THE COMING OF AGE OF THE INTERIONIC ATTRACTION THEORY[1]

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In April, 1912, Milner (34) published his paper entitled "The Virial of a Mixture of Ions," and in May, 1923, Debye and Hückel (11) published their first paper, "Zur Theorie der Elektrolyte." So this meeting falls very close to the tenth and the twenty-first anniversaries of the two most important events in the theoretical study of interionic attraction. If the first publication of a quantitative relation may be considered as the birth of a theory, the interionic attraction theory comes of age next month. The present occasion is then a very fitting one to stop and consider just what this adolescent theory is, what it has already accomplished, what may be expected of it in the future, and what our attitude toward it is to be.

To judge any theory we must consider its predecessors and important contemporaries. In this case we need not go back very far into history, but we may start in 1885 with the two theories introduced in the first great papers of Arrhenius (2). The first, the theory of "ionic dissociation," states that the ions are not formed by the electrical field but exist in considerable quantities in electrolyte solutions in the absence of any external electrical force. This theory has been the basis of all subsequent studies in this field, and every new development has confirmed it. The second theory states that dissolved electrolytes are sharply divided into two parts without transition stages: the ions, which are entirely independent of each other and behave as ideal solutes;

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and the undissociated molecules, in which two or more ions are so tightly held together that they behave as a single ideal solute molecule. This is generally known as the theory of "partial ionic dissociation." The theory is quite symmetrical, however, and we, who are no longer shocked at the idea of free ions, might equally well call it the theory of "partial association." Although it has not at all the standing of the first theory, it has been much more emphasized for the reason that it leads to important quantitative conclusions. Its successes have been so great in many cases that its failures in others were glossed over.

In 1900 van Laar (32, see also 31) showed that, on account of the strong electrostatic forces between ions, they can not be expected to be independent and to behave as ideal solutes. His theory did not attract enough attention to receive a name. Since it denied the existence of completely independent ions we may call it the theory of "complete association." Later Sutherland (53) and Bjerrum (3) emphasized this point of view, and claimed further that the electrostatic action was enough to account for all the behavior of "strong electrolytes," so that they denied also the existence of un-ionized molecules of the electrolyte. Possibly because it seemed more susceptible to experimental proof, this second conclusion has been so much stressed that the whole theory has been called the theory of "complete dissociation." It is interesting to imagine how different the reception would have been had the emphasis been kept on van Laar's more fundamental idea and the name "complete association" given to the theory.

What was the American attitude at this time? For then American physical chemists formed a compact enough group so that they might be said to have an attitude. They came close to accepting the theory of complete ionization even before Sutherland and Bjerrum. How near can best be shown by quoting from an address given by A. A. Noyes in 1904 (36). "Thus the experimental data fully warrant the statement of the principle that *the optical activity and the color of salts in solution, when referred to equivalent quantities, are independent of the concentration and therefore of the degree of ionization of the salts and are additive with respect to the properties of the constituent ions even up to concentrations where a large proportion of the salt is in the un-ionized state.*"

We shall skip the presentation of experimental data familiar to all of you, but then continue to quote, "If there were no other evidence to the contrary, the existence of this general principle, which is also applicable to many other properties, would almost warrant the conclusion that the salts are completely ionized up to the concentration in question, and that the decrease in conductivity is due merely to a change in migration velocity. But in view of the apparently conclusive evidence against such a hypothesis, we can only conclude that the form of union represented by the un-ionized molecules of salts differs essentially from ordinary chemical combination, it being so much less intimate that the ions still exhibit their characteristic properties, in so far as these are not dependent upon their existence as separate aggregates."

By sufficiently emphasizing "separate aggregates" we might read much into that last sentence, but we shall merely note that the American physical chemists stuck to sane middle ground, accepted neither complete ionization nor a partial ionization measurable by conductance, and devoted their attention to the collection of experimental data and to the development of a rigorous thermodynamics independent of any particular picture. Van Laar was also doing the latter, but while van Laar argued, the Americans taught. In particular, Lewis, by developing rigorous equations which took the same form as the inexact ones of the Arrhenius-van't Hoff theories, developed a large audience capable of applying thermodynamics and understanding solution theories.

