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THE USE AND ABUSE OF THE IONIC THEORY[1]

TWENTY-FIVE years have elapsed since Arrhenius advanced the theory that acids, bases and salts in aqueous solution are dissociated into their constituent ions. Now that the storm of contention aroused by this doctine is clearing, it may not be inappropriate to consider in cooler blood this proposition of Arrhenius, to reinspect the foundations, and to weigh without prejudice the pros and cons, the successes and failures of the ionic theory.

To show that an electrolyte in solution suffers a change analogous to dissociation, Arrhenius brought forward evidence of three different kinds. First, he pointed out that the various methods of determining molal concentration in solution (freezing-point, boiling-point, vapor pressure, osmotic pressure), all of which are identical in principle and yield nearly identical results, indicate that in a salt solution the number of molecules dissolved, or less hypothetically the number of mols, is greater than the number calculated from the simple chemical formula of the salt.

The second argument rests upon the observation that in an aqueous solution of a strong electrolyte the properties are purely additive. Thus a dilute solution of hydrochloric acid has no properties which are peculiarly its own. It tastes sour, turns litmus red, dissolves metals, inverts sugar and possesses a number of other well-known properties, all of which are possessed in some degree by every acid. Moreover, it precipitates silver and mercurous salts, and

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[1] Address of chairman of the Section of Physical Chemistry, Baltimore, December 29, 1908.

exhibits other properties which are found in all chloride solutions. In other words, the solution has no properties which are not included in one of two distinct sets, one possessed by all acids, and one by all chlorides. So it seems natural to regard this solution as a mixture of two substances, hydrogen ion, which is present in all acids, and chloride ion, which is present in all chlorides. To illustrate this additive property let me perform this simple and familiar experiment. Here are two solutions in alcohol, one containing cobalt nitrate, the other an equivalent amount of cobalt chloride. One is red, the other a brilliant blue. On pouring these two into equal large volumes of water, the difference in color disappears and both assume the pink color which is typical of aqueous cobalt solutions. Here again are three copper salts, nitrate, chloride and bromide, which in alcohol are respectively blue, green and dark brown, but when poured into equal volumes of water all show the same blue color of the cupric ion.

Finally, the third main argument in favor of ionization is derived from the electrical properties of solutions. Some fifty years ago Clausius believed that the conduction of electricity in electrolytes affords sufficient evidence to show a dissociation into ions. Whether or not we accept this proof, which is perhaps a little metaphysical, other experimental facts such as Kohlrausch's law of the additivity of conductivities at infinite dilutions, the agreement between conclusions drawn from conductivity and transference experiments, and the coincidence in the degree of dissociation calculated from conductivity and from freezing point, all give strong support to the theory of ionic dissociation.

Unfortunately, some over-enthusiastic advocates of the ionic theory, not content with this solid evidence, have superimposed on the theory other extraneous speculations which, when later discredited, have in some quarters brought the parent theory into disrepute. For example, I may mention the *dictum* that all chemical reactions in aqueous solutions are ionic in character, a notion which not only is intrinsically improbable upon theoretical grounds, but has been refuted experimentally by the experiments of Kahlenberg and others. Some too zealous ionists have applied the theory to highly concentrated solutions, without making allowances for the deviations from the laws of the perfect solution which are to be expected there. It would be absurd to class as a dilute solution one which is five or ten times molal, yet we see attempts to apply to a pair such as sodium and potassium nitrates the law of solubility lowering which has been obtained for ideal solutions.

In justice to the author of the ionic theory, it should be noted that he has had no part in these attempts to stretch the theory beyond its elastic limit. In his papers on this subject, brief as they have been, Arrhenius has with great fairness and extraordinary acumen stated, as far as our present limited knowledge permits, the truth, the whole truth, and nothing but the truth about ionic dissociation.

