STATISTICAL MECHANICS OF LIQUID SOLUTIONS[1]

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CONTENTS

I. INTRODUCTION

In the formulation of a molecular theory of solutions, there are two main problems to be considered. The first is the calculation of intermolecular forces from a knowledge of molecular structure, and the second is the correlation of the macroscopic properties of a thermodynamic system with the behavior of a dynamical system, consisting of many molecules executing thermal motion under known intermolecular and external forces. In the calculation of certain types of intermolecular force, for example, between ions and between molecules containing low-frequency electric multipole moments, simple electrostatics suffice. A more comprehensive theory of intermolecular forces is furnished by quantum mechanics. The nature of van der Waals forces between non-polar molecules and of the repulsive forces, which determine molecular size, is now well understood. It is true that computational difficulties stand in the way of exact calculations for all but the simplest molecules. Nevertheless, rather good approximations to the potential of van der Waals force can be obtained in terms of a few simple molecular constants, such as polarizability and ionization potential. What is perhaps more important, the approximate form of the potential of intermolecular force as a function of the molecular coördinates is known.

In the present article, we shall be chiefly concerned with the second problem, which lies within the province of statistical mechanics. In the study of liquids at ordinary temperatures it is usually sufficient to use classical statistical mechanics. This is permissible when the motion of

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the molecules involves only a high frequency and a low frequency type, in the sense of van Vleck's definition. The high frequency type of motion is characterized by the fact that the interval between adjacent energy levels is large relative to kT, the product of Boltzmann's constant and the absolute temperature. Under these circumstances there is no appreciable thermal excitation above the lowest energy state. The low frequency type of motion, on the other hand, is characterized by energy intervals very small relative to kT. The internal motion, electronic and vibrational, of most molecules is of the high frequency type at ordinary temperatures, while the translational and rotational motion is of the low frequency type.

In an earlier article (11) a method for the statistical treatment of liquids was developed on the basis of the classical canonical ensemble. This method provides a suitable basis for the formulation of a general theory of solutions. In addition to yielding a number of new results, it embraces those of older special theories as parts of a unified whole. Both electrolytes and non-electrolytes fit naturally into the scheme. We shall undertake the formulation of the theory as well as a discussion of some of its applications, particularly to electrolyte solutions. While there still remain a number of obstacles to be overcome, the theory is at present sufficiently well developed to yield some interesting results.

II. GENERAL THEORY

The Helmholtz free energy F_N of a liquid solution consisting of N molecules is related to the potential of intermolecular force, V_N, by the method of the canonical ensemble, in the following manner

$$e^{-\beta F_N} = \left[\prod_{s=1}^{\nu} \frac{f_s(T)^{N_s}}{N_s!} \right] Z_N$$

$$Z_N = \int \cdots \int e^{-\beta V_N}\, \mathrm{d}v_1 \cdots \mathrm{d}v_N \tag{1}$$

where β is equal to $1/kT$, and $N_1, \cdots N_\nu$ are the numbers of molecules of the several components of the solution. The function $f_s(T)$ is a product of the internal partition function of a molecule of type s and the classical momentum phase integral associated with its low frequency translational and rotational degrees of freedom. The familiar phase integral Z_N extends over the translational and rotational configuration space of each molecule, bounded by the volume v of the solution. We denote by $\mathrm{d}v_i$ a differential element of this configuration space, divided by 4π for diatomic molecules and linear polyatomic molecules or by $8\pi^2$ for non-linear polyatomic molecules.

It has been previously shown (11) that the chemical potential of a component i of the solution may be expressed in the form

$$\mu_i = -kT \log \left[\frac{f_i(T)}{N_i} \frac{Z_N}{Z_{N-i}} \right] \tag{2}$$

where Z_{N-i} is the phase integral of the system with a single molecule of type i removed, the temperature, volume, and numbers of molecules of the remaining components being the same as in Z_N. We suppose that the potential of intermolecular force may be represented as the sum of terms V_{ik}, each depending upon the relative coördinates of a single molecular pair

$$V_N = \sum_{\substack{i<k\\=1}}^{N} V_{ik} \tag{3}$$

This is no real restriction on the method, for it may be easily extended to include terms V_{ikl} depending upon the coördinates of three molecules, and so on. For simplicity, we shall not include such terms. In treating chemically saturated molecules, terms of the form V_{ikl} are probably needed only when it is desired to take account of the induced or optical polarization of molecules in a system containing ions or dipoles. Such interactions are usually unimportant in comparison with other intermolecular forces. The form of equation 3 might be questioned for the repulsive forces, which operate at small intermolecular distances and determine molecular size. However, these repulsive forces generally act in such a manner as to make the molecules behave as hard impenetrable objects. Thus their rôle consists in making $e^{-\beta V_N}$ vanish whenever the relative coördinates of any molecular pair are within the region of repulsion. This may be accomplished with a potential of the form of equation 3, in which each V_{ik} assumes a large value V_R whenever the relative coördinates of the pair are within the region of repulsion of volume ω_{ik}. Strictly speaking, V_R should be infinite, but for practical purposes it is only necessary to assume it very large relative to kT, a procedure which avoids a certain amount of mathematical hedging.

It is convenient to introduce a fictitious potential

$$\begin{aligned} V_N(\lambda_i) &= V_{N-1} + \lambda_i V_i \\ V_i &= \sum_{k=1}^{N} V_{ik} \end{aligned} \tag{3a}$$

where λ_i is an arbitrary parameter, and V_{N-1} is the potential of intermolecular force in a system containing one less molecule of type i than the original one. Corresponding to $V_N(\lambda_i)$ we may construct a phase integral

$Z_N(\lambda_i)$ which is equal to Z_N when λ_i has the value unity and to Z_{N-i} when λ_i is zero. Following the methods of the earlier paper (11), we finally obtain for the chemical potential of the component i

$$\begin{aligned} \mu_i &= kT \log N_i/v + \sum_{k=1}^{\nu} \frac{N_k}{v} (J_{ik} + G_{ik}) + \varphi_i(T) \\ J_{ik} &= \int_0^1 \int_0^{\omega_{ik}} V_{ik} e^{-\beta W_i^k(\lambda_i)} \, dv_k \, d\lambda_i \\ G_{ik} &= \int_0^1 \int_{\omega_{ik}}^{v} V_{ik} e^{-\beta W_i^k(\lambda_i)} \, dv_k \, d\lambda_i \\ \varphi_i(T) &= -kT \log f_i(T) \end{aligned} \tag{4}$$

where the integral J_{ik} extends only over the region of repulsion ω_{ik}, and G_{ik} extends over the rest of the volume of the solution. The function $W_i^k\,(\lambda_i)$ is the potential of average force between i and k, defined as follows

$$e^{-\beta W_i^k(\lambda_i)} = \frac{v \int \cdots \int e^{-\beta V_N(\lambda_i)} \, dv_1 \cdots dv_{N-2}}{\int \cdots \int e^{-\beta V_N(\lambda_i)} \, dv_1 \cdots dv_{N-1}} \tag{5}$$

where the integral in the numerator extends over all molecules except i and k, while that in the denominator extends over all molecules except i. In the earlier article (11) it is shown that $W_i^k(\lambda_i)$ satisfies the following equation

$$W_i^k(\lambda_i) = \lambda_i V_{ik} + \sum_{l=1}^{\nu} \frac{N_l}{v} \int_0^{\lambda_i} \int_0^{v} V_{il} (e^{-\beta W_{ik}^l(\lambda_i)} e^{-\beta W_i^l(\lambda_i)}) \, dv_l \, d\lambda_i \tag{6}$$

where $W_{ik}^l(\lambda_i)$ is the potential of average force acting on a molecule l in the neighborhood of the fixed pair i and k. It is defined by a relation similar to equation 5. A set of integral equations for the $W_i^k(\lambda_i)$ of the several types of pairs in the solution may be obtained if $W_{ik}^l(\lambda_i)$ is approximated by $W_i^l(\lambda_i) + W_k^l(1)$:

$$W_i^k(\lambda_i) = \lambda_i V_{ik} + \sum_{l=1}^{\nu} \frac{N_l}{v} \int_0^{\lambda_2} \int_0^{v} V_{il} e^{-\beta W_i^l(\lambda_i)} (e^{-\beta W_k^l(1)} - 1) \, dv_l \, d\lambda_i \tag{7}$$

The nature of the superposition approximation, upon which this equation is based, has been discussed elsewhere (11). It may happen that outside the regions of repulsion, βW_i^l and βW_k^l are small enough to permit expansion of the exponentials with the neglect of terms in the second and higher powers of β. When this is done a set of approximate linear integral equations is obtained,

$$
\begin{aligned}
W_i^k(\lambda_i) &= V'_{ik}(\lambda_i) - \beta \sum_{l=1}^{\nu} \frac{N_l}{v} \left\{ \int_0^{\omega'_{il}} K_{il} W_k^l(1)\, \mathrm{d}v_l + \lambda_i \int_{\omega_{il},\omega_{kl}}^{v} V_{il} W_k^l(1)\, \mathrm{d}v_l \right\} \\
V'_{ik}(\lambda_i) &= \lambda_i V_{ik} + \sum_{l=1}^{\nu} \frac{N_l}{v} \left\{ \lambda_i \int_0^{\omega'_{kl}} V_{il}\, \mathrm{d}v_l - \int_0^{\omega_{ikl}} K_{il}\, \mathrm{d}v_l \right\} \qquad (8) \\
K_{il}(\lambda_l) &= \int_0^{\lambda_i} V_{il} e^{-\beta W_i^l(\lambda_i)}\, \mathrm{d}\lambda_i ; \quad l \text{ in } \omega_{il}
\end{aligned}
$$

where ω'_{il} and ω'_{kl} are the non-overlapping parts of the regions of repulsion for l around i and k, and ω_{ikl} is the overlapping part of these regions. Solution of these equations for several types of intermolecular forces has been undertaken. The case of electrolytes will be discussed in a later section of this article. Fortunately we do not need to know K_{il} in this case. Solution has also been attempted for a system of spherical molecules with short-range attractive forces. In this case K_{il} must be known and has been estimated with some success for pure liquids. This work will be reported in a later article.

For the calculation of the integrals G_{ik} and J_{ik} appearing in equation 4, it is necessary to know the potential $W_i^k(\lambda_i)$ both inside and outside the sphere of exclusion ω_{ik}. While considerable progress has been made in the calculation of the G_{ik}, direct attempts to evaluate the J_{ik} have not yet been successful. Inside ω_{ik}, $W_i^k(\lambda_i)$ is of course positive and very large except when λ_i is near zero, so that the integrand $V_{ik}e^{-\beta W_i^k(\lambda_i)}$ has a sharp peak near $\lambda_i = 0$ and vanishes elsewhere. A crude approximation, not valid at liquid densities, is obtained by setting $W_i^k(\lambda_i)$ equal to $\lambda_i V_{ik}$, yielding $J_{ik} = kT\omega_{ik}$. Indirect methods of approach have yielded fair approximations to J_{ik} in pure liquids, but in mixtures the problem has not been solved, except under certain arbitrary assumptions about the entropy of solvation.

