

## On the Theory of Strong Electrolyte Solutions

John G. Kirkwood

Citation: *J. Chem. Phys.* **2**, 767 (1934); doi: 10.1063/1.1749393

View online: <http://dx.doi.org/10.1063/1.1749393>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v2/i11>

Published by the American Institute of Physics.

---

### Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT

**physicstoday**

Comment on any  
*Physics Today* article.

**Measured energy in Japan**  
David von Seggern  
(vonneg@seismo.unr.edu) University of Nevada  
July 2012, page 10  
DIGITAL OBJECT IDENTIFIER  
<http://dx.doi.org/10.1063/PT.3.1619>  
The article by Thorne Lay and Hiroo Kanamori is an interesting one. It discusses the energy released by the 1994 Northridge earthquake. The authors estimate that the earthquake released about 10<sup>15</sup> joules of energy. This is a very large amount of energy, but it is only a fraction of the energy released by a 100-megaton explosion. The authors also discuss the energy released by the 1964 Chilean earthquake. They estimate that this earthquake released about 10<sup>16</sup> joules of energy. This is even larger than the energy released by the 1994 Northridge earthquake. The authors conclude that the energy released by earthquakes is a very small fraction of the energy released by nuclear weapons.

**Comment on this article**  
By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.  
Written by Edgar McCarroll, 14 July 2012 19:59

## On the Theory of Strong Electrolyte Solutions\*

JOHN G. KIRKWOOD, *Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology*

(Received June 15, 1934)

The nature of the approximations involved in the derivation of the Poisson-Boltzmann equation of the Debye-Hückel theory is investigated in detail from the standpoint of classical statistical mechanics. The validity of the initial Debye approximation, under the restrictions originally imposed upon it, is confirmed. Deviations arising from fluctuation terms and van der Waals forces are roughly estimated. An alternative to the Bjerrum method for the treatment of ions of small size and high valence is outlined.

### I.

ALTHOUGH the Debye-Hückel<sup>1</sup> theory furnishes a strikingly satisfactory account of many of the properties of strong electrolyte solutions, it is based upon physical assumptions, which, though plausible, are not in exact accord with the formal theory of statistical mechanics. This discrepancy has exposed the theory to a certain amount of adverse criticism in recent years. Although some of this criticism has certainly been of value in bringing the imperfections of the theory to light, none of it has been very successful in estimating their quantitative importance. It is the object of the present article to investigate in some detail the approximations involved in the derivation of the Debye-Hückel equations from statistical mechanics, and to estimate, insofar as possible, their quantitative importance.

The formulation of a statistical theory of electrolyte solutions offers little difficulty in itself. However, obstacles are immediately encountered in the evaluation of certain phase integrals. Until these are evaluated the theory remains formal and somewhat impotent. In order to obtain integrals, which can be treated with much hope of success, it is necessary to idealize the solvent as a continuous medium characterized only by its dielectric constant. Let us suppose that a solution of volume  $v$  consists of  $N$  ions dissolved in a solvent of dielectric constant  $D$ . Let  $F$  be the Helmholtz free energy,  $E - TS$ , of the solution when all ions bear their full charges  $e_1, \dots, e_N$ , and  $F_0$  be the free energy when all ions are completely discharged. For convenience, we exclude from  $F$  a constant

term of the form  $\sum_{k=1}^N e_k^2/2Db_k$  arising from the self-energy of the ions. If we assume that the system of  $N$  ions, in thermal equilibrium with a temperature  $T$ , can be represented by a classical canonical ensemble, we may write

$$e^{-\beta(F-F_0)} = Z_N/Z_N^0,$$

$$Z_N = \int \dots \int e^{-\beta V_N} dv_1 \dots dv_N, \quad (1)$$

$$Z_N^0 = \int \dots \int e^{-\beta U_N} dv_1 \dots dv_N,$$

where  $\beta$  is equal to  $1/kT$ ,  $V_N$  is the mutual potential energy of the fully charged ions, and  $U_N$  is the mutual potential energy of the completely discharged ions, consisting only of the terms in  $V_N$ , arising from short range van der Waals forces. Integration in the configuration space  $v_k$  of each ion is to be extended over the volume,  $v$ , occupied by the solution.