The theory of interionic attraction was born into a world most of which accepted without any question the theories of Arrhenius and van't Hoff as developed by Ostwald and Nernst. For eleven years the new theory was a feeble and awkward child. Its father thought well of it, but no one else paid it much attention except on one occasion, and then the attention paid was far from favorable. Almost every child passes through a period of rather obnoxious publicity-seeking when it first discovers that certain words can shock the adult ear. Our young theory was no exception. In its sixth year it passed through what we may call the "swear-word episode" or the Ghosh theory (23).

Then at eleven years there was a sudden change from the feeble, awkward child to an elegant, graceful, and powerful youth. The paper of Debye and Hückel is a much more important event in the life of the interionic attraction theory than its birth itself. Since then the growth has been so rapid and in so many directions that we shall not attempt to be chronological in the rest of our description.

Let us stop first to consider how an electrolyte solution differs from one containing only non-electrolytes. The first difference is that the forces between ions fall off much less rapidly with the distance than forces between neutral molecules; and the second is the duality of an electrolyte solution,—the fact that positive and negative ions must always exist together, and in such quantities that the total amount of negative electricity is the same as the total amount of positive. If any ion is isolated from the rest, the solution is divided into two parts with charges of equal magnitudes but of opposite signs. The first problem of the interionic attraction theory is to determine the distribution of that charge

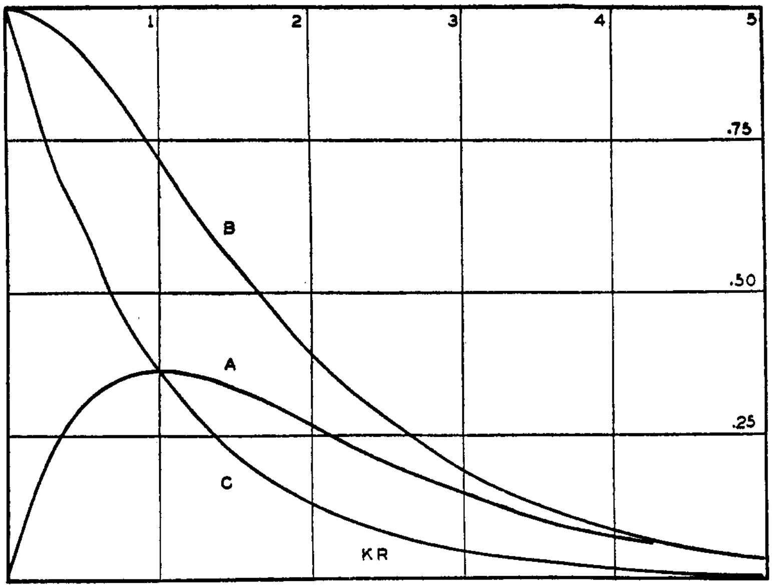

FIG. 1. AVERAGE DISTRIBUTION OF ION ATMOSPHERE

which is not located in the central ion, the charge which Debye calls the "ion atmosphere." It cannot be uniformly distributed throughout space because the total charge, including the central ion, must be uniform. However, it is not closely packed around the central ion.

The average distribution of the ion atmosphere as determined from Debye theory is shown in figure 1, in which the abscissas are the distances from the center of the central ion. For Curve A the ordinates are the fraction of the ion atmosphere contained in a spherical shell of radius R divided by the thickness of the shell. For Curve B the ordinates are the fraction of the ion atmosphere farther from the central ion than R. These are not merely illustrative curves. According to the Debye-Hückel approximation they hold for all values of the concentration, provided that, when the ion atmosphere cannot approach closer than a distance a to the central ion, the unit ordinate for both curves is the value of the B curve for $R = a$, and also that the abscissas be measured as κR, that is, that the unit of length is $1/\kappa$, where κ is the well-known Debye-Hückel function[2]

$$\kappa = \frac{8\pi N\epsilon^2}{1000DkT}\mu$$

The most appropriate measure of the thickness of the ionic atmosphere is the distance at which the A curve reaches its maximum, for more of the ionic atmosphere is there than anywhere else. This distance is $1/\kappa$. We see, however, that almost three-quarters of the atmosphere is at a still greater distance from the central ion. A charge near the central ion has, of course, a greater effect on the potential of the central ion than an equal charge further away. The C curve shows the fraction of the effect of the ion atmosphere on the potential at the central ion produced by that part of the atmosphere farther away than R. This is also accurate for all concentrations provided that the unit ordinate is the value at $R = a$, which is the same in this case as

