

Faraday's law receives striking confirmation from the electrolysis of several solutions arranged in series in contact with each other by means either of porous septa, asbestos wicks, or siphon tubes. Each liquid then acts as an electrode to the adjacent ones, and so at the junction we have separated the anion of one electrolyte and the cation of the next. These in general unite, and if the resulting compound be insoluble, a precipitate is thrown down. Faraday thus precipitated magnesia from its sulphate by electrolysis of a solution of that salt in contact with water, the current passing from the salt solution to the water. Now, in all cases in which the ions unite at the junction, and do not appear free at all, the amount of the cation of one liquid must be chemically equivalent to that of the anion of the succeeding one, and hence obey Faraday's law. Many of the decompositions and combinations thus effected are very interesting, a list showing in a tabulated form the results of experiments by Hisinger and Berzelius, Davy, Daniell, Miller, and others will be found in Wiedemann (*Galv.*, Bd. i. § 368). We can only mention one example which is of theoretical importance. If the positive electrode be in solution of iodic acid which is in contact with dilute sulphuric acid containing the cathode, then at the surface of separation there will be formed I and SO₂, or H and SO₄, according as the I observed at the negative electrode in the electrolysis of HIO₃ solution is an ion or due to secondary action. By the union of the two ions at the junction the latter is shown to be the case; therefore iodic acid is electrolysed as H₂ + (I₂O₅ + O).

We gather at once from the truth of Faraday's law that we can assign to each ion an electrochemical equivalent (which may be referred to as E.C.E.), which will enable us to determine at once the amount of the ion which will be separated by a given quantity of electricity. With the notation already used the E.C.E. of an ion = $\frac{m}{z}$. The value of ϵ —the amount of water decomposed by one C.G.S. electromagnetic unit of electricity—from experiments of Weber, Joule, Bunsen, Casselmann, and Kohlrausch is .00093 gramme (*Wied. Galv.*, Bd. iii. § 1077-1079). The quantity m is one of the chemical equivalents of the ion, usually that deduced from its most stable salts; some metals, indeed, with two series of salts have two E.C.E.s. The following table of the elements gives the values of m and the E.C.E.s in absolute units, as far as they have been experimentally determined. Since m bears a simple ratio to the atomic weight, its value can be corrected by the results of chemical analysis.

Table of Electrochemical Equivalents.

Element.	Atomic Weight.	Electrochemical Equivalent in Hydrogen units (m).	E.C.E. in grammes per C.G.S. unit of Elec. = $\frac{m}{z}$.	Element.	Atomic Weight.	E.C.E. in Hydrogen units (m).	E.C.E. in absolute units = $\frac{m}{z}$.
Al	27.5	9.1(2)	.00094	Mo	96	(3)	...
Sb	122	40.6(2)	.00420	Ni	59	29.5(1)	.00305
As	75	25(2)	.00258	Nb	97.5	(3)	...
Ba	137	65.5	.00708	N	14	(3)	...
Bi	210	71(2)	.00733	Os	199	(3)	...
B	10.9	(2)	...	O	16	8(1)	.00083
Br	80	80(1)	.00826	Pd	106	(3)	...
Cd	112	56(1)	.00578	P	31	(3)	...
Cs	133	133(4)	.01374	Fe	56	28(1)	.00283
Ca	40	20	.00206	K	39.1	39.1(1)	.00404
C	12	(2)	...	Rb	85	(3)	.00878
Ce	92	(2)	...	Ru	101.2	(3)	...
Cl	35.5	35.5(1)	.00368	S	32	(2)	...
Cr	52.5	17.5	.00181	Se	79.5	(3)	...
Co	59	29.5(1)	.00305	Si	28	(2)	...
Cu	63	31.6(1)	.00326	Ag	108	108(1)	.01116
D	96	(2)	...	Na	23	23(1)	.00237
E	19	19(1)	.00196	Sr	87.5	43.7	.00452
F	9.3	(2)	...	Ta	182	(3)	...
Au	196.6	65.5(2)	.00677	Te	129	64.5(2)	.00668
H	1	1	.000103	Tl	204	204(2)	.02108
In	113.4	(2)	...	Th	119	(2)	...
I	127	127(1)	.01312	Sn	118	59.5(2)	.00610
Fe	56	28(1)	.00289	Ti	50	(2)	...
La	92	(2)	...	W	184	(2)	...
Pb	207	103.5(1)	.01069	U	120	(2)	...
Li	7	7	.00072	V	51	(2)	...
Mg	24.3	12(1)	.00124	Zn	65	32.5(1)	.00336
Mn	55	27.5(1)	.00284	Zr	89.5	(2)	...
Hg	200	100(1)	.01033				

