

ments could readily be made by the American and British Associations in 1797, and the final arrangements by the British and French Associations in 1899.

ADDRESS BEFORE SECTION B OF THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE BY THE VICE-PRESIDENT.

THE selection of a subject for presentation in an address such as I am called upon to deliver to-day, seems difficult. A large proportion of those who may listen to me to-day are workers in the same field which interests me and are familiar with the progress in the science of physics. It is, therefore, unlikely that I shall be able to present to you anything which may be new or startling; this I regret, for it seems that it requires something of this character to stimulate interest and research.

The aim of science in its most general sense, is the discovery of truths. Its progress may be expressed by a curve approaching truth asymptotically, probably never in human experience approaching to its *complete* knowledge. So long as investigators find that they are working upon the steep part of the curve where it approaches truth rapidly, there is no lack of interest; this, however, seems to die out quickly when much labor and great patience are required to extend experimentally the curve now more slowly approaching complete knowledge, or straighten out some of its irregularities. As soon as a startlingly new or curious line of investigation is suggested every one pounces upon it and older problems are left far from completion. That we in America are especially inclined to this weakness in physical investigations I believe to be the case. Though investigations have been carried out by a number of American physicists, well-nigh to completion, involving years of painstaking labor, of which we may well be proud, yet I be-

lieve the tendency exists. It is this thought which has led me to select for a brief review a line of study patiently carried on in Europe for a number of years, yet hardly touched upon by physicists in this country. In the last few years the studies in electrolysis and solution have been so fruitful that we can no longer afford to neglect them. It is also remarkable that these studies in electrolysis and molecular physics have been made almost exclusively by chemists, though of equal, if not greater, interest to the physicists; the problem should be attacked by them. To direct your attention then to some of the important work that should be undertaken by physicists is my object in reviewing, in the briefest possible manner, the progress of studies in electrolysis from their beginning to the present time.

Scarce one hundred years have passed since the first note of chemical action having been produced by electricity is to be found. About the middle of the 18th century Pater Beccari obtained metals from oxides between which electric sparks had passed. These results led to no further inquiry at the time, and were passed by almost unnoticed. Priestley, in 1778, critically studied the effect of the passage of the spark through air, noting the production of an acid gas. Cavendish continued these researches, explaining the action in the sense of the Phlogistic Theory of the day. Van Marum, extending Cavendish's investigations, decomposed ammonia, and through a careful study of the chemical changes brought about by the electric spark became converted from Stahl's Phlogiston Theory, stoutly maintained at the time, to Lavoisier's Oxygen Theory. Van Troest and Dieman, in 1739, gave the first unmistakable evidence of electrolytic action in decomposing water by means of the spark. The tendency towards an Electrical Theory of chemical action, fully developed later,

becomes evident from the study of the literature of the day. These investigations were almost exclusively carried on by chemists; but little attention was given to the study of electricity, its nature and physical action; only the chemical results were of interest. The quantity of electricity at the command of the experimentalists at that time, was so small that very definite results in electrolytic action could not be expected.

So far some progress had been made in the production and study of chemical effects resulting from electrical action; *the question of the possibility of the reversal of these effects, the production of electricity from the chemical action*, had not been thought of. Volta was the first one to investigate *that* question. Galvani's discovery given to the world in 1791 in a brochure of 58 pages gave a new stimulus to investigation, now taken in hand by physicists. The perusal of the little work is of great interest in the historical study of electricity. Galvani, as anatomist, looked for the source of electricity to the phenomena of life, believing it to be stored in the living cell. Volta, the trained physicist, sought for it in the material world and gave us the Contact Theory of electricity as distinguished from the Chemical Theory. These two theories have each been as stoutly maintained as controverted by the best experimentalists and thinkers of the century. Volta's great gift to the world was the Voltaic Battery, the study of which, together with the reversibility of the action, has thrown a flood of light upon problems in molecular physics as well as upon chemical action, though the 'contact theory' of electricity of Volta, accepted with modifications by many of the greatest physicists of this century, has undoubtedly been one of the strongest barriers to the progress of later and more satisfactory theories as to the seat of the electromotive force in the battery.

Passing over many important contribu-

tions from co-workers of Volta, laying a foundation for an understanding of the chemical effects of electricity, the most valuable work having perhaps been done by Ritter, we come to Nicholson and Carlisle, who, on the 2d of May, 1800, opened the field for the study of electrolysis by the decomposition of water by means of the current from the Voltaic pile.

Volta seems to have avoided almost purposely the recognition of chemical action associated with the production and action of the current. It is remarkable, at any rate, that such action should have impressed itself most strongly upon all other experimentalists of that day and scarcely be noticed by him.

From this time on we recognize for a considerable period two lines along which electrical problems have been studied. A long list of illustrious physicists from Ermann to Ohm studied the laws and physical effects of current electrical phenomena without questioning the somewhat unsatisfactory theory of Volta as to its source; another list, mostly chemists from Nicholson and Carlisle to Davy and Faraday, sought to determine the source of the current. To trace the development of modern theories historically would demand following both of these lines of research; time forbidding this we will consider but a few of the more important discoveries in each field as required.

