

# A THEORY OF STRONG ELECTROLYTES IN SOLUTION BASED ON A NEW STATISTICS.

## EQUILIBRIUM PHENOMENA: ACTIVITY COEFFICIENTS

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### INTRODUCTION

Following Milner (1912 and 1913), Ghosh (1918) has pointed out rightly that the deviations in the behaviour of solutions of strong electrolytes from that of ideal one are to be explained from the considerations of interionic fields existing in these solutions. But his calculations have been subsequently replaced by a method, generally accepted as more accurate, due to Debye and Hückel (1923). In their calculations, Debye and Hückel have assumed that in the atmosphere of an ion in solution other ions are distributed according to the Boltzmann statistics and have calculated the potential from an approximate evaluation of Poisson's equation for the field (assumed to be of electrostatic nature) for small values of  $\psi$  ( $\epsilon\psi \ll kT$ ). They have also distinguished the available or free (electrical) energy from the total (electrical) potential energy of the assembly and have calculated the former by considering an ideal process of charging and discharging of the ions in the above field. The theoretical values of the mean activity coefficients (and other related quantities) of electrolytes obtained by the method of Debye and Hückel are generally admitted to be in good agreement with experimental results at low concentrations. But the method, as actually put forward by Debye and Hückel, has originally been the subject of criticisms mainly due to the following unsatisfactory features:

- (i) Firstly, the use of Poisson's equation in the present model, which admits fluctuations, requires a priori justifications.
- (ii) Secondly, unusual and sometimes inadmissible (i.e., negative) values are to be taken for the ionic radii in order to obtain a good fit with observations.
- (iii) Thirdly, for high concentrations and for ions of large-valency types, the deviations of the calculated values from those observed are considerably large.
- (iv) Fourthly, Sengupta (1952) has recently pointed out another very simple but fundamental inconsistency in the original calculations of Debye-Hückel. It has been shown that the value of  $\epsilon\psi$  on the surface of ion, which only is of actual significance in calculations, is greater than that of  $kT$  and thus it contradicts the basic assumption of calculation that  $\epsilon\psi \ll kT$ .

Subsequently, Fowler (1927), Kramers (1927), Onsager (1933) and Kirkwood (1934) have justified the use of Poisson's equation in the model of Debye and Hückel from general considerations of statistical mechanics. Müller (1927) and Gronwall with his collaborators (1928) have shown that good fits with experimental values can be obtained with usual and admissible values of the ionic radii, if the Poisson

equation of the Debye-Hückel theory is evaluated more accurately. The question, raised recently by Sengupta, yet remains open.

Recently, Bagchi (1950) has remodelled the Debye-Hückel theory in a completely new line and has claimed to obtain good agreements with experimental values of activity coefficients for almost entire range of concentrations, especially in the case of uni-uni-valent electrolytes. Firstly, in his calculations in place of Boltzmann statistics the law of distribution of ions has been taken as

$$n_{i,r} = \frac{\sum_i n_i}{z_i \epsilon \psi_r e^{\alpha + \frac{\epsilon \psi_r}{kT}} + 1}, \quad \dots \quad \dots \quad \dots \quad (1)$$

where

$n_{i,r}$  = number-density (i.e. number per c.c.) of ions of  $i$ -th type at a point in the solution, where the electrostatic potential energy is  $z_i \epsilon \psi_r$ ,  $\epsilon$  being the electronic charge,  $z_i$  the valency of ions of the  $i$ -th type,  $\psi_r$  the potential;

$n_i$  = number-density (average) of ions in solution;

$\alpha$  = a parameter of distribution;

$k$  = Boltzmann's constant;

$T$  = temperature (absolute).

Secondly, the Poisson-equation has been evaluated \* for small and large values of  $\frac{\epsilon \psi}{kT}$  separately and the solution for large values has been used in calculations after fitting it with that for small values suitably. In other aspects, Bagchi's calculations are similar to those of Debye and Hückel.