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[2] N is Avogadro's number, ϵ the electronic charge, D the dielectric constant, k the Boltzmann constant, T the absolute temperature, and μ the ionic strength in moles per liter.

measuring from the inner edge of the ion atmosphere. The contributions of the neighboring parts are relatively large, but there is still an important share contributed by the distant parts of the atmosphere. As the concentration approaches zero this diagram spreads out in terms of real distances, so that the fraction of the effect produced by the atmosphere within any measurable distance is immeasurably small. It is this effect of far distant molecules, particularly at very small concentrations, which makes electrolyte solutions so different from those containing only non-electrolytes.

Curve C, if turned upside down and mirror-imaged to negative values of R, also shows the potential energy of the central ion due to its atmosphere. We see at once that the removal of the central ion from its equilibrium position requires work. Let us imagine the central ion to be suddenly obliterated. The ion atmosphere would gradually melt away. The time in which the potential of the atmosphere at its center would fall to 1/e'th part of its original value is called the time of relaxation. It depends upon the mobility of the ions and also upon the distances they have to travel, that is, upon the thickness of the ion atmosphere.

Those effects which depend upon the motion of the ions can be calculated from these two properties of the ion atmosphere—its thickness and its time of relaxation. The first of such effects to studied was the conductance. According to the original treatment of Debye and Hückel (12), or to the correction and extension of Onsager (37), the equivalent conductance decreases with increasing concentration for two reasons. The first, called the time of relaxation effect, comes from the fact that the ion atmosphere of a moving ion always lags behind, so that ahead there is always too little of the opposite charge for equilibrium, and behind there is always too much. The second, called the cataphoresis effect, arises from the fact that the ion must move through a medium bearing the opposite charge and therefore moving in the opposite direction. The success with which this picture explains the experimentally measured conductances in dilute solutions will be treated by other contributors to this symposium.

We shall take time, however, to consider the relation of conductance to frequency and to field strength. When an ion reverses its direction due to the reversal of the external field, its motion is aided by the dissymmetry of the atmosphere rather than hindered. As the frequency increases, the gain at the beginning of each tack compensates for more and more of the loss at the end until, when the frequency is great enough, the ion oscillates about its equilibrium position so rapidly that the ion atmosphere helps as much as it hinders, and the time of relaxation decrease in the equivalent conductance disappears. Since the ion atmosphere is always present, the cataphoretic effect is unchanged. The experimental measurements (45, 46) not only show the qualitative effect predicted by Debye and Falkenhagen (17), but they agree quantitatively with the theory as to the magnitude of the effect and the frequency at which it appears. There is also a phase difference between the potential and the current which appears to macroscopic measuring instruments as an increase in the dielectric constant, which is also predicted by the theory as to both magnitude and dependence upon the frequency.

If an ion moves fast enough it may escape completely from its ion atmosphere, so that both causes of diminished mobility disappear and the equivalent conductance approaches that at zero concentration. The rate of change of mobility with changing speed, that is, with changing field strength, also depends upon the time of relaxation. The measurements of Wien (55) are explained by the calculations from the Debye theory (28). It was hoped that such measurements would give an opportunity of distinguishing between incomplete ionization and the physical interionic attraction, but it appears from the measurements with weak acids (57) that the high fields used can also change the ionization equilibrium.

The viscosity is found to increase as a linear function of the square root of the concentration with a factor depending on the thickness of the ionic atmosphere and its time of relaxation (19, 20), and the most accurate experimental measurements check quantitatively. A similar effect has been calculated for the diffusion of ions (38), but no comparison has been made with experiment.

