A SYMPOSIUM ON THE DIELECTRIC PROPERTIES OF MATTER[1]

INTRODUCTION TO THE SYMPOSIUM

J. W. WILLIAMS

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

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The development of knowledge in all branches of physical, analytical, and inorganic chemistry has been so rapid in recent years that it is difficult for any individual to keep in touch with the advances in the fields outside his own specialty. With the desire to perform a service to its members and to chemistry, the Division of Physical and Inorganic Chemistry of the American Chemical Society has taken upon itself the organization of symposia whose purpose is the correlation of the advances of research in the several fields of its scope and the provision of authoritative and critical summaries of those subjects which have had at the same time consistent and rational development and far-reaching consequences. On this occasion we seek to coördinate the knowledge which has become available on the subject of the dielectric properties of matter. Enough of a theoretical background is given so that the reports to follow may serve as a stimulus for investigators and investigations in this important field. Further, it is hoped that useful conclusions have been reached which may prove of value to scientists and engineers confronted with some practical problem.

The first attempt to describe the dielectric constant as an atomic or molecular property is found in the classical theory of Clausius–Mosotti, according to which the volume actually occupied by the molecules is related in a simple way to this constant. The molecules were considered as conducting spheres, and it is not surprising that it has been necessary to modify the Clausius–Mosotti statements by the electron theory and by the dipole theory of dielectric behavior.

The electron theory considers the molecules in a dielectric to be neutral systems of positive and negative electricity, which are bound by quasi-elastic forces with the center of the positive charges at the same point

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within the molecule as the center of the negative charges. If such a molecule is brought into an electrical field it is polarized, and the molecule contains an induced electric moment. Dielectric constant at zero frequency ϵ and molar polarization P can be shown to be related by the same formula which has come to be known as that of Clausius–Mosotti, that is,

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = \frac{4\pi}{3} N\alpha$$

In this formula α is the molecular polarizability, or the electric moment induced by a field of unit strength, and the other symbols have their usual significance.

According to this formula the molar polarization ought to be independent of density and of temperature. If the dielectric constants of gases or vapors are measured at constant density, it is found that for some gases the molar polarization is really constant, but in other cases it decreases with increasing temperature. The substances of the second kind or class have high dielectric constants and low refractive indices, the Maxwell equation $\epsilon = n^2$ is not obeyed, and the molar refraction is smaller than the molar polarization.

In proposing what has now come to be known as the dipole theory Debye (2), in an article published in 1912, modified the Clausius–Mosotti law in such a way as to give an explanation of this and other difficulties. The assumption was made that although the molecule is uncharged, the center of the positive charges may not be at the same point as the center of the negative charges. If this occurs the molecule has a permanent moment, and now can show a polarization not only by electron and atom displacements or distortion, but also by orientation in the electrical field. Furthermore, it may be expected that the amount of orientation created by the field will be larger the smaller the disturbance due to temperature motion. Debye went on to establish the quantitative law for the dependence of orientation with temperature, so that it became possible to obtain the absolute value of the electric moment of gases and properly dissolved molecules from a measurement of the temperature variation of the dielectric constant and density in such systems. This quantitative law takes the form,

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N\left(\alpha + \frac{\mu^2}{3kT}\right) = A + \frac{B}{T}$$

in which μ is the electric moment of the molecule. According to it the molar polarization is made up of two parts, one due to electron and atom displacement which is independent of temperature, and another resulting from the orientation of the permanent moment which is a function of the temperature. The formula will be correct insofar as we can represent the energy of the molecule in an electrical field as a function of no higher than the second degree in the field components and can consider only the most important part of the mean electric moment which is proportional to the field of electric intensity.

An immediate consequence of the new theory was the explanation of the anomalous dispersion or decrease of the dielectric constant with increase in frequency first observed by Drude (4) for liquids in which, as was inferred, the molecules contain special atomic groups like OH and NH_2. Debye (3) reasoned it to be probable that the characteristic property of the liquids with anomalous dispersion in the radio-frequency range is the polarity of their molecules, and that the effect represents the transition of the combined orientation and distortion to a pure distortion of the molecules. A quantitative description of the frequency variation of dielectric constant in liquids was here given.