The position of any ion  $k$  can be specified by a set of configuration coordinates,  $q_k$ , for example the three components of a vector  $\mathbf{r}_k$ , drawn from some arbitrary origin and terminating at the center of the ion  $k$ . For simplicity we assume that the ions have no internal degrees of freedom, and that they are spherically symmetrical. Their mutual potential energy may then be expressed as a function of the configuration coordinates  $q_1 \dots q_N$  in the following manner.

$$V_N = \frac{1}{2} \sum_{k=1}^N [e_k \psi_k(q_k) + U_k(q_k)],$$

$$\psi_k(q_k) = \sum_{\substack{l=1 \\ l \neq k}}^N \frac{e_l}{D |\mathbf{r}_l - \mathbf{r}_k|}, \quad (2)$$

$$U_k(q_k) = \sum_{\substack{l=1 \\ l \neq k}}^N u_{kl}(|\mathbf{r}_k - \mathbf{r}_l|),$$

\* No. 334.

<sup>1</sup> Debye and Hückel, *Phys. Zeits.* **24**, 185, 305 (1923).

where  $e_k$  is the charge on an ion  $k$ , and  $|\mathbf{r}_l - \mathbf{r}_k|$  is the distance between the ion pair  $k$  and  $l$ . Thus  $\psi_k(q_k)$  is the electrostatic potential produced in the interior of the ion  $k$  by the charges on the other ions. The potential of the short range van der Waals and polarization forces can be represented to a very close approximation, as in the theory of imperfect gases, by a sum of terms of the type  $u_{kl}$ , each depending only upon the relative coordinates of the ion pair  $k$  and  $l$ .

Eq. (1) is of course purely formal and is of little value unless it is possible to evaluate the phase integrals  $Z_N$  and  $Z_N^\circ$ . The integral  $Z_N^\circ$ , involving only short range van der Waals forces, may be obtained by the methods employed in the statistical theory of imperfect gases. This method is not applicable in the case of  $Z_N$ , which unfortunately is very difficult to treat. Kramers<sup>2</sup> has attempted to evaluate  $Z_N$  and van Rysselberghe,<sup>3</sup> using a similar method, has attempted to calculate the osmotic pressure directly without the intermediate calculation of  $Z_N$ . Both methods are based upon dimensional considerations, which fail to account satisfactorily for the rôle of the van der Waals forces between the ions. Moreover, unless these forces, which determine the size of the ions, are taken into account,  $Z_N$  clearly diverges. Thus, while very ingenious, the investigations of both Kramers and van Rysselberghe fail to do much more than confirm the Debye-Hückel limiting law at low concentrations, without indicating how a better approximation may be obtained.

Instead of basing the calculation of the free energy  $F$  on a direct determination of  $Z_N$ , it is possible to start from the mean electrostatic potential in an ion, defined as follows:

$$\bar{\psi}_k = \frac{\int \cdots \int \psi_k(q_k) e^{-\beta V_N} dv_1 \cdots dv_N}{\int \cdots \int e^{-\beta V_N} dv_1 \cdots dv_N}. \quad (3)$$

From (1), it is easily demonstrated that

$$\begin{aligned} \partial F / \partial e_k &= \bar{\psi}_k, & (a) \\ \partial \bar{\psi}_k / \partial e_l &= \partial \bar{\psi}_l / \partial e_k. & (b) \end{aligned} \quad (4)$$

These relations have been derived and discussed in detail by Onsager<sup>4</sup> and later by

Halpern.<sup>5</sup> If the charges on the ions are varied in an arbitrary manner, we have from (4a)

$$\delta F = \sum_{k=1}^N \frac{\partial F}{\partial e_k} \delta e_k = \sum_{k=1}^N \bar{\psi}_k \delta e_k. \quad (5)$$

From (4b), the condition of integrability, we may conclude that the integral of  $\delta F$  in any charging process depends only upon the initial and final values of the charges, and not upon the method of charging. Thus the difference  $F - F_0$ , where  $F$  is the free energy of the solution when all ions have the full charges  $e_1 \cdots e_N$ , and  $F_0$ , the free energy when all ions are completely discharged, may be obtained by integrating  $\sum_{k=1}^N \bar{\psi}_k \delta e_k$  along any path. The Debye charging process is the one most commonly employed. In this process, all ions are charged simultaneously by equal fractions of their final charge, so that

$$F - F_0 = \sum_{k=1}^N \int_0^1 e_k \bar{\psi}_k(\lambda e_1, \cdots \lambda e_N) d\lambda. \quad (6)$$

It is often possible to assume that  $F_0$  is the free energy of an ideal solution, or when this is not permissible to treat it by empirical methods, applicable to ordinary non-electrolyte solutions. It is to be emphasized that the charging process need not be attributed physical significance, but can be regarded simply as a mathematical device for calculating the free energy function,  $F$ , defined by Eq. (1). The method outlined here, although somewhat indirect, has distinct advantages, since it is easier to calculate  $\bar{\psi}_k$ , at least approximately, than it is to calculate  $Z_N$ .