It is possible to adopt a point of view so strictly chemical as to take no interest in the foregoing properties because they have no influence on chemical equilibria or reaction rates. Even then these results must be considered important on account of the confirmation they give of the Debye picture of the ion atmosphere. Many theories can account for a decrease with increasing concentration of the equivalent conductance and the activity coefficient. Up to the present the theory of a diffuse ion atmosphere is the only one which has accounted for the proportionality to the square root of the concentration; the fact that this theory gives the proportionality constant accurately in both cases is a strong confirmation of its essential correctness; the fact that it also accounts quantitatively for the time effects by taking into account the mobility of the ions and the distances they must travel seems practically conclusive, and gives us much greater assurance in making use of the picture for equilibrium relations.

These equilibrium relations depend upon the thickness of the ionic atmosphere but not upon the time of relaxation; so they are independent of the mobility of the ions. Debye and Hückel showed that in very dilute solutions the change in the electrical contribution to the chemical potential of a salt is proportional to the square root of the ionic strength with a proportionality factor depending only on the temperature, dielectric constant of the solvent, and the valence of the ions. They calculated the effect on the properties which are directly determined by the chemical potentials (or activities) of the salt and the solvent.

Their treatment has been extended to other properties which can be calculated from the variation of the chemical potentials with external conditions: the heat of dilution, for which the proportionality factor depends also on the temperature coefficients of the dielectric constant and of the volume (26, 4, 1, 33, 22, 46); the heat capacity, which depends also on the second temperature coefficients of these variables (39, 10); and the change of volume on dilution, which depends upon the change in chemical potential and upon the pressure coefficients of the dielectric constant and the volume (40, 41). It has also been applied to the surface tensions of salt solutions (54), but those results need reconsideration. The equilibrium properties, applied to steady state conditions, have also been applied to the rates of reactions involving ions (7, 8, see also 50).

Most of these applications will be considered in the papers which follow. We shall content ourselves with noting that the measurements of properties which depend directly upon the chemical potential agree well with the theory, but that the square-root limiting law holds only for small concentrations. As other coefficients are introduced, the theoretical calculations become less certain, and the measurements in dilute solutions less accurate; apparently the deviations from the calculated limiting slope also become greater, and the square-root limiting law appears to hold to higher concentrations.

The later developments which are concerned with the limiting law are attempts to show that the lack of generality of the original treatment does not affect its conclusions. Debye and Hückel treated a model in which the ions are regarded as rigid spheres, all of the same size, differing from the solvent only in the possession of a charge, and not polarizing the solvent around them; their treatment depends upon the expansion of an exponential in a power series and dropping all but the first two terms, and upon rather unorthodox statistical mechanics. Kramers (30), Fowler (21), and van Rysselberghe (44) have attempted to apply more orthodox methods, and their results indicate that the square-root term is unaffected. Gronwall, La Mer, and Sandved (24) show that the use of the complete exponential does not change the square-root term. Debye and Pauling (15) eliminate polarization as a disturbing factor; and Kirkwood and I show that neither unequal size (48) nor lack of spherical symmetry (49) affect the square-root term. The theoretical as well as the experimental evidence for the quantitative correctness of the limiting law has grown continually stronger.

It seems to me that at present the greatest interest is in the more concentrated solutions. No attempt has been made to extend the theory of non-reversible effects beyond the square-root term. On the other hand, the original Debye-Hückel treatment of equilibrium effects showed how the ratio to the square root of the concentration of the non-ideal part of the chemical potential should decrease with increasing concentration, the more rapidly the larger the ions. It was soon found experimentally that many solutions show a much less rapid decrease or even an increase of this ratio. Two explanations have been offered. The first is incomplete ionization. Probably all of us will agree that this is the correct explanation for weak acids and bases, but in general it is not satisfactory. The second method of explanation is to take into account the error of the simple Debye-Hückel picture for close distances of approach of the ions. Stopping the series expansion with the second term as they do is equivalent to assuming that the average total concentration is independent of the distance from the central ion. Figure 2 shows the total number of ions in each spherical shell and the difference between the numbers of negative and of positive ions, first as calculated by the Debye-Hückel approximation, and second as given by the complete exponential at the limit of zero concentration, which

