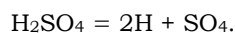


Electrolysis, in the strict sense, is the resolution of a fluid into its proximate constituents by the direct chemical action of the electric current; but the word is now commonly applied to all chemical operations, whether analytic or synthetic, which are performed by the direct action of the current. The phenomena that occur in the electric furnace (q.v.) are often incorrectly said to be "electrolytic"; but in most cases they are not so, electricity being used, in this instance, merely as a means for the production of high temperatures. Most of the chemical reactions that are observed in the electric furnace would occur equally well without the use of electricity, if the same high temperatures could be realized by other means; though in some cases, as in the reduction of metallic aluminum by the Hall process (see ALUMINUM), the fundamental operations really are electrolytic, and the high temperature is required merely to keep the electrolyte in the fluid state. The first recorded observation of a distinctively electrolytic action was made in 1800 by Nicholson and Carlisle, who observed that when the terminal wires of a galvanic battery are immersed in water, bubbles of gas arise from them. The correct explanation of this phenomenon was shortly afterward given by Sir Humphry Davy, who carried out an exhaustive, series of experiments which laid the foundations for the practical knowledge of electrolysis that we have today. Davy demonstrated the tremendous importance of the electrolytic method of analysis, by applying it to study of the alkaline earths and the caustic alkalies. The nature of these substances was not previously understood; but he proved them to be the oxide of previously unknown metals, and prepared the metals themselves in the free state. By passing the electric current through melted potash, for example, he found that bubbles of free oxygen gas were liberated at one of the electrodes, while silvery globules of what is now known as potassium appeared at the other electrode. A few days later he isolated the metal sodium in the same manner, by the electrolysis of soda; and he succeeded, afterward, in demonstrating the compound nature of lime and magnesia also, by the aid of the electric current. As may be imagined, the new method aroused the keenest interest in the scientific world. Napoleon, then at the zenith of his power, offered valuable prizes for discoveries along the same lines, and had large voltaic batteries constructed, in order that French investigators might have every opportunity to carry on the work. The two great Swedish scientists, Berzelius and Hisinger, discovered many new phenomena, and elaborated a general theory of the constitution of chemical substances, based largely upon their behavior under the action of the electric current; and Faraday (q.v.) established the fundamental quantitative laws that hold true in electrolytic decomposition.

Some slight evidence has been adduced which indicates that in certain cases the passage of electricity through solids may be accompanied by slight chemical changes of an electrolytic nature, and phenomena allied to those of electrolysis have been observed in connection with high-tension electrical dis-

charges through gases (see Thomson, "Recent Researches in Electricity and Magnetism," chapter 2 and appendix); but in general, electrolysis is observed only in liquids. All liquids may be divided into three classes, according to their behavior when the attempt is made to pass electricity through them. In the first class belong mercury and the other molten metals, which conduct the current readily, and without any noticeable chemical effects. In the second class belong such substances as carbon disulphide and absolute alcohol which do not conduct the current at all, and hence are not subject to decomposition by it. Absolutely pure water probably belongs to this class, though it becomes a conductor when the smallest quantities of certain impurities are present. Water that is ordinarily called "pure" conducts electricity fairly well, but its conductivity falls off as the purity increases, and Kohlrausch and Heydweiler have shown that water that is distilled in a vacuum, and collected in a glass vessel which has been kept full of distilled water for 10 years in order to dissolve out all the soluble constituents of the glass, has a conductivity almost too small to be measured. The third class of liquids includes all those (such as aqueous solutions of the various metallic salts) in which electric conduction is always accompanied by a definite chemical change. In the present article attention will be confined to this third class, whose constituents are known as "electrolytes" and in which the current is said to flow by "electric conduction."