As a theoretical support to the use of a formula different from that of Boltzmann in Bagchi's calculations, a general formula † for distribution of ions in solutions has been deduced (Dutta and Bagchi, 1950) by applying a general method of statistical mechanics, developed by Dutta (1947, 1948, 1951) in a series of papers on real gases, from the simple assumption that there is a minimum distance to which ions can approach one another, either due to finite size of ions or due to mutual repulsive reaction of like ions. The distribution formulae thus obtained, are

$$n_r^\pm \left( 1 + n_r^\mp b_{+-} \right) = \frac{1}{b_\pm e^{\nu_\pm + \frac{\epsilon_\pm \psi_r}{kT}} + 1}, \quad \dots \quad \dots \quad (2)$$

where

$\epsilon_\pm$ ,  $k$ ,  $T$  have their usual significance,

$\nu_\pm$  = assembly-parameters of distribution,

$n_r^\pm$  = number-densities of positive and negative ions at a point in the solution with potential energy  $\epsilon_\pm \psi_r$ ,

$b_\pm$  = volumes of covering spheres (Deckungssphären) of positive or negative ions due to minimum approach amongst the like ions,

$b_{+-} = b_{-+}$  = the same for unlike ions.

\* This method of evaluation has been originally suggested by Dr. G. Bandyopadhyay of Indian Institute of Technology, Kharagpur (India), to Bagchi and to Dutta, one of the present authors, and the present authors take this opportunity to express their thanks to him.

† This is the same as those obtained by Dutta for real gases (*loc. cit.*).

The formula (2) has recently been used by Bagchi (1952) in calculations of activity coefficients.

If one admits the assumption  $b_{+} \ll b_{\pm}$  which means that the distance of minimum approach of unlike ions is much smaller than those of like ion, and, which appears to be very plausible in the Coulombian field, then the formula (2) reduces to

$$n_{\pm} = \frac{1}{\frac{b_{\pm}}{v_{\pm} + \frac{e_{\pm}\psi_r}{kT}} + 1} \dots \dots \dots (3)$$

Subsequently Eigen and Wicke (1951) have obtained a good agreement between theoretical and observed values of activity coefficients by using in place of Boltzmann statistics, a distribution formula which they have claimed to be new and more general than formula (3). But as shown by Dutta (1952), the distribution formula used by Eigen and Wicke is practically the same as the formula (3), written in a different form with new symbols and with slightly different explanations for the parameters involved. Moreover, in reply to some misleading and confusing remarks \* of Wicke and Eigen (1952), it has been further shown by Dutta (1953) that also the method by which Eigen and Wicke arrive at their distribution formula, is practically similar to that employed by Dutta and Bagchi (1950) in deducing formula (3). Still it is easy to see that the method used by Eigen and Wicke lacks the generality of that of Dutta, developed in the papers (Dutta, 1947, 1948, 1951, Dutta and Bagchi, 1950).

Thus up till now, no detailed calculations, based on the theoretically deduced distribution formula (3) in the original form and with original simple interpretations, has been made. In this paper, we propose to develop a complete scheme for the calculation of mean activity coefficients of electrolytes, starting from the formula (3) and to show clearly, as far as possible, the advantages and the disadvantages of the present method with other existing methods, such as those of Debye and Hückel (1923), Bagchi (1950), and of Eigen and Wicke (1951). For the sake of simplicity, the discussion here will be restricted to the case of uni-uni-valent electrolytes. The extension of the theory to the case of symmetrical electrolytes is obvious, the treatment of the case of non-symmetrical electrolytes is left over for future communications.