Sir Humphrey Davy succeeded in decomposing the fixed alkalis in a fused condition; the separation of the elements from their compounds was by him demonstrated in many experiments.

Before proceeding, however, it may be well to define a few terms used in discussing electrolysis and recall a few of its phenomena.

By electrolysis we mean the chemical changes which result from passing an electric current through a compound, usually in solution or in a state of fusion. The sub-

stance decomposed is called electrolyte. The battery terminals, or source of current, connected by the electrolyte, are called Electrodes—the one bringing the current to the electrolyte the Anode, the one carrying it away the Kathode. As a result of the difference of potential of the electrodes, the materially different constituent parts of the electrolyte are impelled to move towards the electrodes; these wandering particles are called ions; those gathering about or moving towards the anode, anions; those about the kathode, kathions. The chemical changes are observable only at the electrodes. Taking as a simple case, ordinary hydrochloric acid—a compound of hydrogen and chlorine dissolved in water—the passage of the current causes chlorine to appear at the anode and hydrogen at the kathode. The hydrogen and chlorine, while in the solution finding their way to the electrodes, are ions; the chlorine-anion, the hydrogen-kathion. In many cases the action is not so simple. The electrolytic decomposition may be accompanied by chemical action occurring subsequent to or simultaneously with the appearance of the ions at the electrodes; the substance formed differing from the ions actually carried to the electrode. Changes of this character considerably complicate the problem and make the correct interpretation of observed phenomena difficult. This general law may, however, be enunciated: An electrolyte under action of the current is split into two and only two parts, atoms or groups of atoms, no matter how complex its structure may be. These atoms or atomic groups thus separated, are similar to the ones which exchange places in the ordinary chemical reactions. This early observed law led to the theory advocated by Berzelius, that all salts consisted of two atomic groups, one acid the other basic—erroneous, in that the chemical changes subsequent to the electrolytic action were not properly understood.

The wondering attention of early investigators had been directed to the curious phenomenon that the substances resulting from electrolysis appeared only at the electrodes and were not recognizable in the solution between the electrodes. The various theories propounded to explain this vied with one another in improbability. The difficulty of explaining this behavior satisfactorily seems to have led to the abandonment of the problem until, in 1805, Chas. J. D. Freiherr Von Grothuss propounded a theory which gave a sufficiently reasonable explanation to be adhered to for fifty years, even quoted to-day in many text-books. Grothuss conceived that each molecule of a chemical compound acted like a conductor consisting of two parts capable of being separated; these molecules acted upon inductively by the charged electrodes, one group would become positively charged, the other negatively, the nature of the charge being determined by the character of the group, being acted upon by attractions and repulsions, varying inversely as the square of the distance from the electrodes, the electrified *end* particles would be attracted to the electrodes; the remaining groups by separation and recombination would at once form a new series of molecules as before the action, ready for a repetition of the process; no freely charged groups thus remaining in the mass of the solution between the electrodes. This theory demands that the electrical forces between the plates vary inversely as the square of the distance; that, when the force reaches a certain definite magnitude the groups will be separated; a further consequence is that when this critical force is attained all or a very great number of groups will be separated, instantly, for if this attraction be equal to the force holding the groups together, the whole mass will be in unstable equilibrium, and any increase will cause complete separation of all groups.

Important experimental contributions followed one another rapidly, batteries were perfected, many physical actions of the electrical current were studied, the action of the current upon magnets was discovered, measuring instruments for quantitative work were invented, Ohm's law was enunciated, etc., so that when Michael Faraday, Sir Humphrey Davy's man of all work and his successor at the Royal Institute, with matchless experimental genius and wonderful breadth of view, attacked the problem of electro-chemical action, he had at his command the means for quantitative work in this field which enabled him to discover and formulate one of the most important laws of electrolysis. Faraday's charming directness and clearness in the exposition of his work and results contrast refreshingly with the prolix, flowery and mystifying style of his immediate predecessors; it at once stamped him a master of the subject treated. Faraday's original notes are well worth studying; they may be taken as models to-day by many who essay to record experimental results and conclusions. Confusion in terms and errors in inferences occurring in his work are well excusable; from our more extended and accurate knowledge, we are inclined to be unfairly critical. A review of Faraday's work in electrolysis alone would be interesting, for in it we may see foreshadowed many important points in the theories of to-day, though Faraday himself scarcely appreciated them.

The most important law Faraday contributed to the behavior of electrolytes acted upon by a current is stated thus:

The amount of chemical decomposition in electrolysis is proportional to the current and time of its action.

The mass of an ion liberated by a definite quantity of electricity, is directly proportional to its chemical equivalent weight.