Every complex ion has also a definite electrochemical equivalent, usually coinciding with its chemical equivalent. The E.C.E. of an electrolyte is the sum of the E.C.E.s of its component ions.

1 Faraday, *Exp. Res.*, ser. vii.
2 Renault (*l.c. infra*)
3 Either these elements have not been obtained as ions by electrolytic action, or quantitative experiments are wanting.
4 Hensen.

Renault² determined the E.C.E.s by an inverse method. He observed the amount of the metal which, forming the negative pole of a battery with various electrolytes, gave a current equivalent to that produced by the dissolution of a definite amount of zinc in a ZnPt cell, the two currents passing through a differential galvanometer, and thus compared the amounts of elements which generate the same quantity of electricity in combining. It is perhaps necessary to observe that the electrolytic reactions taking place in a galvanic cell which generates a current are in every way identical with those due to a current from an external source sent through the electrolyte. In the former case, the energy of chemical affinity at the electrodes is transformed into the energy of electrical separation, and in the latter the converse is the case.

The Electrochemical Series.

It is evident from all the examples we have given that it is not an accident whether an ion will appear at the anode or cathode; the cations have been all more or less similar in character, and were either metals or more allied to the metals than the corresponding anions, which were bodies like Cl, Br, I, CN, O, &c. Faraday (*Exp. Res.*, 847) was accordingly led to consider that an element or radical was unalterably either an anion or a cation; this, however, was contradicted by the fact that the same element may act as an anion in one solution and a cation in another, as is the case with iodine, which in KI is an anion, but from a solution of iodine bromide (IBr) appears at the cathode. The electrolysis of alloys³ points in the same direction, so that the conclusion is suggested to us that "anion" and "cation" have only relative meanings, and that we might arrange the elements in a series such that, in a compound of an element A with any one of those above it, A would appear as a cation, but in a compound with any of those below, as an anion. To do this by purely electrolytic means is out of the question, as binary electrolytes do not exist for each pair of elements. As far, however, as the series can be thus made out, it is found that, as a rule, if two elements A and B, such that A is above B in the series, be immersed in a simple electrolyte, as dilute H₂SO₄, and connected by means of a wire, the current flows from B to A through the liquid. Hence in unknown cases we may observe the direction of the current when the two elements are immersed in an electrolyte, say H₂SO₄, and determine the relative position in the series.⁴ With the series thus roughly formed, it is observed that the wider two elements are apart the greater is the chemical affinity between the two, and thus that if we have a compound MR, where M is the electro-positive element, a more electro-positive element M' having a greater affinity for R than M tends to replace M from the compound, and a more electro-negative element R' tends to replace R as iron replaces copper from CuSO₄, and chlorine iodine from KI. This further assists us in forming an electrochemical series of the elements, but it is still not very strictly arranged, and many of the members of the series are placed by their analogy to elements whose positions are known. Moreover, it is supposed that the relative position of two elements may vary with the temperature. Thus carbon which is used in batteries as the negative element, is at a full red heat electro-positive even to potassium, or at least reduces the carbonate of that element. Jablochkoff (*Comptes Rendus*, Dec. 3, 1877) describes a cell of which the positive element is coke. The electrolyte is fused sodium or potassium nitrate, and the negative element is a cast-iron vessel containing the fused salt. The current is from coke to cast-iron through the nitrate, and the electromotive force 2 to 3 volts.