#### CHARGE-DENSITY IN ION-ATMOSPHERES

As in the Debye-Hückel theory, attention will be focussed on any one ion (say, of positive charge). The charge-density in the atmosphere of this ion will

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\* After the completion of this manuscript, the attention of the authors has been drawn to some further wrong and misleading remarks of Wicke and Eigen (cf. foot-note, *Zeit. f. Elektro. Chem.*, Bd. 56, No. 6, p. 558 (1952)). Here again Wicke and Eigen have wrongly chosen to identify (as they have done in their previous publications) the distribution formula (3) with the one originally used by Bagchi (1950). The essential difference between these two formulae has already been mentioned in previous publications of Dutta and also of Dutta and Bagchi and has been clearly shown in the present paper. Further to make the impression that formula (3) is the good old Fermi statistics, they have quoted some phrases from Bagchi's paper (1950), whereby it is obvious that they have failed to take proper notice of the relevant lines (at the end of first para) of the paper of Dutta and Bagchi (1950), where the difference of formula (3) from Fermi statistics has been clearly and unequivocally emphasised. For a clear understanding of these differences the papers of Dutta (III, 1951), of Dutta and Bagchi (1950) and a note by Dutta (1953) should be consulted. Again, that formula (3) does actually pass over to Boltzmann statistics, has already been shown in the paper (Dutta, 1951, communicated in 1949) and was therefore omitted in the paper (Dutta and Bagchi, 1950). Finally, the rôle of the very essential concept of the number of occupiable sites in the method of Dutta and Bagchi would have been clear to every one who has had a lance into the papers of Dutta, and of Dutta and Bagchi, which it is apprehended has not been done by Wicke and Eigen.

be calculated by using the formula (3) in place of the Boltzmann statistics. Then, the charge-density at the point in the atmosphere of the ion, where the potential is  $\psi_r$ , will be given by

$$\rho_r = \epsilon (n_r^+ - n_r^-), \quad \dots \quad \dots \quad \dots \quad (4)$$

$$= \epsilon \left\{ \frac{\frac{1}{b_+}}{e^{\nu_+ + \frac{\epsilon\psi_r}{kT}} + 1} - \frac{\frac{1}{b_-}}{e^{\nu_- - \frac{\epsilon\psi_r}{kT}} + 1} \right\}, \quad \dots \quad \dots \quad \dots$$

where  $\epsilon$  is the ionic charge.

$$\text{Therefore, as } \psi_r \rightarrow \infty, \rho \rightarrow -\frac{\epsilon}{b_-}. \quad \dots \quad \dots \quad \dots \quad \dots \quad (6)$$

The above result has a very elegant physical significance. Now  $-\epsilon$  being the charge of negative ion and  $b_-$ , the volume exclusively under command of a single negative ion,  $-\frac{\epsilon}{b_-}$  represents the density of negative charge, if the negative ions are distributed in close packing in the atmosphere of the positive ion under consideration. Again,  $b_-$  represents the crystallographic value (actual or after correcting for hydration), thus, for very large values of  $\psi$ , the distribution of ions is similar to that in crystals. This shows the plausibility of the quasi-lattice model proposed in a previous paper (Dutta, 1953).

Moreover,  $\rho$  as defined by the equation (4) is always bounded. In the Debye-Hückel theory, this is not the case. The unboundedness of  $\rho$  is devoid of physical significance, and so unsatisfactory, mainly due to the following reasons. An infinity of  $\rho$  means an infinite accumulation of negative charges in the close neighbourhood of the ion of positive charge. As soon as two or three negative ions come very near to the positive ion, there will be a shielding effect and the original Coulombian attractive field for negative ions will be transformed into a Coulombian repulsive field, and so, no further accumulation of negative ions is possible. So, the infinite accumulation of charges is unthinkable in the Coulomb field. Again, an infinite accumulation of ions in a certain neighbourhood of the central ion is in direct contradiction to the assumption, (which is simultaneously made in usual theories), that there exists a distance of minimum approach amongst the ions. This unsatisfactory self-contradictory feature of the theory has been easily avoided in the present theory simply by replacing the Boltzmann statistics by the formula (3).

