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ADDRESS OF THE RETIRING PRESIDENT.

RECENT ADVANCES IN THE THEORY OF SOLUTIONS.

BY LAUNCELOT W. ANDREWS.

Ten years ago nothing was known of the molecular magnitudes of substances which could not be converted into the gaseous condition. Concerning the constitution of the much greater number of compounds that exist only as solids or liquids, our ignorance was complete.

Within the period named, a host of investigators, among whom the names of Raoult, Van't Hoff, Nernst, Arrhenius, and Ostwald are the most distinguished, have devoted themselves to studies of the liquid state, and their labors have poured a flood of light into the darkness.

The researches of Raoult may be looked upon as forming the basis of the new movement.

Any study of the liquid state must in the first instance concern itself with the phenomena which limit this state, namely, freezing on the one hand and boiling on the other. It had long been known that, in general, the presence of foreign matter in solution depresses the freezing point of a liquid, and raises its boiling point. Coppet had already paved the way for the quantitative study of the first of these phenomena which Raoult (1886-1888) carried on with great experimental skill and extended to the second.

This investigator, unguided and unbiased by any theory, established the interesting and important fact that the depression of the freezing point of a solvent resulting from the addition of small quantities of a second substance is directly proportional to the number of molecules of the material added, being independent of the kind or weight of these molecules, and that the elevation of boiling point followed the same law. In other words: *first*, the depression of the freezing temperature of a solvent is directly proportional to the amount, and

inversely proportional to the molecular weight of the substance dissolved; *second*, the elevation of the boiling point of a solvent is directly proportional to the amount, and inversely proportional to the molecular weight of the substance dissolved. An important apparent exception to these laws which will be considered later, was found in the case of those substances which are good conductors of the electric current, that is, of electrolytes. The laws were further found to be limited in their application to dilute solutions.

Important as this principle was in furnishing a method for the determination of molecular weight of those compounds, such as the sugars, which can not be converted into vapor, its purely empirical character, and the important apparent exception above stated, prevented for a time its receiving the consideration and acknowledgement which were intrinsically due to it.

It could not meet general acceptance, or be received with confidence until deprived of its empirical character by a general theory connecting the phenomena in question with other known facts, and until its seeming exceptions met a satisfactory explanation.

In due time Van't Hoff enunciated the theory and Arrhenius furnished the explanation.

Raoult's first law may be expressed by the equation

$$m = K | a$$

in which m = the molecular weight of the substance dissolved, a = the *specific depression*, that is the lowering of the freezing temperature due to dissolving one gram of substance in one hundred grams of solvent. K = a constant dependent upon the nature of the solvent only.

Raoult's second law may be expressed by the following similar equation :

$$m = k | E,$$

in which E is the *specific elevation*, or elevation of boiling temperature due to dissolving one gram of substance in one hundred grams of solvent.

Now, Van't Hoff, by means of an imaginary cycle of operations, conceived in analogy with Carnot's famous cycle to which the science of thermodynamics owes so much, showed that the constant, K ; of Raoult's formula must be a function of the temperature and of the heat of fusion of the solvent, of the form

$$K = \frac{2 T^2}{100 L}$$

in which T = the absolute temperature, L = the heat of fusion of the solvent.

For Raoult's second law a similar dependence of the constant upon the temperature and the heat of vaporization was established. To Van't Hoff belongs, therefore, the signal service of bringing the empirical laws of Coppet and Raoult into close connection with the general principles of thermodynamics, from which they are derived as necessary consequences.

This important step greatly stimulated research. Many investigators began to till the field upon which the sod had been so successfully turned; new and convenient methods were devised for the accurate determination of melting and boiling points. In fact, a new technique was developed. An incidental result of this activity is that mercurial thermometers capable of reading to $\frac{1}{1000}$ of a degree centigrade have become articles of commerce. The only compounds whose molecular weights can not be determined by the new methods are the very few which resist solution in all solvents.