Berzelius's final series stands thus:—
Electro-negative.

Oxygen.	Boron.	Mercury.	Thorium.
Sulphur.	Carbon.	Silver.	Zirconium.
Selenium.	Antimony.	Copper.	Aluminium.
Nitrogen.	Tellurium.	Bismuth.	Didymium.
Fluorine.	Tantalum.	Tin.	Yttrium.
Chlorine.	Titanium.	Lead.	Lanthanum.
Bromine.	Silicon.	Cadmium.	Glucinum.
Iodine.	Hydrogen.	Cobalt.	Magnesium.
Phosphorus.	Gold.	Nickel.	Calcium.
Arsenic.	Osmium.	Iron.	Strontium.
Chromium.	Indium.	Zinc.	Barium.
Vanadium.	Platinum.	Manganese.	Lithium.
Molybdenum.	Rhodium.	Uranium.	Sodium.
Tungsten.	Palladium.	Cerium.	Potassium.

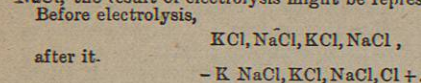
Electro-positive.

1 "Vérification expérimentale de la réciproque de la loi de Faraday, sur la décomposition des électrolytes." Paris, 1867; *Ann. de Chim.* [4] xi. 137.
2 Alloys of tin and lead, potassium and sodium, sodium amalgam, gold amalgam, and fused cast-iron have all been shown to suffer chemical decomposition on the passage of the electric current (*Wied. Galv.*, i. § 328).
3 This is not always conclusive evidence, as the direction of the current for the same two elements sometimes varies with the electrolyte employed, as will be seen by referring to the list of chemico-electric series in Gore, *Electro-metalurgy*, p. 66. The boracic acid series is peculiarly anomalous.

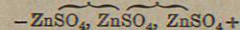
Radicles as NH₄ and SO₄ behave as elements, and have each a definite position in the series.

Theory of Electrolysis.

Any hypothesis which seeks to account for the phenomena of electrolysis has mainly to deal with the two points—(1) that the ions appear only at the electrodes, and (2) that the electricity at the same time is conducted between the electrodes. From the behaviour of electrolytes in contact on the passage of the current we conclude that if we had a series of cells consisting alternately of KCl and NaCl, the result of electrolysis might be represented thus:—



Now, we may suppose similar effects to occur if the cells were all identical, and farther we may consider the collection of molecules in any electrolyte as such a series of cells in contact, and argue the electrolytic process to be a series of decompositions and recombinations along a line of molecules resulting finally in the decomposition of molecules at the electrodes alone. The decomposition of any oxygen salt would be similar with the exception that the one ion is complex. Thus

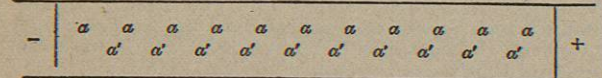


might represent the decomposition of zinc sulphate. This idea of alternate decompositions and recombinations was originally suggested by Grotthuss in 1805, who, however, attributed the separation to attractions, due to the electrodes, varying inversely as the square of the distance. Faraday (*Exp. Res.*, 481-563, series iv.) discusses the theory, and, while denying the attractions of the electrodes defends the idea of decomposition and reformation, chiefly against De la Rive and Riffault and Chompré, and considers that the effect of the passage of the current is due to a change of the chemical affinities of the components of the electrolyte, and he points out (1843 *sgg.*, ser. viii.) that the decomposition is probably preceded by a polarized state of the particles, as explained by him in his theory of electrostatic induction. This is confirmed by experiments of Tribe (*Proc. Roy. Soc.*, 1875-6), who inserted 198 small strips of silver in rows, parallel to the line joining the electrodes in dilute CuSO₄, and observed that copper was deposited on the ends facing the anode, while gas was given off from the other ends; by comparing the amounts of the deposit he explored the electric field, showing that it was roughly similar to the magnetic field due to a north and a south pole.