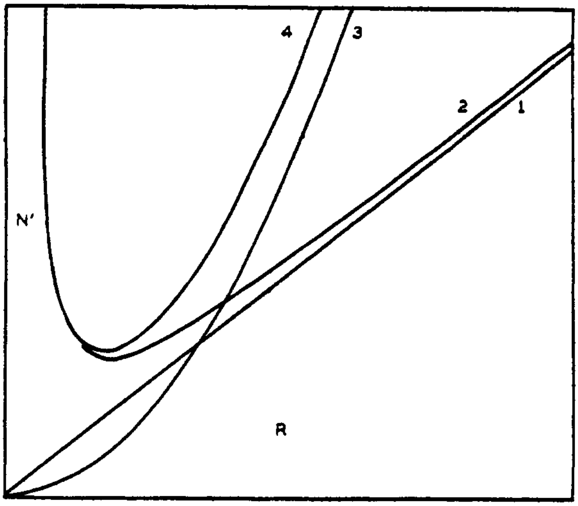

FIG. 2. ION ATMOSPHERE NEAR CENTRAL ION

also gives the approximate distribution for any small concentration. For very close approach the first approximation is seriously in error. Comparing this figure with figure 1 we see that the reason this error does not affect the limiting law is that in figure 2 the distances are in absolute units, so that for small concentrations this figure represents a slice of negligible thickness from the left side of the first.

Bjerrum (5) was the first to undertake the solution of this problem. He notes that the number of ions in the spherical shells near the minimum in the distribution curve must be very small. When the total concentration is small it is probable that, when one ion is closer than this minimum, all the other ions will be so far away that they may be considered equidistant from the first two. Then a second approximation can be made by treating the number of such pairs by the law of mass action. Bjerrum found that the result depends very little upon just where the outer limit to the pairs is placed, but that it is very sensitive to the inner limit. The correction to the first approximation is very small until the lower limit is half the distance to the minimum. It is interesting to note that this is only one-quarter the distance within which the first approximation gives a negative concentration of ions of the same sign as the central ion, showing that the accuracy of an approximation may be very different for different properties. Bjerrum entitled his paper "Ion Association," and his result has the same form as that for compound formation between the ions. As a consequence many have confused his treatment with incomplete ionization. The application of the law of mass action depends not at all upon the existence as a chemical compound of the ions treated as a pair. It might equally well have been used to determine the number of pairs whose separation is between nine and ten times the equilibrium distance. That the association treated by Bjerrum is part of the general association of electrostatic interionic attraction is shown by the fact that the extent of it depends upon the ionic charge, size, and concentration, the dielectric constant of the solvent and the temperature, but upon nothing else.

Müller (35) attacked the same problem by graphic approximation of the unexpanded exponential. Gronwall and La Mer (24, 25) give an analytical solution to the third approximation of a problem differing from the required one only in the fluctuation terms. The three methods give answers which are practically identical. Although the more physical method of Bjerrum lends itself better to qualitative exposition, there is no question but that the Gronwall-La Mer treatment is to be preferred for quantitative calculation with binary salts, where the convergence is rapid. With unsymmetrical salts there might be an advantage in using the analytical results for the symmetrical case with a theorem of Bjerrum that the electrical contribution to the mean chemical potential of the ions is the same for all solutions for which κa and (z_+z_-/kTa) are the same. For the case where there are two types of ions of the same sign but different sizes there is no solution other than the use of such a theorem.

The calculation of these correcting terms gives a quantitative answer to two criticisms which have been raised against the interionic attraction theory. The first is that at small distances from the central ion the electrical density demanded is greater than the total ion density. We have seen that the correction needed on this account is very small up to distances only one-quarter of that at which the difficulty begins, and it is probable that the correction is calculated to a good approximation even to much smaller distances. The second criticism is that it must be erroneous to use the dielectric constant of the solvent to calculate the mutual energy of two molecules so close together that there are no solvent molecules between them: actually such a calculation leads to only a small error whose effect would be to change slightly the number of pairs close together and so change a little the interpretation to be given to the distance a.

The limiting law and the modification of it at higher concentrations depending upon the size of the ions, including the higher term corrections, we will call the charge-charge effects, because they are calculated upon the assumption that an ion differs from the same volume of the solvent only in the possession of its charge.