Now, almost twenty-five years later, we know the modified Clausius–Mosotti equation which describes both temperature and frequency variation to be entirely consistent with the latest quantum theory, and, except in a few special cases, to be fully substantiated by experiment. For reasons not apparent these explanations of temperature and frequency dependence of dielectric constant did not become immediately and widely known. But about a decade ago attention was again called to them, this time in two monumental works, an article in the fifth volume of the Marx *Handbuch der Radiologie* and a monograph, *Polar Molecules,* both written by Debye; at the present time the scope of the subject has been greatly broadened and many important and unique applications have been made to problems of chemistry, physics, and electrical engineering. Because we believe an acquaintance with and a study of this subject to be of value to members of this Division, we have arranged a program to indicate some of the many and varied uses to which the dipole theory has been and will be put in the solution of chemical problems.

Our study may be divided in several ways. We propose here to consider at the same time the actual dielectric behavior of gases, liquids, and solids; electrolyte, non-electrolyte, and dipolar ion solutions; and the application of these ideas to give information about other properties of the several systems. In the arrangements the breadth of the subject has proved a source of considerable difficulty, and it is only to avoid congestion of the program that other important contributions to the subject have been omitted. Especially deserving of mention are recent contributions of Fuoss and Kraus and of Onsager.

In the opening paper Debye gives an account of his recent important work having to do with the properties of pure liquids. It is pointed out that while there remain no essential difficulties in describing the dielectric behavior of gases, the theory developed can not be applied to pure liquids without considerable modification. Binding forces between molecules become of such significance that molecular rotation is restricted and the liquid assumes a quasi-crystalline character. The successful calculation of this binding energy is a large factor in bringing the theory abreast with the rapid progress which has been made in experimental researches having to do with effects of electrical saturation, anomalous dispersion, electric double refraction, interference maxima in the scattering of x-rays, association, specific heat, and other properties, all in the liquid state.

Many of the configurations of which molecules are constituted are strongly polar in character. In the compounds of organic chemistry the dipole moment of these groups proves to be largely independent of the length of the non-polar hydrocarbon chain to which they are attached. The moments of the groups are additive as vectors, with the result depending upon the configuration of the molecule. Thus once more a physical chemical theory finds important application and utility in the chemistry of organic compounds. The Division is fortunate in having a distinguished English chemist, N. V. Sidgwick, to consider in detail the relationship between electric moment and molecular structure. This application of the Debye dipole theory to problems of molecular configuration was early recognized, thoroughly understood, and skillfully used by him.

The available data for the dielectric constants of gases at higher densities are of interest in the theory of dielectrics. Keyes and Oncley show that the results of most investigators are in agreement with the observation that the polarizability of compressed gases may increase by several per cent in some cases, although the simpler gases show little, if any, change. The origin of this increase in polarizability and its significance to the theory of dielectrics and problems involving the molecular field are discussed.

The electric moments of molecules are estimated usually either in the gaseous state or in non-polar solvents. With the contribution of Debye contained in this volume as an aid, we can look forward to the time when molecular behavior in polar solvents will be described, but until now there is no completely satisfactory theory for such polar solutions. In spite of this fact experimental research has made rapid strides, and certain important relationships have been made apparent between the polarity of molecules and the dielectric constants of these solutions. In this field the work of Wyman has been outstanding. He summarizes here the various methods which can be used, and presents data which reveal great regularity and simplicity of behavior.

The amino acids and proteins are constituted of a relatively small number of chemical groups. Recognition of this fact and the realization of its significance has enabled Cohn to point the way in one of the most active fields of research in all biochemistry. In clear and lucid fashion we are shown that the electrostatic forces in biological systems must be considered to involve not only ions but also the dipolar ions. Here, then, the activity coefficients reflect not only Coulomb forces but also the space properties both of ions and of dipolar ions. Since electrostatic forces surrounding ions are of longer range than those surrounding dipolar ions, whereas the latter are larger and contain an appreciable proportion of non-polar groups, interaction between ions, between ions and dipolar ions, and between various dipolar ions reflects such forces as the so-called "salting-out effect" the more, the larger the volume of the dipolar ion in comparison with its electrical moments and the greater the dielectric constant of the solvent. These effects are therefore being studied at high dielectric constants in systems containing many components.

