, benzene, iodide of sulphur, carbon disulphide, glacial acetic acid, fused boracic anhydride, antimonie oxide and oxychloride, the higher halogen salts of tin, liquid sulphurous anhydride, pure water, and pure halogen acids. For others see article ELECTRICITY, p. 51.

In the description of the phenomena, in the typical case of electrolysis given above, it was stated that the amount of chemical decomposition in any time is proportional to the whole quantity of electricity which passes through the liquid in that time; this is true in all cases of electrolysis, and was established by Faraday (*Exp. Res.*, v. 505, and ser. vii.). It forms part of the general law to which his name is attached, but we prefer to consider it separately for reasons that will appear when we discuss the statement of that law. We may put it thus:—If W be the mass of an electrolyte, decomposed by the passage of a quantity E of electricity, then, as long as the ions remain of the same nature,

$$W = KE \dots \dots \dots (1),$$

where K is a constant dependent only on the nature of the electrolyte, and therefore independent of the nature or size of the electrodes and of any secondary actions which may take place.

It is evident that if we can prove the truth of this law for one electrolyte, with ions which do not vary with variations of electromotive force, we shall have a very convenient means of measuring the total amount of electricity which passes through any circuit in a given time by introducing such an electrolyte into the circuit, and measuring the amount of decomposition in the given time. Faraday's law for a single electrolyte

¹ Bleekrode and De la Rue, *Proc. Roy. Soc.*, xxv. p. 323. In fact, disruptive discharge occurs by convection currents, or, if the electrodes be sufficiently near, by spark. Similar phenomena may be observed by immersing the poles of a Holtz machine in paraffin oil.

² In what follows, the term electrolyte is used in its most general sense, to signify any liquid or mixture of liquids through which the current passes, and not necessarily one definite chemical compound. Hence the necessity for the condition that the ions shall not vary, as in mixed electrolytes ions for high electromotive forces are different from those for low (*vid. inf.*).

day demonstrated the truth of the law in the case of dilute sulphuric acid by experiments with vessels in which the products of decomposition of the dilute acid between platinum electrodes could be conveniently collected, either separately or together, and measured (*Exp. Res.*, 714-728.) Such an instrument he called a volta-electrometer, and subsequently a voltmeter. After demonstrating that the amount of decomposition was independent of the size of the electrodes, he connected up two voltmeters A and B, in multiple arc, as in the accompanying diagram, and then passed the whole current through a third C, and found that the amount of decomposition in C was equal to the sum of the amounts in A and B. He therefore applied the voltmeter¹ to measure quantities of electricity in other cases.

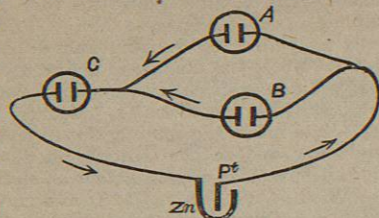


Diagram showing connection of voltmeters.

Various forms of voltmeter have been employed (see Wiedemann, *Galvanismus*, Bd. i. § 317-319). The most accurate is the silver voltmeter of Poggendorf, which consists of a vertical rod of silver with the lower end immersed in a solution of silver nitrate contained in a platinum vessel; the silver is connected with the positive, the platinum vessel with the negative pole of the battery, and the amount of decomposition is ascertained by weighing the platinum vessel with the attached silver before and after the experiment. Buff directly proved the truth of equation (1) for such an instrument by electrolyzing silver nitrate solutions of different strengths between silver electrodes. The currents employed were varied for different experiments, and were measured by a tangent galvanometer, and the quantity E of electricity was deduced by observing the time of passage of the current. (*Ann. d. Chem. u. Pharm.*, xciv. 15.)

We have, then, in order to demonstrate generally the law expressed in equation (1), to measure the amount of the ions set free in any case of electrolysis, while the amount of electricity is measured at the same time by means of a voltmeter included in the circuit. But the measurement of the amount of ions liberated is not always an easy task; in the great majority of cases secondary actions (see above, p. 106) occur, the primary results of electrolysis are obscured, and in order to determine the nature and amount of the ions special apparatus and further investigation are necessary.

Since the ions are liberated at the electrodes the products of secondary action will remain in the immediate neighbourhood if the action be not too long continued. We may therefore determine the ions by collecting any gaseous products, ascertaining the loss or gain in weight of the electrodes, and analysing the electrolyte in the immediate neighbourhood of the electrodes, taking care that the products at the two do not mix by gravitation, by diffusion, or otherwise.

