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Citation: [The Journal of Chemical Physics](#) **1**, 205 (1933); doi: 10.1063/1.1749276

View online: <http://dx.doi.org/10.1063/1.1749276>

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## The Limiting Laws of the Interionic Attraction Theory of Strong Electrolytes

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(Received December 3, 1933)

The various methods of obtaining the limiting laws of strong electrolytes are briefly discussed. It is shown that the dependence of these limiting laws on the temperature, the dielectric constant of the solvent and the volume of the solution can be deduced from the Gibbs-Helmholtz equa-

tion and the virial theorem of Clausius. The Debye-Hückel and the Kramers limiting laws are found to be of the same type as these general limiting laws, with numerical coefficients obtained thanks to the use of the Poisson equation.

### INTRODUCTION

THE common features of the various forms of the interionic attraction theory of ionized solutes are: (1) The assumption of complete ionization at low concentrations (sometimes corrected by the consideration of a partial association of ions of opposite signs)<sup>1</sup>; (2) the assumption that the departure from the properties of perfect solutions is entirely due to the Coulomb attractions and repulsions between ions.

The first step in any theory of ionized solutes is either the direct calculation of the correction that has to be introduced in the expression for the free energy of the system on account of those electrostatic forces; or the calculation of the energy involved in the so-called "charging process" of Debye.<sup>2</sup> Either one of these calculations presents difficulties of theoretical and mathematical nature. Milner<sup>3</sup> tried to solve the problem directly by calculating the virial of a mixture of ions but his calculations are extremely intricate and contain a certain number of approximations. The method of Debye and Hückel is based upon the Poisson equation of electrostatics which is only strictly valid for a continuous distribution of electricity. This procedure is rendered uncertain and weak on account of

fluctuations, a point discussed by Fowler<sup>4</sup> who considers the Debye-Hückel theory as "empirically successful." The more exact form of the Debye-Hückel theory developed by Gronwall,<sup>5</sup> by Gronwall, La Mer and Sandved<sup>6</sup> and by La Mer, Gronwall and Grieff,<sup>7</sup> although much more satisfactory than the original form of the Debye-Hückel theory, also suffers from fluctuations of an unknown order of magnitude since it is also based on the Poisson equation, for which an exact solution is now obtained. The only parameter of the theory, the mean ionic diameter, is found to have more consistent values than in the original Debye-Hückel theory, where absurdly small or even negative values were often found.

A remarkable solution of the problem, "avoiding the pitfalls of Debye and Hückel's method and the tedium of Milner's" (Fowler) has been obtained by Kramers.<sup>8</sup> It consists of a direct calculation of the correction in the free energy due to the electrostatic forces, by means of Gibb's phase integral. The Poisson equation is not used (at least not as the fundamental point of departure of the theory) and hence fluctuations

<sup>1</sup> N. Bjerrum, *Det kgl. danske Vidensk. selskab, Math.-fys. Meddelelser* VII, No. 9 (1926); W. Nernst, *Zeits. f. Elektrochemie* 33, 428 (1927); *Zeits. f. physik. Chemie* 135, 237 (1928) etc.

<sup>2</sup> P. Debye and E. Hückel, *Phys. Zeits.* 24, 185 (1923); 25, 97 (1924); E. Hückel, *Ergebn. d. exakt. Naturwiss.* 3, 199 (1924); W. Orthmann, *ibid.* 6, 155 (1927).

<sup>3</sup> S. R. Milner, *Phil. Mag.* 23, 551 (1912); 25, 743 (1913).

<sup>4</sup> R. H. Fowler, *Statistical Mechanics*, pp. 194-197, 316-325, Cambridge, 1929.

<sup>5</sup> T. H. Gronwall, *Proc. Nat. Acad. Sci.* 13, 198 (1927); *Annals of Math.* 28, 355 (1927).

<sup>6</sup> T. H. Gronwall, V. K. La Mer and K. Sandved, *Phys. Zeits.* 29, 358 (1928).

<sup>7</sup> V. K. La Mer, T. H. Gronwall and L. J. Grieff, *Phys. Chem.* 35, 2245 (1931).