## II.

The foundation for a precise statistical calculation of  $\bar{\psi}_k$ , the mean potential produced in an ion  $k$ , by the other ions in the solution, was laid by Fowler.<sup>6</sup> We shall have occasion to use the mean Poisson equation of Fowler's theory, Eqs. (582) and (584), which we derive here in a slightly different and somewhat more direct manner. From this point on, we depart from Fowler, employing a method of treating the statistical space

<sup>2</sup> H. A. Kramers, Proc. Amst. Acad. Sci. **30**, 145 (1927).

<sup>3</sup> P. van Rysselberghe, J. Chem. Phys. **1**, 205 (1933).

<sup>4</sup> Onsager, Chem. Rev. **13**, 73 (1933).

<sup>5</sup> Halpern, J. Chem. Phys. **2**, 85 (1934).

<sup>6</sup> R. H. Fowler, *Statistical Mechanics*, 8.7, 8.8, Cambridge University Press (1929).

charge around an ion, which leads to somewhat more concrete results.

We begin by considering the electrostatic potential at some fixed point,  $q$ , in the solution

$$\psi(q) = \sum_{l=1}^N (e_l/D |\mathbf{r}_l - \mathbf{r}|), \quad (7)$$

where  $|\mathbf{r}_l - \mathbf{r}_k|$  is the distance of the  $l$ th ion from the point  $q$ . The mean value of  $\psi(q)$ , when a selected ion  $k$  is fixed at a point  $q_k$  is given by

$$\overline{\psi(q)}^k = \frac{\int \dots \int \psi(q) e^{-\beta V_N} dv_1 \dots dv_{N-1}}{\int \dots \int e^{-\beta V_N} dv_1 \dots dv_{N-1}}, \quad (8)$$

where the integrations are extended over the coordinates of all ions except those of the selected ion,  $k$ . We define  $\psi_k(q)$  as the potential at  $q$ , arising from all ions except the fixed ion  $k$ .

$$\psi_k(q) = \psi(q) - e_k/D |\mathbf{r} - \mathbf{r}_k|. \quad (9)$$

The term  $e_k/D |\mathbf{r} - \mathbf{r}_k|$  is a constant as long as ion  $k$  remains fixed, and is unaffected by a mean value operation of the type (8). Suppose that  $\overline{\psi_k(q)}$  has been determined everywhere in the neighborhood of the ion  $k$ , and let  $\overline{\psi_k(q_k)}$  be its value in the interior of the ion  $k$ . From Eqs. (3) and (8) we obtain the relation

$$\frac{\int \overline{\psi_k(q_k)} [\int \dots \int e^{-\beta V_N} dv_1 \dots dv_{N-1}] dv_k}{\int \dots \int e^{-\beta V_N} dv_1 \dots dv_N} = \overline{\psi_k}. \quad (10)$$

If  $\overline{\psi_k(q_k)}$  is independent of  $q_k$ , we may write immediately

$$\overline{\psi_k} = \overline{\psi_k}. \quad (11)$$

We may assume without formal proof that  $\overline{\psi_k}$  is independent of  $q_k$ , that is, of the position of  $k$  relative to the boundaries of the solution, except in a surface region of negligible volume. Otherwise direct contradictions with experiment would result, such as concentration gradients in the bulk of the solution. Therefore Eq. (11) may be accepted as valid, except for a quantity of negligible order.