For instance, if a fused chloride (e.g., $PbCl_2$) be electrolysed with platinum electrodes, no chlorine will be

¹ Many corrections have to be applied to the observations with a water voltmeter in consequence of—(1) the formation of ozone in the collected oxygen; (2) the formation of H_2O_2 ; (3) the solution of the evolved gases in the water, varying with different strengths of acid, and greater for oxygen than hydrogen; (4) the re-combination of the oxygen and hydrogen if in contact with platinum (see Wied. *Galv.*, l.c.). A diagram and description of the water voltmeter will be found in any of the numerous works on the subject.

evolved at the anode, although Pb will be deposited at the cathode; but if the liquid round the anode be analysed, for every 414 grammes of lead at the cathode will be found 339 grammes of $PtCl_4$ round the anode. Now the platinum must have been derived from the anode, which will be found to have lost 197 grammes in weight, consequently the 142 grammes of Cl were derived by the electrolysis from the $PbCl_2$, and hence $PbCl_2$ is electrolysed as $Pb + Cl_2$.

In order to separate the fluids at the two electrodes, various forms of apparatus have been employed. For fused electrolytes a W-shaped tube, which can be divided after the fluid has solidified, is sufficient; with solutions, however, where the solvent introduces new complications the separation is more difficult, owing to the "migration of the ions" and other causes which will be considered below. Daniell and Miller (*Phil. Trans.*, 1844) used a cylindrical glass vessel separated into three compartments by porous clay diaphragms, the two end compartments containing the electrodes, and having tubes for conducting away gaseous products; while Hittorf, in a classical series of experiments (*Pogg. Ann.*, lxxxix. xcvi. ciii. cvi.), used a number of bell-shaped glass vessels fitted to each other with india-rubber washers, the electrodes being inserted in the bottom and top vessels respectively. The lower end of each bell was covered with membrane to prevent mixing of the products; the whole apparatus was filled with the electrolyte to be decomposed; and the products at the two electrodes were known to be separated if the composition of the fluid in one of the intermediate bells remained the same throughout the experiment.

Great numbers of experiments have been made by different experimenters in one or other of the ways mentioned, and they have thus proved that, whatever the electrodes, and whatever the electromotive force, the secondary action at the electrodes has no effect upon the amount of chemical decomposition,² and therefore the law of equation (1) always holds.

We can give here but a few examples of secondary action. A very good account will be found in Wiedemann, Bd. i. § 326-385, with, however, the drawback of the use of an obsolete chemical notation.

(1.) *The ions themselves are set free, but separate into component parts.* That this is the case with oxygen salts, which are separated into the metal and a complex anion which is resolved into oxygen and an anhydride, was pointed out by Daniell (*Phil. Trans.*, 1839), who gave to the SO_4 derived as electro-negative ion from sulphates, the name of oxysulphion, and so on. Many similar cases occur in electrolyses of organic compounds. Thus potassium acetate is electrolysed originally as $KC_2H_3O_2 = K + C_2H_3O_2$; but the anion splits up (partly at least) thus: $2C_2H_3O_2 = C_2H_6 + 2CO_2$. All the potassium salts of the fatty acids behave similarly, so that this becomes a general method of preparing the normal paraffins.

(2.) *The ions appear in an abnormal molecular state.* The deposit of copper in Gladstone and Tribe's ZnCu couple is a black crystalline powder (see p. 114). The most important instance, however, is the formation of ozone in the oxygen liberated at the anode by the electrolysis of acid solutions, which was recognized by Schönbein in 1840, although the smell and powerful oxidizing properties of the gas evolved had previously been noticed by Franklin and Van Marum. The amount of ozone, though very small, may be recognized by all the ordinary tests (KI, indigo, &c.); it diminishes with rise of the temperature at which the electrolysis takes place, and is above 2 per cent. when the electrolyte dilute H_2SO_4 is cooled by ice and salt, and the electrodes are platinum-iridium wires (Soret). With dilute H_2SO_4 at 6° C., 100 c.c. of oxygen contained .00009 gramme ozone, and .00027 gramme at a mean temperature of -9° C.; dilute H_2CrO_4 gave at 0° C. .00052 gramme per 100 c.c. of oxygen (Soret). The amount varies with the different acids, solutions of chromic and permanganic acids giving the largest percentage.

These points are of importance in correcting observations by the water voltmeter.

² Of course, if the products of decomposition be allowed to accumulate until the electrode is surrounded with an envelope of liquid differing from the original electrolyte, the whole character of the decomposition changes.