<sup>8</sup> H. A. Kramers, *Koninkl. Akad. van Wetenschappen te Amsterdam, Afdeling Natuurkunde*, XXXV, No. 10, 1153 (1926).

are avoided. It is shown that up to definite concentrations depending on the valence type of the electrolyte the part of the free energy due to the electrostatic forces, the activity coefficient and the osmotic coefficient are independent of the size of the ions and the Debye-Hückel limiting laws (under their simplest form, corresponding to negligibly small ionic radii) are obtained for the case of extremely low concentrations. Kramers further shows that the treatment given by Debye and Hückel for higher concentrations (finite size of the ions taken into account) cannot be significant because at those concentrations association takes place and reasonings based on the existence of atmospheres of free ions are invalid. It is to be noticed that the Kramers theory is developed without the use of any parameter. Towards the end of his reasoning, however, Kramers uses the Poisson equation in order to determine the numerical value of a constant.

The object of this note is to show that it is possible to obtain directly the general form of the limiting laws of strong electrolytes from the combined use of the Gibbs-Helmholtz formula and the virial theorem of Clausius. It is then shown that the Debye-Hückel and the Kramers limiting laws are particular forms of these general laws.

#### LIMITING LAWS OF PERFECT STRONG ELECTROLYTES

We call "perfect strong electrolyte" a completely ionized solute satisfying the following conditions: (1) The ions are point charges. (2) The departure of the osmotic properties from those of an ideal solution is entirely and only due to the Coulomb forces between the ions. (3) The dielectric constant of the solvent is a function of temperature only.

Let us call  $\epsilon_1, \epsilon_2, \dots, \epsilon_i, \dots$  the charges of the various ions, and  $\psi_1, \psi_2, \dots, \psi_i, \dots$  the electrostatic potentials at the points occupied by the charges  $\epsilon_1, \epsilon_2, \dots, \epsilon_i, \dots$  and due to all the other charges. Thus we have:

$$\psi_i = \frac{1}{D} \left[ \frac{\epsilon_1}{r_{1i}} + \frac{\epsilon_2}{r_{2i}} + \dots + \frac{\epsilon_{i-1}}{r_{i-1,i}} + \frac{\epsilon_{i+1}}{r_{i+1,i}} + \dots \right], \quad (1)$$

$r_{1i}, r_{2i}, \dots, r_{ki}, \dots$  being the distances between

the various ions and the ion  $i$  and  $D$  the dielectric constant of the medium. It is obvious that we are dealing with the time averages of the  $\psi_i$ 's and  $r_{ki}$ 's.

The electrostatic energy  $U_e$  of the system is given by

$$U_e = \frac{1}{2} \sum_i \epsilon_i \psi_i. \quad (2)$$

Let us call  $P$  the osmotic pressure of the solution,  $\bar{P}$  the osmotic pressure of the corresponding ideal solution,  $A$  the Helmholtz free energy or maximum work of the system,  $\bar{A}$  the same quantity for the ideal solution,  $V$  the volume of the solution. We have:

$$P = -(\partial A / \partial V)_T, \quad (3)$$

$$\bar{P} = -(\partial \bar{A} / \partial V)_T. \quad (3')$$

$A$  could be decomposed into  $\bar{A}$  and  $W$ , the energy involved in Debye's charging process<sup>2</sup>:

$$A = \bar{A} + W. \quad (4)$$

From (3), (3') and (4) we deduce:

$$P = \bar{P} - (\partial W / \partial V)_T. \quad (5)$$

The virial theorem of Clausius leads to the equation of state:

$$PV = NkT + \frac{1}{3} \sum_i \sum_k r_{ki} \cdot f(r_{ki}), \quad (6)$$

where  $N$  is the total number of particles in the volume  $V$ ,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $r_{ki}$  is the distance between two particles,  $i$  and  $k$ ,  $f(r_{ki})$  is the force acting on the particle  $i$  on account of particle  $k$ . We have:

$$\bar{P} = NkT / V. \quad (7)$$

We deduce from (5), (6) and (7):

$$-(\partial W / \partial V)_T = (1/3V) \cdot \sum_i \sum_k r_{ki} f(r_{ki}). \quad (8)$$