The quantity of electricity which is required to decompose a certain amount of a

certain electrolyte is equal to the quantity which would be produced by recombining the separated ions in a battery.

The latter law, clearly showing the reversibility of the process, at once makes the problem one capable of theoretical treatment from the standpoint of conservation of energy and has brought most abundant fruit in later years. Faraday, in the main, accepted Grothuss' hypothesis, differing from him in the conception of the character and manner of action of the forces. Faraday showed experimentally, by measuring the change of potential between the electrodes, that Grothuss' conception of attracting and repelling forces, varying inversely as the square of the distance, was untenable; he (Faraday) assumed that through the action of the electrodes the chemical affinities of the combined ions were so changed or weakened that they acquired a greater attraction for the plates and their neighboring opposite ions; that decomposition and recombination occurred along the entire line. With Grothuss, he assumes that each liberated ion has a definite quantity of electricity belonging to it. This theory then demands that the action of the constituent parts of the electrolyte extend to considerable distance, and that the effect of the electrode is to modify or weaken the chemical affinity between the groups so that decomposition results. Faraday leans to the opinion that chemical and electrical forces are identical, and in considering the reversibility of the process becomes an advocate of the chemical theory of the Voltaic cell.

Faraday, though somewhat confused in his nomenclature, brings out very clearly the relations between quantity of electricity and quantity of material separated, and electrical potential and chemical affinity, though at that time the concept of energy and work done, as a function of both potential and quantity of electricity, was not clearly established.

To review the work of Faraday in electro-chemistry alone, and the influence it had in the development of the more modern theories, would require more time than is allotted to us; the most important contribution in this subject has alone been mentioned.

In 1851 Williamson, from purely chemical evidence in the manner of the formation of some ethers, was led to believe that in solutions there is a constant interchange of atoms or groups of atoms between molecules, equivalent to dissociation and recombination, a view differing from those previously held, where this condition was supposed to be brought about by the action of the electric current. Williamson made no application of this conception to electrolysis.

Clausius, in 1857, applying the ideas growing out of the Kinetic Theory to solutions, points out the weaknesses of previously advocated theories; he shows that Grothuss' hypothesis, as well as its modifications by Daniell and Faraday, are not in accord with experimental results from accurate measurements. He shows that the hypothesis that the decomposition or tearing apart of the groups of atoms in the molecule by the electric forces, before transfer of electricity takes place, is untenable.

Clausius assumes that the molecules in the liquid stored with energy, move with varying velocities; that collisions will occur which may cause the separation of the molecules into atomic groups for a short time; that during the period of separation these groups charged with opposite kinds of electricity peculiar to the groups will, under the influence of the electrode, be directed towards the electrodes in their path and thus become carriers of electricity; he ascribes to the liquid the conditions of dissociation due to fortuitous impacts always occurring, whether the solution be under the influence of external electrical forces or not; that the function of the electric forces is but

directive, the effect being, the disturbance of the internal kinetic equilibrium.

The principle of the conservation of energy, developed and applied in thermodynamic relations, influenced the manner of looking upon and interpreting electrochemical processes. The most prominent names associated with the application of this great principle are Joule, Helmholtz, Willard Gibbs, Thomson, Boscha, Favre and others. Much attention was now given to the problem: What is the cause of the electromotive force? The distribution of the energy in the electric circuit, including battery, electrolytic cell and conductors, was investigated in the light of the energy concept and attacked from the mathematical or dynamical side. Weaknesses in older theories were glaringly revealed if searched in the light of this principle. The dependence of the electromotive force upon the entropy term in the equations was shown, and its consequent variation with temperature.

The contributions of Willard Gibbs in this field are the most important, though scarcely appreciated; published in the Transactions of the Connecticut Academy, 1876-78, they were not very accessible and not generally known. This great work anticipated the many discoveries since made experimentally, in a manner all but final in its comprehensiveness and completeness, opened out and suggested experimental investigations only partially undertaken and beginning to be carried out to-day. Why it was and is not more fully appreciated is probably due to its concentration; in the compass of some 300 pages and in 700 equations the entire subject of molecular dynamics is treated. The treatise was too rich to be grasped in its day; it is only beginning to be properly estimated twenty years after its first appearance.

About 1853 Hittorf quantitatively investigated, with great care, the change of con-

centration in solutions of electrolytes about the electrodes when a current passes. This phenomenon had been noticed and studied to some extent by Daniell and others, without, however, having been made use of in explaining the nature of electrolytic action. Hittorf's studies and conclusion bring us into the very midst of the modern views of electrolysis. Taking a simple case, let two electrodes of copper be placed vertically over one another in a solution of copper sulphate, pass a current through the cell making the lower plate the anode; no very noticeable change occurs other than that copper is dissolved at the anode and deposited at the kathode; if after the current has passed for a short time it is interrupted and the electrode short circuited through a galvanometer, a current will for a short time flow in the cell from kathode to anode, that is, in a direction opposite to the one which has passed through in electrolyzing. The counter-electromotive force in this case can not result from polarization at the electrodes, for no change has been brought about at their surfaces, such as a gas deposit in the case of decomposition in acidulated water with platinum electrodes. If the electrolyzing current be continued for some time it will be seen that the solution about the anode has become more concentrated and more dilute about the kathode; the total quantity of copper salt in the solution having, however, remained the same, the counter-electromotive force above referred to is due to this change in concentration.