The molecular state of the deposit varies very much with the density of the current, i.e., the current strength per unit area of electrode (Bunsen, *Pogg. Ann.*, xci. 619). With small current density the metals are deposited as well-shaped crystals; on increasing the density, reguline metal (similar to the metal when smelted) is obtained, but with great density the deposit is amorphous, botryoidal, or pulverulent. With some metals, the molecular state differs with the solutions from which they are deposited. Thus silver from dilute solution of the nitrate, with great current density, appears as a black powder, becoming grey-white and crystalline when the current ceases (Wied., *Galv.*, Bd. 1. § 336a) but from solution of potassium silver cyanide it is electrolysed as reguline metal. Gold and platinum exhibit a similar behaviour. For a good instance of amorphous deposit, see the account of Gore's explosive antimony in his *Electrometallurgy*, p. 103.

(3.) *The ions very frequently react upon the electrodes and produce in some cases very interesting chemical actions.* If the cation and cathode are both metals, an alloy of the two is the usual if not universal result. This is well known in the case of the electrolysis of many metals and salts with mercury electrodes, and the combination of the hydrogen set free by electrolysis with electrodes of palladium, nickel, and iron may be similarly regarded; and perhaps the compounds derived when ammonium salts are decomposed with a mercury cathode. Copper, when deposited on platinum, alloys with it to a certain extent, the alloy penetrating to a considerable depth (Gore, *Electro-metallurgy*, p. 47). Faraday noticed the combination of tin and lead with platinum electrodes in the electrolysis of the fused salts of those metals.

The action of the anion upon the anode furnished Faraday with an accurate and convenient means of estimating the amount of chemical decomposition produced by a definite quantity of electricity, and thereby of confirming the law given by equation (1) (*Exp. Res.*, 807-822). Thus by varying the anodes, while the cathode remained the same, in the decomposition of acidulated water he found the amount of hydrogen liberated at the cathode, and therefore the chemical decomposition, independent of the nature of the electrodes; and by electrolyzing various chlorides, as of silver, tin, lead, with an anode of the same metals respectively, he was enabled to determine very accurately the amount of chlorine separated. We shall have more to say on the bearing of this hereafter. The oxygen liberated by the electrolysis of acidulated water frequently unites with the anode; even if this is of carbon it becomes oxidized to CO and CO_2 ; this was noticed by Faraday (*Exp. Res.*, 744), and is interesting as showing the active state of the oxygen when separated.

Electro-capillary phenomena.

But perhaps the most interesting examples of the action of the ions on the electrodes are furnished by the capillary phenomena exhibited by mercury in contact with dilute acid, on the passage of the current. If we have a drop of water upon a surface of Hg, and the water be connected with the positive, while the Hg is connected with the negative pole of a battery, the water will gather itself up into a spherical drop, and on reversing the current will spread itself over the metal. This phenomenon is supposed by Wiedemann to be due, in the former case, to the reduction of a film of oxide on the surface of the Hg by the liberated H, thereby giving a cleaner surface with a higher capillary constant, and, in the latter, to the oxidation of the surface by the liberated oxygen, and this view is borne out by numerous experiments. Thus a reducing agent, such as crystal of sodium thio-sulphate ($Na_2S_2O_3$), introduced into the drop of water produces similar contraction of the drop, while an oxidizing agent, as $K_2Cr_2O_7$, produces on the contrary a similar dispersion. A drop of Hg in dilute sulphuric acid, connected with the positive pole of a battery, while the negative electrode is near it, extends toward that electrode on the passage of the current, becoming covered with a film of suboxide, which then dissolves in the H_2SO_4 , and leaves again a bright surface, when the drop returns to its original position, and a series of oscillations are thus set up (see Wied. *Galv.*, i. 368 *seq.*). With solutions of alkaline cyanides containing mercury Gore obtained oscillations producing sounds (*Elec.-Metall.*, p. 197; *Proc. Roy. Soc.*, 1862). It was observed by Erman that a drop of mercury in a horizontal tube, with dilute acid on both sides, moved at the passage of the electric current through the tube towards the negative electrode. These phenomena have been investigated further by Lippmann (*Pogg. Ann.*, cxlix. 547, trans. in *Phil. Mag.* [4] xvii. 281). One of the forms of his apparatus is as follows. A glass tube A, drawn out to a short capillary point of about $\frac{1}{17}$ mm. radius, contains mercury which penetrates into the fine point and partly fills it, the remainder being filled with dilute H_2SO_4 , into which the capillary opening dips; below the electrolyte is a surface of mercury, serving as the positive electrode, sufficiently broad for the capillary effects there to be neglected. The negative electrode is the mercury in the tube A. Lippmann showed by this apparatus that, in order to compensate the change in the capillary constant of the mercury produced by a definite electromotive force of polarization, a definite increase of pressure on the mercury in A is required. As for an electromotive force of polarization equivalent to a Daniell cell the

compensating pressure was 260 mm., and as the quantity of electricity required to polarize the electrodes is very small, this apparatus, when once it has been graduated by observing the compensating pressure for known electromotive forces, may evidently be employed as a sensitive and convenient electrometer for electromotive forces less than the maximum of polarization of the electrodes.