It is necessary, in the discussion of electrolytic phenomena, to distinguish between the primary effects of the passage of the electric current through an electrolyte, and the various secondary effects that may also occur; and while it is not always easy (nor even possible), in actual work, to determine, definitely, what the primary effects are, one or two cases may be cited which will serve to illustrate the difference between primary and secondary effects sufficiently for present purposes. If a current of electricity is passed through melted chloride of lead, $PbCl_2$, the primary effect of the electrolysis is the resolution of the chlorid into its constituent elements, in accordance with the equation $PbCl_2 = Pb + 2Cl$, metallic lead being deposited upon the cathode. If carbon electrodes are used, free chlorine will also appear at the anode; but if platinum electrodes are used, little or no free chlorine will be obtained, because the gas will combine with the metal of the anode in this case, with the formation of platinum tetrachlorid. The combination of the chlorine with the platinum is an example of secondary action. Again, in the electrolysis of sulphuric acid, H_2SO_4 , it is known that the primary effect is the resolution of the acid into hydrogen and the radical "sulphion," SO_4 in accordance with the equation



The hydrogen goes to the cathode, where it is set free. The sulphion goes to the anode, but it is not capable of existence in the free state, and hence some secondary reaction is inevitable. If the acid is dilute, and the an-

ode is of platinum, the sulphion combines with water at the instant of its liberation, according to the equation $\text{SO}_4 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{O}$. In this case, therefore, the effect of the secondary action is to regenerate a molecule of sulphuric acid, and simultaneously set free an atom of oxygen; and the evident products of the electrolysis are merely hydrogen and oxygen, which appear at the cathode and anode, respectively. If the acid is concentrated instead of dilute, the secondary action just described will still occur to some extent so long as the acid is not absolutely anhydrous, but free sulphur dioxide is also liberated at the anode in this case; and finally, under certain conditions, sulphur itself may be obtained at the cathode. The secondary chemical changes that occur in an electrolytic cell depend upon the nature of the electrolyte, upon the concentration of the solution, upon the temperature, and upon the strength of the current to which the primary chemical effects are due. They are often complicated and of an unexpected nature; and it is to the study of these secondary changes, under varying conditions, that industrial electrolytic chemistry must look for its further advancement.

No primary chemical changes whatever are to be observed, in an electrolytic cell, save at the electrodes; though secondary changes may occur elsewhere, on account of the diffusion of the immediate products of decomposition through the liquid of the cell. The primary changes do not depend in the smallest degree upon the size of the electrodes, nor upon any other factor save the total quantity of electricity that passes through the cell. If a series of cells, containing electrodes of various sizes and filled with a given solution in different states of concentration, be placed simultaneously in the same circuit, so that the same identical current traverses them all, the primary products of decomposition will be the same in all, both in nature and in quantity. Moreover, if the same experiment be repeated when the several cells are filled with solutions of diverse natures, the primary products will necessarily be different from one another in kind, but when their quantitative relations are examined, it is found that they are liberated in precisely equivalent proportions. For example, if one cell contains chlorid of sodium and another contains nitrate of silver, then the quantity of chlorine liberated in the first cell is precisely sufficient to unite with the metallic silver liberated in the second one, so as to produce chlorid of silver without excess of either chlorine or silver. This statement needs one simple qualification, however, before it can be applied universally. If the two cells considered contain mercuric nitrate, $\text{Hg}(\text{NO}_3)_2$, and mercurous nitrate, HgNO_3 , respectively, then for every ounce of mercury that is deposited from the mercuric salt, two ounces will be deposited, simultaneously, from the mercurous salt. Obviously the quantities of Hg and of NO_3 , that are liberated in the two cases cannot both be the same; and it is the NO_3 and not the Hg, which is liberated in equal quantities. In general, the "chemical equivalence" of an element is defined as the atomic weight of the element, divided by the

valency that the element has, in the compound under consideration; and the quantities of the various elements that are liberated by a given quantity of electricity are proportional to the "chemical equivalents" of the elements, as they occur in the compounds that are submitted to electrolysis, rather than to the "atomic weights" of these elements. The number of grams of an element that are liberated, electrolytically, by one C.G.S. unit of electricity, is called the "C.G.S. electrochemical equivalent" of that element. The electrochemical equivalent of silver is known by experiment to be about 0.01118; and the electrochemical equivalent of any other element may be found from this by simple proportion, as explained above. For many purposes it is more convenient to know what weight of a given element will be deposited in one minute, by a current whose intensity is one ampere. This is given, in the accompanying table, for the more important elements. The elements are here divided, for convenience, into those that are electro-positive, and those that are electro-negative; the former being those that usually appear at the cathode, and the latter those that usually appear at the anode. This classification is not very valuable in the case of complicated compounds, but it answers for the simpler ones. The data given in the table refer to the primary products of decomposition; but it is sufficiently evident that they apply equally well, so long as the visible product of the decomposition is all of one kind, whether it is primary or secondary. In the electrolysis of sulphuric acid, for example, "sulphion" is the primary product at the anode; but sulphion is incapable of independent existence, and the only visible product at the anode is oxygen, so long, as the acid is sufficiently dilute. In this case the quantity of oxygen that is liberated can be computed precisely as though the oxygen were itself the primary product. When, as in the electrolysis of concentrated sulphuric acid, more secondary products than one are obtained, the case is more involved. In general, however, we must remember that it is only with reference to the primary products that the electrolytic nature of the decomposition need be considered; for the secondary reactions are merely those of ordinary chemistry.