Against the excess of zeal in some advocates of the theory may be balanced the dogmatism of others who for *a priori* reasons have declared it absurd that a substance like potassium chloride, bound together presumably by an enormous affinity, could break spontaneously into its constituent parts. Instead of attempting to refute such circular reasoning, let us return rather to the consideration of that experimental material upon which are based the three main arguments for the ionic theory. Here a careful scrutiny reveals facts which, disconcerting as they may be, no fair advocate of ionic dissociation can afford to ignore.

The first of these unpleasant facts is that the values for the degree of dissociation of strong electrolytes calculated on the one hand from freezing points, and on the other from conductivities, while usually fairly concordant, frequently differ by an amount far greater than the experimental error. For half normal solutions of lithium chloride, magnesium chloride and calcium ferrocyanide, the degrees of dissociation calculated from the freezing points are 94 per cent., 99 per cent. and 2 per cent., while from conductivities we calculate 71 per cent., 62 per cent. and 20 per cent., respectively. Of course these are moderately concentrated solutions and at higher dilutions the discrepancies become less. Moreover, it is not unlikely that the attempts to explain such facts, by assumptions of hydration, association, and the like, may ultimately be successful, but in the meantime these facts can not be neglected.

In the second place, the additivity of the properties of electrolytic solutions, striking as it is, seems to prove too much. If it is an argument for the dissociation of electrolytes, it seems to be an argument for complete dissociation. Why should the properties of a normal solution of potassium chloride be simply those of potassium and chloride ions if, as measurements of conductivity show, it is 25 per cent. undissociated? Why should the undissociated part have no individual properties of its own? It is easy to see why completely dissociated acids and bases should give the same heat of neutralization, since we regard this heat as simply due to the union of hydrogen and hydroxide ions, but half-normal potassium and sodium hydroxides give essentially the same heat of neutralization with an acid, although they are 20 per cent. undissociated. Half-normal barium hydroxide gives the same, although 40 per cent. undissociated. Copper sulphate as dilute as one tenth normal is still more than half undissociated, but its color is nearly the pure color of cupric ion. Indeed in all the strong electrolytes the partial volume, heat capacity, internal energy, viscosity, refractive index, rotary power, in fact practically all the significant physical properties of the undissociated part of the electrolyte, seem practically identical with the properties of the constituent ions. If we had no other criterion for the degree of dissociation, these facts would undoubtedly lead us to regard salts, up to a concentration of normal or half normal, as completely dissociated.

Finally, the phenomena of electrical conduction present several puzzling, and as yet unexplained, features. For example, attention has recently been called to the interesting fact that the two ions which in aqueous solution possess by far the greatest mobility, are the ions of water itself, hydrogen and hydroxide. This might possibly be regarded as chance if it had not also been found that in other solvents a similar condition exists. Thus in methyl alcohol, the methylate ion moves with unusual velocity. To explain this curious fact, it has been suggested that the ions of the solvent have a mode of progress different from that of other ions, due to their ability to pass *virtually* through the molecules of solvent. This view, in a certain sense, requires a return to a modified Grotthus theory, and if accepted, necessitates the conclusion that the process of conduction is not quite so simple as it may have seemed to the original advocates of the ionic theory.

Perhaps the most vulnerable point in the whole armor of the ionist is reached when we attempt to apply the mass law to the dissociation of strong electrolytes. The mass law derived rigorously only for the perfect solution could hardly be expected to be exactly true in the case of actual solutions. We might therefore expect certain small deviations from the mass law, but are in no way prepared for the startling discrepancies which are in fact observed. This discrepancy is sufficiently marked in the case of salts of the simplest type, like potassium nitrate or sodium chloride, but is most striking in the case of some salts of a higher type. The following table gives for three electrolytes the values of the "mass law constant" (*K*) at different molal concentrations (*C*). We see that when the concentration changes one thousand fold, *K* changes one hundred fold in the case of potassium chloride and one million fold in the case of potassium ferrocyanide! For the weak electrolyte, acetic acid, it is a real constant.