From (1) and (2) we find:

$$\sum_i \sum_k r_{ki} f(r_{ki}) = (1/D) \sum_i \sum_k r_{ki} (\epsilon_i \epsilon_k / r_{ik}^2)$$

or

$$\sum_i \sum_k r_{ki} f(r_{ki}) = \frac{1}{2} \sum_i \epsilon_i \psi_i. \quad (9)$$

Eq. (8) gives then:

$$-(\partial W / \partial V)_T = (1/6V) \cdot \sum_i \epsilon_i \psi_i. \quad (10)$$

But since  $W$  is the energy spent in charging the ions against the potentials  $\psi_i$ , we have:

$$W = \sum_i \int_0^{\epsilon_i} \psi_i d\epsilon_i. \quad (11)$$

Eq. (10) becomes then:

$$-\frac{\partial}{\partial V} \left[ \sum_i \int_0^{\epsilon_i} \psi_i d\epsilon_i \right] = \frac{1}{6V} \cdot \sum_i \epsilon_i \psi_i. \quad (12)$$

We have for the ion  $i$ :

$$-\int_0^{\epsilon_i} \frac{\partial \psi_i}{\partial V} \cdot d\epsilon_i = \frac{1}{6V} \epsilon_i \psi_i. \quad (13)$$

Differentiating with regard to  $\epsilon_i$ :

$$\psi_i = -\epsilon_i \cdot \partial \psi_i / \partial \epsilon_i - 6V \cdot \partial \psi_i / \partial V. \quad (14)$$

Integrating:

$$\psi_i = (1/\epsilon_i) \cdot f_1(\epsilon_i/V^{1/6}), \quad (15)$$

we obtain

$$\Delta U = U_e \left[ 1 + \frac{T}{D} \cdot \frac{dD}{dT} \right] = W - T \left( \frac{\partial W}{\partial T} \right)_V \quad (21)$$

or:

$$\frac{1}{2} \sum_i \epsilon_i \psi_i \left[ 1 + \frac{T}{D} \cdot \frac{dD}{dT} \right] = \sum_i \int_0^{\epsilon_i} \psi_i d\epsilon_i - T \cdot \frac{\partial}{\partial T} \left[ \sum_i \int_0^{\epsilon_i} \psi_i d\epsilon_i \right]. \quad (22)$$

For the ion  $i$ :

$$\frac{1}{2} \epsilon_i \psi_i \left[ 1 + \frac{T}{D} \cdot \frac{dD}{dT} \right] = \int_0^{\epsilon_i} \psi_i d\epsilon_i - T \int_0^{\epsilon_i} \frac{\partial \psi_i}{\partial T} d\epsilon_i. \quad (23)$$

Differentiating with regard to  $\epsilon_i$ :

$$\left( 1 + \frac{T}{D} \cdot \frac{dD}{dT} \right) \left( \frac{1}{2} \psi_i + \frac{1}{2} \epsilon_i \frac{\partial \psi_i}{\partial \epsilon_i} \right) = \psi_i - T \frac{\partial \psi_i}{\partial T} \quad (24)$$

or:

$$\psi_i \left[ 1 - \frac{T}{D} \cdot \frac{dD}{dT} \right] = \epsilon_i \left[ 1 + \frac{T}{D} \cdot \frac{dD}{dT} \right] \cdot \frac{\partial \psi_i}{\partial \epsilon_i} + 2T \cdot \frac{\partial \psi_i}{\partial T}. \quad (25)$$

Integrating ( $D$  is a function of  $T$  only):

$$\psi_i = T^{1/2} D^{-1/2} \cdot f(\epsilon_i/T^{1/2} D^{1/2}) \quad (26)$$

$f_2(\epsilon_i/T^{1/2} D^{1/2})$  being an arbitrary function of  $\epsilon_i/T^{1/2} D^{1/2}$ . Let us expand expressions (15) and (26) into infinite series, according to Maclaurin's formula. We get:

$$\psi_i = \frac{1}{\epsilon_i} \left[ f_1(0) + \frac{\epsilon_i}{V^{1/6}} \cdot f_1'(0) + \frac{1}{2!} \cdot \frac{\epsilon_i^2}{V^{1/3}} \cdot f_1''(0) + \frac{1}{3!} \cdot \frac{\epsilon_i^3}{V^{1/2}} \cdot f_1'''(0) + \dots \right] \quad (27)$$

$$\psi_i = T^{1/2} D^{-1/2} \left[ f_2(0) + \frac{\epsilon_i}{T^{1/2} D^{1/2}} \cdot f_2'(0) + \frac{1}{2!} \cdot \frac{\epsilon_i^2}{T D} \cdot f_2''(0) + \frac{1}{3!} \cdot \frac{\epsilon_i^3}{T^{3/2} D^{3/2}} \cdot f_2'''(0) + \dots \right]. \quad (28)$$