We return to equation 4 for the chemical potential, which we write in the following form

$$
\begin{aligned}
\mu_i &= kT \log x_i + \sum_{k=1}^{\nu} \frac{N_k}{v} G_{ik} + \mu_i^* \\
\mu_i^* &= kT \log \bar{v} + \sum_{k=1}^{\nu} \frac{N_k}{v} J_{ik} + \varphi_i(T)
\end{aligned}
\qquad (9)
$$

where $\bar{v}$ is the mean molal volume of the solution, and $x_1, \cdots x_2$ are the mole fractions of the several components. Let us now suppose that our solution contains N'_i molecules which are of the same shape and volume as molecules of type i but which exert no attractive forces on their neighbors. Although such molecules may have arbitrary shape, we shall find it convenient to refer to them as hard spheres. For a hard sphere all G_{ik} are zero. Referring again to equation 4, we find for the chemical potential of a hard sphere

$$\mu_i' = kT \log x_i' - kT \log \bar{v}' + \sum_{k=1}^{\nu+1} \frac{N_k}{v} J_{ik} + \varphi_i(T) \tag{10}$$

where x_i' is the mole fraction of the hard spheres and $\bar{v}'$ is the mean molal volume of the solution augmented by N_i' hard spheres, the summation over all components of course including them. We now observe that the limit of

$$\mu_i' - kT \log x_i'$$

as $x_i' \rightarrow 0$ is simply μ_i^* of equation 9. Thus μ_i^* is the non-ideal part of the chemical potential of hard spheres of type i at infinite dilution in a solvent consisting of the solution under investigation.[2]

For thermodynamic purposes, it is convenient to choose some reference value of the chemical potential, μ_i^0, and to define an activity coefficient which measures the departure of $\mu_i - \mu_i^0$ from its ideal value $kT \log x_i$. When the mole fraction of the component is large, or when solutions are to be studied in which its mole fraction varies over a wide range, it is customary to choose μ_i^0 as the chemical potential of the pure liquid component at the same temperature and pressure as the solution,

$$\mu_i = kT \log f_i x_i + \mu_i^0 \tag{11}$$

where the activity coefficient f_i approaches unity as the mole fraction x_i tends to unity. On the other hand, if one component, the solvent, is present in large excess at all compositions of interest, it is convenient to choose the reference value, μ_i^0, for a solute component as the limit of $\mu_i - kT \log x_i$ as the mole fraction of the solvent, x_s, approaches unity.

$$\begin{aligned} \mu_i &= kT \log \gamma_i x_i + \mu_i^0 \\ \mu_i^0 &= \lim_{x_s \rightarrow 1} \mu_i - kT \log x_i \end{aligned} \tag{12}$$

where γ_i is an activity coefficient which approaches unity as the solution becomes infinitely dilute with respect to all solute species. It is often convenient to use the molarity or the concentration of species i in place of its mole fraction. In dilute solution these variables are nearly proportional

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[2] The formal and thermodynamic aspects of the separation of the chemical potential into parts arising from different types of intermolecular force are discussed by Bell and Gatty (Phil. Mag. **19**, 66 (1935)). Our hard sphere species corresponds to the solute with "limited interaction" of Bell and Gatty.

to one another and the corresponding activity coefficients are nearly equal. From equation 9, we obtain for the first choice of μ_i^0, the chemical potential of pure liquid i,

$$\mu_i^0 = NG_{ii}^0/\bar{v}_i^0 + \mu_i^{*0}$$

where G_{ii}^0 is to be calculated with a distribution function $e^{-\beta \overset{k}{W}_i(\lambda_i)}$ appropriate to the pure liquid component and μ_i^* is the non-ideal part of the chemical potential of a hard sphere of the same size as molecules of type i, at infinite dilution in pure i. By subtraction and use of the relation

$$1/\bar{v}_i = N_i/v + \sum_{\substack{k \neq i \\ =1}}^{\nu} N_k \bar{v}_k / v\bar{v}_i$$

we obtain

$$\begin{aligned} kT \log f_i/f_i^* &= \sum_{k=1}^{\nu} \frac{N_k}{v}\left(G_{ik} - \frac{\bar{v}_k}{\bar{v}_i} G_{ii}\right) + \frac{NG_{ii}}{\bar{v}_i} - \frac{NG_{ii}^0}{\bar{v}_i^0} \\ kT \log f_i^* &= \mu_i^* - \mu_i^{*0} \end{aligned} \tag{13}$$

If the μ_i^0 is chosen at infinite dilution in a solvent s, we have

$$\mu_i^0 = NG_{is}^0/\bar{v}_s^0 + \mu_i^{*(s)} \tag{14}$$

where $\mu_i^{*(s)}$ is the chemical potential of a hard sphere of type i at infinite dilution in the pure solvent. We then obtain for the activity coefficient γ_i the following expression.

$$\begin{aligned} kT \log \frac{\gamma_i}{\gamma_i^*} &= \sum_{\substack{k=1 \\ \neq s}}^{\nu} \frac{N_k}{v}\left(G_{ik} - \frac{\bar{v}_k}{\bar{v}_s} G_{is}\right) + \frac{NG_{is}}{\bar{v}_s} - \frac{NG_{is}^0}{\bar{v}_s^0} \\ kT \log \gamma_i^* &= \mu_i^* - \mu_i^{*(s)} \end{aligned} \tag{15}$$

For exact calculations, we must be able to say something about the chemical potential μ_i^* of the hard spheres. Since direct calculations of the J_{ik} have not yet been successful, only provisional statements about μ_i^* may be made. At this point it is of interest to mention an empirical means of estimating $\mu_i^* - \mu_i^{*(s)}$ similar to a method due to Scatchard (18), who recognized the need for such a correction in the case of electrolytes. He proposed to use the solubilities of the noble gases for this purpose. The noble gases approximate hard spheres, at least in polar solvents, since their attractive forces are weak relative to those between polar molecules. In the present formulation γ_i^* would be equal to the limit of p^*/p_0^* as the pressure of the noble gas tends to zero, where p^* and p_0^* are the gas fugacities in equilibrium with equal mole fractions of the dissolved gas in the actual solution and in the pure solvent. This limit is equal to K/K_0, the ratio of the Henry's law constants of the gas for the solution and for the pure solvent. By a process of size interpolation among the several noble gases, it should be possible to pick a value appropriate to the size of a given solute molecule. Given the data, this would at least provide a means of estimating errors introduced by the customary neglect of the term $\mu_i^* - \mu_i^{*(s)}$ in theories of dilute solutions.[3]

There is another method of estimating μ_i^*, based upon certain assumptions about the entropy of solvation of a hard sphere. From thermodynamics we know that μ_i is equal to $\bar{H}_i - T\bar{S}_i$ or to an adequate approximation in condensed system, $\bar{E}_i - T\bar{S}_i$, where $\bar{H}_i$, $\bar{E}_i$, and $\bar{S}_i$ are the partial molal heat content, energy, and entropy of component i. Now the energy of a solution is easily calculated as

$$E = \frac{1}{2}\sum_{\substack{k,l\\=1}}^{\nu} \frac{N_k N_l}{v} B_{kl} + \sum_{k=1}^{N} N_k E_k^0(T) \qquad (16)$$

$$B_{kl} = \int_{\omega_{kl}}^{v} V_{kl}\, e^{-\beta W_k^l(1)}\, dv_l$$

where $E_k^0(T)$ is the sum of the internal energy and the average rotational and translational kinetic energy of a molecule of type k, depending only on the temperature. The B_{ik} are calculated with the distribution function $W_i^k(1)$, which always makes $e^{-\beta W_i^k(1)}$ vanish in the region of repulsion ω_{ik}, so that no contribution to the integral arises from this region. The B_{ik} all vanish for a hard sphere. If we imagine hard spheres of type i to be present, they can influence the energy of the solution only by their effect on the volume and on the relative distribution of the other molecules. Neglecting the latter effect, and calculating $\bar{E}_i^*$ for a hard sphere of type i, we obtain

$$\bar{E}_i^* = \left(\frac{\partial E}{\partial N_i}\right)_{T,p,N_k\cdots} = -\frac{\bar{v}_i^*}{2v^2}\sum_{\substack{k,l\\=1}}^{\nu} N_k N_l B_{kl} + E_i^0(T) \qquad (17)$$

where, since $\bar{E}_i^*$ is to be taken at infinite dilution with respect to the hard spheres, the B_{kl} and v are those of the actual solution. The partial molal volume $\bar{v}_i^*$ of the hard spheres is not necessarily equal to $\bar{v}_i$, that of the actual species i, but in many cases the two will be very nearly equal. We now tentatively assume that $\bar{S}_i^*$ is the same for all solutions and pure liquids at the same temperature and pressure, remembering that $\bar{S}_i^*$ is the

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[3] A similar method was first proposed by Bjerrum and his coworkers (Trans. Faraday Soc. **23,** 445 (1927); Z. physik. Chem. **127A,** 358 (1927); **159,** 194 (1932)).

non-ideal part of the partial molal entropy of the hard spheres at infinite dilution in the given solution. This assumption cannot as yet be justified by exact reasoning, and it probably is not valid or only approximately valid when one has to do with components of unequal molecular size. When applied to solutions whose components are identical in molecular size and shape, the assumption is entirely reasonable, for since the hard sphere exerts no attractive forces on the other molecules of the solution, its motion in the system is determined solely by the repulsive forces exerted on it by the other molecules, in other words by their size, shape, and packing. Under this assumption the chemical potential of a hard sphere depends upon the solution in which it is immersed only through $\bar{E}_i^*$. This term arises from the pushing of the other molecules of the solution apart, an effect which may be likened to that of the introduction of a microscopic bubble into the solution. The corresponding values of f_i^* and γ_i^* are the following

$$\begin{aligned} kT \log f_i^* &= -\frac{\bar{v}_i^*}{2}\left[\sum_{\substack{k,l\\=1}}^{\nu} \frac{N_k N_l}{v^2} B_{kl} - \frac{N^2 B_{ii}^0}{\bar{v}_i^{0\,2}}\right] \\ k \log \gamma_i^* &= -\frac{\bar{v}_i^*}{2}\left[\sum_{\substack{k,l\\=1}}^{\nu} \frac{N_k N_l}{v^2} B_{kl} - \frac{N^2 B_{is}^0}{\bar{v}_s^2}\right] \end{aligned} \tag{18}$$

where $\bar{v}_i^*$ is assumed to have the same value in the solution and in the reference liquid, in the first case pure liquid i, and in the second pure solvent. For future reference, we shall express $kT \log \gamma_i^*$ in a form suitable for dilute solutions in which only solute concentrations appear.

$$\begin{aligned} kT \log \gamma_i^* = &-\frac{\bar{v}_i^*}{\bar{v}_s^2} \sum_{\substack{k=1\\ \neq s}}^{\nu} \frac{N_k}{v} [\bar{v}_s B_{ks} - \bar{v}_k B_{ss}] \\ &- \frac{\bar{v}_i^*}{2\bar{v}_s^2} \sum_{\substack{k,\,l\\ \neq s}}^{\nu} \frac{N_k N_l}{v^2} [\bar{v}_s^2 B_{kl} + \bar{v}_l^2 B_{ss} - 2\bar{v}_k \bar{v}_l B_{ks}] \end{aligned} \tag{19}$$

where all molal volumes are assumed independent of composition.

