

ELECTROLYTES

Edited by
B. PESCE

ELECTROLYTES

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PREFACE

ALTHOUGH the field of electrolytes still has a vital and stimulating appeal for research scientists, it has rarely been discussed in Congresses held over the past few years.

Apart from the 'General Discussion' on the interactions in ionic solutions held in September 1957 at the Faraday Society, Oxford, no post-war Congress of international standing has dealt with electrolytes.

But there are obviously several reasons for holding the Symposium on electrolytes within the frame of the 47th Reunion of the Italian Society for Scientific Progress (Società Italiana per il Progresso delle Scienze; S.I.P.S.). Some aspects of this subject either were not taken up in the discussion in the Autumn of 1957 by the Faraday Society or, if they were, a wider examination and estimate of successive or collateral developments appeared to be opportune and justified.

Only a few indications can, of course, be given as examples here; the consideration of molecular forces at short range, above all active in the field of concentrated solutions; the treatment of some typical cases of ionic equilibrium in non-aqueous or mixed solvents; the quantitative elaboration of some basic problems (such as the accurate numerical solution of the Poisson-Boltzmann equation and the calculation of some thermodynamic quantities of strong electrolytes); the behaviour of polyelectrolytes in the electrical field; the ultrasonic behaviour and the ion-solvent interaction. But the wide, fundamental studies in the field of electrical conductance should, in particular, be indicated with the brilliant results obtained during the last five years mainly due to R. M. Fuoss, C. A. Kraus, L. Onsager and their schools. It is not only a question of notable theoretical developments which are really conclusive, but, 'granted the high precision obtainable in conductance work, of a powerful instrument for the penetration of the molecular structure and the interactions.'

Finally, another justification—but not the last—should be noted. With this Symposium, the S.I.P.S. wanted to remember Svante Arrhenius on the centenary of his birth and to give homage to Peter Debye—the main author of the electrostatic theory of electrolytes—who, by his active participation in the Symposium, has stirred up extensive and lively interest in it. In this way the Symposium brings together the two most important names in the electrolyte field.

The S.I.P.S. expresses its keen appreciation and gratitude to R. M. Fuoss who has with devoted care undertaken the scientific organisation of the Symposium.

September 1961

B. PESCE

CONTENTS

	PAGE
Molecular Forces	1
P. DEBYE	
Topological Methods in the Cluster Theory of Ionic Solutions	7
E. MEERON	
The Electrical Properties of Ice	27
L. ONSAGER and M. DUPUIS	
The Accurate Numerical Solution of the Poisson-Boltzmann Equation	47
E. A. GUGGENHEIM	
Solvation of Electrolytes in Dioxane-Water Mixtures	62
E. GRÜNWARD	
The Interaction of Two Ions at Small Separations in an Aqueous Medium	77
S. LEVINE and G. M. BELL	
The Transport of an Electrolyte during the Diffusion of a Non-Electrolyte	96
F. J. KELLY and R. H. STOKES	
Contributo allo Studio delle Giunzioni Interliquido negli Elettroliti	101
R. PIONTELLI	
Zur Theorie der Leitfähigkeit Starker Elektrolyte	109
H. FALKENHAGEN und G. KELBG	
Ionic Association and the Fuoss-Onsager Conductance Equation	119
R. L. KAY	
Solvent-Solute Interaction in Dilute Electrolytic Solutions	132
H. SADEK, E. HIRSCH and R. M. FUOSS	
The Behaviour of Carboxylic Acids in Mixed Solvents	146
T. SHEDLOVSKY	
Acid Ionization Constants of Alcohols in the Solvents Water and Deuterium Oxide	152
F. A. LONG and P. BALLINGER	
A Test of the Hammett Relation	165
R. A. ROBINSON	
Electronic Structure of Strong and Weak Electrolytes	170
K. FAJANS	
Dissociation Constants of Carboxylic Acids in Formamide	176
M. MANDEL and P. DECROLY	