One easily finds that  $f_1(0) = 0$ ,  $f_2(0) = 0$ ,  $f_1'(0) = 0$ . Hence, introducing the Boltzmann constant, so

<sup>9</sup> N. Bjerrum, Zeits. f. physik. Chemie 119, 145 (1926); see W. Orthmann, reference 2, p. 181.

$f_1(\epsilon_i/V^{1/6})$  being an arbitrary function of  $\epsilon_i/V^{1/6}$ . According to Bjerrum<sup>9</sup> the heat of dilution of an electrolyte is given by:

$$\Delta U = U_e [1 + (T/D) \cdot dD/dT]. \quad (16)$$

$\Delta U$  is the heat evolved when the solution of volume  $V$  is diluted to an infinite volume.

If the solution were perfect,  $\Delta U$  would be zero. The Gibbs-Helmholtz formula gives:

$$\Delta U = A - T \cdot (\partial A / \partial T)_V. \quad (17)$$

But

$$A = \bar{A} + W. \quad (18)$$

Hence:

$$\Delta U = \bar{A} - T(\partial \bar{A} / \partial T)_V + W - T \cdot (\partial W / \partial T)_V. \quad (19)$$

Since

$$\bar{A} - T(\partial \bar{A} / \partial T)_V = \Delta \bar{U} = 0 \quad (20)$$

as to make the  $C$ 's dimensionless:

$$\psi_i = C_1 \frac{\epsilon_i}{DV^{\frac{1}{3}}} + C_2 \frac{\epsilon_i^2}{(kT)^{\frac{1}{3}} D^{\frac{1}{3}} V^{\frac{1}{3}}} + C_3 \frac{\epsilon_i^3}{(kT) D^2 V^{\frac{1}{3}}} + \dots \quad (29)$$

or:

$$\psi_i = \sum_{m=1}^{m=\infty} C_m \cdot \frac{\epsilon_i^m}{(kT)^{(m-1)/2} \cdot D^{(m+1)/2} \cdot V^{(m+1)/6}}.$$

The  $C_m$ 's are constants depending on the total number of ions, their valences, etc. Their determination requires calculations of the type of those of Debye and Hückel, of Milner and of Kramers.

In the case of negligibly small ionic radii Debye and Hückel found:

$$\psi_i = -(\epsilon_i/D) \cdot ((4\pi\epsilon^2/DkT) \cdot \sum N_i z_i^2 / V)^{\frac{1}{2}}, \quad (30)$$

$\epsilon$  being the elementary quantum of electricity,  $N_i$  the total number of ions of the kind  $i$ ,  $z_i$  the valence of these ions.

One sees that Eq. (29) reduces to (30) when:

$$C_1 = C_3 = C_4 = \dots = 0$$

and

$$C_2 = -(4\pi \cdot \sum N_i z_i^2 / z_i^2)^{\frac{1}{2}}. \quad (31)$$

The value of  $W$  obtained by Kramers is the following:

$$W = \frac{1}{2} N k T \ln \omega(x). \quad (32)$$

$N$  is the total number of ions,  $\omega(x)$  is a function whose dependence on  $x$  is defined as follows:

$$\omega = e^t (1 + 3t)^{-1}, \quad (33)$$

$$(4\pi/9)x = t^2 (1 + 3t)^{-3} \quad (34)$$

and

$$x = [(\epsilon^2/DkTN) \cdot \sum N_i z_i^2]^{\frac{1}{2}} \cdot N/V. \quad (35)$$

When  $x$  is much smaller than 1, we have:

$$\omega = 1 - (2/3)(4\pi x)^{\frac{1}{2}} - (5/18) \cdot 4\pi x - \dots, \quad (36)$$

$$-\ln \omega = (2/3)(4\pi x)^{\frac{1}{2}} + \frac{1}{2} 4\pi x + \dots, \quad (37)$$

$$W = -\sum (N_i z_i^2 / 3) \cdot \epsilon^2 \kappa / D - \dots \quad (38)$$

with  $\kappa = ((4\pi\epsilon^2/DkT) \cdot \sum N_i z_i^2 / V)^{\frac{1}{2}}$ . The first term of  $W$  is the value found by Debye and Hückel for this quantity in the limiting case of negligibly small ionic radii.