Scatchard (17) and Hildebrand and Wood (8, 9) have proposed an equation for non-electrolyte mixtures, based upon two primary assumptions: (a) the entropy of mixing is ideal; (b) the probability distribution is the same for all molecular pairs in the solution and is independent of composition. In our notation the Scatchard–Hildebrand equation may be written

$$kT \log f_i = \frac{\bar{v}_i}{2} \sum_{\substack{k,\,l\\ =1}}^{\nu} \frac{N_k N_l \bar{v}_k \bar{v}_l}{v^2} \left[\frac{2B_{ik}^0}{\bar{v}_i \bar{v}_k} - \frac{B_{kl}^0}{\bar{v}_k \bar{v}_l} - \frac{B_{ii}^0}{\bar{v}_i^2}\right] \tag{20}$$

where the partial molal volumes are assumed independent of composition and the B_{kl}^0 are computed with a distribution function appropriate to any one of the pure liquid components. It is interesting to note the conditions under which our equations 13 and 18 reduce to the Scatchard–Hildebrand equation. This occurs when all $W_i^k(\lambda_i)$ are independent not only of composition, but also of λ_i. When the $W_i^k(\lambda_i)$ are independent of composition the term

$$G_{ii}/\bar{v}_i - G/{}^0_{ii}\bar{v}_i^0$$

vanishes. When they are independent of λ_i, the G_{ik} reduce to the corresponding B_{ik}. If, in addition, we suppose that the partial molal volume $\bar{v}_i^*$ is equal to $\bar{v}_i$, and that all $\bar{v}_k$ are independent of composition, our equations 9 and 18 reduce to equation 20 after some algebraic transformations involving the relation

$$1/\bar{v}_i = \left(N_i + \sum_{k \neq i}^{\nu} N_k\bar{v}_k/\bar{v}_i\right) \Big/ v$$

An investigation of the $W_i^k(\lambda_i)$ in liquids consisting of spherical molecules with short-range attractive forces, now in progress, has shown that when the attractive forces between different components do not differ greatly, the function $W_i^k(\lambda_i)$ is determined primarily by molecular size. This conclusion is not especially remarkable, and has been reached by others on qualitative grounds. However, when this is true, we find that $W_i^k(\lambda_i)$ is practically independent of λ_i except when λ_i is nearly zero, which requires the G_{ik} to reduce effectively to the B_{ik}. When all components of the solution are of the same molecular size, $W_i^k(\lambda_i)$ also becomes independent of composition, and the two major conditions for the validity of the Scatchard–Hildebrand equation are fulfilled.

Guggenheim (6) has developed an interesting theory of solutions, which makes no attempt to go into the fine points of molecular distribution. His theory bears a marked resemblance to lattice theories of the solid state, as does a somewhat earlier theory of Heitler (7). Guggenheim confirms the Scatchard–Hildebrand equation for equal molecular sizes and random distribution of pairs of the type previously discussed. He also proposes an approximate method for taking departures from random distribution into account when the attractive forces between like and unlike pairs are considerably different. Guggenheim's approach is quite different from ours and in many ways simpler. However, while it is probably adequate to deal with problems concerning the energy of mixing and solution, it fails to take account of the non-ideal entropy of mixing in a formally satisfactory manner. We shall present briefly an extension of the Guggenheim theory, which takes formal account of the entropy of mixing, a step which is necessary in estimating its possibilities.

Guggenheim assumes that as in crystals V_N, the potential of intermolecular forces, has a number of sharp minima of equal depth in the configuration space of the system of N molecules. In perfect crystals, there are just $\prod_{s=1}^{\nu} N_s!$ of these minima, one for each permutation of molecules of the same species, which just cancels out this factor in the denominator of the right-hand side of equation 1. On the other hand, in some liquid mixtures, where attractive forces between like and unlike molecules are not very different from those between like molecules, the minima in V_N occur for permutations of unlike molecules as well so that they are $\left(\sum_{s=1}^{\nu} N_s\right)!$ in number. The phase integral of equation 1 is then equal to $\left(\sum_{s=1}^{\nu} N_s\right)! I_N$, where I_N is the value of Z_N taken over the region in the neighborhood of one of the minima. From equation 1 we then obtain for the free energy of the solution

$$F_N = + \sum_{k=1}^{\nu} N_k kT \log x_k - kT \log I_N + \sum_{k=1}^{\nu} N_k \varphi_k(T) \tag{21}$$

where factorials have been approximated by Sterling's formula. Guggenheim then approximates I_N by $e^{-\beta \bar{V}_N} v^N$ where $\bar{V}_N$ is its value at the minimum (also the average potential energy in this theory), and v is a proper volume in which a molecule is free to move. For the theory to be of value, the dependence of this quantity v on composition must be investigated. Guggenheim applies his theory only to cases in which it is reasonable to assume v independent of composition. However, it is possible to get a deeper insight into this question in the following manner. In order to evaluate I_N by peak integration, it is necessary to expand V_N in a Taylor's series in normal coördinates $q_1 \cdots q_{3N}$ specifying the displacement of the system of N molecules from the point in configuration space corresponding to the minimum value of V_N and the maximum of $e^{-\beta V_N}$,

$$V_N = \bar{V}_N + \tfrac{1}{2} \sum_{s=1}^{3N} \left(\frac{\partial^2 V_N}{\partial q_s^2}\right)_0 q_s^2 + \cdots\cdots \tag{22}$$

where the linear terms in the q_k do not appear, since all first derivatives of V_N vanish at the minimum, and, by the use of normal coördinates, all cross derivatives $(\partial^2 V_N/\partial q_s \partial q_k)_0$ are made to vanish. The derivatives $(\partial^2 V_N/\partial q_i^2)_0$ are equal to $2\pi^2 M_s \nu_s^2$, where M_s is a function of the masses of the N molecules, and the ν_s is one of the normal frequencies, in terms of which the vibration of the system around the position of minimum V_N is described, in other words one of the Debye frequencies of the solution. In the peak integration, the q_s are followed to range between $-\infty$ and $+\infty$ with the result

$$I_N = e^{-\beta \bar{V}_N} \left[\prod_{s=1}^{3N} \cdot \frac{1}{\nu_s} \right] \prod_{s=1}^{3N} \left(\frac{kT}{2\pi M_s} \right)^{1/2} \tag{23}$$

Substitution of this expression into equation 21 gives

$$F_N = \sum_{k=1}^{\nu} N_k \, kT \log x_k + \bar{V}_N + \sum_{s=1}^{3N} kT \log \nu_s + \sum_{k=1}^{\nu} N_k \varphi_k(T) \tag{24}$$

where the factors $(kT/2\pi M_s)^{1/2}$ are absorbed into the temperature functions $\varphi_k(T)$. Thus Guggenheim's effective volume v is proportional to the mean reciprocal of the Debye frequencies of the solution

$$\log v = \frac{1}{N} \sum_{s=1}^{3N} \log \nu_s^{-1} \tag{25}$$

except for an additive constant dependent only on the temperature. It is no easy task to determine the dependence of the mean Debye frequency on composition, and it should be pointed out that not only molecular size, but also the attractive forces must enter into such a calculation. However, in a nearly ideal solution, where the assumption of approximately equal depths for all minima of V_N is justified, it is reasonable to suppose that v is rather insensitive to changes in composition of the solution. This is not necessarily true in Guggenheim's extension of his theory to take into account the inequalities in the depths of the minima for unequal attractive forces. Moreover, in the latter case the Debye frequencies must be averaged, not only over all normal modes for a single permutation of the molecules, but also over all such permutations. It appears that an exact treatment of the entropy of mixing, into which the v must enter, is even more difficult by the Guggenheim method than by our own.

III. THE RÔLE OF ELECTROSTATIC FORCES

We shall for the present be concerned with moderately dilute solutions. Let us denote γ_i/γ_i^* by γ_i'. It is also convenient to write equation 15 in a slightly different form.

$$kT \log \gamma_i' = \sum_{\substack{k \neq s \\ =1}}^{\nu} \frac{N_k}{v} G_{ik} + \frac{N_s}{v} G_{is} - \frac{N G_{is}^0}{\bar{v}_s^0} \tag{26}$$

We shall not attempt to calculate the hard sphere contribution γ_i^*, but we should remember that to obtain the true activity coefficient γ_i' must be multiplied by this quantity. An estimate of γ_i^* in dilute solutions is given by equation 19.

In this section we shall be particularly interested in solutions containing ions and dipoles. While for non-polar solutions the difference between G_{is} and G_{is}^0 may often be ignored, this is not true in solutions containing ions or dipole molecules, for the pair distribution functions $W_i^k(\lambda_i)$ are no longer even approximately independent of composition. Let us consider a solution consisting of a mixed electrolyte furnishing ν ionic species of charges e_k in a solvent consisting of dipole molecules. The potentials of intermolecular force for the different types of molecular pairs are the following,

$$\begin{aligned} V_{ik} &= e_i e_k / r_{ik} \\ V_{is} &= e_i \boldsymbol{\mu}_s \cdot \nabla_s \left(\frac{1}{r_{is}}\right) \end{aligned} \tag{27}$$

where r_{ik} is the distance between the ion pair i and k, and r_{is} is the distance between anion i and a solvent molecule of dipole moment $\boldsymbol{\mu}_s$. For $N_s G_{is}/v$, we have from equations 4 and 27

$$\frac{N_s G_{is}}{v} = \int_0^1 \int_{\omega_{is}}^v \frac{N_s}{v} e_i \boldsymbol{\mu}_s \cdot \nabla_s \left(\frac{1}{r_{is}}\right) e^{-\beta W_i^s(\lambda_i)} \, dv_s \, do_s \tag{28}$$

where for clearness we indicate the orientation of a solvent molecule explicitly, do_s being a normalized differential element of its orientation space, while dv_s refers only to its translational configuration space. We remark that

$$\frac{N_s e^{-\beta W_i^s(\lambda_i)}}{v}$$

is the average density of solvent molecules having a specified orientation at a specified distance, r_{is}, from ion i. Thus the integral

$$(N_s/v) \int \boldsymbol{\mu}_s \, e^{-\beta W_i^s(\lambda_i)} \, do_s$$

is the average density of electric moment or local polarization ${}^i\mathbf{P}$ of the solvent in the vicinity of ion i, charged to a fraction λ_i of its full charge e_i, and we may write

$$\frac{N_s G_{is}}{v} = \int_0^1 \int_{\omega_{is}}^v e_i \, {}^i\mathbf{P} \cdot \nabla_s \left(\frac{1}{r_{is}}\right) dv_s \, d\lambda_i \tag{29}$$

If ${}^i\mathbf{D}(r_{is})$ is the local dielectric displacement, we may define a local dielectric constant, ${}^i\epsilon$ by the relation

$$ {}^i\mathbf{P} = \frac{1}{4\pi}\,\frac{{}^i\epsilon - 1}{{}^i\epsilon}\,{}^i\mathbf{D} \tag{30} $$

where the local dielectric constant, ${}^i\epsilon$, may of course differ from the macroscopic dielectric constant, ϵ, of the solution and may depend upon ${}^i\mathbf{D}$ if there is electrical saturation. Except for possible terms of dipole symmetry, the local dielectric displacement is equal to the sum of $-\lambda_i e_i \nabla_s(1/r_{is})$ and the mean values of $-e_k\nabla_s(1/r_{ks})$, arising from the other ions k, averaged with i fixed

$$ {}^i\mathbf{D}\,(r_{is}) = -\,\lambda_i e_i\,\nabla_s\left(\frac{1}{r_{is}}\right) - \sum_{k=1}^{\nu} \frac{N_k}{v}\,e_k \int_{\omega_{ik}}^{v} \nabla_s\left(\frac{1}{r_{ks}}\right) e^{-\beta W_i^k(\lambda_i)}\,dv_k \tag{31} $$