Hittorf's Many investigators have suggested additions to Grotthuss's Theory. hypothesis (see Wiedemann, i. 421, a.), and in particular Hittorf (*Pogg. Ann.*, lxxxix.) has expanded it to explain the migration of the ions in salt solutions investigated by him. He supposes that the molecules are equal distances apart, and that the ions when separated travel with different velocities to the points of recombination, and consequently those points are not the middle points between pairs of adjacent molecules. He thus considers that

the cation travels $\frac{1}{n}$ th of the distance between molecules while the anion travels $(1 - \frac{1}{n})$ th of the distance.

If then we suppose the ions separated at the electrodes to be removed, we may imagine the positions of the particles in the medium of solution before and after electrolysis to be represented by a a' respectively, thus (where n = 4):—



the effect will be the same as if (1) the particle nearest the negative electrode were removed, and all the other particles in the line moved towards that electrode $\frac{1}{n}$ th of the distance between the particles, or as if (2) the particle at the positive electrode were removed, and all the rest shifted $(1 - \frac{1}{n})$ th part of the distance between the particles towards it. If we suppose the solvent separated by a porous wall into two portions, we shall have after electrolysis in the portion containing the cathode (on the first supposition) corresponding to deposition of one equivalent of hydrogen in the voltameter—

- (1) a gain of one equivalent of cation deposited;
- (2) a loss of one equivalent of salt since the decomposed molecules are supposed taken from there;
- (3) a gain of $\frac{1}{n}$ equivalent of salt due to translation.

Hence the whole increase in the amount of the cation, free and combined, due to electrolysis is $\frac{1}{n}$ equivalent.

In the portion containing the anode we shall have—(1) a gain of one equivalent of anion set free, and (2) a loss of $\frac{1}{n}$ equivalent of electrolyte due to the translation; and hence the whole increase in the amount of anion free and combined round the anode is $(1 - \frac{1}{n})$ equivalent. The same results are obtained if the second supposition be made. Hence the n here used is identical with the n used above in the account of the phenomena of migration of the ions. D'Almeida considered that the phenomena were due to the fact that round the positive electrode an envelope of free acid was formed by electrolysis, and that this became a second electrolyte in contact with the salt solution. It is also evident that by supposing the salt to be electrolysed in a hydrated state, *i.e.* combined with a number of molecules of water which may travel with either the anion or cation, an explanation of the phenomena may be arrived at (Burgoin, *Bull. Soc. Chim.* [2] xvii. 244). Hittorf explained the remarkable cases of the iodides of zinc and cadmium by a somewhat similar assumption (*v. supra*, p. 110).

F. Kohlrausch (*Nacht. v. d. K. Ges. d. Wiss.*, Göttingen, 17 Mai 1876, 4 April 1877) has recently pointed out a most remarkable relation between the migration constants and the conductivities of extremely dilute solutions containing electrochemically equivalent amounts of haloid or oxygen salts. Thus if l_1, l_2 be the conductivities of such solutions of two salts MR, MR' containing one component M the same in both, and if n_1, n_2 be the corresponding migration constants of the ion M, then Kohlrausch shows that the equation $\frac{l_1}{n_1} = \frac{l_2}{n_2}$ holds with remarkable accuracy for many salts. The quantities l_1, l_2 are called the "specific molecular conductivities" of the solutions, and are defined by the equation $l = \frac{k}{\mu}$, where k is the specific conductivity of a very dilute solution at 18° C. referred to mercury, and μ is the ratio of the number of grammes of salt per unit of volume of solution to its electrochemical equivalent in hydrogen units. The results are in accordance with the hypothesis that the conductivity of an electrolyte is proportional to the sum of the oppositely directed velocities of the anion and cation; the velocity of any ion is supposed to depend on the friction of the surrounding fluid, and is accordingly constant for the same ion in different solutions if these are extremely dilute. A table of relative velocities can be formed from the migration constants of Hittorf, Wiedemann, and Weiske; a multiple of these velocities gives numbers such that the sum of those corresponding to two ions gives a value for the molecular conductivity of a solution of the compound of the two ions agreeing very closely with the experimental determinations of Kohlrausch and Grotthuss.