Acetic Acid		KCl		$K_4Fe(CN)_6$	
C	*K*	*C*	*K*	*C*	*K*
.001	.00177	.0001	.0075	.0005	.7
.004	.00180	.001	.035	.002	18.0
.01	.00179	.01	.132	.012	1171.0
.02	.00179	.1	.495	.1	41190.0
.1	.00180	1.0	2.22	.4	842100.0

This extraordinary divergence from the mass law, of which I have chosen the most extreme case known in aqueous solution, is, however, found to an even more startling degree in the case of non-aqueous solutions. To the extremely bizarre conductivity curves there obtained few have had the temerity to apply in full the principles derived from the ionic theory. Nevertheless, we are beginning to realize that the phenomena of aqueous solutions are but special instances of the widely varying phenomena occurring in other solvents; and it seems unlikely that a satisfactory understanding of the behavior of aqueous solutions can come except through a careful study of non-aqueous solutions. At present our quantitative knowledge of such solutions is extremely limited, and does not encourage the belief that we have in any sense a final answer to the problem of solutions.

These, then, are some of the weak points of the ionic theory as it stands to-day. If the case were to rest here I am afraid it would be difficult to bring in a verdict for the theory of dissociation. Indeed many scientists, on the basis of such evidence, have decided to close the hearing and to class the ionic theory with other ingenious hypotheses that have failed to stand the test of experience. But these men have not applied the one criterion by which in the end every scientific proposition must be judged—the test of serviceability. After all, what have we said except that the ionic theory is not complete? But perfection is rare in the science of chemistry. Our scientific theories do not, as a rule, spring full-armed from the brow of their creator. They are subject to slow and gradual growth, and we must candidly admit that the ionic theory in its growth has reached the "awkward age." Instead, however, of judging it according to the standard of perfection, let us simply ask what it has accomplished, and what it may accomplish in scientific service.

When we examine a little more critically the unfavorable features which we have mentioned, we find that they enter chiefly in the application of the theory to strong electrolytes. If we consider the weak electrolytes, like ammonia, acetic acid and most of the organic substances, of which a large number have been investigated, we find a remarkably satisfactory state of affairs. For these the mass law has generally been shown to hold with remarkable accuracy. Indeed it is hardly too much to say that every prediction from the ionic theory has been quantitatively verified for all the weak electrolytes which have been carefully investigated. The degrees of dissociation obtained in different ways are in complete accord; the properties are additive only just in as far as the electrolytes are ionized; the electrical properties seem entirely normal. Here, then, is an enormous field in which the whole theory of Arrhenius may be quantitatively applied, with perfect safety, to a wide variety of problems.

Again, in the case of strong electrolytes at high dilution, the theory of ionic dissociation is completely in accord with all known facts. The agreement between transference numbers measured directly and those calculated from the conductivities at infinite dilution is eminently satisfactory. There can hardly be any question that with increasing dilution the ratio of the molal concentration to that calculated when no dissociation is assumed approaches just two for binary, and just three for ternary salts. Is there any other hypothesis which will account for this cardinal fact?

Any valid criticism of the ionic theory must, therefore, be based upon its application to solutions of strong electrolytes at moderately high concentrations. Here the problem is unquestionably one of great difficulty. Even the simple question of determining the true degree of dissociation is one which still permits much divergence of opinion. One of the suggestions which has been made to account for some of the anomalies of the strong electrolytes is that, owing to the change in the mobility of the ions with the concentration, the conductivity is not a correct measure of the degree of dissociation. In some cases, especially in the case of the hydrogen ion, this supposition has indeed been definitely verified. Yet in the majority of cases it seems very unlikely that we may thus explain the extraordinary discrepancies such as those that I have pointed out in the application of the mass law to strong electrolytes. I have shown in another place that while conductivity may not indeed be an absolutely reliable measure of the concentration of the ions, it furnishes, nevertheless, the only way that we have of determining them. Every other method which has been used gives a measure, not of the real concentration, but rather of the escaping tendency, or activity, which may not in all cases be proportional to the concentration. I believe that we shall make no great error in assuming that the degree of dissociation calculated from the conductivities is in most cases substantially correct and that the lack of fulfilment of the requirements of the mass law for strong electrolytes is due to deviation of one or more of the dissolved substances from the laws of the perfect solution. This assumption is by no means inherently improbable. In fact, in the case of many non-electrolytes we find marked deviations from the ideal laws even at small concentrations.