Debye's Salt Effect Theory applied to Aqueous Solutions of Electrolytes and Urea, 1/Electrolytes with Common Anion and Cations of Various Valencies M. SARNOWSKI and B. BARANOWSKI.	187
Sulla Carica Superficiale di Alcune Soluzioni Elettrolitiche S. BORDI e F. VANNEL	196
On the Configurational Stability of DNA in Diluted Solution A. M. LIQUORI, F. ASCOLI, C. BOTRÉ, V. CRESCENZI and A. MELE	201
Investigation of Transport Numbers by Measurement of the e.m.f. of Galvanic Cells with Second Class Electrodes S. LENGVEL	208
Counterion Binding by Macro-ions U. P. STRAUSS	215
Untersuchungen zur Statistisch-Mechanischen Theorie Starker Elektrolyte G. KELBG	226
Ricerche Sull'Effetto Cinetico Primario di Sale V. CARASSITI e C. DEJAK	230
Influenza del Raggio dei Controioni sull'Associazione in Soluzione di Polimetacrilato V. CRESCENZI, A. DE CHIRICO and A. RIPAMONTI	248
Hydrogen Halides in Polar Organic Solvents G. J. JANZ and S. S. DANYLUK	255
Ricerche Sulla Teoria delle Soluzioni Concentrate di Elettroliti Forti XXIV C. DEJAK	266
Ricerche Sulla Teoria delle Soluzioni Concentrate di Elettroliti Forti XXV C. DEJAK	281
Electrolytical Conductance of Some Picrates in Alcohol Mixtures F. ACCASCINA and S. PETRUCCI	292
Ultrasonic Behaviour of Liquid Systems F. ACCASCINA and S. SCHIAVO.	301
Structure and Kinetic Properties of Polyelectrolytes in Solution, determined from Relaxation Phenomena in Electric Fields M. EIGEN and G. SCHWARZ	309
Über Integrale Verdünnungswärmen Starker Elektrolyte im Gebiet des Debye-Hückelschen Grenzesetzes E. LANGE	336
Sur l'Apport des Effets Électrostatiques à une Théorie de la Cinétique des Réactions J. E. DUBOIS et J. BARTHEL	343
Author Index	353
Subject Index	359

MOLECULAR FORCES

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NOWADAYS it is a foregone conclusion that all molecular forces are electrical in origin. If this is accepted we can try to order the different types of such forces starting with Coulomb's fundamental law of electrostatics. According to this law the potential energy between two charges is proportional to the first power of their reciprocal distance r , so we are dealing with long-range interaction. This interaction decreases so slowly with increasing distance that a gas of constant density of particles with a Coulombic interaction could not exist. One of the fundamental parameters to be considered in the discussion of the equation of state and in the classical Van der Waals' approximation connected with his parameter a , is the potential energy of one molecule with respect to its surroundings. The integral

$$\int \frac{d\tau}{r}$$

in which $d\tau$ is an element of volume, diverges if r becomes infinite, so the potential energy of that single molecule we are considering would increase to infinity with increasing volume of a gas of such particles. If we had a sphere of radius R and we would suppose our gas with Coulombic interaction to fill that sphere with constant density, this situation could not persist since every particle would be pushed away from the center with a force proportional to the distance from this center. We know that this is what actually happens, for an electrical charge on a conductor is wholly distributed on its surface.

The Coulombic long-range interaction, however, can lead to an equilibrium situation of constant particle density, when we mix positively and negatively charged particles in such a way that the total charge of the assembly is zero. This is the situation which exists in a solution of a totally dissociated electrolyte. However, we have to recognize that under the influence of the Coulombic forces some long-range order of the relative arrangement of positive and negative particles must exist. In the immediate vicinity of a positive particle and in the average, more negative than positive particles will be found and vice-versa. At the same time it is clear that this arrangement will depend strongly on the kinetic energy of the particles, that is on the temperature.