Again, when  $\psi_r \rightarrow 0$ , the distribution is (on average) uniform, i.e.,

$$\frac{\frac{1}{b_+}}{e^{\nu_+ + 1}} = n_0^+ = n_0^- = \frac{\frac{1}{b_-}}{e^{\nu_- + 1}} = n_0 \text{ (say)}, \quad \dots \quad \dots \quad (7)$$

Then, for small values of  $\psi_r$  we have up to the first order

$$\rho = -\frac{2\epsilon^2}{kT} n_0 \left( 1 - n_0 \frac{b_+ + b_-}{2} \right). \quad \dots \quad \dots \quad \dots \quad (8)$$

#### THE INTER-IONIC FIELD

Now, as in the theory of Debye and Hückel, the potential for the inter-ionic field will be taken to satisfy the Poisson equation,

$$\nabla^2 \psi = -\frac{4\pi}{D} \rho, \quad \dots \quad \dots \quad \dots \quad (9)$$

subject to boundary conditions

$$\psi \rightarrow 0 \text{ as } r \rightarrow \infty, \quad \dots \dots \dots (10)$$

and, 
$$\int \left( \frac{d\psi}{dr} \right) dS = - \frac{4\pi}{D} \epsilon \text{ (Gauss' theorem).} \dots \dots \dots (11)$$

It is more convenient to introduce a dimensionless variable and we shall take

$$\lambda = \frac{\epsilon\psi}{kT}, \quad \dots \dots \dots (12)$$

then (9) becomes

$$\nabla^2 \lambda = - \frac{4\pi \epsilon}{D kT} \rho. \quad \dots \dots \dots (13)$$

Substituting the values of  $\rho$  we can write the differential equation in simpler forms for large and for small values of  $\lambda$  as follows:—

When  $\lambda \sim 0$ , 
$$\nabla^2 \lambda = \kappa^2 \lambda, \quad \dots \dots \dots (14)$$

and when  $\lambda \sim \infty$ , 
$$\nabla^2 \lambda = \kappa^2 m_+, \quad \dots \dots \dots (15)$$

where 
$$\kappa^2 = \frac{8\pi\epsilon^2}{D kT} n_0 \left( 1 - n_0 \frac{b_+ + b_-}{2} \right), \quad \dots \dots \dots (16)$$

and 
$$m_+ = \frac{1}{b_-(2n_0) \left( 1 - n_0 \frac{b_+ + b_-}{2} \right)}. \quad \dots \dots \dots (17)$$

One important point should be noted in this connection. As already mentioned after Sengupta (1953), it is known that the value of  $\lambda$  (when calculated from the expression for  $\lambda$  obtained by Debye and Hückel in their original calculations based on the assumption  $\lambda \ll 1$ ) on the surface of the ion is in almost all cases greater than one. This inconsistency necessitates the approximate evaluation of the Poisson's equation for large values of  $\lambda$ , but this is not possible in Debye-Hückel theory as  $\rho$  is unbounded when  $\psi \rightarrow \infty$ . On the other hand, in the present development, as also in those of Bagchi, and of Eigen and Wicke, the evaluation of  $\lambda$  for large values is easy. This may be looked upon as an advantageous feature in these developments, entirely due to the replacing of Boltzmann formula by a new one, and may be looked upon as one of the main reason of their success.

Now, in Bagchi's original calculations, he writes the equations of the field as

$$\nabla^2 \lambda' = \kappa'^2 \lambda', \quad \dots \dots \dots (14a)$$

and 
$$\nabla^2 \lambda' = \kappa'^2 m'_+, \quad \dots \dots \dots (15a)$$

where 
$$\kappa'^2 = \frac{4\pi\epsilon^2}{D kT}, \quad \dots \dots \dots (16a)$$

$$m'_+ = m'_-, \quad \dots \dots \dots (17a)$$

$$\lambda' = \frac{\lambda}{2} = \frac{\epsilon\psi}{2kT}.$$

Thus, the material difference, between the equations in Bagchi's calculations and those in the present one, is in the factor

$$\left( 1 - n_0 \frac{b_+ + b_-}{2} \right)$$

When 
$$n_0 \frac{b_+ + b_-}{2} \text{ is } \ll 1,$$

and so can be neglected, they become practically same. The omission of this factor in Bagchi's calculations may be the reason of the necessity of using large values of ionic radii.