If we must conclude that one of the substances present in a solution of an electrolyte is abnormal in its behavior, we are inclined at first to suspect the ions, which on account of their peculiar electrical condition might be expected to differ materially from ordinary substances. But this view proves to be untenable. As far as we can judge, the ions seem to obey, at least to a fair degree of approximation, the laws of the perfect solution, and thus we are forced to place the responsibility for the observed anomalies chiefly upon the undissociated part of the electrolyte.

The correctness of this idea may be tested by applying the simple laws of solutions to those cases where the properties of the undissociated substances may be eliminated from consideration. Every such test, which our present experimental material permits, substantiates this hypothesis. Thus, for example, when we consider the equilibrium between a dissolved salt and the ions in its saturated solution we need not consider the undissociated portion. Assuming that the ions are normal in behavior, we are led at once to the principle of the constancy of the solubility product, the substantial correctness of which has been demonstrated by the experiments of Noyes, and the more recent work of Stieglitz. An entirely similar method which depended upon the elimination of the undissociated electrolyte was employed by Rothmund in his study of the dissociation of picric acid.

Another deduction which is similarly justified is that the product of the hydrogen and hydroxide ion concentrations is a constant, in any dilute aqueous solution, and this important constant has been obtained by several independent methods, all in excellent agreement. Finally the Nernst equation for the electromotive force of a concentration cell gives very satisfactory results when we consider only the ion concentrations. If, however, we apply an equation similarly obtained to the undissociated portion of the electrolyte we obtain results which are by no means corroborated by experiment.

A few years ago I had occasion to make a calculation which involved simultaneously the application of all the principles which I have just enumerated, the Nernst equation, the solubility product, the dissociation constant of water. By the aid of these it was possible to calculate from the decomposition pressure of silver oxide the potential of the oxygen electrode. The potential thus obtained differed more than one tenth of a volt from the value previously accepted, but was in perfect agreement with the results of the independent investigations published during the same year by Haber and by Nernst. The calculation would obviously have been vitiated if any one of the principles used had been unreliable.

To review the service rendered by these simple generalizations deduced from the ionic theory would be to summarize a very considerable part of the exact work in physical chemistry published during the past two decades. In the study of chemical equilibrium and reaction velocity, especially in the process of rationalizing quantitative analysis, these principles are of daily service.

While therefore many difficult problems relating to the application of the ionic theory remain to be solved, this theory must even at the present time be regarded as established on a sound working basis. Advance will come through the exact quantitative study of the properties of aqueous, and especially of non-aqueous, solutions. After this work is completed it is not improbable that our views of the nature of solutions will be greatly changed, but I venture to predict that the later and better theories will not be substitutes for, but rather developments of, the simple hypothesis of Arrhenius.

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THE COLLEGES OF THE UNITED STATES AND THE CAMPAIGN AGAINST TUBERCULOSIS[1]

THE colleges and universities of the United States are social forces of such power that the campaign against tuberculosis can not ignore them: it needs their help, it seeks to enlist them among its strongest allies. And the campaign is so reasonable, so timely, and already so efficient, that it may confidently expect the cooperation of the colleges of the country, as, indeed, it depends on the cooperation of all intelligent men and women interested in the betterment of man.

First in importance among the aids which the higher schools are giving is perhaps the investigation of fundamental

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[1] Read before the International Congress on Tuberculosis, Washington, D. C.