Another class of solutions shows a decrease with increasing concentration of the ratio of the non-ideal part of the chemical potential to the square root of the concentration much greater than that calculated by Debye and Hückel. In many cases the non-ideal term even passes through a minimum and then increases to a large positive value. This also has received both physical and chemical explanations. The chemical explanation is that the ions are solvated. The physical explanation is that there is a mutual energy of ions and neutral molecules which can be expressed in terms of the charge and size of the ions and the dielectric constant and volume of the neutral molecules. Debye (13) modified his original derivation of the chemical potential from the electrostatic potential to avoid an error copied from Milner. The new treatment reduces for zero concentration to the form of Born's result (16) for the transfer of an ion from a vacuum to a solution. Debye and McAulay (14, see also 16) have applied this same treatment to ions in mixtures of non-electrolytes with different dielectric constants to explain salting-out effects, and Hückel (27, see also 48) extended the treatment to the action of ions on each other. Since this effect depends upon the charge of an ion and the dielectric properties of another molecule, which may be charged or uncharged, we will call it the charge-molecule effect. Kirkwood has developed the treatment given in our joint paper to obtain a solution for a spherical molecule with any distribution of charges which will reduce many charge-molecule effects to the same basis as the Debye-Hückel approximation for charge-charge effects and should be very useful for unsymmetrical ions. Unfortunately this was done too late for inclusion in this symposium.

Even for symmetrical monatomic ions the properties at high concentrations are very far from being additive for the ions (18). To explain this fact it is necessary to include a third effect. The most probable one is the same type of behavior as that shown by a mixture of non-electrolytes. If the rare gases were soluble enough in water we should expect them to show positive deviations from Raoult's law proportional to the squares of their molal volumes (47). The rare gas type ions appear to show this effect, and for two large ions it is large relative to the electrical effects at moderate concentrations (48). It corresponds to an activity coefficient decreasing with increasing ion concentration. More complex ions, particularly in non-aqueous solvents, might show an increase. We shall call this the molecule-molecule effect because it does not depend at all upon the ionic charges. The theory that such effects are chemical in nature has also been upheld strenuously, but it is now generally abandoned for non-electrolyte mixtures.

We have seen that much of the behavior of ionic solutions may be explained in either of two ways,—chemical or physical. For all effects which depend upon close approach they may be regarded as two ways of looking at the same thing. The simple chemical picture assumes that two molecules which interact with each other to form a compound do not react with a third molecule; the simple physical picture assumes that each interacts with the third as though the other were not there. Generally the truth lies somewhere between the two and may be approximated by improvements on either. For most ionic solutions it appears that the truth lies so much nearer to the simple physical picture that the chemical picture may be objected to as giving a distorted view. Certainly it may be criticized as giving a hazy and indefinite view. This is partly because we have no definition of a simple molecule such that we know what one is in a liquid, and partly because no attempt has been made to correlate the extent of compound formation with any other properties of the reactants. Under these circumstances chemical association is merely another word for an activity coefficient decreasing with increasing concentration, and solvation another word for activity coefficient increasing with increasing concentration. In the present state of knowledge it is greatly to be recommended that, in liquid solutions at least, chemical action be used as an explanation only for effects which cannot be accounted for in other ways.

The other classification seems to me to lead to positive results. It is convenient to think of an ion as an electrical charge superimposed upon a neutral molecule, which acts like other molecules except as its behavior is modified by the fact that it must always accompany the charge. It is certain that non-electrolyte mixtures deviate from the laws of ideal solutions, and that the forces which cause these deviations persist in electrolyte solutions. It is equally certain that, when ions are introduced, new forces come into play which lead to the salting in or salting out of non-electrolytes, and another set of forces which lead to the salting in of ions. We have labelled these three classes: molecule-molecule, charge-molecule, charge-charge.

There appear to be three ways to determine to which class a given effect belongs. The first method is to compare the measured value of some property with that calculated theoretically over a range of concentration of a single substance. The difficulties are that, aside from the square-root limiting law, each of the three classes has the same general behavior: each is proportional to the concentration multiplied by a function which decreases rather slowly with increasing concentration; the form of each function is not very accurately determined because of the approximations which must be introduced; and each depends upon at least one parameter difficult to determine independently. In spite of these difficulties it would be possible, with a slight modification of a method already used (48), to obtain very fair results for the chemical potential of any alkali halide in aqueous solution without using a single measurement on any of these solutions. The method appears less satisfactory for those ions which do not have the noble gas structure, and probably for solvents with a lower dielectric constant than water. The simple methods used thus far are entirely inadequate to account for the behavior of those cases where a proton may shift from one molecule to another, that is, for weak acids and bases. However it is poor science to ignore an effect because we do not know how to calculate it accurately, and we should recognize that all three effects are always present.

