A SYMPOSIUM ON ELECTROLYTES[1]

INTRODUCTION TO THE SYMPOSIUM

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The past decade has witnessed advances in our knowledge of solutions and particularly of electrolytic solutions, which are second in importance only to the revolutionary innovations introduced fifty years ago by van't Hoff, Arrhenius, Ostwald, and Nernst. In view of the far reaching consequences of the important contributions of Debye and Hückel, it is eminently fitting that this symposium is being held on the tenth anniversary of the appearance of their fundamental papers.

During the past decade the problems of electrolytes have been subjected to a consistent and rational thermodynamic analysis, using methods which have proven to be well adapted for expressing the results of the more powerful tools of statistical mechanics. As a result the main features of the interaction problem have been solved sufficiently well for dilute aqueous solutions, so that today there are few who doubt the utility of considering strong electrolytes as practically completely dissociated in such solvents. The interpretation of the behavior of electrolytes in low dielectric solvents constitutes the pressing problem of the present. Here again statistical mechanics is the guiding light. The important paper of Fuoss and Kraus (1) presented at this symposium had already been accepted for publication elsewhere and unfortunately does not appear in the present list.

The prompt and cordial reception which the theory of Debye

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[1] This symposium on electrolytes was held by the Division of Physical and Inorganic Chemistry at the eighty-fifth meeting of the American Chemical Society in Washington, D. C., in March, 1933.

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and Hückel received was due in no small measure to the fact that several investigators had just deduced on non-mathematical grounds the essential features of the theory which Debye and Hückel, working quite independently, presented in a single equation as a mathematical result of similar initial postulates. I refer to the discovery of the principle of ionic strength by Lewis and Randall in 1921 and to the principle of electric charge types enunciated by Brönsted as a result of the extensive experimental studies made in his laboratory. Reasoning from fundamental principles and guided by the data, Brönsted predicted in 1922 the form which the limiting law must assume and the universal character of the theoretical constant. It was the writer's good fortune to be engaged in the determination of the value of this constant, when the paper of Debye and Hückel appeared predicting the numerical value we were finding experimentally.

The rare skill with which Brönsted has utilized these principles in unravelling the still more subtle problems of neutral salt catalysis and of acid and basic catalysis constitutes one of the most brilliant chemical achievements of the decade. These kinetic aspects have been treated in detail in recent symposia published in This Journal (2), so that the present symposium will be confined primarily to non-kinetic problems.

In the opening paper Scatchard (p. 7) reviews the subject from the historical point of view in a most engaging manner, and develops the Debye picture of the ionic atmosphere which is applied to reversible and non-reversible processes. His presentation of the chemical and physical views of association is timely and should be of aid in dissipating the fog of confusion with which some writers have enveloped the subject. In a later paper with Prentiss (p. 139) an objective evaluation of certain data is presented.

The precise measurement of transference number has long been recognized as a master key for interpreting the intricacies of conductance data, but in contrast to the latter the measurements remained notoriously difficult, inaccurate, and meager until MacInnes and his collaborators developed the moving boundary technique into a precision method. In their paper, MacInnes, Shedlowsky, and Longsworth (p. 29) report conductance data to 3×10^{-5} M with an accuracy of 0.02 per cent, along with transference data of comparable accuracy—a notable advance over Kohlrausch's classic achievements. The Arrhenius theory postulated a constant transference number, which was not always in agreement with the available data. It is highly significant that the variations in transference number which are obtained by the refined methods now available are in the direction and magnitude predicted by Onsager's form of the interionic attraction theory. By utilizing the results on strong electrolytes MacInnes and his collaborators have revised the dissociation constants of weak electrolytes, with the result that conductance data are now in perfect agreement with purely thermodynamic data.

Onsager's paper (p. 73), a searching critique of the statistical foundations of the Debye theory, merits a careful study by anyone who wishes to penetrate the subject. The first important result is equation 9 which states that the potential to be employed in the distribution law is the *potential of the average force.* The Guntelberg single ion charging process and the Debye form of the charging process are shown to be equally valid procedures.