Substitution of equations 30 and 31 in equation 29 yields

$$ \begin{aligned} \frac{N_s G_{is}}{v} &= -\int_0^1\int_{\omega_{ik}}^{v} \lambda_i\,\frac{{}^i\epsilon - 1}{4\pi\,{}^i\epsilon}\,\frac{e_i^2}{r_{is}^4}\,dv_s\,d\lambda_i \\ &\quad - \sum_{k=1}^{\nu} \frac{N_k e_i e_k}{v} \int_0^1\int_{\omega_{ik}}^{v}\int_{\omega_{is}}^{v} \frac{{}^i\epsilon - 1}{4\pi\,{}^i\epsilon}\,\nabla_s\left(\frac{1}{r_{is}}\right)\cdot\nabla_s\left(\frac{1}{r_{ks}}\right) e^{-\beta W_i^k(\lambda_i)}\,dv_s\,dv_k\,d\lambda_i \end{aligned} \tag{31a} $$

We remark that if the regions of repulsion ω_{ik} and ω_{is} are small spheres of arbitrary radius, it is easy to carry out the integration over s by means of Green's theorem, which transforms it to a surface integral on the spheres, ω_{is}.

$$ \int_{\omega_{is}}^{v} \nabla_s\left(\frac{1}{r_{is}}\right)\cdot\nabla_s\left(\frac{1}{r_{ks}}\right) = \frac{4\pi}{r_{ik}} \tag{32} $$

Using this relation, we may write

$$ \begin{aligned} \frac{N_s G_{is}}{v} &= \sum_{k=1}^{\nu} \frac{N_k}{v}\,[G_{ik}^{(s)} - G_{ik}] + A_{is} \\ G_{ik} &= \int_0^1\int_{\omega_{ik}}^{v} \frac{e_i e_k}{r_{ik}}\,e^{-\beta W_i^k(\lambda_i)}\,dv_k\,d\lambda_i \\ G_{ik}^{(s)} &= \int_0^1\int_{\omega_{ik}}^{v} V_{ik}^{(s)}\,e^{-\beta W_i^k(\lambda_i)}\,dv_k\,d\lambda_i \\ V_{ik}^{(s)} &= \frac{e_i e_k}{\epsilon r_{ik}} + \frac{e_i e_k}{4\pi}\int_{\omega_{is}}^{v} \frac{\epsilon - {}^i\epsilon}{\epsilon\,{}^i\epsilon}\,\nabla_s\left(\frac{1}{r_{is}}\right)\cdot\nabla_s\left(\frac{1}{r_{ks}}\right) dv_s \\ A_{is} &= -\frac{e_i^2}{4\pi}\int_0^1\int_{\omega_{is}}^{v} \frac{{}^i\epsilon - 1}{{}^i\epsilon}\,\frac{1}{r_{is}^4}\,dv_s\,d\lambda_i \end{aligned} \tag{33} $$

where ϵ is the macroscopic dielectric constant of the solution. If the deviation of the local dielectric constant ${}^i\epsilon$ from ϵ can be neglected, $V_{ik}^{(s)}$ reduces simply to $e_ie_k/\epsilon r_{ik}$, the electrostatic energy of a pair of charges in a uniform dielectric continuum. As the distance r_{ik} increases, ${}^i\epsilon$ must approach ϵ. Near ion i, it may be expected to deviate from ϵ, owing to electrical saturation and to variations of the local density of the solvent from its average density. To investigate this effect from a molecular point of view, it is necessary to study the potential of average force and torque on a solvent dipole in the vicinity of an ion. Without detailed calculation, it is easy to see that the deviation of $V_{ik}^{(s)}$ from $e_ie_k/\epsilon r_{ik}$ will have only the effect of imposing a short-range force upon the Coulomb force, for since $\epsilon - {}^i\epsilon$ approaches zero at large values of r_{ik}, the integral certainly decreases more rapidly than $1/r_{ik}$.

For an ionic constituent of an electrolyte solution in a polar solvent we may therefore write

$$\left.\begin{aligned} kT\log\gamma_i' &= \sum_{k=1}^{\nu}\frac{N_k}{v}G_{ik}^{(s)} + A_{is} - A_{is}^0 \\ A_{is} - A_{is}^0 &= \frac{e_i^2}{4\pi}\int_0^1\int_{\omega_{is}}^{v}\left[\frac{1}{{}^i\epsilon} - \frac{1}{{}^i\epsilon_0}\right]\frac{1}{r_{is}^4}\,\mathrm{d}v_s\,\mathrm{d}\lambda_i \end{aligned}\right. \tag{34}$$

where ${}^i\epsilon_0$ is the local dielectric constant of the pure solvent near an ion i at infinite dilution. We have assumed that the polarization of the solution was due entirely to the permanent dipole moments of the solvent molecules, and have ignored the small contribution due to induced polarization of the solvent and the solute. This may be taken into account by introducing terms of the form V_{iks} into V_N, where V_{iks} is of the form $\alpha_s\nabla_s(1/r_{is})\cdot\nabla_s(1/r_{ks})$, α_s being the polarizability of a solvent molecule. By an analysis similar to the preceding one, equation 34 is again obtained, the local dielectric constant ${}^i\epsilon$ including the effect of induced polarization. It should also be mentioned that short-range van der Waals forces between the ions can be included by adding their potential to $V_{ik}^{(s)}$. It is possible to take account of the influence of the solvent on the potential of average force $W_i^k(\lambda_i)$, through the potential $V_{ik}^{(s)}$. We may write equation 6 for a pair of solute molecules in the following form.

$$\left.\begin{aligned} W_i^k(\lambda_i) = \lambda_i V_{ik} &+ \sum_{l=1}^{\nu}\frac{N_l}{v}\int_0^{\lambda_i}\int_0^{v} V_{il}\left(e^{-\beta W_k^l(\lambda_i)} - e^{-\beta W_i^l(\lambda_i)}\right)\mathrm{d}v_l\,\mathrm{d}\lambda_i \\ &+ \frac{N_s}{v}\int_0^{\lambda_i}\int_0^{v} V_{is}\left(e^{-\beta W_{ik}^s(\lambda_i)} - e^{-\beta W_i^s(\lambda_i)}\right)\mathrm{d}v_s\,\mathrm{d}o_s\,\mathrm{d}\lambda_i \end{aligned}\right\} \tag{35}$$

The last integral

$$(N_s/v) \int^{\lambda_i} \int_0^v V_{is}\, e^{-\beta W_i^s(\lambda_i)}\, \mathrm{d}v_s\, \mathrm{d}o_s\, \mathrm{d}\lambda_i$$

is equal to $N_s G_{is}/v$ and is given by equation 33. To obtain the first integral we proceed in a similar manner

$$\frac{N_s}{v} \int^{o_s} V_{is}\, e^{-\beta W_{ik}^s(\lambda_i)}\, \mathrm{d}o_s = e_i\, {}^{ik}\mathbf{P} \cdot \nabla_s \left(\frac{1}{r_{is}}\right) \tag{36}$$

where ${}^{ik}\mathbf{P}$ is the average local polarization of the solvent near the fixed ion pair i and k. There will be a corresponding local dielectric constant ${}^{ik}\epsilon$, and the dielectric displacement is

$${}^{ik}\mathbf{D} = -\lambda_i e_i \nabla_s \left(\frac{1}{r_{is}}\right) - e_k \nabla_s \left(\frac{1}{r_{ks}}\right) - \sum_{l=1}^{\nu} \frac{N_l}{v} \int^v e_l \nabla_s \left(\frac{1}{r_{sl}}\right) e^{-\beta W_{ik}^l(\lambda_i)}\, \mathrm{d}v_l \tag{37}$$

Substitution of $[({}^{ik}\epsilon - 1)/4\pi\, {}^{ik}\epsilon]\, {}^{ik}\mathbf{D}$ for ${}^{ik}\mathbf{P}$ in equation 36 and integration over s leads to an expression similar to equation 33, with some additional terms. Finally one obtains equation 35 in the following form

$$\begin{aligned} W_i^k(\lambda_i) = {} & \lambda_i V_{ik}^{(s)}({}^{ik}\epsilon) + A_{is}({}^{ik}\epsilon) - A_{is}({}^{i}\epsilon) \\ & + \sum_{l=1}^{\nu} \frac{N_l}{v} \int_0^{\lambda_i} \int [V_{il}^{(s)}({}^{ik}\epsilon)\, e^{-\beta W_{ik}^l(\lambda_i)} - V_{il}^{(s)}({}^{i}\epsilon)\, e^{-\beta W_i^l(\lambda_i)}]\, \mathrm{d}v_l\, \mathrm{d}\lambda_i \end{aligned} \tag{38}$$

where $V_{ik}^{(s)}$ and A_{is} are again given by equation 33, the notation $V_{ik}^{(s)}({}^{ik}\epsilon)$ meaning that the local dielectric constant ${}^{ik}\epsilon$ appears instead of ${}^{i}\epsilon$. Finally, if the deviations of the local dielectric constants from the macroscopic dielectric constant can be neglected, the equation takes the form

$$\begin{gathered} W_i^k(\lambda_i) = \lambda_i V_{ik}^{(s)} + \sum_{l=1}^{\nu} \frac{N_l}{v} \int_0^{\lambda_i} \int_0^v V_{il}^{(s)}\, [e^{-\beta W_{ik}^l(\lambda_i)} - e^{-\beta W_i^l(\lambda_i)}]\, \mathrm{d}v_l\, \mathrm{d}\lambda_i \\ V_{ik}^{(s)} = V_{ik}/\epsilon \end{gathered} \tag{39}$$

the equation for the potential of average force between a pair of ions, in which the solvent plays the rôle of a dielectric continuum, the sole effect of which is to multiply the V_{ik} by a factor $1/\epsilon$. We shall presently undertake the solution of equation 39 with certain approximations.