Hittorf, from 1853 to 1859, examined in a most careful manner the behavior of many electrolytes, and by a series of analyses of the solutions determined this change of concentration due to the passage of the current. His patient labor has only within the last few years received proper recognition.

All theories which so far had survived

the test, conceived that the electricity was conveyed by a migration of particles, called ions by Faraday; whether these particles received their changes by contact with the electrodes or contained definite inherent quantities of electricity, the charges being the same for all ions, need not be considered at this time.

The first step toward the decisive establishment of the fact of the migration of the ions towards the plate would be an experimental measurement of the rate of migration; this was accomplished by Hittorf and led to the enunciation of these laws:

1. The change in concentration due to current, is determined by the motion which the ions have in the unchanged solution.

2. The unlike ions must have different velocities to produce such change in concentration.

3. The numbers which express ionic velocities mean the relative distance through which the ions move between the salt molecules, or express their relative velocities in reference to the solution, the change in concentration being a function of the relative ionic velocities. Hittorf's analyses enabled him to give their numerical values. A great many such have been made by him, Nernst, Loeb and others; these results show that in dilute solutions the relative velocities of the ions are independent of the difference in potential between the electrodes (if the current be steady), and that they are only slightly affected by temperature.

Hittorf points out that a knowledge of the specific resistance of electrolytes should give valuable information in reference to the nature of electrolytic action. Horsford, Wiedemann and Beez made such measurements; their methods were, however, imperfect; it remained for P. Kohlrausch to devise a method, using an alternating current, by means of which accurate results were obtained. Kohlrausch's work shows

an amount of patience and experimental skill rarely found ; his contributions will remain classical. In connection with Hittorf's work, Kohlrausch recognized that, according to Faraday's law, the conductivity should be represented by sums of the velocities of the ions, each carrying its electric charge. Thus, having from experimental data on conduction the sum of the velocities, and from Hittorf's migration constants, based upon changes in concentration, the ratio of the ionic velocities, the absolute velocities of the ions would be calculable. Inasmuch as the quantities he was to deal with were groups of atoms or molecules he determined at once to make the molecule his unit of quantity, and not mass alone. This expedient simplified the comparison of results and has been neglected by physicists. The comparison of results obtained by making the molecule the unit, revealed at a glance relations between the physical behavior of different substances which would have been obscure if the mass had been chosen as unit. The selection of the most convenient proper unit is of great importance in the interpretation of results and the enunciation of physical laws.

Kohlrausch expressed the concentration in *gramme molecules* per unit volume of solution, the unit solution containing a number of grammes of the electrolyte equal to the number expressing the chemical equivalent on the hydrogen scale, in one litre of water. The measurements were then made upon solutions, the relative numbers of molecules in which were known. The ratio between the conductivity and the number of *gramme molecules* contained in the solution will then give molecular conductivities.

The results of such measurements show, that as dilution increases there is an increase in molecular conductivity, that in very dilute solutions it approximates a limiting value. This increase of conductivity is considerable for bad conductors, less so for

good conductors. The limiting value in dilute solutions of good conductors can be reached. In bad conductors, even at the extremest dilution accessible to measurement, the molecular conductivity is still far from the limiting value.

In general there is an increase of conductivity with increase of temperature, usually amounting to about 2 per cent. per degree Centigrade.

The conductivity of equivalent quantities of neutral salts is of much the same order of magnitude, usually reaching the limiting value at a dilution of $\frac{1}{2000}$ *gramme equivalent*.

From Kohlrausch's numerical values and Hittorf's constants, the absolute velocity of a large number of ions was calculated. It appears from this, that the velocity of the ion in very dilute solutions depends only upon its own nature and not upon the nature of the ions with which it may have been associated ; thus the velocity of the Chlorine ion was found to be the same whether determined from solutions of KCl, NaCl, HCl, etc.

This important general law was also found, that the conductivities of neutral salts are additively composed of two values, one depending only upon the metal or positive ion, the other upon the acid radical or negative ion. According to this law the conductivity of a neutral salt can be calculated from a knowledge of the velocities of the ions independently, a test which has been applied in many cases with very satisfactory results when checked experimentally. For quite a number of compounds, however, the computed results were much too high an abnormality to be discussed later. This law confirms the idea of independent migration of the ions.

Kohlrausch's numbers expressing velocities were checked by some exceedingly ingenious experiments by Oliver Lodge and Wethan. By a change in the color of the

solution of two layers the migration of the ions could be directly measured, these results agree surprisingly well with Kohlrausch's, considering the widely different conditions and the difficulty of measurement.