We may mention one other example of the action of the ions upon the electrodes. An iron wire is usually attacked by dilute HNO_3 (sp. gr. 1.3); but if previously to its being immersed in that liquid it is employed as the anode in the electrolysis of diluted oxygen acids, the nitric acid has no longer any effect upon it, not even tarnishing the surface, and the wire differs from ordinary iron in being strongly electro-negative to it, and indeed to copper, in dilute acids (Martens, *Pogg. Ann.*, lxi. 121). It is then said to be in the passive state, and is considered to be covered with a film of oxide which is strongly electro-negative, and insoluble in dilute nitric acid (Faraday, *Phil. Mag.*, ix. p. 60, 1836, x. p. 175, 1837; Beetz, *Pogg. Ann.*, lxii. 234, lxiii. 415). De Regnon, however (*Comptes Rendus*, lxxix. 299), attributes the phenomena to polarization. This peculiar state may be induced by various processes; Keir (*Phil. Trans.*, 1790) observed it when an iron wire was dipped into strong nitric acid (sp. gr. 1.5), by which its surface is not attacked. A more dilute solution has the same effect (Schönbein, *Pogg. Ann.*, xxxviii. 444), if the wire be immersed several times, or if the solution contain chromic or sulphuric and permanganic acids (Boutmy and Chateau, *Cosmos*, xix. 117). Iron when dipped in very strong solution of $AgNO_3$ does not precipitate the silver, and is electro-negative even to that metal. Another method of rendering iron passive, evidently the same in principle as the one first mentioned, is to touch the iron wire immersed in dilute nitric acid, by carbon, platinum, or other electro-negative element itself in contact with the liquid; and on the contrary, passive iron becomes active if it be touched by a body electro-positive to it, as copper or zinc. If a passive wire be partly immersed in the dilute acid, and an active wire in contact with it be slowly introduced into the liquid, the latter becomes passive too; but if they touch under the liquid, both are rendered active. Iron is rendered passive also by heating in a current of oxygen or an oxidizing flame until it is tarnished. On the other hand, the passive metal becomes active under the influence of any reducing action upon its surface, whether by deposition of H upon it by electrolysis, by heating the metal in a reducing flame, or by abrading the surface. One modification of the electrolytic method is to touch the metal in dilute nitric acid, for a moment, with a copper wire. The point touched becomes immediately active, and therefore electro-positive to the rest, and so currents are set up from active to passive metal through the acid, which accordingly reverse the state of both parts, and a curious series of oscillations result, ending in the whole becoming active. (Schönbein, l.c. Compare these with the phenomena of alternation of passive and active states of iron, and of the oxidized and bright surfaces of amalgamated zinc described by Joule, *Phil. Mag.*, 1844, i. 106.)

Iron is not the only metal which behaves thus. Nickel, cobalt, tin, bismuth, and even copper, all exhibit similar phenomena in strong HNO_3 , and as positive electrodes; and aluminium thus treated is electro-negative even to passive iron (see Wiedemann, *Galv.*, Bd. i. § 539-542).

(4.) *The ions act upon the fluid surrounding the electrodes.* Secondary actions of this kind in both fused and dissolved electrolytes nearly always occur unless the ions combine with the electrodes; thus perchlorides, if such exist, are formed from the chlorides, and perchlorates from chlorates at the anode (Kolbe). At the cathode the secondary actions are cases of reduction; thus if solution of potassium iodide be electrolysed, corresponding to 1 equivalent of iodine at the anode, there will appear not only 1 equivalent of H, at the cathode, but an equivalent of KHO as well, so that the potassium liberated from the iodine must have acted upon the water and formed KHO. If ammonium chloride be electrolysed, the chlorine at the anode reacts upon the NH_4Cl , giving free nitrogen and nitrogen-chloride. The electrolysis of ammonium nitrate is still more interesting, as NH_3 and H are separated at the cathode, where the hydrogen reduces the nitric acid of the nitrate, and nitrogen is evolved, while at the anode NO_2 is deposited, which forms with the water nitric acid and oxygen, the latter reacting upon the ammonia of the nitrate, again evolving nitrogen, so that that element appears at both poles,—at one mixed with ammonia, at the other with oxygen (Miller). Some of the reactions investigated by Kolbe and Burgoin with organic salts are very interesting, but more exclusively to the chemist. The oxidizing and reducing actions are very powerful, as the bodies probably act in the "nascent state."