In order to explain the conduction of electricity during electrolysis Hypotheses several hypotheses have been suggested, which involve the idea thesis of continuity of electricity, even in the molecules. On this view conduction the elementary atoms when recombining carry with them a certain quantity of electricity, which, indeed, by Faraday's law, must be the same for every group of atoms constituting a chemical equivalent. Berzelius, for example, considers that when two atoms, e.g., H and Cl, unite to form HCl, electric distribution takes place similar to that of magnetism in a bar magnet, H being the positive pole, Cl the negative. The hypothetical positive pole is then attracted by the negative electrode, and the attraction is so great at the electrode itself as to overcome the chemical affinity of the H for Cl, and separation is the result, while the electricity of the electrode and of the H combine and are neutralized. The liberated chlorine atom then behaves in the same way towards its next neighbour, and so the current of electricity is set up.

For an account of the allied theories see Wiedemann, *l.c.*, and see also Clerk Maxwell's remarks upon the subject (*Elec. Mag.*, vol. i. § 259 *sgg.*). These hypotheses nearly all involve the idea, more or less defined, of a statical molecule, *i.e.* a molecule at rest relatively to other molecules, and consisting of relatively fixed atoms; but while we regard heat as the energy of molecular motion, this notion of a molecule cannot be sustained, and accordingly the above hypothesis can serve, as Maxwell suggests, merely to give precision to our ideas. Clausius (*Pogg. Ann.*, cl. 338), however, has applied the kinetic hypothesis of the constitution of bodies to electrolysis, and from his suggestions we can form some conception of the method of proceeding in electrolytic action. He supposes the molecules in the ordinary state to be in a state of agitation, and the atoms composing the molecules to be also in motion, sometimes separating, sometimes recombining with other separated atoms, so that decomposition and recombinations are continually going on, but in no definite direction. The mean result is an apparent state of equilibrium. When, however, an electromotive force acts upon the electrolyte,

no matter how small it is, it causes the atoms, when liberated as usual, to tend in one direction, viz., along the lines of force. Hence the collection of the ions at the electrodes, where they will separate if the electromotive force be sufficient to prevent them reacting and again recombining,—in other words, sufficient to bear the polarization. This, though by no means a complete theory, is indeed applicable to ultimate atoms, and is the only one which admits decomposition for all electromotive forces. Clausius shows that the finite electromotive force is necessary to maintain the ions in the free state at the electrodes.

One theory, which we must mention because it accounts at once for conduction, the migration of the ions, and "electric endosmose," is that due to Quincke (*Pogg. Ann.*, cxiii. extended in cxliv), who considers the ions of each molecule charged with quantities of electricity ϵ and ϵ' ; then the force K tending to separate the ions from each other $= -\frac{d\psi}{dx}(B\epsilon - B'\epsilon')$, where B and B' are constants, and $\frac{d\psi}{dx}$ is the electromotive force per unit of length of the electrolyte, and is consequently $= -\frac{i}{qk}$, where i is the current intensity, q the sectional area of the electrolyte, and k its specific conductivity; so that $K = \frac{i}{qk}(B\epsilon - B'\epsilon')$, and electrolysis takes place when this is greater than the force of chemical affinity. This is a weak point of the theory, as a finite electromotive force would be required to produce any decomposition or polarization.