#### SCHEME FOR EVALUATION OF $\lambda$

Here we shall take the approximate solution of the equation (9) subject to the boundary conditions (10) and (11) to be given by the integrals  $\lambda_1$  and  $\lambda_2$  of (13) and (14) respectively for different ranges of values of  $\psi$ , when the constants of integration have been determined from the following relations.

$$(\lambda_1)_{\xi_1} = m_+ = (\lambda_2)_{\xi_1}, \quad \dots \quad (18)$$

$$\left( \frac{d\lambda_1}{d\xi} \right)_{\xi_1} = \left( \frac{d\lambda_2}{d\xi} \right)_{\xi_1}, \quad \dots \quad (19)$$

$$\lambda \rightarrow 0 \text{ as } r \rightarrow \infty, \quad \dots \quad (20)$$

and also from the Gauss's theorem,

$$\int_s \left( \frac{d\psi}{dr} \right) dS = - \frac{4\pi}{D} \epsilon, \quad \dots \quad (21)$$

where

$$\xi = \kappa r. \quad \dots \quad (22)$$

Now, since  $\lambda \rightarrow 0$  as  $\xi \rightarrow \infty$ , so  $\lambda_1$  is given by

$$\lambda_1 = B \frac{e^{-\xi}}{\xi} \dots \quad (23)$$

The other solution is of the form

$$\lambda_2 = m_+ \left[ \frac{\xi^2}{6} + C + \frac{H}{\xi} \right]. \quad \dots \quad (24)$$

Now, so far as the use of the condition (21) is concerned there will appear a practical difficulty. A priori there is nothing to decide from the beginning which of the integrals,  $\lambda_1$  and  $\lambda_2$  will represent  $\lambda$  close to the surface (i.e. at  $r = a$ ) and so is to be used in the equation (21). Here, it is also to be remembered that in calculations of activity coefficients and other related thermodynamics quantities, the value of  $\lambda$ , close to the surface of the ion, is of actual importance. So, the actual procedure is a bit round-about and may be sketched as follows:—

Now, for sufficiently low concentrations,  $m_+$  is a large number and the expression for  $\kappa^2$  reduces to that of Debye-Hückel. Again from the finding of Sengupta (1952), it is known that the values of  $\lambda$  on the surface of ions, from (23), are not large. Then, since  $\lambda$  increases monotonically from 0 as  $r$  decreases from infinity, so the surface value of  $\lambda$ , being less than  $m_+$ , will be reached before  $\lambda$  attains the value  $m_+$ . Thus  $\lambda$  will be taken to be represented by  $\lambda_1$  where  $B$  has been determined from (21). Thus, we get near the surface

$$\lambda = \lambda_1 = \frac{\epsilon^2}{DkT} \frac{e^{\kappa a_+}}{1 + \kappa a_+} \frac{e^{-\kappa r}}{r} \dots \quad (25)$$

Now, since the Poisson equation does not represent the field within the ion, which again is not of any interest for the present discussion, so, in the case under consideration  $\lambda$  is given by  $\lambda_1$ , and  $\lambda_2$  is devoid of any significance.

Thus the expression for potential is same as that in the original calculations of Debye and Hückel and so will yield the usually accepted limiting laws. For this reason, in this paper, calculations of activity coefficients for small concentrations have been omitted.

For comparatively high concentrations,  $m_+$  is of the order of unity and may be less than the surface value of  $\lambda$ . Thus,  $\lambda$  reaches the value  $m_+$  earlier, so  $\lambda$  near the surface is expected to be given by  $\lambda_2$  and so

$$\lambda = \lambda_2 = m_+ \left[ \frac{\xi^2}{6} + C + \frac{H}{\xi} \right], \quad \dots \dots \dots (26)$$

where  $C$ ,  $H$ , and  $\xi_1$  (argument of  $\lambda$  corresponding to  $\lambda = m_+$ ) are to be determined from the equations (17), (18) and (19). In a manner, similar to that of Bagchi,  $C$  and  $H$  are found to be

$$H = \frac{\epsilon^2 \kappa}{m_+ D k T} + \frac{\kappa^3 a_+^3}{3}, \quad \dots \dots \dots (27)$$

$$= \frac{g_+}{3} \text{ (say)}, \quad \dots \dots \dots (28)$$

$$\xi_1 = (1 + g_+)^{\frac{1}{2}} - 1, \quad \dots \dots \dots (29)$$

$$C = \frac{1}{2} \{ 1 - (1 + g_+)^{\frac{3}{2}} \}. \quad \dots \dots \dots (30)$$