Solutions of acetate and nitrate of lead, when electrolysed by currents of small density, deposit at the positive electrode hydrated peroxide of lead as a black powder. If a polished iron plate be used as the anode, the deposit shows prismatic colours depending on the thickness, and the process has been applied in the arts to colour metallic toys, under the name of metallochromy. If a fine wire as cathode be placed vertically above the anode plate,

the colours are arranged in circles long known as Nobili's rings. Similar phenomena are exhibited by salts of bismuth, nickel, cobalt, and manganese, all of which are precipitated as peroxides, usually hydrated (Wernicke, *Pogg. Ann.*, cxli. 109), upon the anode by the action of the oxygen liberated by the passage of electricity. Silver is also thrown down as a black peroxide, together with some oxygen from a solution of sulphate and nitrate, and iron behaves somewhat similarly in an ammoniacal solution of the protoxide in vacuo.

Such secondary actions vary very conspicuously with the density of the current and the temperature. Bunsen (*Pogg. Ann.*, xci.) electrolysed solution of chromic chloride, and by increasing the current density obtained in succession H, Cr₂O₃, CrO₃, and metallic Cr at the cathode; the reason for this is evidently that with high current densities the supply of ions in any time is greater than can take part in secondary action, and hence some of the original ion is deposited. A rise of temperature favours chemical action, and promotes rapid mixture of the ions with the solution at the same time; so the higher the temperature the greater is the current density required to isolate the ions. From concentrated sulphuric acid, for instance, below 80° only H and O are obtained; between 80° and 90° oxygen is given off at the anode, while at the cathode H and S, due to reduction of H₂SO₄ by hydrogen, appear; above 90° sulphur alone is deposited at the cathode (Warburg, *Pogg. Ann.*, cxxxv. 114).

Mixed electro-lytes.

Instructive and important cases of secondary action occur when the electric current is made to traverse a mixture of several solutions. Magnus (*Pogg. Ann.*, cii. 23) determined by experiments on dilute CuSO₄ solution, in an apparatus with a porous diaphragm of clay, colloid paper, or animal membrane, specially arranged that the lines of flow should be parallel, and the current density therefore uniform, that there was a limiting value of the density above which both copper and hydrogen appeared at the cathode, but below only copper. His results show that this density is independent of length of the electrolyte and material of the electrodes, but varies directly as the size of the electrodes. The specific resistance of the constituents, as well as the relative position of the two ions in the "electro-chemical series" (*vid. inf.*), are of great importance, the electro-negative metal always appearing first.

In order to determine whether the current traversed both electrolytes or only one, Hittorf (*Pogg. Ann.*, ciii. 48), with the apparatus above described (p. 108), electrolysed mixed solutions of potassium chloride and iodide in different proportions, and arrived at the important conclusion that for all densities the current traversed both electrolytes, as it were in multiple arc (though the resistance of the mixture apparently bears no definite relation to the resistances of its constituents except for some of the haloid salts); but the products liberated depend on the secondary action at the electrode, and hence on the current density. The formation of an envelope of liquid of altered composition would also introduce complications (Smee, *Phil. Mag.*, xxv. 437). Buff, by experimenting on solution of HCl, with a small amount of H₂SO₄, substantially confirms Hittorf's results (*Ann. d. Chem. u. Pharm.*, cv. 156).

These considerations are, of course, especially useful in effecting the deposition of alloys by electrolysis. The possibility of so doing appears to depend upon the composition of the solution employed. An acid solution of Cu and Zn deposits only copper, but the addition of potassium cyanide determines the deposition of brass. Gore (*Electro-metallurgy*, p. 51) points out that, in order to deposit an alloy of two metals, there must be no electric separation when the two metals are in contact with the liquid; if indeed such were the case, a deposit of the two metals, say of Cu and Zn, would immediately act as a CuZn couple (see p. 114), and the electro-negative metal alone would be deposited at the expense of the electro-positive.