We may rewrite Eq. (8), which defines  $\overline{\psi(q)}$ , in a somewhat different manner.

$$\begin{aligned} \overline{\psi(q)}^k &= \sum_{\substack{l=1 \\ l \neq k}}^N \int \frac{\rho_l(q_l)}{D |\mathbf{r}_l - \mathbf{r}|} dv_l + \frac{e_k}{D |\mathbf{r} - \mathbf{r}_k|}, \\ \overline{\rho_l(q_l)}^k &= e_l \frac{\int \dots \int e^{-\beta [V_{N-1} + V_l(q_l)]} dv_1 \dots dv_{N-2}}{\int \dots \int e^{-\beta V_N} dv_1 \dots dv_{N-1}}. \end{aligned} \quad (12)$$

In the expression for  $\overline{\rho_l(q_l)}^k$ , the coordinates of both  $k$  and  $l$  remain fixed in the integral in the numerator, while only those of  $k$  remain fixed in the integral in the denominator. For clearness we have expressed  $V_N$  as a sum of two terms,  $V_{N-1}$ , which is independent of  $q_l$ , and  $V_l(q_l)$  which is given by

$$V_l(q_l) = e_l \psi_l(q_l) + U_l(q_l).$$

This is merely a rearrangement of terms, which may be carried out for any one of the  $N$  ions. Eq. (12) is precisely the solution of the following Poisson equation:<sup>7</sup>

$$\nabla^2 \overline{\psi(q)}^k = -(4\pi/D) \overline{\rho(q)}^k,$$

<sup>7</sup> The passage from (12) to (13) follows from a well-known transformation in potential theory, depending upon the fact that  $\nabla^2 |\mathbf{r}_l - \mathbf{r}|^{-1}$  is zero except when  $\mathbf{r}_l = \mathbf{r}$ , where it has a singularity. Thus in any integral of the form

$$\int F(q_l) \nabla^2 |\mathbf{r}_l - \mathbf{r}|^{-1} dv_l$$

$$\overline{\rho(q)} = \sum_{l=1}^N e_l \frac{\int \dots \int e^{-\beta[V_{N-1} + V_l(q)]} dv_1 \dots dv_{N-2}}{\int \dots \int e^{-\beta V_N} dv_1 \dots dv_{N-1}}. \quad (13)$$

In general, there will be several ion types present in the solution. If  $N_i$  be the number of ions of the  $i$ th type,  $N_i/v$  is the bulk concentration  $C_i$  of that type. Moreover,  $\overline{\rho_i(q)}$  is the same function  $\overline{\rho_i(q)}$  for all ions of the  $i$ th type. Therefore we may write

$$\overline{\rho(q)} = \sum_i C_i e_i \zeta_{ki}(q), \quad (14)$$

$$\zeta_{ki}(q) = \frac{v \overline{\rho_i(q)}}{e_i} = \frac{v \int \dots \int e^{-\beta[V_{N-1} + V_i(q)]} dv_1 \dots dv_{N-2}}{\int \dots \int e^{-\beta V_N} dv_1 \dots dv_{N-1}}$$

and the Poisson Eq. (13) becomes  $\Delta^2 \psi(q) = -(4\pi/D) \sum_i C_i e_i \zeta_{ki}(q), \quad (15)$

where the sum is extended over all ion types. Properly, the selected ion  $k$  should be omitted from the sum, but its omission would alter the concentration of the type to which it belongs by a quantity of the order  $C_i/N_i$ , which can be ignored altogether.

It is sometimes convenient to define a function  $V_{ki}$  by means of the following relation

$$e^{-\beta V_{ki}} = \zeta_{ki}. \quad (16)$$

It may be shown that  $V_{ki}$  is the potential of the mean force acting on the ion  $i$  at the point  $q$ .<sup>4</sup> When the  $\zeta_{ki}$  are expressed in the form (16), Eq. (15) becomes identical in form with Fowler's Eqs. (583) and (584). From Eqs. (14) and (16) one obtains by differentiation of  $\zeta_{ki}$

$$\begin{aligned} \nabla^2 V_{ki} + 4\pi e_i \rho_{ki}/D &= -\beta [\overline{ik(\nabla V_i)^2} - (\nabla V_{ki})^2], \\ \rho_{ki} &= -\frac{D}{4\pi e_i} \overline{ik \nabla^2 V_i}, \end{aligned} \quad (17)$$

where the mean values are taken with the ion  $i$  fixed at the point  $q$  and the ion  $k$  fixed at the point  $q_k$ . Eq. (17) is identical with Fowler's Eqs. (585) and (586). If the quantities  $\rho_{ki}$  and  $\overline{ik(\nabla V_i)^2}$  were known,  $\overline{ik\psi(q)}$  could be determined by the simultaneous solution of Eqs. (15), (16), and (17) with appropriate boundary conditions. Unfortunately, we do not have the necessary information about  $\rho_{ki}$  and  $\overline{ik(\nabla V_i)^2}$ , nor does there seem to be any practicable means of obtaining it. For this reason, we prefer to study the charge density  $\overline{ik\psi(q)}$  of Eq. (14) by another method, which utilizes the properties of the functions  $\zeta_{ki}$  themselves and not those of their derivatives.