About 1887 electro-chemistry entered into a new stage of progress; the central figure among those who were mainly active in bringing about this development was Svante Arrhenius, who, together with Ostwald and others, advanced a theory of electrolytic action, explaining very satisfactorily many well-known phenomena. Arrhenius' theory involves the general idea contained in the theory of Clausius and Williamson, namely, that the solution contains the electrolyte dissociated into ions before the current is forced through it. Arrhenius adds that this dissociation is affected by solution or fusion, and that the ions contain charges of positive and negative electricity dependent upon their nature, but of equal quantity in every ion. While in this state, that is, as ions, they move in an irregular manner between the molecules of the solvent and the undissociated molecules of the electrolyte, now attaching themselves to one another and again separating, upon the whole maintaining a condition of Kinetic equilibrium. As soon as brought under the influence of the electrodes of different potential, they are impelled in definite directions, the anions towards the anode, the kathions towards the kathode.

The first work done by the current is the overcoming of the viscous resistances of the medium, not an inconsiderable amount; thus a portion of the energy of the current is fritted into heat.

At the electrodes another kind of work has to be done; either the charges have to be removed from the ions, changing them into the molecular condition, or new ions must be produced from the material of the electrode and the solvent, for kathions ar-

iving the formation of anions or for anions kathions.

Undissociated molecules of the electrolyte take no part directly in electrolysis, except in so far as they may alter the viscous resistance of the solution.

The fact that molecular conductivity increases with dilution means, that as infinite dilution is approached complete dissociation or ionization of the electrolyte is effected.

The ratio between molecular conductivity at greater concentration and infinite dilution, expresses the degree of dissociation or ionization. The conductivity can always be expressed by the sum of the velocities of the ions into a coefficient expressive of the degree of dissociation: $C=A(u+v)$. In the limiting case $A=1$ and the conductivity is measured by the sum of the ionic velocities, this in accord with Kohlrausch's law.

One of the important points in this theory is that solution effects dissociation. Chemically pure substances, such as HCl in the liquid state, should not be electrolyzed; such is found to be the case. The curious fact that pure HCl and pure water alone are non-conductors, but become electrolytic conductors when mixed, is not rationally explained, other than that dissociation results. Why it takes place we do not know; that some change in the associated energy always takes place we do know. In general, unless some chemical change occurs, solution is accompanied by refrigeration, except in the case of gases. It is probable, then, that some of the heat energy taken from the mixture is concerned in this dissociation.

In the case of fused substances heat may be a considerable factor in dissociation.

The question whence come the electric charges upon the ions is not solved. Whether they are inherent in the molecule and become free by ionization or whether

they result from the work done upon the molecules in dissociation is not known. Some progress has been made towards the solution of the question by Ostwald, who succeeded in measuring the heat energy of ionization in a few cases. This problem is one that should be carefully studied.

An objection to the theory of the existence of free ions in a solution has been urged from the chemical side, namely, that the ions possess different properties from the atoms, or atomic groups. It seemed remarkable that a potassium ion should be capable of existing in water without combining with the oxygen, as would be the case in the ordinary atomic or molecular condition. If we consider, however, that the amount of associated energy in the two conditions is different, it is not difficult to imagine different properties. We know, for instance, that negatively charged zinc will not act on hydrochloric acid; that several elements exist in well-known allotropic conditions, showing quite different properties. We explain this by different amounts of associated energy, which, in some cases, is quite measurable.

The difficulty of applying Ohm's law in the case of Grotthus' and Faraday's theories disappears in case of the dissociation theory; it rather becomes a necessary consequence of it.

Considering now a few phenomena not directly involved in electrolysis, evidence in favor of the dissociation theory may be found.

Substances form solutions when a homogeneous mixture results, the constituents of which can not be separated by mechanical means, the proportion between the parts being continuously variable between certain limits, with a corresponding continuous variation in properties.

According to the state of aggregation of the dissolved substance before solution, energy changes usually become apparent,

either in temperature changes, contraction of the volume, or the like, when solution is affected. As a rule, such energy changes occur in the same sense when solutions of different concentrations are mixed, until a point is reached, with very dilute solutions, when they no longer are observable. The substance in the solution is then very small in amount as compared with the solvent.