Here I do not have to repeat the argument which in 1923 led to the recognition that the size of the ionic atmosphere which surrounds every ion in a solution, which contains per cm^3 a mixture of n_1 ions of charge e_1 , n_2 ions of charge e_2 , etc., can be characterized by a length λ to be calculated from the relation

$$\frac{1}{\lambda^2} = \frac{4\pi}{DkT} \sum n_i e_i^2$$

in which D is the dielectric constant of the solvent, k Boltzmann's constant and T the absolute temperature.¹ For a millimolar solution of a uni-univalent electrolyte in water with a dielectric constant 80 this is very nearly 100 Å at room temperature.

In the sum $\sum n_i e_i^2$ we recognize the equivalent of and the basis for G. N. Lewis's ionic strength. The fact that λ itself is proportional to the reciprocal of the square root of the total concentration we can recognize as the reason why the activity of an ion in diluted solutions decreases also proportionally to the square root of the concentration. However, this dependence on the square root not only exists for quantities which are important for reversible processes at low concentrations; it also crops up in irreversible processes. Kohlrausch deduced this dependence, long before any theoretical reason for it was known, as the best representation for his experimental results on the conductivity of solutions of strong electrolytes.^{2, 3} Taking it for granted that in such solutions it is not the degree of dissociation (which is very nearly 100 per cent) but the mobility of the ions which decreases with the concentration, leads to a consideration of the effect of the ionic atmosphere on the mobility. It is well known how, also in 1923, the discussion of this interaction furnished an explanation of the law of Kohlrausch and how largely due to the continuing efforts of Onsager and Fuoss the conductivity-concentration relations due to electrostatic interaction now are well established and thoroughly understood.⁴ The same concept has also led to the understanding of two newer effects: the Wien effect⁵ which is based on the increase of the ionic mobility with the field strength and the dependence of the conductivity on the frequency, as predicted together with Falkenhagen,⁶ which depends on the existence of a finite relaxation-time of the ionic atmosphere.⁷

There is no doubt that the Coulombic interaction of the ions is the clue to the understanding of the behavior of solutions of strong electrolytes as long as highly diluted solutions are being considered. However, it is equally evident that for more concentrated solutions other molecular interactions of shorter range begin to be important. When we wish to develop a theory of electrolyte solutions which can be applied to higher concentrations, it becomes imperative to consider next to Coulombic all these other molecular interactions.

An electric structure one step more complicated than a single charge is the

dipole, with zero total charge but finite moment. A high percentage of all molecules carry permanent electric dipole moments. If two such molecules of dipole-moment μ are at a distance r their mutual potential energy is proportional to μ^2/r^3 and is at the same time a function of their mutual orientation. Averaged over all possible orientations with no preference for any special situation the potential energy is zero. However, if two such molecules are at shorter distances from each other there is a preference for orientation, which makes the relative orientations with negative potential energy more probable than those for which this energy has positive values and this preference will be the more pronounced the lower the temperature is. All in all we are therefore led to a finite average potential energy of a central molecule in a surrounding gas of constant density. However, this potential energy is a function of the temperature, it goes to zero when the temperature is high enough. All the experimental evidence connected with the equation of state does not give support to such a model. Part of the interaction of polar molecules will certainly be of the type here considered, but there must still be another interaction which gives a mutual Van der Waals' attraction, and which is essentially independent of the temperature.

Such independence becomes understandable if we remember the fact that all molecules are polarizable. The polarizability α of a molecule is defined as the quotient of the electric moment it acquires and the electric field which induces this moment. In a gas containing n molecules per cm^3 , the so-defined polarizability is connected with the refractive index ν by the relation

$$\nu^2 - 1 = 4\pi n\alpha$$

It has the dimension of a volume and is of the same order of magnitude as the actual volume occupied by the molecule which itself is connected with Van der Waals' constant b . If such a molecule is brought into an electric field to a place where the field-strength is E , its potential energy due to its polarizability is

$$-\frac{\alpha}{2}E^2$$

Since the electric field around a polar molecule is proportional to $1/r^3$, two such molecules, each being polarizable, will show a negative and therefore attractive interaction-energy proportional to $1/r^6$. This interaction energy will have a finite average value when averaged over all orientations, even when no preference of orientation should exist.