Not only when the solute molecules are ions, but whenever the attractive forces between them are principally electrostatic in nature, equations 39 and 34 may be used for the calculation of the potential of average force and the activity coefficients, the $G_{ik}^{(s)}$ being given by

$$G_{ik}^{(s)} = \int_0^1 \int_{\omega_{ik}}^v V_{ik}^{(s)}\, e^{-\beta W_i^k(\lambda_i)}\, \mathrm{d}v_k\, \mathrm{d}\lambda_i \tag{40}$$

If the local dielectric constants are approximated by the macroscopic dielectric constant, $V_{ik}^{(s)}$ is reduced to V_{ik}/ϵ. Electrostatic forces between solute molecules are generally of predominant importance only for electrolytes and polar molecules. The three most important types of interaction are therefore those between two ions, between an ion and a dipole, and between dipoles. The first has already been considered. The other two types of forces have potential $V_{ik}^{(s)}$ of the form

$$
\begin{aligned}
V_{ik}^{(s)} &= \frac{e_i}{\epsilon}\,\mu_k\cdot\nabla_k\left(\frac{1}{r_{ik}}\right);\ \text{ion–dipole}\\
V_{ik}^{(s)} &= \frac{1}{\epsilon}\,(\mu_i\cdot\nabla_i)(\mu_k\cdot\nabla_k)\left(\frac{1}{r_{ik}}\right);\ \text{dipole–dipole}
\end{aligned}
\tag{41}
$$

It should be remembered, however, that it is a much poorer approximation to neglect the deviation of the local dielectric constant from the macroscopic one, in the case of ion–dipole and dipole–dipole interaction than in the case of ion–ion interaction, since the former are themselves short-range forces. Also, the effect of the discontinuity of the dielectric constant at the surface of the dipole molecule has been neglected in the above expressions (41), the dipole having been supposed to consist of a pair of charges encased in non-overlapping small spheres, since otherwise the dielectric displacement $\mathfrak{D}$ of equation 31 cannot be expressed simply as a sum of Coulomb terms arising from the individual charges of the molecules, but there will be contributions arising from the effect of the cavity made by the molecule in the statistical continuum of the solvent. The effect of the cavity can be calculated easily only if the local dielectric constant is assumed to be ϵ, and the boundary conditions of electrostatics are applied at the surface of the molecule. (Continuity of the potential, the tangential component of the electric field, and the normal component of the dielectric displacement.) For dipole molecules of spherical shape, this leads to corrected expressions for $V_{ik}^{(s)}$.

$$
\begin{aligned}
V_{ik}^{(s)} &= \left[\frac{3\epsilon}{2\epsilon+1}\right]\frac{e_i}{\epsilon}\,\mu_k\cdot\nabla_k\left(\frac{1}{r_{ik}}\right);\ \text{ion–dipole}\\
V_{ik}^{(s)} &= \left[\frac{3\epsilon}{2\epsilon+1}\right]^2\frac{1}{\epsilon}\,(\mu_i\cdot\nabla_i)(\mu_k\cdot\nabla_k)\left(\frac{1}{r_{ik}}\right);\ \text{dipole–dipole}
\end{aligned}
\tag{42}
$$

The method also leads to an expression for the polarization energy of solvent by a dipole molecule. If the molecule is a sphere, we obtain

$$
A_{is} = \frac{\mu_i^2}{a^3}\,\frac{1-\epsilon}{2\epsilon+1}
\tag{43}
$$

The potentials of ion–dipole and dipole–dipole interaction are those of short-range forces. For this reason $W_i^k(\lambda_i)$ of equation 39 may be approximated by $\lambda_i V_{ik}^{(s)}$ for an ion–dipole or a dipole–dipole pair. With this approximation, the integrals $G_{ik}^{(s)}$ take the form

$$G_{ik}^{(s)} = kT \int_{\omega_{ik}}^{v} (1 - e^{-\beta V_{ik}^{(s)}})\, dv_k \tag{44}$$

a form reminiscent of the second virial coefficient of gases. If the salting-out term $A_{is} - A_{is}^0$, depending upon the influence of the solute on the dielectric constant of the solution is ignored, the following limiting law for the activity coefficient of a dipole molecule i in a dilute solution, is obtained

$$\log \gamma_i' = \sum_{k=1}^{\nu} \frac{N_k}{v} \int_{\omega_{ik}}^{v} (1 - e^{-\beta V_{ik}^{(s)}})\, dv_k \tag{45}$$

where the sum extends over all solute components of the solution, which may include both ions and dipoles. It should be pointed out that this is not a true limiting law for the salting-out term $A_{is} - A_{is}^0$ and the hard sphere factor γ_i^* (equation 19) both contain terms proportional to the solute concentrations N_k/v. Only when these additional terms are small, can equation 45 be a good approximation. This probably is only true for large dipoles such as zwitterions, the electric moments of which are very large in comparison with those of the solute molecules, or perhaps for smaller dipoles when the solvent is non-polar. Equation 45 was first proposed by Fuoss (4) for solutions containing only dipole solutes. His argument was based upon the van't Hoff analogy between the osmotic pressure of a solution and the pressure which the solute would exert as a gas in the same volume. Fuoss' calculation of the osmotic pressure therefore closely parallels the Keesom theory of the equation of state of dipole gases. Fuoss has given asymptotic expressions for the integral

$$\int_{\omega_{ik}}^{v} (1 - e^{-\beta V_{ik}^{(s)}})\, dv_k$$

for elongated elliptical molecules, and has tabulated it for spherical dipole molecules as a function of the parameter $\mu^2/\epsilon a^3 kT$, where μ is the dipole moment and a is the molecular diameter.

One of the most interesting applications of equation 45 is found in the study of the influence of electrolytes upon the activity coefficients of the aliphatic amino acids. It is well established that these acids exist in zwitterionic form in solvents of high dielectric constant. Zwitterions differ from true ions in that they possess no resultant charge, but they are characterized by dipole moments of great magnitude, of the order of 15.0×10^{-18} E.S.U. for α-amino acids. Calculation of $\log \gamma_i$ for spherical zwitterions with the use of equations 42 and 45 leads to a limiting law in agreement with that obtained by the author (13) on the basis of the Debye–Hückel theory. The calculations have been extended to non-spherical zwitterions, account being taken of the finite separation of the charged groups. The resulting formulas have been applied with success to experimental results of Cohn (2) and his coworkers on the influence of salts upon the solubilities of the amino acids and their peptides. This work will be reported in detail at a later time.

It is of interest to remark that a better approximation to the salting-out term $A_{is} - A_{is}^0$, which represents the difference between the energy of polarization in the given solution and in the pure solvent, can be obtained by incorporating a term to take care of it in $V_{ik}^{(s)}$. This may be done by taking the sizes of both molecules i and k into account in the calculation of their electrostatic energy $V_{ik}^{(s)}$ in a medium of dielectric constant ϵ. If the molecules are spherical in shape and a_{is} and a_{ks} are the radii of the respective cavities which they form in the solvent, one obtains for ions the following expression for $V_{ik}^{(s)}$, by applying the boundary conditions of electrostatics

$$V_{ik}^{(s)} = \frac{e_i e_k}{\epsilon r_{ik}} - \frac{1}{2} \frac{e_i^2 a_{ks}^3 + e_k^2 a_{is}^3}{2\epsilon + 1} \frac{\epsilon - 1}{\epsilon} \frac{1}{r_{ik}^4} \tag{46}$$

Similar, but more complicated, expressions may be obtained for ion–dipole and dipole–dipole pairs. If these $V_{ik}^{(s)}$ are used in equation 34, salting out is automatically taken care of and the term $A_{is} - A_{is}^0$, a cruder estimate of the effect, does not appear.

IV. STRONG ELECTROLYTES

The potential of mean force $W_i^k(\lambda_i)$ between a pair of ions cannot be approximated by $\lambda_i V_{ik}^{(s)}$, because the long-range character of the interionic forces causes the

$$\int_{\omega_{ik}}^{\infty} (1 - e^{-\beta V_{ik}^{(s)}})\, dv_k$$

to diverge. We therefore turn to equation 39 for a better approximation. Equation 39 differs from equation 4 only by the substitution of $V_{ik}^{(s)}$ and $V_{il}^{(s)}$ for V_{ik} and V_{il}. By the same set of approximations,

$$W_{ik}^l(\lambda_i) = W_i^l(\lambda_i) + W_k^l(1)$$

and expansion of the exponentials, equation 39 may be transformed into a linear equation like equation 7. Introducing $e_i e_l / \epsilon r_{il}$ for the $V_{il}^{(s)}$, we obtain for ions of equal size

$$W_i^k(\lambda_i) = \lambda_i \frac{e_i e_k}{\epsilon r_{ik}} - \frac{\lambda_i}{kT} \sum_{l=1}^{\nu} \frac{N_l}{v} e_i e_l \int_{\omega_{ik}, \omega_{il}}^{v} \frac{W_k^l(1)}{r_{il}}\, dv_l \tag{47}$$

where the integrals over the regions of repulsion are omitted for brevity. For ions of equal size, they vanish because of electrical neutrality

$$\sum_{l=1}^{\nu} N_l e_l = 0$$

when the solutions $W_i^k(\lambda_i)$ have the form

$$W_i^k(\lambda_i) = \lambda_i \frac{e_i e_k}{\epsilon} g(r_{ik}) \tag{48}$$

where $g(r_{ik})$ is the same function for all ionic species. A more general solution of equation 7 may be obtained by adding to equation 48 a term independent of the ionic charges, $W_i^{k^0}(\lambda_i)$ satisfying the equation

$$\begin{aligned} W_i^{k^0}(\lambda_i) &= u(r_{ik}) - \sum_{l=1}^{\nu} \frac{N_l}{v} \int_0^{\omega'_{il}} K_{il} W_k^{l^0}(1)\, dv_l \\ u(r_{ik}) &= -\sum_{l=1}^{\nu} \frac{N_l}{v} \int_0^{\omega_{ikl}} K_{il}\, dv_l \end{aligned} \tag{49}$$

Thus $W_i^{k^0}(\lambda_i)$ is just the potential of average force between a pair of hard spheres. We shall be interested here only in the part of $W_i^k(\lambda_i)$ dependent upon the ionic charges. It is interesting to remark that a rather tedious analysis shows that the terms neglected in approximating W_{ik}^l by $W_i^l + W_k^l$ are of the same magnitude as the non-linear terms neglected in the expansion of exponentials to obtain equations 47 and 49, so that equations 7, 47, and 49 are exact as linear approximations to equations 4 and 39.