It is a well-known fact that when solutions of different concentration are carefully superposed, the molecules of the dissolved substance pass from the more concentrated to the more dilute solution, until finally a uniform degree of concentration is attained, when a condition of kinetic equilibrium is maintained. This diffusion phenomenon in liquids is similar to that in gases, only it progresses much slower. In the case of gases the dynamics of the process is pretty well understood and satisfactorily explained by the kinetic theory, the mixture of the gases resulting from the projectile energy of the molecules. In the case of liquids it has been variously explained; in general, however, the molecular attraction between the solvent and the dissolved substance has been assumed as the cause. Van't Hoff has recently offered an explanation along the same kinetic lines so satisfactorily applied in gases. The force tending to produce diffusion must be measurable as a pressure, if it exist; if then, the two solutions are separated by a semi-permeable membrane which will allow but one of the two constituents to pass, this pressure will become measurable upon the membrane. The production of such semi-permeable septa is a matter of very great difficulty, but has been accomplished to a very perfect degree for some substances. The general method of making such measurements is familiar to all physicists. Traube, Pfeffer, De Vries, Tammen and Pringsheim, from 1867 to 1885, have succeeded in producing semi-permeable membranes of great perfection,

and with improved apparatus have made many measurements of very satisfactory character. These results show, that equimolecular solutions of non-electrolytes show equal osmotic pressures. The osmotic pressure is directly proportional to concentration (expressed in gramme equivalents). The osmotic pressure is proportional to the absolute temperature.

The similarity of these laws to those of gaseous pressure, is at once apparent. Van't Hoff further, upon the bases of absolute measurements and the applications of the ordinary equations for properties of gases, enunciates the laws: That the molecules of the dissolved substance exert pressures in osmotic action, equal to the pressure which would be exerted by the same number of molecules in the gaseous state upon the sides of a containing vessel of the volume of the solution, the temperature remaining the same.

Osmotic pressure seems then to be merely a molecular kinetic effect. On this assumption thermodynamic considerations led to the same result as experiment.

The first two laws of osmotic pressure could be satisfactorily explained under the ordinary supposition of molecular attraction; the last two, however, are difficult to reconcile with any explanation other than the one that the pressure is due to molecular impact.

The osmotic pressure of electrolytes is considerably greater than that of non-electrolytes; in dilute solutions they, however, follow the same laws of variation. In quite a number of binary compounds it is just twice as great numerically as in the non-electrolytes. The behavior is, as though the number of molecules contained in the electrolyte solution per gramme equivalent, was greater than in non-electrolytes. If we imagine that solution has dissociated the molecule into two groups, the anomaly is easily explained. There is evidence here,

independent of electrolytic behavior, that electrolytes are dissociated in solution.

Blagden, as early as 1788, recognized that salts in solution lowered the freezing point of water; his experiments were made mainly on sea water. He found that in very dilute solutions, the lowering of the freezing point was very nearly proportionate to the amount of substance dissolved. Riedorf, Coppett and Raoult carefully studied the subject and found that the molecular depression of the freezing point was equal for salts of similar composition. For non-electrolytes, equimolecular solutions of different salts gave very nearly the same values, showing, that the effect was purely a molecular one independent of the nature of the substance.

The problem may be treated from the dynamical point of view upon this supposition: Knowing the osmotic pressure and imagining the change in state in the nature of a reversible cycle, the necessary energy changes are calculable. The depression of the freezing point calculated in this way for a number of substances gave values closely agreeing with experiment. The evidence that this effect is purely a molecular kinetic process is very strong.

Electrolytes cause a depression of the freezing point, experimentally determined, far greater than non-electrolytes; we have here another evidence of dissociation by solution.

The investigation of the effect of substances in solution upon vapor pressure and boiling point made by Berthelot, Beckmann, Raoult, Ciamician, Ostwald and others lead to precisely similar laws.

We may summarize these laws thus: Equimolecular solutions of different substances made with equal masses of the same solvent, show equal osmotic pressure, equal relative diminution of vapor pressure, equal elevation of boiling point and equal depression of the freezing point.

Electrolytes give greater values than non-electrolytes. The effect is as though there was present a greater number of molecules than indicated by the amount of substance dissolved. Binary compounds in dilute solutions, give nearly twice the numerical values found in solutions of non-electrolytes.

From these experimental results the theory of dissociation of electrolytes by solution and the electrolytic conduction by directing the migrating ions seems very strong.

Chemical evidence can not be reviewed here; the evidence is, however, fully as strong or even stronger than that considered.

Reversing the phenomena of electrolytic decomposition, Nernst applies these concepts to the battery problem. We will apply the theory to one or two simple cases only.

When two solutions of the same electrolyte are brought in contact electrical differences manifest themselves. The mere statement, that the cause for such difference in potential is contact, is unsatisfactory. Nernst reasons in this wise: The ions in virtue of osmotic pressure will diffuse; migrating with different velocities, as shown by Hittorf, they will diffuse at different rates; there will result, therefore, an excess of anions in the one solution and kathions in the other; the ions possessing characteristic electric charges, there will be found an excess of positive electricity in the one solution and an accumulation of negative electricity in the other solution. If an indifferent electrode be immersed in each solution, connected through a conducting circuit, there must result a current. We have here a battery giving an electrical current as a result of osmotic pressure. The necessary conditions for the production of the current are, that the ions have different velocities and exert osmotic pressure; that in solution we have the molecules dissociated or ionized; that the energy associated if current

flows, is less at the close of the operation than at the beginning.