CALCULATIONS OF AVAILABLE (OR FREE) ENERGY

Here, to calculate the free energy after Debye and Hückel, we shall consider the ideal process of charging and discharging. Of course, we shall think that the charge of the ion is on the surface of the ion, and so, the processes of charging and discharging are occurring on the surface of the ion instead of on the geometrical surface of the covering sphere (Deckungssphären) of the ion, as has been considered in the Debye-Hückel theory. Thus, for high concentrations,

$$\psi_2(a_+) = \frac{kT}{\epsilon} \lambda_2(a_+) = \frac{kT}{\epsilon} \frac{m_+ \kappa^2 a_+^2}{2} + \frac{\epsilon}{D a_+} + \frac{m_+ kT}{2\epsilon} \{ 1 - (1 + g_+)^{\frac{3}{2}} \} \dots (31)$$

The potential due to the ion-atmosphere on the surface of ion is

$$\psi_2^*(a_+) = \frac{kT m_+}{2\epsilon} \left[ \kappa^2 a_+^2 + \{ 1 - (1 + g_+)^{\frac{3}{2}} \} \right]. \quad \dots \dots (32)$$

The work done in charging

$$\begin{aligned} W_+ &= \int_0^1 \epsilon \left[ \psi_2^*(a_+) \right]_{\epsilon x} dx \\ &= \frac{kT m_+}{2} \left\{ \kappa^2 a_+^2 \int_0^1 x dx + \int_0^1 \frac{1 - (1 + g_+ x^3)^{\frac{3}{2}}}{x} dx \right\} \\ &= \frac{kT m_+}{2} \left\{ \frac{1}{2} \kappa^2 a_+^2 + P + \phi_+(g_+) \right\}, \quad \dots \dots \dots (33) \end{aligned}$$

where

$$P = \frac{1}{2} + \frac{1}{\sqrt{3}} \tan^{-1} \sqrt{3} - \frac{1}{2} \log_e 3 \equiv 5551, \quad \dots \quad (34)$$

and,

$$\begin{aligned} \phi_+(g_+) &= \frac{1}{2} \log \left[ (1+g_+)^{\frac{1}{2}} + (1+g_+)^{\frac{1}{2}} + 1 \right] - \frac{1}{2}(1+g_+)^{\frac{1}{2}} \\ &\quad - \frac{1}{\sqrt{3}} \tan^{-1} \frac{2(1+g_+)^{\frac{1}{2}} + 1}{\sqrt{3}}. \quad \dots \quad (35) \end{aligned}$$

A similar expression is obtained for  $W_-$  and the total work done in charging all the ions is given by:

$$\begin{aligned} W &= n_0 (W_+ + W_-) \\ &= \frac{kT}{2} n_0 \left[ \frac{1}{2} (\kappa^2 m_+ a_+^2 + \kappa^2 m_- a_-^2) + P(m_+ + m_-) + (\phi_+ m_+ + \phi_- m_-) \right]. \quad \dots \quad (36) \end{aligned}$$

#### ACTIVITY COEFFICIENTS

Now, for convenience of calculations as in other theories we shall take

$$n_0^+ = n_0^- = n_0 = n_+ = n_-, \quad \dots \quad (37)$$

where  $n_+$  and  $n_-$  are average number of positive and negative ions.