Although the amount of a salt decomposed by the passage of a given quantity of electricity is the same whether the salt be fused or dissolved in alcohol, water, or other solvent, yet the presence of the solvent produces an important effect upon the electrolyte, which should not be lost sight of in quantitative experiments. The phenomenon is known as the "migration of the ions" (Hittorf), or the "unequal transfer of the ions" (Miller). Suppose, for example, we electrolyse a solution of CuSO₄ containing 16 grammes of salt per cubic centimetre, in a vessel separated by a porous diaphragm into two portions A and B. Let electricity be passed through the solution between platinum electrodes from B to A, until 1.59 grammes of CuSO₄ have been decomposed. Then—

- (1) 1.59 g. of CuSO₄ has been removed from the solution;
- (2) .63 g. of Cu has been deposited on the platinum cathode;
- (3) .16 g. of O has been evolved at the anode, and .80 g. of SO₂ absorbed there by the water of the solution.

Now, had the electrolyte been a single fused compound, no complication could have arisen; the liquid remaining must still have been homogeneous (except for the presence of the ions near one or other electrode). But when the salt is dissolved, it is important to

consider from what part of the solution the salt has been removed. Suppose that of the CuSO₄ decomposed $\frac{1}{n}$ th was taken from the vessel B, and therefore $\frac{n-1}{n}$ ths from A. The result of electrolysis may then be exhibited thus (assuming that no diffusion takes place through the diaphragm):—

	In A.	In B.
Before Electrolysis	x g. CuSO ₄ .	y g. CuSO ₄ .
After "	$(x - \frac{n-1}{n} \cdot 1.59)$ g. CuSO ₄ + .63 g. Cu, including Cu deposited.	$(y - \frac{1}{n} \cdot 1.59)$ g. CuSO ₄ + .96 g. SO ₂ , including oxygen collected.

If the volumes of the two vessels are equal, x and y are of course equal, since the fluid is originally homogeneous.

Hence A will gain $\frac{1}{n}$ ·63 g. Cu, and lose $\frac{n-1}{n}$ ·96 g. SO₂.

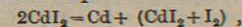
B will lose $\frac{1}{n}$ ·63 g. Cu, and gain $\frac{n-1}{n}$ ·96 g. SO₂.

We may therefore state the result thus:—For every equivalent of copper deposited upon the cathode the entire gain of copper in the vessel A is $\frac{1}{n}$ th equivalent, and the entire gain of SO₂ in B is $\frac{n-1}{n}$ equiv. The experiment shows that the entire gain of copper in A is .276 × .63 g., and the gain of SO₂ in B is .724 × .96 g.; and hence, for solutions of CuSO₄ of that strength, $\frac{1}{n} = .276$, and consequently $\frac{n-1}{n} = .724$, so that, of the CuSO₄ decomposed, 72.4 per cent. is taken from A, and 27.6 per cent. from B, and the solution round the cathode is weakened much faster than that round the anode. This will be observable by the depth of the blue colour of the solution. If the anode be of copper and be vertically above the cathode, the effect is well seen; for although the total amount of CuSO₄ in solution remains constant, the difference of colour at the two electrodes is very apparent, and, if the action be continued, strong dark-blue solution drops down in thin streams from the anode through the more dilute (Magnus).

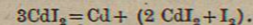
The value of n differs for different salts, and usually for solutions of the same salt of different strengths, though in some cases, as K₂SO₄, KNO₃, NaCl, and KCl, the variations for great difference of concentration are very slight. The following table shows a few of the results obtained by Hittorf, with the apparatus described above, by which errors due to diffusion were avoided. The numbers in the third column indicate what is called above $\frac{n-1}{n}$, i.e., the total excess in equivalents of the anion in the vessel containing the anodes corresponding to a decomposition of one equivalent of salt; or, except in the last few cases, that part of the salt decomposed which is taken from the vessel containing the cathode.

Salt.	No. of cc. of solvent containing one gramme of salt.	$\frac{n-1}{n}$
HCl	2.9	.319
HCl	36.2	.168
HCl	140.9	.171
HCl	2125.9	.210
HBr	8.6	.178
HIO ₃	13.3	.102
K ₂ SO ₄	11.8	.500
K ₂ SO ₄	412.8	.499
NaCl	20.7	.684
Fe ₂ Cl ₆	25.25	.600
CdI ₂	4.2	1.14
CdI ₂	116.7	.613
CdI ₂ in alcohol	1.1	2.103
CdI ₂ in alcohol	37.2	1.313
ZnI ₂ in alcohol	0.5	2.16