This was the way by which temperature-independent attraction as a result of electrical interaction was introduced.⁸ However, not all molecules carry permanent dipole-moments. The remark that molecules with charge zero and dipole moment zero could and will still carry an electrical field around them due to a quadrupole moment is no way out. This is clear as soon as we think of monatomic gases which consist of atoms in which the average

negative charge density has central symmetry around the positive nucleus with the result that the outside electric field vanishes altogether.

At this point in the development, London⁹ saved the situation by remarking that we should not apply classical Maxwell theory but quantum theory and accept that even around atoms of a monatomic gas, the same as for all kinds of molecules, there is an instantaneous and rapidly changing electric field, that will polarize a neighbouring atom or molecule. The radiation which according to Maxwell's equations is unavoidable in such a case, does not exist in reality. For large enough distances the instantaneous field will be that of a dipole and, just as in the case of the permanent dipole, we will end up with a mutual energy of attraction which for large distances is proportional to the reciprocal sixth power of the distance and which is universal.

It is interesting to see how much experimental evidence is available for this molecular attraction and its electrical interpretation.

In the field of chemistry it can be remarked that when in a mixture of two liquids, like for instance water and ethylether, the last component is salted out by the addition of a salt, this effect is a demonstration of a potential energy measured by $-(\alpha/2)E^2$. For around the ions in which the salt is dissociated we will have very strong and inhomogeneous electrical fields of a field strength of the order of 10^6 V/cm even in water with its high dielectric constant. Around every ion a separation of molecules will occur because the more polarizable are attracted more strongly to positions of high field strength in the immediate vicinity of the ions. Recently, Prock and McConkey¹⁰ have shown experimentally that such a separation occurs under the influence of an artificial inhomogeneous electric field in the case of polystyrene dissolved in cyclohexane.

In the van't Hoff laboratory in Utrecht as well as in other laboratories it has been possible to show experimentally the existence of Van der Waals' forces between plates of different materials at large distances of the order of the wavelength of the light. Especially convincing are experiments published in *Physica* 1958, **24**, 751, by M. J. Sparnaay in which the Van der Waals' attraction between metal plates was measured. Here it is shown that the London force per cm^2 of opposing metal plates is proportional to the 4th power of their reciprocal distance. Even the observed absolute magnitude of the force coincides with Casimir's theoretical prediction.¹¹ At a distance of 3000 Å it is still 1.6 dyn/cm².

Finally, it has been shown recently that the range of molecular forces can be measured by observing the angular dissymmetry of light scattered in the vicinity of the critical point. The theoretical background of this development is already contained in the thesis of Zernike (Amsterdam 1916), in which attention is drawn to the fact that thermal density fluctuations in neighboring points of a liquid cannot be totally independent from each other but must show correlation. The average correlation-distance usually is only of the

order of a few molecular diameters as shown experimentally in the case of X-ray scattering of liquids. However, this distance becomes much larger in the vicinity of the critical point. A convincing demonstration of the existence of such large correlation-distances is provided by experiments of Zimm¹² and of Fürth and Williams.¹³ In both cases the angular distribution of visible light scattered by liquid mixtures in the vicinity of their critical mixing point was investigated. Especially in the case investigated by Zimm (carbon tetrachloride and perfluoro-methyl-cyclohexane) concentration of the scattered intensity in the direction of the primary light was observed which increased strongly when the temperature approached the critical temperature. From this dissymmetry the correlation length, in this case pertinent for fluctuations of composition, can be calculated and reaches about 1400 Å for a temperature distance of 0.02°C from the critical temperature. It can be shown that between this correlation-length L and the range of molecular forces l the relation