Nernst and Helmholtz calculated the electromotive force for such cells from the experimental data of osmotic pressure and ionic velocities, obtaining results agreeing very well with electrical measurements.

It would, perhaps, be expected from the above that the current would continue until the concentration had become uniform; such, however, will not be the case in the battery just described, for the kathions at the kathode and the anions at the anode will now develop electrostatic attractions which can not be overcome by the electromotive force of the battery.

Modifying the cell so that, in place of indifferent electrodes, we use electrodes of the metal, the salt solutions of which surround it, a battery results which will continue in operation until uniform concentration results. In this case the kathions will, at the kathode, by giving up their electric charges, become metallic, the electrode becoming positively charged; at the anode metallic particles will go into solution as kathions. This ionization involves energy changes. The kathions there produced, carrying positive charges with them, leave the electrode negatively charged.

In a battery, such as described, three differences of potential result; one at the surfaces of the solutions differing in concentration, and a difference of potential between the surfaces of the electrodes and the solution, the first having been explained as originating from osmotic pressure. Nernst explains the latter as resulting from a solution pressure. Just as a liquid evaporates from the surface until the vapor pressure becomes equal to the vaporization tension, so in solution will a salt dissolve until the osmotic pressure becomes equal to the solution tension of the salt. In the same way Nernst supposes that each metal has a tendency to convert atoms of the

metal into ions in solution as soon as it is immersed in an electrolyte; this has been termed electrolytic solution tension. Osmotic pressure and solution tension thus become analogous concepts. Three conditions are possible in the battery cell:

1. If the solution tension be greater than the osmotic pressure the metallic plate acts like a salt mass in a dilute solution. Kathions will be thrown into the solution positively charged, leaving an equal negative charge upon the electrode; at the surface of separation between solution and electrode we shall have positive kathions upon one side and negatively charged metal upon the other, these exerting electrical forces, a condition will be reached when they are equal to the solution tension, further action will then cease until the kathions are discharged or made metallic.

2. If the osmotic and solution pressures are equal, no difference in potential will result; as when a mass of salt is introduced into a saturated solution, of itself no change takes place in equilibrium.

3. When the osmotic pressure is greater than the solution tension, kathions will be projected upon the plate and made metallic, the electrode becoming positively charged and the solution negatively, similar to the action which takes place when a solid salt is brought into contact with a supersaturated solution where salt particles will be deposited.

The determination of the relative values of solution pressures is comparatively simple, the determination of their absolute values very difficult. In the case of mercury and a saturated solution of calcium chloride, the absolute value has been determined with considerable accuracy from the effect upon tension phenomena in the mercury surface, fully discussed by Lippman, Helmholtz and Paschen. Ostwald and Planke obtained, values by two methods based upon this action agreeing very well.

With this value as a basis others have been determined. Applying those values experimentally obtained, together with the ones for osmotic pressure, in calculating the electromotive force of a number of well-known cells, an excellent agreement with experimentally determined values is found.

It will be impossible in this review to apply these theories to the various forms of batteries known, and to many phenomena of electrolysis which we have no space even to mention; the theories briefly reviewed have borne rich fruit in the more satisfactory explanation of electrolytic action. Many problems still remain to be attacked, while some have been but now appreciated.

The development of the solution and dissociation theories gives no explanation of the forces and conditions which cause solution or ionization, though some attempts have been made in this direction. Thus, J. J. Thomson has shown that if the attractions between the ions in the molecule is due to electrical forces it will be weakened, if the molecules be immersed in a medium of high specific inductive capacity. Experimental evidence, in so far as it goes, shows that in liquids of high specific inductive capacity, ionization is most complete. This is one of the problems to be systematically studied.

With the solution of the older problems new ones present themselves. This is the effect of any comprehensive good theory. Many new problems in molecular physics and electrolysis are suggested through Arrhenius's, Van't Hoff's and Nernst's theories. Their development and solution will not be one of chance, however, to be stumbled upon by daring or blind groping, but by intelligent, painstaking research. A bird's-eye view of the field is given us through these theories, in filling in the detail and contours, the chance explorer must give way to the systematic investigator.

Until within the last three or four years,

the systematic and careful amassing of experimental data for building up or verifying these theories, was done by a few European workers, mostly chemists; since Willard Gibbs's theoretical work bearing upon this subject, scarcely a single addition of importance has come from American workers; in fact, it seems that much of the work done abroad is scarcely known to American physicists. It is to be regretted that in the history of the development of this branch of electrical science hardly an American name will appear.

There, however, remains much to be done, and contributions from this side will I trust be made.

Whether electrolytic action ever occurs in solids, is a question which I do not believe has been definitely settled. If such action ever does take place, the theories just considered will have to be modified. Some very curious phenomena in glass, subjected to the action of the electric currents, have been noticed; the claim has been made that glass has actually been electrolyzed, though the evidence so far is not conclusive. The very interesting changes of conductivity with variation in temperature, exhaustively studied by Thomas Gray, indicate molecular changes which may be due to dissociation. The form of the equation for change in conductivity with temperature shows a maximum with reversal, considerably below the fusing point. A similar peculiarity is noticed in alloys. The systematic study of this seems important.