The forces on the ions when separated, and hence their respective velocities, will be proportional to ϵ and ϵ' . This will account for the migration of the ions, for which ϵ and ϵ' are supposed unequal and of different signs in all cases except ZnI and CdI, &c., for which $(1 - \frac{1}{n})$ is greater than unity; for these ϵ and ϵ' may be of the same sign. If, on the other hand, ϵ be the amount of free electricity on a molecule of the electrolyte (supposed of high resistance) in contact with the glass, then $-B\frac{d\psi}{dx}$ will represent the force urging the fluid in the positive direction of the current, and perhaps producing endosmose, since ϵ will be positive except for turpentine oil. So the motion of particles may be similarly explained by supposing ϵ to be the charge on them due to contact with the fluid; this is negative with particles in water, and positive for all particles except sulphur in turpentine oil. The results thus obtained will be found to agree closely with the experiments mentioned above (p. 111); and the quantitative results also agree, since the force on a particle equals $B\frac{i}{qk}\epsilon$, and therefore varies as the current density i , and inversely as the conductivity k .

An application of electrolysis, which has already proved to be of great value in chemistry, has been introduced of late years by Gladstone and Tribe. In a paper read before the British Association in 1872 (*Trans. of Sections*, p. 75, see *Proc. Roy. Soc.*, vol. xx. p. 218) they showed that although zinc alone does not decompose distilled water, yet if zinc foil be immersed in dilute solution of cupric sulphate, and be thereby coated with metallic copper, which is thrown down as a black crystalline powder, containing traces of zinc only if the time of immersion be very long (*Journal Chem. Soc.*, 1873, p. 452), and if the zinc copper couple thus produced be immersed in distilled water at ordinary temperature, about 4 cc. of H can be collected per hour. The hydrogen is seen by the microscope to collect upon the copper crystals, while the zinc is oxidized, and forms a hydrate. The rate of evolution of hydrogen varies with the temperature; the relation may be exhibited by a curve very similar to the curve of tension of water vapour. Gladstone and Tribe have found this a powerful method of acting upon many organic bodies, particularly the halogen compounds of the alcohol radicles. In all cases either new reactions were set up, or the temperature at which reaction takes place was very much lower than with ordinary zinc (see the series of papers by Gladstone and Tribe in the *Jour. Chem. Soc.*, 1873-6). To the chemist the ZnCu couple affords an exceedingly convenient way of arranging electrolysis, since the whole may be contained in one vessel. For the copper in the arrangement, gold or platinum may with great advantage be substituted by immersing zinc foil in solutions of the chlorides.

This easily explains the well-known custom of generating hydrogen from zinc and sulphuric acid, to which a little CuSO₄ is added; and the "local action" in batteries, when currents pass from one part to the other of the same mass of metal and consequently energy is expended for which no external equivalent is obtained, may be similarly referred to the difference of composition of the metals in the two places. It should be remembered that Davy suggested the preservation of the copper sheathing of ships by attaching plates of Zn; the same object is now achieved by using an alloy of the two metals.

The application of the principle of the conservation of energy to electrolysis has already produced valuable results; research, how-

ever, in this direction is rendered difficult on account of the great number of circumstances which have to be taken into account, in computing the balance of energy expended and work done; the chemical composition and physical state of the electrolyte; the molecular condition of the ions, and the secondary actions at the electrodes have all to be taken into account. For a notice of the present state of this branch of the subject the reader is referred to the article ELECTRICITY. (W. N. S.)

ELECTRO-METALLURGY, a term introduced by the late Mr Alfred Smee to include all processes in which electricity is applied to the working of metals. It is far more appropriate than the French equivalent *galvanoplastie*, or the German *Galvanoplastik*, since the metals are certainly not rendered plastic under galvanic action, though it is true that in electrolysis, which forms one branch of electro-metallurgy, the metal is deposited in moulds, and can thus be used to reproduce works of plastic art.