$$L^2 = \frac{l^2}{\frac{T}{T_c} - 1}$$

holds, in which T is the absolute temperature and T_c the critical temperature.¹⁴ The range l in Zimm's mixture is 14.7 Å. We have here the interesting case that a length of the order of 10 Å can be measured as a result of an interference effect observed in using waves of a wavelength of the order of 3000 Å. It is probable that in favorable cases not only the range but the curve representing the mutual energy between two molecules as a function of their distance apart may be derived from the angular intensity distribution of the scattered light.

It seems to me that essential progress in the theory of concentrated solutions of electrolytes can only be achieved if sufficient attention is paid to the existence of short-range molecular forces on top of the long-range Coulombic interaction. It is for this reason that I have given preference to the general subject of molecular forces as an introduction to the deliberations of this symposium.

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TOPOLOGICAL METHODS IN THE CLUSTER THEORY OF IONIC SOLUTIONS

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THE TWO methods most often employed in the theoretical evaluation of radial distribution functions and potentials of average force in ionic solutions are, first, solutions of certain integral equations and, second, expansions in powers of ion number densities. The second method may also be used for direct evaluation of osmotic pressure in ionic solutions.¹ The terms evaluated by Mayer were later shown to form the first member of a general series in which the Debye-Hückel limiting law is the zeroth order term. Similar expansions were obtained for potentials of average force and radial distribution functions.² On the other hand, the evaluation of potentials of average force through solution of integral equations, as was done for example by Kirkwood and Poirier,³ can be done rigorously only for completely linearized equations, for which superposition in potentials of average force, called the Kirkwood superposition principle, is rigorously valid. The Kirkwood superposition principle, however, becomes just an *ad hoc* approximation when it is used in the exact, non-linearized equations. Solution of the linearized integral equations for Coulombic systems yields just the Debye-Hückel screened potential, thus showing that the Kirkwood superposition principle, implicit in the original formulation of the Debye-Hückel theory, is valid for this linearized form of potential of average force. The present paper is concerned mainly with the evaluation of *all* terms in the particle number density expansion of potentials of average force for which the Kirkwood superposition principle is valid. We shall see that these terms are given by the solution of a new integral equation. Furthermore, departures from superposition will be shown to be given by a series of cluster integrals remarkably similar to the original density expansions which give us departures of the actual system from ideality. Thus, in a sense, we have here a combination of the two basic methods for evaluation of potentials of average force and distribution functions. However, we would like to note that the

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developments which we shall discuss are by no means complete. Our principal aim here is to note the possibilities of some new lines of thought.

In describing a multicomponent system such as an ionic solution, we shall find it convenient to use a contracted notation.

$$\mathbf{n} = n_1! n_2! \dots n_s! \quad (1)$$

$$\mathbf{x}^{\mathbf{n}} = x_1^{n_1} x_2^{n_2} \dots x_s^{n_s} \quad (2)$$

$$\int f(\mathbf{n}) d(\mathbf{n}) = \int \dots \int f_{1,2,\dots,n_s}(\mathbf{r}_1, \dots, \mathbf{r}_{n_s}) d\mathbf{r}_1, \dots, d\mathbf{r}_{n_s} \quad (3)$$

Here the boldface letter \mathbf{n} denotes a set of n particles of s kinds, n_i of kind i . The boldface letter \mathbf{x} denotes a set of quantities pertaining to the s kinds of particles, such as a set of s number densities. Using this notation we can write out the expansions of the potential of average force, radial distribution function and osmotic pressure in solutions:

$$g(ik) = g_{ik}(R_{ik}) = \exp \left\{ -\frac{1}{kT} U(ik) \right\} \left[1 + \sum_{\mathbf{n} \neq 1} \frac{\rho^{\mathbf{n}}}{n!} \int P(ik; \mathbf{n}) d(\mathbf{n}) \right] \quad (4)$$

$$f(jl) = \exp \left\{ -\frac{1}{kT} U(jl) \right\} - 1 \quad (5)$$

$\rho = \rho_1, \rho_2, \dots, \rho_s$ ion number densities.