Then, on using the usual expression for the ionic activity coefficient, viz.,

$$\log f_+ = \frac{1}{kT} \frac{\partial W}{\partial n_+}, \quad \dots \quad (38)$$

we get from the equation (36)

$$\begin{aligned} \log f_+ &= \frac{m_+}{2} \left\{ \frac{1}{2} \kappa^2 a_+^2 + (P + \phi_+) (1 - n_+ D_+) + E_+(g_+) n_+ D_+ \right\} \\ &\quad + \frac{m_-}{2} \{ E_-(g_-) n_- D_+ - n_- D_+ (P + \phi_-) \}, \quad \dots \quad (39) \end{aligned}$$

where

$$D_+ = \frac{1 - 2n_0 b_+}{2n_0 \left( 1 - n_0 \frac{b_+ + b_-}{2} \right)}, \quad \dots \quad (40)$$

$$\begin{aligned} \text{and} \quad E_+(g_+) &= \frac{1}{2} \frac{\frac{g_+}{(1+g_+)^{\frac{1}{2}}} + \frac{g_+}{2(1+g_+)^{\frac{1}{2}}}}{(1+g_+)^{\frac{1}{2}} + (1+g_+)^{\frac{1}{2}} + 1} - \frac{g_+}{2(1+g_+)^{\frac{1}{2}}} \\ &\quad - \frac{g_+}{3(1+g_+)^{\frac{1}{2}} \left[ 1 + \frac{1}{3} \{ 2(1+g_+)^{\frac{1}{2}} + 1 \}^2 \right]} \quad \dots \quad (41) \\ &\equiv \frac{1}{2} \{ 1 - (1+g_+)^{\frac{1}{2}} \}, \end{aligned}$$

A similar expression is also obtained for  $\log f_-$ .



Then, finally,

$$\log f_{\pm} = \frac{1}{2} \left[ \frac{m_+}{2} \left\{ \frac{1}{2} \kappa^2 a_+^2 + (P + \phi_+) \left[ 1 - n_0(D_+ + D_-) \right] + E_+ n_0(D_+ + D_-) \right\} + \frac{m_-}{2} \left\{ \frac{1}{2} \kappa^2 a_-^2 + (P + \phi_-) \left[ 1 - n_0(D_+ + D_-) \right] + E_- n_0(D_+ + D_-) \right\} \right] \dots \quad (42)$$

COMPARISON WITH EXPERIMENTAL DATA

Consistent with our interpretation for  $b_{\pm}$  given in the papers (Dutta and Bagchi, 1950, Dutta, 1951-53) they will be taken as the volumes of exclusion (volumes of covering spheres, overlapping being neglected), i.e.,

$$b_{\pm} = \frac{4}{3} \pi (2a_{\pm})^3, \quad \dots \dots \dots \quad (43)$$

where  $a_{\pm}$  are the ionic radii in the ordinary sense (i.e., either the crystallographic or the effective values due to hydration). Now, according to the accepted views, it is known that in the solutions, the effective ionic radii, on account of hydration are greater than the crystallographic values, and their differences are more and more prominent, the smaller the ionic radii (crystallographic), for ions of the same charge. So in this paper, for  $\text{Cs}^+$  we have taken the crystallographic value for the radius and for  $\text{K}^+$  and  $\text{Na}^+$  a value nearly equal to that due to hydration (Eucken, 1948). The values of the mean molar activity coefficients of the three electrolytes  $\text{CsCl}$ ,  $\text{KCl}$  and  $\text{NaCl}$  at  $25^\circ\text{C}$ . as calculated according to the equation (42) are compared to the corresponding experimental values (molal).

TABLE 1  
Variation of activity coefficient\* with concentration

			1 m.	1.5 m.	2 m.	2.5 m.	3 m.	3.5 m.	4 m.
CsCl	$a_{\text{Cs}^+} = 1.67 \text{ \AA}$	Obs.	.543	.514	.495	.485	.480	.476	.474
	$a_{\text{Cl}^-} = 1.81 \text{ \AA}$	Cal.	.531	.484	.466	.459	.460	.468	.480
KCl	$a_{\text{K}^+} = 2.15 \text{ \AA}$	Obs.	.605	.585	.575	.572	.573		
	$a_{\text{Cl}^-} = 1.81 \text{ \AA}$	Cal.	.554	.532	.532	.546	.579		
NaCl	$a_{\text{Na}^+} = 2.66 \text{ \AA}$	Obs.	.658	.659	.671				
	$a_{\text{Cl}^-} = 1.81 \text{ \AA}$	Cal.	.65	.65	.72				