It is interesting to note that the numerous molecular weight determinations thus made show that the great majority of substances have the same molecular weights in the liquid as in the gaseous form, but few being more complex, and that most substances not capable of vaporization without decomposition possess, in fact, when in solution, the relatively simple constitution which had previously been assigned to them on insufficient chemical grounds alone. Among the many other valuable results attained may be mentioned the conclusion that the permanganates are salts of the simple acid $H Mn O_4$ and not of the more complex molecule $H_2 Mn_2 O_8$ and that chromic acid exists in solution as dichromic acid $H_2 Cr_2 O_7$. The further conclusion, that most of the true metallic elements resemble mercury in that they consist of monatomic molecules, and differ in this respect from the non-metallic elements whose molecules are complex, has recently been confirmed, in several cases, by vapor density and other independent determinations. The most important theoretical development due to Van't Hoff is the close analogy shown by him to exist between a gas, on the one hand, and a solution on the other. We may summarize the points of analogy as follows:

a. A gas fills uniformly the space to which it is confined. A dissolved substance fills uniformly the space (that is the solvent) to which it is confined. The main difference is that the distribution takes place much more slowly in the second case than in the first.

b. A gas exerts a uniform pressure upon limiting surfaces. A solution exerts a uniform *osmotic* pressure. In both cases we have, at a constant temperature, an analogous relation; for the gas, pressure \times volume = a constant, and for the solution, *osmotic* pressure \times volume = a constant.

c. All gases contain the same number of molecules in the same space at the same temperature and pressure (Avogadro's Law). *All solutions of substances in a given solvent contain the same number of molecules of the dissolved substance in the same space at the same temperature and osmotic pressure* (Van't Hoff's Law). Further, to put the analogy in its most general form, the pressure exerted by a given amount of substance in the state of a gas throughout a given volume is identical with the *osmotic* pressure which the same amount of that substance would exert, or the same number of molecules of any other compound, if dissolved in the given volume of any solvent.

It is to be noted that, as the familiar "Laws" of Boyle and Charles are not valid for high states of condensation of the gases, (in full analogy), the corresponding laws for liquids are only valid for relatively dilute solutions.

The analogy referred to between the gaseous and liquid states is, in a word, not merely a superficial one, useful only for purposes of illustration, but is of such a profound and far-reaching character that all known laws affecting the gases may be directly applied, *mutatis mutandis*, to the liquid state.

From this analogy the laws of Raoult may be derived, the reasoning differing only in form from that previously referred to. Aqueous solutions of salts, acids and bases, in general, all electrolytic solutions constitute an apparent exception to these laws, inasmuch as the indicated molecular weight is much less than that calculated from the ordinary chemical formulæ. Therefore we must conclude, either that the laws of Raoult are not universally valid and that the theory of Van't Hoff is incomplete, or else that, in the case of electrolytic solutions, the ordinary chemical molecules are split up into two or more parts. The latter hypothesis is that adopted by Arrhenius and defended and adopted with such fruitful results under the name

of the Electrolytic Dissociation Theory by its author, together with Nernst and Ostwald.

The main features of the theory may be stated as follows: It assumes that when a salt, such as sodium chloride, is dissolved in water, a certain number of the salt molecules separate into, primarily, two simple parts or ions, in this case sodium and chlorine, charged respectively with positive and negative electricity. These ions are to be thought of as playing the part of new atoms or radicals for the time being, capable of independent motion throughout the solution. This separation or dissociation of molecules into ions is going on continuously and is accompanied by a continuous re-association of ions into molecules. These opposite actions must, when the conditions are constant, ultimately balance one another, the number of molecules dissociated in the unit of time, becoming exactly equal to the number reproduced in the same period from the ions; as in a region of constant population the number of deaths must equal the number of births.

In the solution, this state of equilibrium is reached very rapidly, in fact, as we measure time, instantaneously.

If, in such a solution we plunge a pair of positive and negative electrodes, the previously existing equilibrium will be disturbed, for the negative ions will be attracted to the positive electrode, while the positive ions travel to the negative electrode. As each ion carries its electric charge and deposits it upon the electrode, we have the phenomenon of an electric current passing through the solution. As the ions are thus removed from the solution their place is supplied by fresh dissociation of molecules. It is important to bear in mind that Arrhenius' Theory affords a simple and rational explanation of the fact that those solutions of compounds, which, by methods based on Raoult's law, give results for the molecular weight of the substance dissolved that are below normal, are all capable of electrolysis.