Here $g(ik)$ denotes the radial distribution function of particles i and k . $U(ik)$ is the direct interaction potential of particles i and k . The integrands $P(ik; \mathbf{n})$, called P -sums, are sums of certain products of f -functions, $f(jl)$, defined in terms of topological connexions among particles of the set \mathbf{n} and particles i and k . We say that two particles, such as j and l , are directly connected when the f -function containing their coordinates appears in the product. Then the P -sum is defined as the sum of all possible products of f functions in which every particle of the set \mathbf{n} is connected independently to both particles i and k , that is, in which we can pass from every particle of the set \mathbf{n} to particles i and k by paths involving different sets of intermediate particles. These sums may be represented graphically. In Fig. 1 we have a graphical representation of products appearing in the integrands in the first and second terms of our expansion of the radial distribution function. Each particle here is denoted by a small circle, called a node, and each f -function containing the relative coordinates of two given particles is denoted by a heavy line connecting the corresponding nodes. The numerical coefficients before each graph denote the number of times a corresponding product appears in the P -sum, and are a direct result of the fact that products corresponding to topologically identical graphs, differing only in the numbering of particles of the set \mathbf{n} , give the same result on integration. We note that when the number densities tend to zero, the radial distribution function

becomes simply the well-known Boltzmann factor which represents the probability of finding the two particles at the given relative configuration, if these two particles constitute the entire system. Thus the first term in the density expansion of the radial distribution function includes the statistical effect of the simultaneous interaction of particles i and k with a third particle; the second term includes the interaction with two other particles, and so on

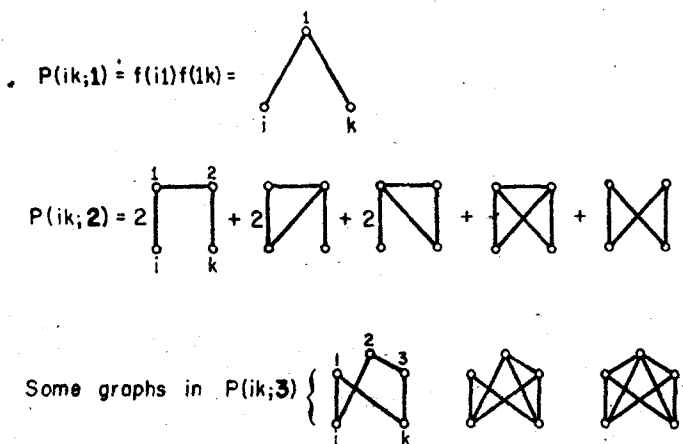


FIG. 1

The potential of average force acting between particles i and k , denoted here by $W(ik)$, is related to the radial distribution function in the same way as the direct pair potential is related to the Boltzmann factor.

$$W(ik) = W_{ik}(R_{ik}) = -kT \ln g(ik) \quad (6)$$

$$g(ik) = \exp \left\{ -\frac{1}{kT} W(ik) \right\} \quad (7)$$

$$W(ik) = U(ik) - kT \sum_{n \geq 1} \frac{\rho^n}{n!} \int Q(ik; n) d(n) \quad (8)$$

It has been shown that the potential of average force can be expanded in powers of particles number densities as shown here. The Q -sums, $Q(ik; n)$, are sums of products of f -functions, defined in the same way as the P -sums, but with the further restriction that particles of the set n must be connected among themselves without involving the two particles i and k . Graphs describing some of the Q -sums are given in Fig. 2. As we see, the last graph of the second P -sum is missing from the corresponding Q -sum because in that graph particles one and two are not connected one to the other without involving particles i and k . The pressure or, in the case of a solution, the osmotic pressure can likewise be expressed in terms of a density expansion.