The most generally accepted theory with regard to the nature of electrolytes is that which is known as the "ionic theory," and which teaches that a salt whose solution is capable of electrolysis becomes more or less completely dissociated when it is dissolved, the respective parts into which its molecules subdivide being known as "ions." This aspect of the phenomena of solution is considered in the article SOLUTION (q.v.), and in the present place we need dwell only on those features of the ionic theory which have an immediate bearing on the subject of electrolysis. The ions into which the electrolyte is resolved, upon solution, are supposed to be associated with definite charges of electricity, which cling to the ions so long as the dissociation persists, and can only be neutralized by causing the ions to come together again so as to re-form a

GRAMS LIBERATED PER AMPERE PER MINUTE.

Element	Atomic Weight	Velocity	Chemical Equivalent	Grams per Ampere per Minute
Electro-positive:				
Aluminum.....	26.9	3	8.97	0.00562
Copper (cupric)	63.1	2	31.6	0.0198
(cuprous)	63.1	1	63.1	0.0395
Gold.....	195.7	3	65.2	0.0408
Hydrogen	1.0	1	1.00	0.00626
Iron (ferric)	55.6	3	18.5	0.0116
(ferrous)	55.6	2	27.8	0.0174
Lead.....	205.4	2	102.7	0.0643
Mercury (mercuric)	198.8	2	99.4	0.0623
(mercurous) .	198.8	1	198.8	0.1245
Nickel	58.3	2	29.1	0.0182
Potassium.....	38.9	1	38.9	0.0244
Silver	107.1	1	107.1	0.0671
Sodium	22.9	1	22.9	0.0143
Tin (stannic)	117.6	4	29.4	0.0184
(stannous).....	117.6	2	58.8	0.0368
Zinc	64.9	2	32.4	0.0203
Electro-negative:				
Bromine	79.4	1	79.4	0.0497
Chlorine.....	35.2	1	35.2	0.0221
Iodine	125.9	1	125.9	0.0789
Nitrogen.....	13.9	3	4.63	0.00290
Oxygen.....	15.9	2	7.95	0.00948

molecule of the original salt, or to enter into other chemical combinations with one another; neutralization being effected, in such cases, by the actual discharge of the equal and opposite electricities into one another, as the re-combining ions come together. What the ions are, into which a given salt dissociates when it is dissolved, can only be discovered by inference from certain kinds of experiments for which reference must be made to the books cited in the article SOLUTION. Our knowledge on this point is still far from complete, but we know what the ions are in most of the simpler electrolytes. When potassium hydroxid, KOH, is dissolved in water, it becomes dissociated, or "ionized," into the ions K and OH. At first thought it appears to be impossible to admit that potassium, which has so great an affinity for water, can exist in the free state in a solution; but it must be remembered that the potassium "ion" differs from the ordinary potassium atom by the possession of a definite and considerable electric charge, which modifies its chemical behavior profoundly. As the solution is concentrated by evaporation, the potassium ions and the hydroxyl ions (OH) come together, discharge into each other, and unite to form potassium hydroxid, KOH, which is deposited in the solid form. (Some of the hydroxid remains in solution as such, the dissociation never being complete except in exceedingly dilute solutions; but this point is not essential to our present purpose, and for its further elucidation reference must be made to the article SOLUTION.) In the ionized state, the potassium is charged positively and the hydroxyl negatively; and, in general, any ion which appears at the cathode during electrolysis is charged positively in the free solution, and any ion which appears at the anode is

charged negatively. Moreover, the phenomena of electrolysis prove that any given ion is always associated with the same identical charge of electricity, no matter what the salt may have been from which the ion was obtained, provided the ion has the same valency in each of the salts that are compared. The potassium ion in a solution of potassium chlorid, for example, carries precisely the same charge as the potassium ion in a solution of potassium nitrate, or of potassium carbonate. We may therefore regard the free ions in a solution as so many little buckets filled with electricity, all the buckets having identically the same capacity.