The familiar Poisson-Boltzmann equation of the Debye-Hückel theory follows immediately from Eqs. (15) and (16) when  $e_i \overline{ik\psi(q)}$  is substituted for  $V_{ki}$  in  $\zeta_{ki}$ . This is admittedly an approximation, for it involves the assumption that the potential of the mean force is equal to the mean potential. However, the approximation

$$V_{ki} = e_i \overline{ik\psi(q)} \quad (18)$$

the integrand is zero except in the immediate neighborhood of the point  $\mathbf{r}_l = \mathbf{r}$ . The integral in the vicinity of this point may be transformed by Green's theorem and evaluated as  $J = -4\pi F(q)$ . This may be represented symbolically by saying that  $\nabla^2 |\mathbf{r}_l - \mathbf{r}|^{-1}$  is a delta-function

$$\nabla^2 |\mathbf{r}_l - \mathbf{r}|^{-1} = -4\pi \delta(\mathbf{r}_l - \mathbf{r}),$$

where  $\delta(\mathbf{r}_l - \mathbf{r})$  has the property

$$\int F(q_l) \delta(\mathbf{r}_l - \mathbf{r}) dv_l = F(q).$$

Thus the  $\rho(x)$  in the integrand of Fowler's Eq. (584) is simply

$$-4\pi \sum_{\substack{l=1 \\ \neq k}}^N \delta(\mathbf{r}_l - \mathbf{r}).$$

is by no means as objectionable as the approximation attributed to Debye and Hückel by Fowler (*Statistical Mechanics*, Eq. (587))

$$\nabla^2 V_{ki} = -(4\pi e_i/D) \overline{\rho(q)} = e_i \nabla^2 \overline{\psi(q)}. \quad (19)$$

Thus two functions may be approximately equal over a large interval even though their second derivatives are not. The approximate validity of (18), for example at large distances from the selected ion  $k$ , is not subject to the validity of (19) nor would it even follow from (19), unless all boundary values of the two functions  $e_i \overline{\psi(q)}$  and  $V_{ki}$  were equal.

Fowler's criticism of the Debye-Hückel theory was based upon Eqs. (17) and (19). In order for these equations to be consistent it is necessary that  $\beta[(\nabla V_i)^2 - (\nabla V_{ki})^2] + 4\pi e_i \rho_{ki}/D$  be equal to  $4\pi e_i \overline{\rho(q)}/D$ . If  $\rho_{ki}$  and  $\overline{\rho(q)}$  were approximately equal, the fluctuation in the force acting upon the ion  $i$  would have to be small. However, it turns out that this requirement is not necessary, for  $\rho_{ki}$  is quite different from  $\overline{\rho(q)}$  and always much smaller. As Onsager<sup>4</sup> has pointed out Eq. (17) is meaningless, unless van der Waals forces of the repulsive type are taken into account. By the method employed in the derivation of Eq. (13), it is readily shown<sup>8</sup> that these repulsive forces, which give the ions their finite size, cause the Coulomb contribution to  $\rho_{ki}$  to vanish. Thus Eq. (17) should actually be written in the following manner:

$$-\beta[(\nabla V_i)^2 - (\nabla V_{ki})^2] = \nabla^2 V_{ki} - \nabla^2 U_i, \quad (17a)$$

where  $U_i(q)$  is the potential of the short range forces acting upon the ion  $i$ . This circumstance makes it even more difficult to determine whether Eqs. (17) and (19) are consistent, but it removes the restriction that the fluctuation in the force must be small. Finally, when it is emphasized that Debye and Hückel wished to obtain a differential equation for  $\overline{\psi(q)}$ , not  $V_{ki}$ , and that their result follows directly from Eqs. (15) and (18), it becomes clear that the adequacy of their approximation should not be judged on the basis of Eq. (19). Thus to conclude that the two functions  $V_{ki}$  and  $e_i \overline{\psi(q)}$  could not be approximately equal in an extensive region of the solution simply because their second derivatives may not be equal, would to say the least, put the Debye-Hückel approximation in an unjustifiably unfavorable light.