$$\frac{P}{kT} = \sum_{i=1}^n \rho_i \left[1 - \frac{\partial}{\partial \rho_i} A(\rho) \right] + A(\rho), \quad A(\rho) = \sum_{n \geq 2} \frac{\rho^n}{n!} \int R(n) d(n-1) \quad (9)$$

$$F_s = -kTV A(\rho) \quad V = \text{volume} \quad (10)$$

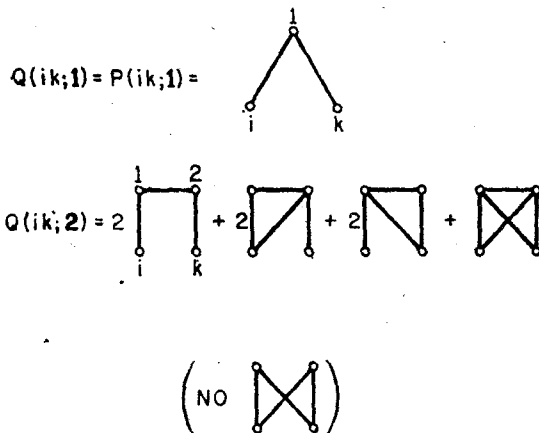


FIG. 2

The integrations here are carried out over the coordinates of all particles of the set n , except one, with respect to the coordinates of that one particle. The integrands $R(n)$ are sums of all possible products of f -functions in which every particle of n is connected to every other particle of this set by at least two independent paths. These are depicted graphically in Fig. 3. The expansion

$$R(2) = \text{---} \quad R(3) = \text{triangle} \quad R(4) = 3 \text{ square} + 6 \text{ square with diagonal} + \text{square with both diagonals}$$

FIG. 3

sion $A(\rho)$ itself has a definite physical meaning, since the Helmholtz configurational free energy is simply related to it, as seen from the last equation here. The chemical potentials of the individual species can likewise be easily obtained from the free energy. The cluster integrals in all three of these expansions diverge for ionic solutions owing to the long range of the Coulombic forces. By proper classification and summation of graphs the cluster expansions are converted into convergent expansions in which the Debye-Hückel screened potentials appear instead of the direct Coulombic interaction potentials.²

$$W(ik) = U^*(ik) + e_i e_k \frac{e^{-\kappa r}}{Dr} - kT \sum_{n \geq 1} \frac{\rho^n}{n!} \int \theta(ik;n) d(n) \quad (11)$$

$$\psi(jl) = \exp \left\{ -\frac{1}{kT} \left[U^*(jl) + e_j e_l \frac{e^{-kr}}{Dr} \right] \right\} - k(jl) - 1 \quad (12)$$

$$k(jl) = -e_j e_l \frac{e^{-kr}}{DkTr} \quad (13)$$

$$\kappa^2 = \frac{4\pi}{Dkt} \sum_{j=1}^s \rho_j e_j^2 \quad (14)$$

Here $U^*(ik)$ is the short-range non-Coulombic interaction of ions i and k , e_i and e_k are the charges on ions i and k , respectively, and D is the dielectric constant of the solution. The functions $\theta(ik; n)$ are sums of products of functions $\psi(jl)$ and $k(jl)$, that is, ψ -bonds and k -bonds. These products are defined just like the Q -sums which appear in the density expansion of the