Let us calculate  $\psi_i$  from (32) and (37). We have:

$$\psi_i = (z_i / \sum N_i z_i^2) \cdot \partial W / \partial \epsilon_i. \quad (39)$$

This gives:

$$\psi_i = -\frac{\epsilon_i}{D} \cdot \left( \frac{4\pi\epsilon^2}{DkT} \cdot \frac{\sum N_i z_i^2}{V} \right)^{\frac{1}{2}} - \frac{\epsilon_i}{D} \cdot \frac{6\pi\epsilon^4}{(DkT)^2} \cdot \frac{(\sum N_i z_i^2)^2}{NV} - \dots \quad (40)$$

Comparing with Eq. (29) we see that:

$$C_1 = C_3 = C_4 = C_6 = \dots = 0$$

and

$$C_2 = -(4\pi \cdot \sum N_i z_i^2 / z_i^2)^{\frac{1}{2}}, \\ C_5 = -6\pi \cdot (\sum N_i z_i^2)^2 / N z_i^4, \text{ etc.} \quad (41)$$

From Eq. (29) we could deduce, if the  $C_m$ 's were known, the osmotic coefficient  $g$  and the activity coefficient  $f$  by means of the following relations:

$$g = P/\bar{P} = 1 - (\partial W / \partial V)_T, \quad (42)$$

$$W = \sum_i \left[ N_i \sum_{m=1}^{\infty} \frac{C_{i,m} \epsilon_i^{m+1}}{(m+1)(kT)^{(m-1)/2} \cdot D^{(m+1)/2} \cdot V^{(m+1)/6}} \right], \quad (43)$$

$$\ln f_i = (1/kT) \cdot \partial W / \partial N_i. \quad (44)$$

The activity coefficient of the salt  $ij$  will be given by:

$$f = [f_i^{v_i} \cdot f_j^{v_j}]^{1/v}, \quad (45)$$

$v_i$  and  $v_j$  being the numbers of ions  $i$  and  $j$  into which the salt  $ij$  dissociates,  $v$  being the sum of

$v_i$  and  $v_j$ . It is seen that  $g$  and  $f$  are given by series. If these series are reduced to their first terms,  $g$  and  $f$  will be given by expressions analogous to those of Debye and Hückel, exactly as in the Kramers theory. This approximation is justified at very low concentrations and for not too small values of  $D$ . It happens that these first

terms are also obtained when the Poisson equation is integrated according to the method of Debye and Hückel (hyperbolic sine replaced by its argument), i.e., when in the case of 1-1 electrolytes, for instance, the equation

$$\Delta\psi = -(4\pi n\epsilon/D)(e^{-\epsilon\psi/kT} - e^{\epsilon\psi/kT}) \quad (46)$$

is arbitrarily replaced by

$$\Delta\psi = 8\pi n\epsilon^2\psi/DkT. \quad (47)$$

This result cannot be considered as anything more than a coincidence, since La Mer, Gronwall and Sandved<sup>6</sup> have shown that if the exact integration of the Eq. (46) is carried out, the value of  $\psi_i$  and hence that of the electrostatic

energy of the mixture of ions become infinite when the radius of the ions becomes infinitely small. This would tend to show that the Poisson equation as applied to electrolytes is meaningless in this case.

Summing up we may say that the reasonings developed in this paper show how far it is possible to go in the solution of the problem of electrolytes without using more statistics than what is involved in the virial theorem and without using the Poisson equation. These reasonings also show that, insofar as their dependence on the temperature, the dielectric constant of the solvent and the volume of the solution is concerned, the limiting laws of Debye-Hückel and of Kramers are essentially correct.