It may be of interest to follow out some of the consequences of the theory and compare them with observed facts. Since both the conductivity of the solution and its departure from Raoult's law are due to the presence of ions, that is to the dissociation of molecules, we might infer that on comparing two salts, one of which gives an aqueous solution of high conductivity and the other low, the latter would nearly conform to Raoult's law, the former not. This is in fact the case. For

example, mercuric chloride gives, in water, a freezing point depression nearly corresponding to its normal molecular weight, and the solution is a very poor conductor, while sodium chloride gives a depression corresponding to nearly half its normal molecular weight, showing a nearly complete dissociation into ions, and the solution is of high electric conductivity.

The conception of an aqueous solution of such a substance as common salt, which presents it to the mind as consisting of separated atoms of sodium and chlorine freely moving about in the water, is so contrary to preconceived notions upon which we were brought up that it is at first difficult to grasp. It must be remembered, however, that the ions, sodium and chlorine, are totally different things from the elements of the same name. The ions are atoms highly charged with electricity, which they lose as soon as they unite, to form molecules or separate in the elemental state.

Moreover the ions, although free, are not independent. It is impossible, for example, to remove, as by diffusion or otherwise, from a solution any number of positive ions without removing a corresponding number of negative ions, because of the attraction due to the powerful opposite charges. The new theory explains clearly many things which were incomprehensible on the old theory of electrolysis. According to the old view, the electric current decomposed the electrolyte. Now, to do this, a certain assignable electro-motive force must be supposed to be necessary. To break any stated bond some definite force must be applied. But, in point of fact, the feeblest electro-motive force will send a current through any electrolyte, and therefore will separate its constituents. There is no critical electro-motive force which must be applied to cause decomposition. The new theory assumes that the electric current does not cause any decomposition at all, but simply moves through space the ions which had already been separated by the act of solution, and to do this the lowest assignable E. M. F. must suffice.

The ratio of the conductivity of a solution to its concentration increases with increasing dilution in such fashion so as to approach a maximum value for infinite dilution. This change in conductivity is a consequence of the fact that the degree of dissociation increases with increasing dilution, so that in the most highly dilute solutions, practically all the molecules of the dissolved substance are in the dissociated condition. The

assumption is made that all ordinary chemical reactions occurring with inconceivable rapidity in solutions are in reality reactions between ions and not between molecules, the latter requiring an appreciable time for reaction. Thus, a solution of sodium chloride gives an immediate precipitate of silver chloride when treated with silver nitrate, whereas, under the same conditions, chloroform, in spite of its much larger percentage of chlorine, gives no reaction; the reason being that the sodium chloride is dissociated and contains chlorine ions, while the chloroform is not dissociated, and therefore contains none. We have, therefore, for the first time, an adequate explanation of the familiar fact that the usual reactions of an element are not manifested by *all* the compounds containing that element.

It would be aside from the purpose of the present paper to discuss in detail the electrolytic dissociation theory. My object has been simply to sketch in the briefest way one of the most recent developments of chemical thought and probably the most important, historically, of the last half of the nineteenth century.

Is there any question as to what reception should be accorded to the new view?

To say of any doctrine or theory, old or new, "It is true," is to assume for human intellect a finality of judgment which it can never possess. To ask, "Is it fruitful?" is the only legitimate question, upon the answer to which every scientific hypothesis must stand or fall. A doctrine that makes possible a more comprehensive grasp of phenomena already known, and serves as a trusty guide to the investigator in the discovery of new facts, does all that any theory can do. It becomes the genuinely scientific man, then, to accept the services of the latest theory so long as it *is* serviceable, much as he would accept the aid of a beast of burden to carry him across a ford, not carpingly or with irrelevant questions as to pedigree or absolute truth, nor with a demand for everlasting life, but gratefully, demanding only that it should have strength to reach the other shore.