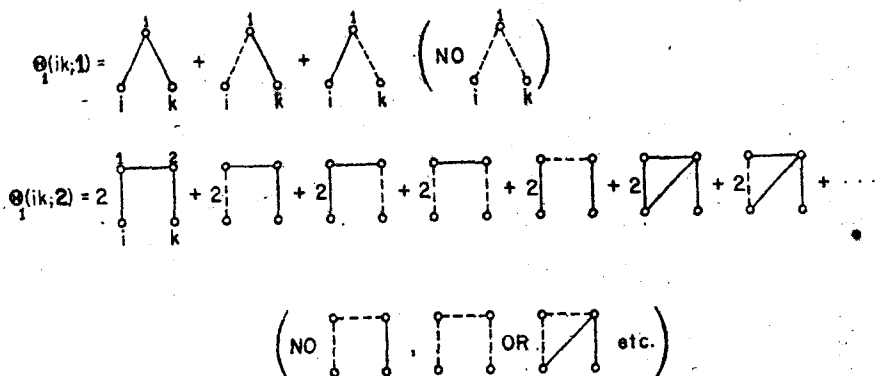


FIG. 4

potential of average force, but connexions are now made through all combinations of ψ -bonds and k -bonds. However, a further restriction is now imposed by excluding all graphs which involve chains of k -bonds, that is, rows of ions each of which is connected only to the preceding one and to the following one by k -bonds. We say that all k -bonds in our graphs are isolated. Examples are represented graphically in Fig. 4; the solid lines denote ψ -bonds, and the dashed ones describe k -bonds. We see here examples of the excluded type of graph which we have just discussed.

The radial distribution function in an ionic solution is expanded in a similar manner.

$$g(ik) = \exp \left\{ -\frac{1}{kT} \left[U^*(ik) + e_i e_k \frac{e^{-kr}}{Dr} \right] \right\} \left[1 + \sum_{n \geq 1} \frac{\rho^n}{n!} \int \eta(ik; n) d(n) \right] \quad (15)$$

$$\eta(ik; 1) = \theta(ik; 1) \quad (16)$$

The integrands here, called η -sums, are defined just like the P -sums in the ordinary density expansion, except that connexions now are made through all possible combinations of ψ -bonds and isolated k -bonds, that is, with the exclusion of combinations containing k -bond chains (Fig. 5). We see that

$$\eta(ik; 2) = \Theta(ik; 2) + \text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \dots$$

FIG. 5

the Debye-Hückel distribution function occupies here a place analogous to that of the Boltzmann factor in the ordinary density expansion.

The osmotic pressure of ionic solutions is given by

$$\frac{P}{kT} = \rho_i = \frac{\kappa^3}{24\pi} + a(\rho) - \sum_{i=1}^i \rho_i \frac{\partial}{\partial \rho_i} a(\rho) \quad (17)$$

$$a(\rho) = \sum_{n \geq 2}^{\infty} \frac{\rho^n}{n!} \int \Omega(n) d(n) \quad (18)$$

$$\Omega(2) = \psi(ik) - \frac{1}{2}k^2(ik) \quad (19)$$

Again, the integrands here, the Ω -sums, are defined in the same way as the R -sums of the ordinary virial expansion of pressure, with connexions made through all possible combinations of ψ -bonds and isolated k -bonds (Fig. 6).

$$\Omega(3) = \text{triangle diagram} + 3 \text{ triangle diagram} + \left(\text{NO triangle diagram} \text{ etc.} \right)$$

FIG. 6

Here the Debye-Hückel limiting law for osmotic pressure of ionic solutions plays a role analogous to that of the osmotic pressure of an ideal solution in the virial expansion. We might say that the ionic solution described by the Debye-Hückel limiting law can be defined as the Debye-Hückel model, and the series of our modified cluster integrals describes the deviations of the actual solution from the Debye-Hückel model just as the series of the ordinary cluster integrals describes deviations of the actual solution from the ideal solution model. This analogy applies also to the potentials of average force and distribution functions. We have on one hand density expansions of potentials of average force and distribution functions involving direct pair potentials, Boltzmann factors and Mayer's f -functions, equations (4) through (9), and on the other hand we have our new expansions, involving Debye-Hückel screened potentials radial distribution functions, and the new ψ -functions, equations (11) through (19). Of course, our new expansions