We now introduce the form of equation 48 into equation 47. Since all ions are assumed identical as to size and shape, ω_{ik} and ω_{il} are independent of the ionic species l, as are the integrals

$$\int_{\omega_{ik}, \omega_{il}}^{\infty} [g(r_{kl})/r_{il}]\, dv_l$$

so that equation 47 becomes

$$\begin{aligned} g(R) &= \frac{1}{R} - \frac{\kappa^2}{4\pi} \int_{\omega_{13}, \omega_{23}}^{\infty} \frac{g(r_{13})}{r_{23}}\, dv_3 \\ \kappa^2 &= \frac{4\pi}{\epsilon kT} \sum_{l=1}^{\nu} \frac{N_l e_l^2}{v} \end{aligned} \tag{50}$$

where R, r_{13}, and r_{23} have been introduced for r_{ik}, r_{kl}, and r_{il}. We remark that κ is identical with the corresponding function in the Debye–Hückel theory. We now assume that the ions are spherical in shape so that ω_{13} and ω_{23} are spherical regions of equal radius a, separated by a distance R, which are to be excluded from the region of integration in equation 50. Introducing r_{13} and r_{23} as variables of integration, we have

$$dv_3 = (2\pi/R)r_{13}r_{23}dr_{13}dr_{23}$$

By integration over r_{23}, with proper regard to the influence of ω_{23} upon the limits of integration, we obtain the following integral equation. For simplicity we designate the single remaining variable of integration, r_{13}, by r.

$$\begin{aligned} g(R) &= \varphi(R)/R \\ \varphi(R) &= 1 - \kappa^2 \int_a^\infty K(R, r)\varphi(r)\,dr \end{aligned} \tag{51}$$

where the kernel $K(R, r)$ has the form

$$\begin{array}{lll} a \leq R < 2a\colon K(R, r) & = (r + R - a)/2 & a \leq r < R + a \\ & = R & R + a \leq r < \infty \\ 2a \leq R < \infty\colon K(R, r) & = r & a \leq r < R - a \\ & = (r + R - a)/2 & R - a \leq r < R + a \\ & = R & R + a \leq r < \infty \end{array} \tag{52}$$

If we had neglected the size of one of the ions and extended the integration over ω_{23}, the kernel $K(R, r)$ would have the simpler form

$$\begin{aligned} & a \leq R < \infty \\ & K(R, r) = r\,;\, a \leq r < R \\ & \qquad\quad = R;\, R \leq r < \infty \end{aligned} \tag{53}$$

With the approximate kernel (53), equation 51 is equivalent to the linear Poisson–Boltzmann equation with boundary conditions, of the Debye–Hückel theory. The unique solution is

$$\varphi(R) = \frac{e^{-\kappa(R-a)}}{1 + \kappa a} \tag{54}$$

a result which may be verified by direct substitution. The corresponding value of $W_i^k(\lambda_i, R)$ is

$$W_i^k(\lambda_i, R) = \frac{\lambda_i e_i e_k}{\epsilon R} \frac{e^{-\kappa(R-a)}}{1 + \kappa a} \tag{55}$$

With the omission of the salting-out term and the hard sphere term, the activity coefficient of a spherical ion of type i may be obtained from equations 40, 33, and 34,

$$kT \log \gamma_i' = \frac{4\pi e_i}{\epsilon} \sum_{k=1}^{\nu} \frac{N_k}{v} e_k \int_0^1 \int_a^\infty R(e^{-\beta W_i^k(\lambda_i)} - 1)\,dR d\lambda_i \tag{56}$$

where, because of electrical neutrality of the solution, the vanishing term $(4\pi e_i/\epsilon) \sum_{k=1}^{\nu} (N_k e_k)/v \int_0^1 \int_a^\infty R\mathrm{d}R\mathrm{d}\lambda_i$ has been subtracted from the left-hand side of equation 56. If $W_i^k(\lambda_i, R)$ has the form 48, and non-linear terms in the expansion of the exponential can be neglected, we have

$$kT \log \gamma_i' = -\frac{e_i^2}{2\epsilon} \kappa^2 \int_a^\infty \varphi(R)\,\mathrm{d}R \tag{57}$$

where $\varphi(R)$ satisfies the integral equation 51. With the solution 54 corresponding to the approximate kernel 53, in which the size of one of the ions is neglected, we obtain the Debye–Hückel (3) result

$$kT \log \gamma_i' = -\frac{e_i^2}{2\epsilon} \frac{\kappa}{1 + \kappa a} \tag{58}$$

The mean activity coefficient of any electrolyte which may be formed from the ions in the solution may be calculated from the individual ion activity coefficients in the usual way.

The solution of equation 51 with the kernel 52, which takes the sizes of both ions of the pair into account, is considerably more difficult. It is found that the solution may be expressed in the form

$$\varphi(R) = \sum_{n=1}^{\infty} A_n e^{-z_n R} \tag{59}$$

where the sum extends over all roots z_n, with positive real parts, of the transcendental equation

$$z^2 - \kappa^2 \cosh za = 0 \tag{60}$$

It is convenient to order the roots according to the magnitudes of their real parts. Several of the denumerably infinite set of roots are tabulated below:

$$z_n = \alpha_n + i\beta_n$$

κa	0.10	1.00	1.03	2.00
$\alpha_1 a$	0.10	1.62	2.07	1.06
$\beta_1 a$	0.00	0.00	0.00	+2.08
$\alpha_2 a$	9.88	2.56	2.07	1.06
$\beta_2 a$	0.00	0.00	0.00	−2.08
$\alpha_3 a$	11.11	6.26		4.84
$\beta_3 a$	±14.42	±14.90		±15.07

When κa is less than 1.03, there are two real roots, one of which remains very nearly equal to κa in dilute solutions. At κa equal to 1.03, the real roots merge into a repeated root, while for greater values of κa, all roots are complex. For small values of κa, all roots except z_1 have very large real parts, so that their contributions to $\varphi(R)$, equal to e^{-z_nR}, will decay rapidly as R increases, and so can be important only for small values of R. In more concentrated solutions, $\kappa a > 1.03$, all roots are complex, imparting to $\varphi(R)$ an oscillatory form, characteristic of radial distribution functions in liquids.

By substitution of the form 59 in the integral equation 51 with the kernel 52 for $R > 2a$, it is found that only one condition is imposed upon the coefficient A_n.

$$\sum_{n=1}^{\infty} \frac{A_n}{z_n^2} e^{z_n a}(1 + z_n a) = 1/\kappa^2 \tag{61}$$

However, in order that 59 be a solution in the interval $a \leq R < 2a$, an infinite set of conditions is imposed upon the A_n. Since the e^{-z_nR} doubtless form a complete set of functions, they could be orthogonalized by linear combination in the interval $a \leq R < 2a$, and the properties of orthogonal sets could be used in conjunction with the integral equation for the determination of the A_n. However, this process is rather laborious and cumbersome. A better method, suggested to the writer by Dr. Warschawski of Cornell University, is to calculate the Laplace transform $\int_0^\infty \varphi(R)e^{-uR}dR$, which is then inverted by means of the Fourier integral theorem. This procedure transforms the integral equation 51 entirely onto the interval $a \leq R < 2a$. Although the resulting integral equation cannot be solved in finite terms, it leads immediately to the desired set of linear relations between the A_n, for a solution of the form 59.

We shall be content here with the construction of an approximate solution, involving only the first two terms of the series 59. Using the two roots z_n with smallest real parts, we can make the solution

$$\varphi(R) = A_1 e^{-z_1(R-a)} + A_2 e^{-z_2(R-a)} \tag{62}$$

fit at the two ends of the interval, $R = a$ and $R = 2a$, and everywhere outside, $R > 2a$. By substitution in equation 51 with the kernel appropriate to $a \leq R < 2a$, the condition that equation 62 be a solution at $R = a$ imposes one linear relation upon the coefficients. A second relation is furnished by equation 61, and we remember that any linear combination of the form 59 is a solution of $R = 2a$ and for all greater values of R. After making some transformations with the aid of equation 60, we have

$$\begin{aligned} A_1(1 + z_1 a)/z_1^2 + A_2(1 + z_2 a)/z_2^2 &= 1/\kappa^2 \\ A_1 e^{z_1 a}/z_1^2 + A_2 e^{z_2 a}/z_2^2 &= 1/\kappa^2 \end{aligned} \tag{63}$$

with solutions

$$\begin{aligned} A_1 &= \frac{z_1^2}{\kappa^2} \frac{e^{-z_1 a} - e^{-(z_1+z_2)a}(1 + z_2 a)}{(1 + z_1 a)e^{-z_1 a} - (1 + z_2 a)e^{-z_2 a}} \\ A_2 &= \frac{z_2^2}{\kappa^2} \frac{e^{-z_2 a} - e^{-(z_1+z_2)a}(1 + z_1 a)}{(1 + z_2 a)e^{-z_2 a}(1 + z_1 a)e^{-z_1 a}} \end{aligned} \tag{64}$$

when $\kappa a < 1.03$, z_1 and z_2 are real, equal to α_1 and α_2. $W_i^k(\lambda_i, R)$ and log γ_i' may be computed by substitution of equations 62 and 64 into 48 and 57.

$$W_i^k(\lambda_i, R) = \lambda_i \frac{e_i e_k}{\epsilon R} [A_1 e^{-\alpha_1(R-a)} + A_2 e^{-\alpha_2(R-a)}] \tag{65}$$

For the activity coefficient, we obtain

$$kT \log \gamma_i' = -\frac{e_i^2}{2\epsilon} \frac{\alpha_1 e^{-\alpha_1 a}(1 - e^{-\alpha_2 a}) - \alpha_2 e^{-\alpha_2 a}(1 - e^{-\alpha_1 a})}{(1 + \alpha_1 a)e^{-\alpha_1 a} - (1 + \alpha_2 a)e^{-\alpha_2 a}} \tag{66}$$

In dilute solutions, reference to the table of roots shows that $(\alpha_2 a - \alpha_1 a)$ is very large, amounting to about 9.0. Under these circumstances all terms involving $e^{-\alpha_2 a}$ are completely negligible and we have

$$kT \log \gamma_i' = -\frac{e_i^2}{2\epsilon} \frac{\alpha_1}{1 + \alpha_1 a} \tag{67}$$

a result which differs from the Debye–Hückel expression only by the appearance of α_1 instead of κ. But in dilute solutions α_1 differs inappreciably from κ so that the Debye–Hückel result is obtained. When κa is equal to 1.03, the roots z_1 and z_2 merge into a repeated root, and equations 63 have no solutions. However, the expressions 65 and 66 for $W_i^k(\lambda_i, R)$ and the activity coefficient both converge for $\kappa a = 1.03$, although A_1 and A_2 individually diverge. Beyond $\kappa a = 1.03$, the roots z_1 and z_2 become complex conjugates, $\alpha \pm i\beta$ and equations 63 again have solutions. Then $W_i^k(\lambda_i, R)$ takes the form

$$\begin{aligned} W_i^k(\lambda_i, R) &= \lambda_i \frac{e_i e_k}{\epsilon R} e^{-\alpha(R-a)}[A_1 \cos \beta(R - a) + A_2 \sin \beta(R - a)] \\ A_1 &= \frac{1}{\kappa^2} \frac{(\alpha^2 - \beta^2)[\sin \beta a - \beta a e^{-\alpha a}] - 2\alpha\beta[\cos \beta a - (1 + \alpha a)e^{-\alpha a}]}{(1 + \alpha a) \sin \beta a - \beta a \cos \beta a} \\ A_2 &= \frac{1}{\kappa^2} \frac{(\alpha^2 - \beta^2)[\cos \beta a - (1 + \alpha a)e^{-\alpha a}] + 2\alpha\beta[\sin \beta a - \beta a e^{-\alpha a}]}{(1 + \alpha a) \sin \beta a - \beta a \cos \beta a} \end{aligned} \tag{68}$$

For the activity coefficient, we obtain the expression

$$kT \log \gamma_i' = -\frac{e_i^2}{2\epsilon} \frac{\alpha \sin \beta a - \beta(\cos \beta a - e^{-\alpha a})}{(1 + \alpha a) \sin \beta a - \beta a \cos \beta a} \tag{69}$$

In figure 1, equations 66 and 69 are compared with the Debye–Hückel formula (58). In dilute and moderately dilute solutions, $\kappa a < 0.5$, $\log \gamma_i'$ does not differ much from the Debye–Hückel value. However, at higher concentrations, $\kappa a > 1.03$, the deviation becomes appreciable, and $\log \gamma_i'$ fails to approach the Debye–Hückel asymptotic value $-e_i^2/\epsilon akT$.