According to this view, the ions act as mere carriers of electricity, and electrolysis is not simply an accompaniment of conduction through an electrolyte, but the very means by which this conduction is effected. The electric circuit in which the electrolysis occurs may be likened to a brook. If the metallic circuit is interrupted by the insertion of a solution of some kind, the solution so inserted corresponds to a dam in the brook, through which no water can pass by direct flow. The analogy is fairly complete when the solution does not contain free ions, for then it will not act as an electrolyte, and no current can pass. Sugar, for example, does not dissociate to any appreciable extent when it is dissolved, and hence a solution which contains nothing but pure water and pure sugar cannot conduct electricity, and merely acts as an impassable barrier to the current. When the solution contains a salt (such as sodium chlorid) which is largely or wholly dissociated, the free ions act like a molecular bucket brigade, passing the water across the dam in the brook, or the electricity across the gap between the two electrodes in the electrolytic cell. In the electrolysis of copper sulphate, for example, the phenomena are as follows: The formula of the sulphate is CuSO_4 , and the free ions in the solution (and hence also the primary results of the decomposition) are copper and "sulphion" SO_4 ; the copper ion being charged positively, and the sulphion ion negatively. The electrodes that are immersed in the electrolytic cell are also kept continuously charged by the battery (or dynamo) with which they are connected; the cathode being negative and the anode positive. The positively charged copper ions in the solution are therefore attracted by the negatively charged cathode, just as a positively charged pith ball is attracted by a negatively charged body in the air. Hence they move towards the cathode, and when they reach it they discharge their electricity upon it, thereby ceasing to be ions, and becoming transformed into atoms of ordinary copper, which are perforce deposited upon the cathode. The sulphion ions simultaneously move toward the anode, upon which they discharge the negative electricity that they carry. The ionic charge is essential to the continued existence of the sulphion, however, and when this charge is lost, the sulphion must either break up into sulphur dioxide and free oxygen, or else combine with some other substance to form a new compound. If the anode is made of platinum or carbon, the sulphion usually combines with a molecule of water with the

liberation of free oxygen, as already explained in connection with the electrolysis of dilute sulphuric acid; but if the anode is made of a material that is less resistant to chemical action, the sulphion may combine with the anode itself instead of with a molecule of water. For example, when the anode is of copper, the sulphion, at the moment that it loses its electric charge, combines with an atom of the anode so as to form a molecule of copper sulphate.

The solvent, according to this theory, is to be regarded as an insulator, through which the electricity is passed by the ionic bucket-brigade. There is no real "conduction" through an electrolyte; but the positive charges that the ions bring to the cathode diminish the charge of the cathode so that more negative electricity must flow to it from the battery (or the dynamo), in order to maintain its potential; and, similarly, the negative charges that the ions carry to the anode require a constant supply of positive electricity from the battery, in order that the potential of the anode may be maintained. The general effect upon the circuit, therefore, is the same as though there were an actual conduction of electricity through the electrolyte. (For a further elaboration of the ionic theory of electrolysis, consult Whetham, 'Solution and Electrolysis.' See also SOLUTION.

By a detailed study of the secondary chemical actions that occur when salt solutions are electrolyzed, it has been found to be possible to isolate many of the metallic elements by electrolysis, when they are present in a mixed solution; and a promising system of "electro-chemical analysis" has been based upon this fact. Copper may be separated from cadmium, for example, by electrolyzing a solution of their mixed salts, in which free nitric acid is present, the copper being obtained in the metallic form, while the cadmium remains in solution. If the same solution is neutralized by potassium hydroxid, and then electrolyzed after the addition of potassium cyanide, the cadmium is deposited, while the copper remains in solution. The successful application of the principles of electrolysis to analysis requires an extensive knowledge of the secondary reactions that occur at the electrodes, however, as well as a full understanding of various practical conditions that must be carefully attended to. For these consult: Smith, 'Electro-Chemical Analysis' (1903), together with the references therein given. See ELECTRIC FURNACES; ELECTRO CHEMICAL INDUSTRIES; ELECTRO-CHEMISTRY; ELECTRON; SOLUTION.