The iodides of zinc and cadmium are anomalous, but it may be supposed that they are decomposed as double salts thus:—



or



The total increase in the amount of an ion in one part of a vessel divided by a porous partition is also affected by a mechanical vector transference of the electrolyte through the pores of the diaphragm, or endosmose generally in the positive direction of the current, which is very noticeable in cases of electrolytes of high resistance. This was discovered by Reuss in 1807, and observed by Porret soon after-

wards; it has been investigated by Wiedemann (*Pogg. Ann.*, lxxxvii. 321), and Quincke (*Pogg. Ann.*, cxiii. 513). The former worked with a porous cell, and estimated the effect either by the quantity of the electrolyte which passed through the wall of the cell, the pressure remaining constant, or by the rise of pressure in the porous cell measured by a mercury manometer. A current of moderate intensity through distilled water caused 17.77 g. of the electrolyte to pass through the diaphragm towards the cathode in a quarter of an hour, and with a 19 per cent. solution of CuSO₄, a pressure of 176.5 mm. was observed in the cell containing the cathode, due to the current of a battery of Daniell's cells. Quincke, however, employed, instead of a porous cell, a capillary tube without diaphragm, open at one end, and connected with a reservoir at the other containing one electrode, while the other electrode consisted of one of several pieces of platinum wire, sealed into the tube in various positions. His current was obtained from either a Leyden battery or 40 to 80 Grove's cells. The two ways of experimenting gave concordant results, and showed that the pressure on the cathode vessel varies as the electromotive force between the electrodes, and so diminishes with the resistance if the current be kept constant. It is also, in Quincke's apparatus, inversely proportional to the square of the diameter of the tube, and, for tubes of the same sectional area, is greatly increased by increasing the perimeter. The direction of motion is, as stated above, usually towards the cathode, and is immediately reversed on a reversal of the current, and stops when the circuit is broken. The rate of transfer is increased by coating the tube with shellac; it is different for different fluids, and with certain specimens of absolute alcohol, and with turpentine oil, the direction is reversed, unless in the latter case the tube is coated with sulphur, when the direction is as before.

Motion of foreign particles.

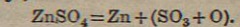
Intimately connected with these phenomena is the motion of solid particles contained in fluids of high resistance. Faraday observed the motion of silk threads in water, and Jürgensen made many experiments on the subject with a capillary tube in the form of three sides of a rectangle with bulbs at the two corners which contained the electrodes; in one was a porous diaphragm as well. Quincke (*l.c.*) used a similar apparatus to this, as well as the one described above, and observed by means of a microscope a double motion of particles of starch contained in water subject to the action of an electric machine. Near the sides of the tube the particles moved towards the negative electrode, but in the middle in the opposite direction; on turning the machine more quickly the particles near the sides gradually lost their velocity, and then began to move towards the positive electrode in common with those in the middle. So that it is highly probable that near the sides the particles are, in the first instance carried along by the motion of the fluid there, but on increasing the current the friction of the liquid in contact with the tube prevents its velocity increasing so fast as that of the particles in the opposite direction, and ultimately the motion of the particles in that direction becomes apparent. Similar phenomena are observed with many finely divided bodies suspended in water, as gold, copper, graphite, silica, feldspar, sulphur, lycopodium, &c., as well as minute drops of liquid, as CS₂, and oil of turpentine, and bubbles of oxygen, marsh gas, &c. All these are urged in water towards the positive electrode, but in oil of turpentine the direction is reversed except in the case of particles of sulphur; the direction is also reversed for silica in carbon disulphide.

Faraday's law for different electro-lytes.

Considering now our first equation $W = KE$ established, K being, as stated, dependent only on the nature of the electrolyte, we proceed to examine the constant K and its value for different electrolytes. The primary investigation is due to Faraday, who found that if A and B be two electrolytes, and if a quantity E of electricity decomposes a mass X of A and Y of B , then X and Y are chemically equivalent, that is, are the amounts of A and B which would take part in a double decomposition between them. According to this view we have for any electrolyte $W = \mu \epsilon E$, where μ is the amount of the electrolyte chemically equivalent to 1 gramme of water, and ϵ is the number of grammes of water decomposed by a unit of electricity, and is called the electrochemical equivalent of water. This appears to be always true, but the law as usually stated refers to the amounts of the ions separated. The most general statement which the facts allow is the following, known as Faraday's law:—*In any electrolytic decomposition whatever, the mass w of one at least (usually of each) of the ions, simple or complex, separated by the passage of a quantity of electricity E , is chemically equivalent to the amount of hydrogen separated by the same quantity of electricity in a water voltameter, and hence $w = m h E$, where m is the chemi-*

cal equivalent of the ion, and h the electrochemical equivalent of hydrogen.