The periodic factor in $W_i^k(\lambda_i, R)$, for $\kappa a > 1.03$, is particularly interesting. As κa increases, the real part, α, of z_1 and z_2 diminishes, and the

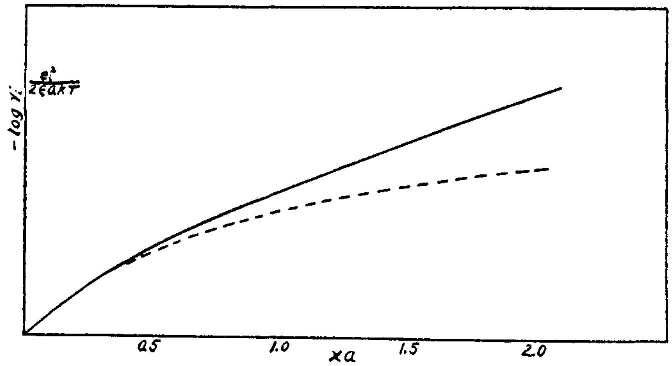

FIG. 1

- - - - - - Debye–Hückel equation 58
———— Equations 66 and 69.

exponential decay becomes less rapid. In other words the ionic atmosphere expands. At the same time the period of oscillation $2\pi/\beta$, at first very long, tends to a distance slightly exceeding the ionic diameter, a. When κa becomes equal to 2.79, α vanishes and equation 68 is no longer a solution of 51. At higher concentrations, a liquid type of distribution function, if one exists at all, must be constructed from the higher roots of equation 60. For values of κa just less than 2.79, the exponential factor is effectively unity over many molecular diameters, and the corresponding distribution is suggestive of a microcrystalline distribution, with "local" long-range order extending over many molecular diameters. This brings up the intriguing question: Do very concentrated electrolyte solutions ($\kappa a > 2.79$) possess long-range crystalline order in the distribution of the ions, which they contain? A loosely bound statistical lattice might still leave the solution with the elastic properties of a viscous fluid, manifesting itself chiefly in the optical properties. The answer to this question is probably in the negative, for the solution 68, in which only the first two roots of equation 60 are employed, very likely has only qualitative significance at very high concentrations. The value, $\kappa a = 2.79$, predicted by equation 68 as the limiting concentration for a liquid type of distribution seems altogether too low. Thus in a uni-univalent electrolyte solution with $e_i^2/\epsilon akT$ equal to unity, this value of κa corresponds to a volume about 2.3 times greater than the ions would occupy if packed in a face-centered cubic lattice, with an interionic distance equal to the diameter a.

Better approximations to the solution of equation 51, may be obtained by including terms e^{-z_nR} involving the higher roots of equation 60. The best way to do this is to employ a general method based upon the Laplace transformation. However, the method employed here could be extended by including the terms e^{-z_nR} involving the first m roots (ordered according to the magnitude of their real parts) and determining the coefficients A_n by making the sum $\sum_{n=1}^{m} A_n e^{-z_n(R-a)}$ a solution of equation 51 at m points on the interval $a \leq R < 2a$. However, even an exact solution of equation 51, although a step in the right direction, could be applied only with caution to very concentrated electrolyte solutions. There is always the question of the error arising from approximating the local dielectric constant by the macroscopic one. This error is doubtless serious when the mole fraction of the electrolyte becomes comparable with that of the solvent. Moreover, even if the macroscopic dielectric constant can be used, it may become so small in very concentrated solutions that it is not permissible to approximate the exponentials in equation 39 by the first two terms of their series expansions. Under these circumstances equation 51 no longer furnishes an adequate approximation to $W_i^k(\lambda_i)$. Another point should be borne in mind. The γ_i' of equation 57 is not the actual activity coefficient, but must be corrected for salting out and multiplied by the hard sphere factor γ_i^*, before comparison with experiment can be made. These latter influences are not negligible in comparison with the pure electrostatic effect, at very high concentrations.

In spite of the fact that equation 51 can be attributed only to qualitative significance in extremely concentrated solutions, it seems reasonable to suppose that it can be used quantitatively in moderately dilute solutions, let us say up to concentrations of 1 mole per liter, as long as $e_ie_k/\epsilon akT$ is small relative to unity for all ion pairs. When this condition is not fulfilled, either equation 39 must be solved without expansion of the exponentials, or a method of the Bjerrum (1) type must be used. Since the error involved in approximating W_{ik}^l by $W_i^l + W_k^l$ is of the same order of magnitude as the non-linear terms in the expansion of the exponentials of equation 39, the former method is almost hopelessly complicated. The Bjerrum method seems therefore to be the most promising.

V. STATISTICAL MASS ACTION AND THE BJERRUM THEORY OF ION ASSOCIATION

If the potential V_{ik} has a minimum of depth large relative to kT for certain values of the relative coördinates of the molecular pair i and k, and if for this configuration, they exert together only a small attractive force upon neighboring molecules, W_i^k may be approximated by an expression which leads to simple mass action. It is a matter of considerable interest to investigate the nature of this approximation.

Reference to equation 18 of "Statistical Mechanics of Fluid Mixtures" (11) allows us to write the chemical potential of a component i in the form

$$\begin{aligned} \mu_i &= kT \log f_i(1) C_i + \varphi_i(T) \\ kT \log f_i(\lambda) &= \int_0^\lambda \overline{V_i(t)}\, \mathrm{d}t = \sum_{k=1}^{\nu} \frac{N_k}{v} \int_0^\lambda \int_0^v V_{ik} e^{-\beta W_i^k(t,1)}\, \mathrm{d}v_k\, \mathrm{d}t \end{aligned} \tag{70}$$

where C_i is the concentration of component i, in any units, conversion factors being absorbed into $\varphi_i(T)$, and $f_i(\lambda)$ is the activity coefficient of a partially coupled molecule i. Let us now consider a potential of average force $W_i^k(\lambda_i, \lambda_k)$, defined for a potential of intermolecular force $V_N(\lambda_i, \lambda_k)$ (equation 7, "Statistical Mechanics of Fluid Mixtures"), in which only the coupling parameters λ_i and λ_k for a single pair of molecules differ from unity.

$$\begin{aligned} e^{-\beta W_i^k(\lambda_i,\lambda_k)} &= \frac{v^2 \int \cdots \int e^{-\beta V_N(\lambda_i,\lambda_k)}\, \mathrm{d}v_1 \cdots \mathrm{d}v_{N-2}}{\int \cdots \int e^{-\beta V_N(\lambda_i,\lambda_k)}\, \mathrm{d}v_1 \cdots \mathrm{d}v_N} \\ V_N(\lambda_i, \lambda_k) &= V_{N-2} + \lambda_i \lambda_k V_{ik} + \lambda_i V_i' + \lambda_k V_k' \\ V_i' = \sum_{\substack{l=1 \\ \neq k}}^{N} V_{il} & \qquad V_k' = \sum_{\substack{l=1 \\ \neq i}}^{N} V_{kl} \end{aligned} \tag{71}$$

Equations similar to equation 29 ("Statistical Mechanics of Fluid Mixtures") may be obtained by partial differentiation of equation 71

$$\begin{aligned} \frac{\partial W_i^k(\lambda_i, \lambda_k)}{\partial \lambda_i} &= \lambda_k V_{ik} + {}^{ik}\overline{V_i'(\lambda_i, \lambda_k)} - \overline{V_i'(\lambda_i)} \\ \frac{\partial W_i^k(\lambda_i, \lambda_k)}{\partial \lambda_k} &= \lambda_i V_{ik} + {}^{ik}\overline{V_k'(\lambda_i, \lambda_k)} - \overline{V_k'(\lambda_k)} \end{aligned} \tag{72}$$

It is unnecessary to indicate the dependence of $\overline{V_i'(\lambda_i, \lambda_k)}$ on λ_k since, except for a term of zero order, it will be independent of the coupling with any single molecule of type k. On the other hand $\overline{{}^{ik}V_i'(\lambda_i, \lambda_k)}$, an average with i and k held fixed, will depend on both λ_i and λ_k when the two molecules are in each other's neighborhood. In order to calculate $W_i^k(\lambda, 1)$, we remember that $W_i^k(\lambda_i, \lambda_k)$ must vanish when either λ_i or λ_k is zero. We choose a path of integration in the (λ_i, λ_k) plane consisting of the straight line $\lambda_i = \lambda t$; $\lambda_k = t$ extending from the origin to the point $(\lambda, 1)$. Using this path and the partial derivatives of equation 72, we obtain

$$\begin{aligned} W_i^k(\lambda, 1) = \lambda V_{ik} + \int_0^1 [\lambda\, {}^{ik}\overline{V_i'(\lambda t, t)} + {}^{ik}\overline{V_k'(\lambda t, t)}]\, \mathrm{d}t \\ - \int_0^\lambda \overline{V_i'(t)}\, \mathrm{d}t - \int_0^1 \overline{V_k'(t)}\, \mathrm{d}t \end{aligned} \tag{73}$$

We note that $\lambda V_i' + V_k'$ is the mutual potential energy of the molecular pair i and k with all the other molecules of the solution. Let us write

$$kT \log f_{ik}(\lambda, 1, q_{ik}) = \int_0^1 [\lambda\, {}^{ik}\overline{V_i'(\lambda t, t)} + {}^{ik}\overline{V_k'(\lambda t, t)}]\, \mathrm{d}t \tag{74}$$

By reference to equation 70, we see that $f_{ik}(\lambda, 1, q_{ik})$ could be interpreted as an activity coefficient of the compound molecule (ik), in which the relative coördinates q_{ik} of the pair have some fixed value. This interpretation, while correct is, however, unessential. Referring again to equation 70 and remembering that $\overline{V_i'(t)}$ and $\overline{V_k'(t)}$ can be identified with $\overline{V_i(t)}$ and $\overline{V_k(t)}$ (since in an average in which no molecules are held fixed, any single term $\overline{V_{ik}}$ is of negligible order), we may write equation 73 in the form

$$W_i^k(\lambda, 1) = \lambda V_{ik} + kT \log \frac{f_{ik}(\lambda, 1, q_{ik})}{f_i(\lambda) f_k(1)} \tag{74}$$

The usefulness of this expression is apparent, for if V_{ik} has a deep minimum for some particular configuration q_{ik}, and at the same time f_{ik} is practically unity, $W_i^k(\lambda, 1)$ can be approximated by $\lambda V_{ik} - kT \log f_i(\lambda) f_k(1)$. As will presently be shown, it is this approximation which leads to simple mass action.