Now it may be said that the fitting of a set of experimental data by suitable adjustment of an arbitrary parameter (the radius of the volume of exclusion), as it is done by Eigen and Wicke (1951), Bagchi (1950), is not conclusive. To avoid this criticism the calculated values for mean molar activity coefficients and the

\* The experimental data given above are all taken from H. S. Harned and B. B. Owen Physical Chemistry of Electrolytic Solutions, Reinhold Publishing Corporation, New York, 1950 (2nd Ed.), p. 562.

corresponding observed values for molal activity coefficients for KCl at different temperatures with values of ionic radii used in the above fitting, have been tabulated in Table 2. The agreement in this case also is good.

TABLE 2  
Variation of activity coefficient \* for KCl with temperature

Temp. (°C)		0	5	10	15	20	25	30	35	40
·5 m.	Obs.	·642	·646	·648	·650	·651	·651	·651	·648	·646
	Cal.	·615	·619	·626	·633	·640	·649	·658	·666	·675
3 m.	Obs.	·539	·549	·556	·562	·567	·571	·573	·574	·573
	Cal.	·538	·546	·555	·563	·571	·579	·586	·593	·601

### CONCLUSION

In conclusion, the following features of the present theory may be stressed as satisfactory, new and important:

I. The distribution formula for ions in the electric field used in the paper has been deduced in a simple manner by a general statistical method from the plausible assumptions, viz.:

- (i) there is a distance of minimum approach between the ions (at least in average),
- (ii) the average gradient of the field is such that its change with distances of the order of ionic diameter can be neglected.

II. The charge-density  $\rho$  is always bounded as required for consistency with the assumptions of existence of the interionic Coulombian field and that of a distance of minimum approach.

III. Every quantity involved in the theory has a precise physical significance.

IV. As already mentioned in a note (Dutta, 1952), good agreement with experimental results have been obtained with usually accepted values of ionic radii, (in Bagchi's calculation large values are to be taken) and without using any quantity as adjustable arbitrary parameters (Eigen and Wicke have taken the number of occupiable sites suitably as a parameter).

V. For low concentrations, the method developed here yields the Debye-Hückel limiting laws.

The unsatisfactory feature of the theory, as it appears to the authors at present, is the approximate evaluation of Poisson's equation as it is done here.

In Table 1, the values of activity coefficients for KC and NaCl cannot be calculated at concentrations higher than 3 m. and 2 m. respectively, since then  $n_0(b_+ + b_-) > 1$  so that  $\kappa^2 < 0$ , and so, the nature of the differential equations will be changed. This is so, as near about this concentration overlapping (which is neglected) is significant, and correction should be done for it, as it is done in (Dutta, 1952) for imperfect gases.

In the present paper, for large concentrations, we have used only the solution  $\lambda_2$  corresponding to large values of  $\lambda$ . Consistency of calculations demand that  $(\lambda)_a$  must be seen to be less than the corresponding  $m_i$ . If it is not satisfied then  $\lambda_1$ , corresponding to small values of  $\lambda$ , is to be taken for  $\lambda$  and calculations are to

\* Experimental values from Harned and Owen, *loc. cit.*, p. 558.

be made afresh. By this, some further betterments in the agreement between calculated and observed values are expected, and will be done in future communications.

### SUMMARY

In this paper, a complete scheme of calculation of activity coefficients has been sketched based on the new statistics proposed in the papers of Dutta and in the paper of Dutta and Bagchi. The agreement of the observed and the calculated values of activity coefficients is found to be good. The values of the activity coefficients for different concentrations and for different temperatures have been calculated and have been given in two tables. Here some inconsistencies of the other existing theories, mainly, of the theory of Debye and Hückel, have been pointed out and how these can be avoided easily in the present development has been clearly shown.

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