The second method is to make the comparison with the same effect for several compounds, preferably including the theoretical calculations. It is desirable that the compounds should be simple enough so that some of their properties may be determined in other ways. This was the method adopted for the study of the alkali halides discussed above. Later in the symposium Prentiss and I are attempting to make a purely objective study of some dilute solutions from this point of view.

The third method is to compare two or more properties of the same solution, for example the change in partial free energy and the corresponding heat content, or the change in free energy and its temperature coefficient. For the charge-charge effect in aqueous solutions the free energy and heat content changes have opposite signs in the limiting law. If the collision diameter is independent of the temperature, the ratio of heat content to free energy increases for the higher terms, and it is physically improbable that the diameter ever changes rapidly enough with increasing temperature to decrease the ratio greatly.

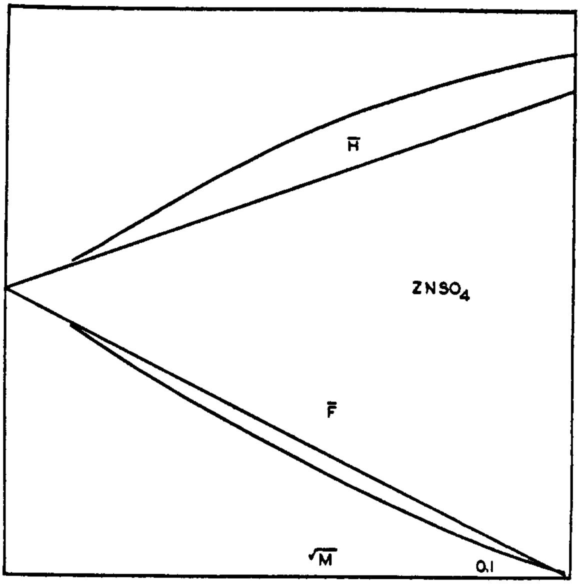

FIG. 3. PARTIAL FREE ENERGIES AND HEAT CONTENTS OF ZINC SULFATE

Theoretically the charge-molecule effect should give a free energy change nearly proportional to the temperature, the ratio decreasing or increasing slightly depending on the change of dielectric constant with the temperature. Experimentally we know that the salting out of non-electrolytes is almost independent of the temperature, increasing slightly in some cases and decreasing in others. Then the heat content change is almost zero.

The molecule-molecule effect can be treated only empirically. For non-electrolyte mixtures we know that the non-ideal free energy change is either nearly independent of the temperature or decreases with increasing temperature; that the heat content change has the same sign as the free energy change and is equal to it in magnitude or larger. This corresponds to the old rule that all dissociations increase with increasing temperature.

Figure 3 shows the two properties for very dilute zinc sulfate solutions (9, 10). It is clear that these meet our specifications for a charge-charge effect, though this appears to be no longer true in more concentrated solutions.