In chemistry the extraordinary importance of solubility is universally recognized. Much of the recent progress made in solution theory has resulted because investigators have learned how to take into account the polarization, dispersion, and repulsive forces between the ions, and the forces of interaction between ions and solvent molecules, and between different solvent molecules. In short, the foundation of a general theory of intermolecular forces has been laid.

The two contributions which follow are concerned with solubility problems. In the first of these, Kirkwood treats the statistical mechanics of liquids and liquid solutions in convincing fashion. Relations between the more important thermodynamic functions of fluids, and the potentials of intermolecular force are formulated in terms of the probability distribution function of molecular pairs. The potential of average force, which determines the distribution of pairs, satisfies an integral equation, which has been solved in certain cases. Special attention is devoted in one of the chapters of this article to a consideration of the nature of the Debye–Hückel method and its application to electrolytes and to mixtures of electrolytes and dipole ions. The treatment shows Debye's theory to be a direct, proper, and logical consequence of statistical laws; at the same time it suggests the ways for its elaboration in more complicated systems.

Numerous investigators have attempted to treat theoretically the properties of concentrated solutions of strong electrolytes. Profound knowledge of the statistical mechanics of solutions and long continued effort have enabled Scatchard to make contributions of importance to this difficult subject. In the present instance it is shown that if the dielectric constant appearing in the Debye electrolyte theory behaves like that of a polar–non-polar mixture, the thickness of the ion atmosphere is proportional to the square root of the volume of the solvent. The chemical potentials in aqueous alkali halide solutions now may be calculated from the radii of the ions and two other parameters. Where more complex ions are involved much progress is made by the application of a general theorem of statistical mechanics, the Debye–Hückel limiting law, and an extension of the Brönsted principle of specific ion interaction.

In his theory of the frequency behavior of the dielectric constant, we have seen that Debye could explain the anomalous dispersion in liquids known since the experimental work of Drude. A problem now attracting much attention has to do with anomalous dispersion effects in certain crystalline solids and its theoretical explanation. In his admirable review of the dielectric constants of solids, Smyth points out that the molecules of some solids possess freedom to turn in an electrical field so as to orient their dipoles in the field and give a high dielectric constant, like that of a polar liquid. In ionic solids the dielectric constant is high because the displacement of ions in a field occurs more readily than that of electrons bound in a molecule, but in molecular solids the shift of charge is mainly a displacement of electrons and the susceptibility is low.

Pioneer work of Brönsted (1) dealing with the effect of the concentration of electrolyte upon reaction rate, has given new impetus to the study of the effect of acids and bases in catalyzing certain reactions. With this work as guiding principle, exact kinetic data for such reactions as the decomposition of nitramide, the inversion of sucrose, and the mutarotation of glucose have received ready interpretation. In the report which forms the last article of the proceedings, La Mer describes studies of these reactions in deuterium oxide, which lead him to conclude that the kinetic effects are primarily the result of displacements in the exchange equilibria between proto and deutero forms of the substrate or of the catalyst. The importance of exchange reactions in solution is demonstrated as well in the case of certain electromotive force studies. Conductance change as solvent is varied from ordinary water to deuterium oxide is determined by the viscosity difference.

The consummate skill with which Debye was able with his dipole theory to remove the difficulties of the Clausius–Mosotti and electron theories, and to explain the anomalous dispersion effects, constitutes one of the most brilliant achievements in all physical chemistry. In printed article and by personal association he has suggested applications of this theory which have meant much in the development of modern physical and organic chemistry. We consider it fitting, then, that we dedicate to him this printed record of the proceedings of the symposium.

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