It was observed as far back as the beginning of the present century that certain metals could be "revived" from solutions of their salts on the passage of a current of electricity. The germ of the art of electro-metallurgy may undoubtedly be traced to the early experiments of Wollaston, Cruickshank, Brugnatelli, and Davy; but it remained undeveloped until the late Professor Daniell devised that particular form of battery which bears his name, and which he described in the *Philosophical Transactions* for 1836. A Daniell's cell consists, in its usual form, of a copper vessel containing a saturated solution of blue vitriol or sulphate of copper, in which is placed a porous cylinder containing dilute sulphuric acid; a rod of amalgamated zinc is immersed in the acid, and on the two metals being connected by means of a conductor, electrical action is immediately set up. The zinc, which forms the positive or generating element, is dissolved, with formation of sulphate of zinc; whilst the blue vitriol is reduced, and its copper deposited, in metallic form, upon the surface of the copper containing vessel, which forms the negative or conducting element of the combination. Any one using this form of battery can hardly fail to observe that the copper which is thus deposited takes the exact shape of the surface on which it is thrown down, and indeed presents a faithful counterpart of even the slightest scratch or indentation. Mr De la Rue incidentally called attention to this fact in a paper published in the *Philosophical Magazine* in 1836, but it does not appear that any practical application was at the time suggested by this observation. Indeed, the earliest notice of electro-metallurgy as an art came from abroad two or three years later.

Sturgeon's *Annals of Electricity* for March 1839 contained a letter from Mr Guggsworth, announcing that Professor Jacobi, of St Petersburg, had recently discovered a means of producing copies of engraved copper-plates by the agency of electricity. This was the first news of the new art which appeared in England, and it evidently referred to the paper which Jacobi communicated to the St Petersburg Academy of Sciences on October 5, 1838, and in which he explained his process. In the *Athenæum* of May 4, 1839, there was a short paragraph relating to Jacobi's discovery, and public attention in this country was thus drawn to the subject. Only four days after the appearance of this paragraph, Mr Thomas Spencer, of Liverpool, gave notice to the local Polytechnic Society that he would read a paper on a similar discovery of his own. This paper was not read, however, until September 13; and although the author wished to describe his process before the British Association at Birmingham in August, it appears that his communication was never brought before the meeting. In Mr Spencer's paper, which was eventually published by the Liverpool Polytechnic, he states that his attention was first directed to the subject by mere accident: he had used a copper coin, instead of a plain piece of copper, in a

modification of Daniell's cell, and on removing the deposited metal he was struck with the faithful copy of the coin which it presented, though of course the copy was in intaglio instead of relief. Yet even this observation was allowed to remain unproductive until another accident called his attention to it afresh. Some varnish having been spilt upon the copper element of a Daniell's cell, it was found that no copper was thrown down upon the surface thus protected by a non-conducting medium; hence it was obvious that the experimentalist had it in his power to direct the deposition of the metal as he pleased; and this led Mr Spencer to prosecute a series of experiments by which he was at length able to obtain exact copies of medals, engraved copper plates, and similar objects. It should be mentioned that between the date on which he announced his paper and the date on which it was actually read, Mr C. J. Jordan, a printer, described experiments which he had made in the preceding year very similar to those of Spencer. This announcement was made in a letter published in the *London Mechanics' Magazine* for June 8, 1839. It thus appears that three experimentalists were close upon the same track about the same time, but it is generally admitted that among these competitors Mr Spencer has the merit of having been the earliest to bring his process to perfection, and to demonstrate its practical value.

Soon after the appearance of Mr Spencer's paper, it became a fashionable amusement to copy coins, seals, and medals by the new process. These copies in metal are termed *electrotypes*. The apparatus employed in the early days of the art, and which may still be conveniently used for small electrotypes, is similar in principle to a single Daniell's cell. It usually consists of a glazed earthenware jar containing a solution of sulphate of copper, which is kept saturated by having crystals of the salt lodged on a perforated shelf, so that they dip just below the surface of the solution. A smaller porous cylinder, containing very dilute sulphuric acid, in which a rod of amalgamated zinc is placed, stands in the jar, and is therefore surrounded by the solution of sulphate of copper. The object to be copied is attached by a copper wire to the zinc, and is immersed in the cupric solution. It thus forms the negative element of a galvanic couple, and a current of electricity passes from the zinc through the two liquids and the intervening porous partition to the object, and thence back to the zinc through the wire, thus completing the circuit. During this action, the zinc dissolves, and sulphate of zinc is formed; at the same time the copper solution is decomposed, and its copper deposited upon the metallic surface of the object to be coated,—the solution thus becoming weaker as it loses its copper, but having its strength renewed by consumption of fresh crystals of blue vitriol. To avoid the complete incrustation of the metal or other object, one side of it is coated with varnish or some other protective medium, so that the deposition of copper takes place only on such parts as are exposed. The deposit may be easily removed when sufficiently thick, and will be found to present an exact counterpart of the original, every raised line being represented by a corresponding depression. To obtain a facsimile of the original it is therefore necessary to treat this matrix in the same way that the original was treated, and this second deposit will of course present the natural relief. Another method consists in taking a mould of the original coin in fusible metal, and then depositing copper upon this die, so as to obtain at once a direct copy of the original.