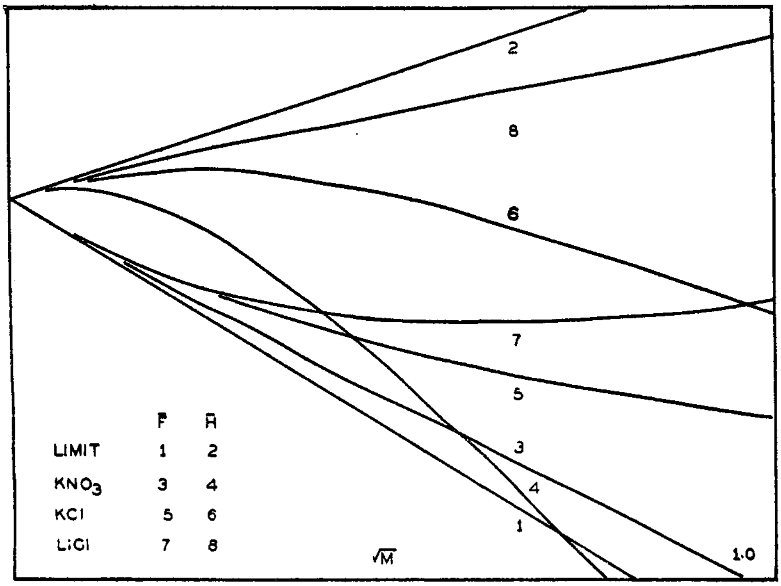

FIG. 4. PARTIAL FREE ENERGIES AND HEAT CONTENTS OF SOME 1-1 SALTS

Figure 4 shows the corresponding effects for three uni-univalent salts. In the more concentrated solutions these must be taken as merely illustrative, for the free energy change is measured at the freezing point (51, 52), and the heat content change at 18°C. (42). For potassium nitrate, the limiting law appears of course as a charge-charge effect, but beyond that the heat content change is also negative and so much larger than the free energy change that the two curves cross. There is obviously a very large molecule-molecule effect. The great excess of heat content over free energy may be explained by a charge-molecule effect of the opposite sign, which contributes to the free energy but not to the heat content.

The fact that there are at least three factors is shown clearly by the lithium chloride and potassium chloride curves. The heat content curve for lithium chloride and the free energy curve for potassium chloride are approximately what we should calculate for the charge-charge effect for either. Then the molecule-molecule effect must be small for lithium chloride, but the great difference in the free energy curve shows a large charge-molecule effect. For potassium chloride on the other hand, the molecule-molecule and charge-molecule effects nearly balance in the free energy change, but the large molecule-molecule effect shown by the heat content change indicates that the charge-molecule effect must also be large.

It is interesting to see how weak acids and bases fit into this classification. The dissociation constants are nearly independent of the temperature, often passing through a maximum between 0°C. and 100°C. That means that the free energy change is nearly proportional to the temperature, and that the heat content change is nearly zero. We should then classify it as a charge-molecule effect, or better as a mixture, perhaps of all three, in which the charge-charge and molecule-molecule effects almost cancel in the heat content change.

It is too early to insist that this classification will be useful in all cases, but there is no question that these results do show the existence of at least three factors. Perhaps the most obvious point to be drawn is that the problem is a very complex one and must be attacked from every possible point of view. It seems to me that very interesting results might be obtained from precision measurements of conductance and its temperature coefficient. There are such measurements, but I find none of great precision. The charge-molecule effects appear not to influence the conductance greatly, but it should be possible to distinguish between charge-charge and molecule-molecule effects. Rudolphi (43) in 1895 suggested an equation which contains the first square-root limiting law for the conductance of strong electrolytes, and classified the salts into those which give constants decreasing with the temperature and those whose constants are practically unchanged. I question whether it would be worth while to analyze existing data by modern methods, but it does seem that advantage should be taken of the great precision now obtainable in conductance measurements.

I have tried to make the story of the past and present of the interionic attraction theory a portrayal of ideas. In so brief a survey of a large field it has been necessary to omit the mathematics necessary to express these ideas precisely, and to discuss the experimental data with which such expression must correspond only when it appears that they would not otherwise be discussed in this symposium. The story of the future will depend much more upon mathematics and experiments. With regard to the experiments it is not difficult to prophesy that we shall continue to have more and better data. To predict the development of a theory, either in ideas or in mathematical treatment, is harder than to predict the weather. We may say that any truly satisfactory solution must wait a development that can express chemical action in precise physical terms and one that can treat a liquid taking into account the existence as molecules of every species present. How long this will be in coming, and whether it will require only an extension of mathematical methods or will need also new physical ideas, are questions which we cannot answer at present.

In the meantime progress will be made by developing different phases of the theory along different lines. It will be desirable to use every available method, and this will lead to some confusion for it will be difficult to avoid counting the same effect twice as expressed in different terms. I believe that the future will not change the results of the theory as it concerns the limiting law. The treatment of more concentrated solutions will doubtless undergo considerable change, though I believe that here also the main lines have now been correctly laid out.

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