From now on, we shall limit our attention to a system of only two components. Using equations 70 and 74, and separating the region of integration for unlike pairs into a region v_0 for small values of their relative coördinates and $v - v_0$ for large values, we may write

$$\begin{aligned} kT \frac{\mathrm{d} \log f_1(\lambda)}{\mathrm{d}\lambda} &= C_2 f_1(\lambda) f_2(1) \int_0^{v_0} \frac{V_{12}}{f_{12}} e^{-\beta\lambda V_{12}}\, \mathrm{d}v + kT \frac{\mathrm{d} \log \overline{f_1(\lambda)}}{\mathrm{d}\lambda} \\ kT \log \overline{f_1(\lambda)} &= C_2 \int_0^\lambda \int_{v_0}^v V_{12} e^{-\beta W_1^2(t,1)}\, \mathrm{d}v\, \mathrm{d}t + C_1 \int_0^\lambda \int_0^v V_{11} e^{-\beta W_1^1(t,1)}\, \mathrm{d}v\, \mathrm{d}t \end{aligned} \tag{75}$$

where C_1 and C_2 are the bulk concentrations of the two components in molecules per cubic centimeter. The expression 74 has been introduced only for W_1^2 in the region v_0. It could have been used for all W_i^k, but this would not be a very useful procedure. A similar equation may be constructed for $f_2(\lambda)$. Integration of equation 75 and the similar one for $f_2(\lambda)$ with regard for the fact that $f_1(0)$ and $f_2(0)$ have the value unity, leads to the result

$$\frac{1}{f_1} - \frac{1}{\bar{f}_1} = K_1 f_2 C_2$$

$$\frac{1}{f_2} - \frac{1}{\bar{f}_2} = K_2 f_1 C_1$$

$$K_1 = -\frac{1}{kT}\int_0^1 \int_0^{v_0} V_{12}\, g_{12}(t, 1)^{-1} e^{-\beta t V_{12}}\, \mathrm{d}v\, \mathrm{d}t \tag{76}$$

$$K_2 = -\frac{1}{kT}\int_0^1 \int_0^{v_0} V_{12}\, g_{21}(t, 1)^{-1} e^{-\beta t V_{12}}\, \mathrm{d}v\, \mathrm{d}t$$

$$g_{12}(t, 1) = \frac{f_{12}(t, 1, q_{12})\overline{f_1(1)}}{\overline{f_1(t)}}; \qquad g_{21}(t, 1) = \frac{f_{12}(1, t, q_{12})\overline{f_2(1)}}{\overline{f_2(t)}}$$

where all activity coefficients refer to $\lambda = 1$, since it is these that we finally desire. The functions K_1 and K_2 depend in general upon the composition of the solution. We shall assume them to be equal. It seems probable that this could be proved generally true, and it is certainly true when $e^{-\beta t V_{12}}$ has a strong peak at $t = 1$, the most important case. We now define quantities C_{12} and $\bar{f}_{12}$ by the relations

$$f_1 C_1 = \bar{f}_1(C_1 - C_{12})$$

$$f_2 C_2 = \bar{f}_2(C_2 - C_{12}) \tag{77}$$

$$\bar{f}_{12} = \frac{K}{K_1} = \frac{K}{K_2}$$

where K is an arbitrarily chosen equilibrium constant. Equations 77 over-define C_{12}, but substitution in equations 76 shows that both relations are satisfied. The substitution leads to the following equation for C_{12}

$$\frac{\bar{f}_{12} C_{12}}{\bar{f}_1 \bar{f}_2 (C_1 - C_{12})(C_2 - C_{12})} = K \tag{78}$$

which is the generalized mass action equation, C_{12} having a phenomenological interpretation as the concentration of compound pairs defined with reference to the equilibrium constant K. Up to this point we have made use of purely formal operations, and, except for the assumption of equality of K_1 and K_2, the results are rigorously true within the frame of classical statistical mechanics. While equation 78 could of course be written down at once, on formal thermodynamic grounds, our rather tedious analysis is necessary for the correlation of the activity coefficients $\bar{f}_1$, $\bar{f}_2$, and $\bar{f}_{12}$ with intermolecular forces.

A suitable choice of the equilibrium constant K is evidently the following

$$K = \int_0^{v_0} (e^{-\beta V_{12}} - 1)\,\mathrm{d}v$$

$$\bar{f}_{12} = \frac{\int_0^1 \int_0^{v_0} V_{12} e^{-\beta t V_{12}}\,\mathrm{d}v\,\mathrm{d}t}{\int_0^1 \int_0^{v_0} V_{12} g_{12}^{-1} e^{-\beta t V_{12}}\,\mathrm{d}v\,\mathrm{d}t} \tag{79}$$

With this equilibrium constant, we obtain simple mass action if $\bar{f}_1$, $\bar{f}_2$, and $\bar{f}_{12}(t, 1)$ do not deviate appreciably from unity. Again, if V_{12} has a sharp minimum of depth large relative to kT, inside v_0, $e^{-\beta t V_{12}}$ will have a sharp peak for this configuration as well as at $t = 1$ in the interval $0 \leq t \leq 1$, and we have

$$\bar{f}_{12} = f_{12}(1, 1, q_{12}^0) \tag{80}$$

where q_{12}^0 specifies the relative coördinates of the pair at which V_{12} has its minimum. It may happen that $\bar{f}_{12}$, $\bar{f}_1$, $\bar{f}_2$ do not deviate much from unity, or much less from unity than f_1 or f_2, so that simple mass action will furnish a good first approximation in the calculation of f_1 and f_2. This will be true for an ion pair when $-e_i e_k/\epsilon a k T$ is large relative to unity, since $\bar{f}_{12}$ is then the activity coefficient of a dipole under the influence of ions. Again in the case of a pair of dipole molecules, for which V_{12} has a sharp minimum in the antiparallel orientation, $\bar{f}_{12}$ will be the activity coefficient of a quadrupole in the presence of dipoles. The choice of v_0 is arbitrary. Any change in $\bar{f}_{12}$ caused by a change in v_0 will be compensated by changes in $\bar{f}_1$ and $\bar{f}_2$. However, the method is likely to prove useful only when V_{12} has such a deep maximum that K and $\bar{f}_{12}$ are very insensitive to the choice of v_0. For short-range forces, v_0 may conveniently be expanded to include the entire volume v of the solution, provided $\bar{f}_{12}$ does not differ sensibly from unity for any configuration in which V_{12} differs effectively from zero. This is not true of interionic forces.

We shall now discuss the application of the theory just outlined to electrolyte solutions. When certain conditions are fulfilled it leads to the theory of ionic association first proposed by Bjerrum (1), and so successfully extended and applied by Kraus and Fuoss (14). Although we have considered a system of only two components, an argument similar to that used in section II allows us to apply the theory to two solute components in the presence of an excess of solvent, $V_{ik}^{(s)}$ replacing the V_{ik}, and $\mu_i^0(T, p)$, the non-ideal part of the chemical potential at infinite dilution, replacing $\varphi_i(T)$ as the reference value of the chemical potential. For brevity we shall omit the superscript s on the V_{ik} in what follows. We shall consider a uni-univalent electrolyte at a molecular concentration C in a solvent of dielectric constant ϵ. The bulk concentrations of both positive and negative ions are then both equal to C. Under these circumstances, we obtain from equations 77 and 78 for the activity coefficient of either ionic species, also $f_{\pm}$, the mean activity coefficient,

$$f_1 = (1 - \alpha)\bar{f}_1$$
$$\frac{\bar{f}_{12}\,\alpha}{\bar{f}_1\bar{f}_2\,(1 - \alpha)^2} = Kc \tag{81}$$
$$K = 4\pi \int_a^{r_0} \left(e^{e_1^2/\epsilon r kT} - 1\right) r^2\, dr$$

where v_0 is taken as a sphere of radius r_0, and α is equal to c_{12}/c. For the present we suppose merely that r_0 is chosen so that W_1^2/kT is small relative to unity for all greater values of the interionic distance, so that the exponentials in equation 75 defining $\bar{f}_1$ may be expanded with retention of only the first two terms. For ions of the same valence type, we may suppose that for distances less than r_0, W_1^1/kT is large and positive relative to unity so that $e^{-\beta W_1^1}$ is effectively zero, while outside r_0 the exponential may be expanded. Taking account of electrical neutrality, we then have

$$kT \log \bar{f}_1 = -\kappa^2 \int_0^1 \int_{r_0}^{\infty} [W_1^1(t, 1) - W_1^2(t, 1)]\, r\, dr\, dt \tag{82}$$

where κ is the Debye kappa for a uni-univalent electrolyte. It would be necessary to have recourse to equation 39 for a satisfactory investigation of W_1^2 and W_1^1 when $r > r_0$. Since this involves difficulties which have not yet been overcome, we shall limit ourselves to some semi-quantitative remarks. By analogy with the simple Debye formula, equation 58, Bjerrum assumed

$$kT \log \bar{f}_1 = -\frac{e_1^2}{2\epsilon}\frac{\kappa'}{1 + \kappa' r_0}$$
$$\kappa' = (1 - \alpha)^{1/2}\,\kappa \tag{83}$$

where κ' is an effective kappa, computed with the concentration of "free" ions, $c - c_{12}$. This result follows from equation 82 if the potentials of average force have the form

$$W_1^1(t, 1) = -W_1^2(t, 1) = t\,\frac{e_1^2(1 - \alpha)}{\epsilon R}\,\frac{e^{-\kappa'(R - r_0)}}{1 + \kappa' r_0} \tag{84}$$

It may be verified without difficulty that $W_1^1 = e_1\overline{\psi(R)}$ and $W_1^2 = -e_1\overline{\psi(R)}$ where $\overline{\psi(R)}$ is the mean electrostatic potential in the neighborhood of a sphere of radius r_0 containing a total charge $te_1(1 - \alpha)$; when the Poisson-Boltzmann equation holds for $r > r_0$ and the boundary conditions of electrostatics are satisfied at $r = r_0$. This is a reasonable approximation, for $\pm e_1(1 - \alpha)$ is indeed the average charge carried by the sphere r_0 around any ion, α being the probability that an ion is "associated," that is, that another ion of opposite charge lies within the sphere, r_0. Further, the appearance of the effective kappa, κ', means that the other ions in the solution screen with this same average charge, $\pm e_1(1 - \alpha)$. With the Bjerrum result, equation 83, we obtain

$$\log \bar{f}_1 = - \frac{e_1^2}{2\epsilon kT} \frac{\kappa'}{1 + \kappa' r_0} + \log (1 - \alpha) \tag{85}$$

where α is to be calculated by equation 81. In the original Bjerrum theory $\bar{f}_{12}$ was assumed to be unity. Fuoss, however, has made estimates of $\bar{f}_{12}$ by considering the interaction of an ion pair in contact with remaining "free" ions in the solution. It is difficult to judge the adequacy of Bjerrum's approximation to $\bar{f}_1$. It is probably adequate in dilute solutions, when α is small relative to unity, but should be used with caution for values of α intermediate between zero and unity. When α is nearly unity, it is again adequate, for then it is sufficient to know that $\bar{f}_1$ is virtually unity and its form as a function of concentration is unimportant.

We have remarked that r_0 must be sufficiently large to permit the expansion of $e^{-\beta W_1^2}$ and $e^{-\beta W_1^1}$ for greater interionic distances. This condition is satisfied by Bjerrum's value

$$r_0 = e_1^2/2\epsilon kT$$

Otherwise the choice of r_0 is arbitrary, any change being absorbed in $\bar{f}_{12}$, $\bar{f}_1$, and $\bar{f}_2$. However, it should be remembered that an unfortunate choice of r_0, for example too large a value, can make it impossible to approximate $\bar{f}_{12}$ by unity or by the activity coefficient of a dipole consisting of an ion pair in contact. The simple Bjerrum theory will be useful only when this can be done. If $e^{-\beta V_{12}}$ has a strong peak when the ions are in contact, both K and $\bar{f}_{12}$ are very insensitive to the choice of r_0, provided it remains a length of molecular order of magnitude, and under these circumstances the theory leads to unambiguous results. An illuminating discussion of this point has been made by Fuoss (5), with the aid of a distribution function, specifying the probability that an ion pair be separated by a distance R, while no other ions be within the sphere of radius R.

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