Since water contains $\frac{1}{8}$ th its weight of hydrogen $h = \frac{1}{8} \epsilon$. Faraday admitted as electrolytes only bodies containing an equal number of equivalents of their components, and accordingly found that the amount of either ion was equivalent to the hydrogen evolved in a voltameter included in the circuit. The seventh series of *Experimental Researches* was devoted to proving this most important law. Two methods were adopted—(1) by collecting and measuring the products of decomposition, a voltameter being included in the circuit, and (2) by introducing an anode with which the anion could combine (as for instance a Pb anode in fused PbCl₂, a silver one in fused AgCl), and determining the loss in weight of the anode. By these means the law was proved for simple fused electrolytes, such as the chlorides, &c. Daniell extended it to oxygen salt solutions, and showed that they were decomposed into a metal and a complex ion, this last splitting up into oxygen and an anhydride which united with water to form the corresponding acid, e.g.,



Matteucci and E. Becquerel added a large amount of evidence in defence of the law, which was demonstrated with great accuracy (to $\frac{1}{2}$ per cent.) by Soret (*Ann. de Chim. et de Phys.*, [3] xlii. 257) for a series of copper salts; and by Buff for great variations of current strength with silver compounds.

So long as we confine ourselves to normal salts there is little difficulty about the statement of the relation; even with such compounds as the series of phosphates, the double cyanides, &c., which are decomposed as in the following table, the amount of either ion may be considered equivalent to the H of the voltameter.

Electrolyte.	Anion corresponding to H in voltameter.	Cation.	Observer
Na ₂ PO ₄	$\frac{P_2O_5}{3} + \frac{O}{2}$	Na.	Hittorf
NaPO ₃	$\frac{P_2O_5}{2} + \frac{O}{2}$	Na.	Daniell and Miller, <i>Phil. Trans.</i> , 1844, p. 1
Na ₄ P ₂ O ₇	$\frac{P_2O_5}{4} + \frac{O}{2}$	Na.	
Na ₂ HPO ₄	$(\frac{P_2O_5}{4} + \frac{H_2O}{4}) + \frac{O}{2}$	Na.	
NaHNH ₂ PO ₄	$(\frac{P_2O_5}{4} + \frac{H_2O}{4}) + \frac{O}{2}$	Na.	
K ₄ FeCy ₆	$\frac{FeCy_2}{2} + Cy$	K.	Hittorf
KAgCy ₂	$\frac{AgCy + Cy}{2} + \frac{O}{2}$	K.	
K ₂ Al ₂ (SO ₄)	$(\frac{Al_2SO_4}{2} + \frac{SO_3}{2} + \frac{O}{2})$	K.	

Faraday's law is nearly always true for both ions, but there are, as before stated, examples of elements forming two series of electrolysable salts, especially when dissolved in water. In these cases the electro-negative ion is usually equivalent to the H of the voltameter, or we may consider that the chemical equivalent of the positive ion varies, while that of the negative ion remains unchanged in the different combinations; so that ferric chloride may be regarded as a dichloride with formula FeCl₂, where $fe = \frac{2}{3} Fe$; cuprous chloride CuCl, where $cu = 2Cu$, and so on. Considerable confusion, too, arose from the arbitrary numbers for chemical equivalents which formerly obtained, and which caused such compounds as Al₂Cl₆, SbCl₃, AuCl₃, to appear anomalous, and warranted E. Becquerel (*Ann. de Chim. et de Phys.*, [3] t. xi. p. 178) in considering that generally the amount of electro-negative ion alone was equivalent to the H of the voltameter.³ This was borne out by his electrolysis of 2N₂O₄, 7PbO, 3H₂O, and N₂O₄, 2PbO, H₂O, which gave $\frac{1}{2}$ and $\frac{1}{2}$ an equivalent of Pb at the cathode respectively; but the law as thus modified fails in the case of K₂Cr₂O₇, which gives $K + (CrO_3 + \frac{1}{2}O)$ both in the melted and dissolved state, and in that of Na₂S₂, which gives $Na + (S_2 + \frac{1}{2}S)$, and also for basic acetate of lead.

¹ This oxygen is set free.
² The well-known deposit of silver in electro-plating is due to secondary action of the K.
³ The chemical equivalents of Al, Sb, Au were taken to be 13.5, 61.98 respectively, instead of 9.1, 40.6, 65.5 as now