The paradox to which the late Dr. T. H. Gronwall and the writer called attention some six years ago, namely, that the two procedures do not yield the same result when applied to the general solution of the Poisson-Boltzmann equation, is attributed by Onsager to an inconsistency in the fundamental equation. Halpern (3), working independently of Onsager, has reached the same conclusion.

Stated physically it appears that the average distribution of charge produced by a pair of ions i and j at a distance r is not always the precise sum of the charges induced by the two ions separately. From Halpern's studies it appears that this will occur whenever the individual ion diameters differ or the valences are not symmetrical. The assumption of spherical symmetry about one ion precludes the similar and simultaneous assumption for the other ion when in the presence of the first. In other words, the fields of individual ions cannot in general be exactly superimposed except for extremely dilute solutions where the limiting law is an adequate approximation.

It is indeed comforting to learn from Onsager that most of the error due to the neglect of fluctuation terms cancels out.

One of the criticisms which could be justly levelled against physical chemistry has been the great concern for aqueous chemistry to the unwarranted exclusion of the non-aqueous. Downes and the writer (p. 47) point out the inadequacy of the classical concepts of acids and bases for understanding their behavior in non-aqueous solvents. The complete absence of acid and basic properties makes the hydrocarbons a most interesting and important type of solvent for investigating the behavior of acid and bases. For this reason we have chosen benzene as a typical example of such an extreme type of solvent for the application of indicator and electrometric methods for the determination of acid strengths. Quantitative measurements, which recognize the influence of association, are reported for a series of sixteen acid–base systems and the results compared with those in aqueous solution.

Hammett (p. 61) treats the problem of the dissociation constants of bases which are too weak for measurement in water from a similar viewpoint. By using concentrated sulfuric acid as a typical acid solvent he demonstrates how the latent basic properties of oxygen-bearing compounds like ketones and aldehydes can be subjected to quantitative study.

The Kilpatricks (p. 131) have chosen acetonitrile as an example of a weakly basic solvent and by indicator methods have correlated the strengths of many acid–base systems in this solvent.

The salting-out effect is a phenomenon of wide application that has been studied for many years. It represents the interaction of ions upon neutral molecules. Gross (p. 91) surveys this broad field and proposes a theory of the antagonistic action of cations and anions as an explanation of "salting out" and "salting in."

Long familiarity with the subject makes Young (p. 103) particularly well qualified to discuss the errors which enter into the intricate calculation of the activity coefficients of concentrated solutions from freezing point data. It appears that the discrepancies between the E.M.F. and freezing point computations which still persist after Young's improved treatment are due primarily to inaccuracies in the original data.

Thermodynamics teaches that the relatively minute changes in volume and compressibility of the solvent which are produced by the addition of a solute are correlated with the changes in the thermal property of heat capacity. The interionic attraction theory predicts that these properties should involve the first and second derivatives of the dielectric constant with respect to volume, temperature, or pressure as the case may be. Unfortunately the numerical values of these derivatives are uncertain, owing to experimental inaccuracies, so that quantitative comparisons with theory are necessarily of doubtful significance. Nevertheless it appears that the experimental data on molal volumes, heat capacities, and compressibilities may often be represented by comparatively simple formulas involving only the square root of the concentration for considerable range. Gucker in his paper (p. 111) discusses these interesting results for this new yet difficult field of investigation.

The Division of Physical and Inorganic Chemistry of The American Chemical Society is much indebted to its Chairman of the year, Professor W. A. Noyes, Jr. for initiating this successful symposium and for his untiring efforts in its organization.

REFERENCES

(1) FUOSS AND KRAUS: J. Am. Chem. Soc. **55**, 1019, 2387 (1933).
(2) Chem. Rev. **5**, 231–338 (1928); **10**, 1–264 (1932).
(3) HALPERN, OTTO: Phys. Rev. **43**, 495 (1933).