Careful study of heat absorption when salts are dissolved should be made. Much work has been done in this direction. A careful examination and comparison of results, however, convinces one that the methods and manner of conducting the investigation must have been widely different, for the results vary in a most astonishing manner; at any rate, definite conclusions cannot be based upon them. If ionization

requires energy, it is more than likely that some will be taken from the solution in the form of heat. In very dilute solutions dissociation of the electrolyte seems complete, while in concentrated solutions it is incomplete. A careful determination of the heat absorption per molecule, when the salt is dissolved in concentrated or dilute solutions, might give valuable results. The problem is very complicated, yet it should be attacked.

That gases can conduct electrolytically seems fairly certain. This field is scarcely entered and may well be studied.

The peculiar behavior of charged plates under the influence of violet light seems likely to involve electrolytic action and bear upon dissociation questions.

So multitudes of problems suggest themselves, the study of which may tend to crystallize the theories of dissociation and solution, so promising at this time, into more perfect form. It can scarcely be doubted that the remarkable connection, evident when the phenomena of solution, modification of freezing and boiling point, osmotic pressure, optical rotation, chemical equilibrium and stability, metathetical reaction, thermal neutrality, electrical conductivity and electrolysis are considered, taking the molecular equivalent mass as the unit, indicates a very near relationship of these processes. The power of Arrhenius's dissociation theory, Van't Hoff's solution theory, together with the conceptions of Hittorf, Clausius, Nernst and Ostwald in explaining the dynamics of molecular action, is most promising. Whether more accurate and more plentiful quantitative studies of these so closely related phenomena will lead to closer concordance or greater divergence of the numerical values obtained, and thus strengthen or reveal weaknesses in the theories, must remain to be seen.

These theories, if fastened, will have a marked influence both upon the chemical

and physical conceptions of the structure of complex molecules. They seem to demand essentially a condition of kinetic equilibrium between molecules and atoms; inter-atomic distances we shall have to consider greater than was our wont; atomic and molecular influences must extend to considerable distances. Geometrical static arrangement of atoms or groups of atoms seems incompatible with their behavior. The relation of atoms in the molecule seems rather to be orbital, permitting of ready rearrangement and readjustment by relatively slight disturbing causes, capable of returning to former relations promptly, involving various quantities of energy. All our inferences in reference to molecular magnitudes will have to be interpreted as effective merely, and not actual in the sense of space occupied.

The one central pillar upon and about which all physical science is erected to-day, the conservation of energy, stands unchanged and, if possible, more clearly defined and strengthened than ever in these tests.

I repeat, may American physicists take up these problems and add their share to the development of these epoch-making theories.

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THE CORNELL EXPEDITION TO GREENLAND.

THE Cornell party, which accompanied Lieut. Peary on the steamer *Hope*, left Sydney, July 16th, and passed the entire eastern coast of Labrador near the land, with one stop at the island of Turnavik. Entering Hudson Strait a stop of several days was made at Big Island and the neighboring coast of Baffin Land. From here an unsuccessful attempt was made to penetrate the ice which stretched across the mouth of the Cumberland Sound, after

which the ship steamed across to Disco Island, on the Greenland coast. A stop was made there, another in the Vaigat Strait and a third at Umanak. After a brief stop at Upernavik, the party was landed, August 7th, on the Nugsuak peninsula, Latitude $74^{\circ} 7'$, about 80 miles north of Upernavik. The party remained there until September 7th, and then returned, following practically the same route and making nearly the same stops as those made on the northern passage on the Greenland coast. On the American side a stop of two or three days was made in Cumberland Sound, where the conditions closely resemble those in Hudson Strait.

The main object of the expedition was to study the geology of a small area in some detail; but collections of plants, insects, marine invertebrates and birds were also made. In connection with this work considerable dredging was done.

Briefly stated, the principal geological results are as follows: At Turnavik, on the Labrador coast, evidence of recent glaciation is abundant. The hills are all rounded; there has been little post-glacial decay, and the transported boulders, as well as the bed rock, are very fresh. Upon exposed rock faces, unprotected from the weather, glacial striæ are still very distinct. Granting equality of weathering, this region has been much more recently glaciated than regions of similar geological structure in New England. The amount of glacial carving has not been sufficient to lower the surface of the gneiss to the level of the pre-glacial decay in the trap-dike valleys.

Until the northern end of the Labrador peninsula is approached evidence of glaciation in the form of rounded contours is so distinct that it may be seen from a ship several miles from land. At Cape Mugford, Table Mountain and vicinity, in Latitude $58^{\circ} 59'$, the topography changes to the angular type, and this highland portion of the