Considerable extension was given to the process by a discovery, apparently trivial, which was first announced by Mr Murray at a meeting of the Royal Institution in January 1840. He found that an electro-deposit of metal

could be formed upon almost any material if its surface was rendered a conductor of electricity by a thin coating of graphite or "black-lead." Instead, therefore, of copying a coin in fusible metal, or indeed in any metallic medium, it is simply necessary to take a cast in plaster-of-Paris, wax, gutta-percha, or other convenient material, and then to coat the surface with finely-powdered black-lead, applied with a camel-hair pencil. Medals in high relief, with much undercutting, or busts and statuettes, may be copied in electrotype by first taking moulds in a mixture of glue and treacle, which forms an elastic composition capable of stretching sufficiently to permit of removal from the object but afterwards regaining its original shape.

About the same time that Murray suggested the use of black-lead, Mr Mason made a great step in the art by introducing the use of a separate battery. Daniell's cell, in consequence of its regular and constant action, is the favourite form of electric generator. The copper cylinder of this arrangement is connected with a plate of copper placed in a trough containing a solution of sulphate of copper, to which a small quantity of free sulphuric acid is commonly added; whilst the zinc rod of the cell is connected with the objects on which the copper is to be deposited, and which are also suspended in the bath of cupric solution. The current enters the bath at the surface of the copper plate, which is the *anode* or positive pole of the combination, and passes through the solution to the suspended medals which constitute the *cathode* or negative pole. As fast as the copper is thrown down upon these objects, and the solution is therefore impoverished, a fresh supply is obtained by solution of the copper plate; this copper is consequently dissolved just as quickly as the electrotypes are produced, and no supply of crystals is needed, as in the case of the Daniell cell. The great advantage of using a separate battery is that several objects may be coated at the same time, since it is only necessary to attach them to a metal rod in connection with the battery. Almost any form of galvanic arrangement may be employed by the metallurgist as a generator of electricity. But as the exciting liquid in a battery needs to be replenished from time to time, and as the zinc plates also wear out, its use is attended with more or less inconvenience in the workshop, and the electro-metallurgist has therefore turned his attention to other sources of electricity. Indeed, as far back as 1842, when the art was but in its infancy, a patent was taken out by Mr J. S. Woolwich for the use of a magneto-electrical apparatus; and of late years powerful machines in which electricity is excited by means of magnetism have been introduced into electro-metallurgical establishments. When a bar of soft iron, surrounded by a coil of insulated copper wire, is rotated between the poles of a magnet, a current of electricity is induced in the coil at every magnetization and demagnetization of the core. By means of a commutator, these alternating currents in opposite directions may be converted into a constant stream of electricity, available for the deposition of metals by electrolysis. The armatures are rotated by mechanical means, such as the use of a steam-engine, and hence the electricity is ultimately produced by conversion of mechanical work.

In the machine constructed by Mr Wilde, which has been largely employed by electro-metallurgists, a small magneto-electric apparatus, with permanent magnet, is employed to excite the electromagnet of a much larger machine. The induced current of the second machine is stronger than that of the first in proportion as the electromagnet is more powerful than the permanent magnet; this second current may then be used to excite another electromagnet, and hence by means of this principle of accumulation, currents of great energy may be obtained. The