### III.

Solution of the Poisson Eq. (15) requires a knowledge of the mean charge density,  $\overline{\rho(q)}$ , which is expressible in terms of the functions  $\zeta_{ki}$ . We shall now investigate the relation of these functions to

<sup>8</sup> The density function  $\rho_{ki}$  in Eq. (17) is equal to  $-\frac{D}{4\pi e_i} \nabla^2 V_i(q)$ .

$$\overline{\nabla^2 V_i} = \frac{\int \dots \int \nabla^2 V_i(q) e^{-\beta V_N(q_i=q)} dv_1 \dots dv_{N-2}}{\int \dots \int e^{-\beta V_N(q_i=q)} dv_1 \dots dv_{N-2}}, \quad (a)$$

where the ions  $i$  and  $k$  remain fixed during the averaging process. Since

$$V_i(q) = e_i \sum_{\substack{l=1 \\ \neq i}}^N \frac{e_l}{D|\mathbf{r}_l - \mathbf{r}|} + U_i(q), \quad (b)$$

we may write (see reference 7)

$$\nabla^2 V_i = -\frac{4\pi e_i}{D} \sum_{\substack{l=1 \\ \neq i}}^N e_l \delta(\mathbf{r}_l - \mathbf{r}) + \nabla^2 U_i. \quad (c)$$

Thus

$$\overline{\nabla^2 V_i} = -\frac{4\pi e_i}{D} \sum_{\substack{l=1 \\ \neq i}}^N e_l \frac{\int \dots \int e^{-\beta V_N(q_l=q_i=q)} dv_1 \dots dv_{N-3}}{\int \dots \int e^{-\beta V_N(q_i=q)} dv_1 \dots dv_{N-2}} + \overline{\nabla^2 U_i}. \quad (d)$$

Now due to van der Waals forces  $V_N$  contains terms of the form  $u_{il}(q_i - q_l)$ . Whenever any  $|q_i - q_l|$  becomes zero as for example when  $q_i = q_l = q$ , there is always a term which becomes positively infinite and makes  $e^{-\beta V_N(q_i=q_l)}$  vanish. Thus the first term of (d), arising from electrostatic forces, always vanishes and we are left with

$$\rho_{ki} = -(D/4\pi e_i) \overline{\nabla^2 U_i}. \quad (e)$$

the mean potential  ${}^k\overline{\psi(q)}$ . The method to be employed is in certain respects similar to a general method proposed by Onsager.<sup>4</sup> We differentiate  $\zeta_{ki}$  with respect to  $e_i$ , the charge on the ion  $i$ . Remembering Eqs. (2) and (14), we obtain

$$\frac{\partial \zeta_{ki}}{\partial e_i} = -\beta \zeta_{ki} [{}^{ik}\overline{\psi_i(q)} - {}^k\overline{\psi_i(q_i)}], \quad (20)$$

$${}^k\overline{\psi_i(q_i)} = \frac{\int \cdots \int \psi_i(q_i) e^{-\beta V_N} dv_1 \cdots dv_{N-1}}{\int \cdots \int e^{-\beta V_N} dv_1 \cdots dv_{N-1}}, \quad {}^{ik}\overline{\psi_i(q)} = \frac{\int \cdots \int \psi_i(q) e^{-\beta [V_{N-1} + V_i(q)]} dv_1 \cdots dv_{N-2}}{\int \cdots \int e^{-\beta [V_{N-1} + V_i(q)]} dv_1 \cdots dv_{N-2}}. \quad (21)$$

Thus  ${}^{ik}\overline{\psi_i(q)}$  is the mean value of the potential at the point  $q$ , when the ion  $i$  is fixed at that point, and the ion  $k$  is fixed at the point  $q_k$ . The subscript  $i$  in  $\psi_i(q)$  means as before that the term,  $e_i/D|\mathbf{r}_i - \mathbf{r}|$  is omitted. For certain purposes it is convenient to express this potential in a somewhat different form. The mean potential at any point  $q'$ , when the ions  $i$  and  $k$  are fixed at any points  $q_i$  and  $q_k$  is

$${}^{ik}\overline{\psi_i(q'; q_i, q_k)} = \frac{\int \cdots \int \psi_i(q') e^{-\beta V_N(q_i, \cdots, q_k, \cdots)} dv_1 \cdots dv_{N-2}}{\int \cdots \int e^{-\beta V_N(q_i, \cdots, q_k, \cdots)} dv_1 \cdots dv_{N-2}}. \quad (22)$$

The potential  ${}^{ik}\overline{\psi_i(q)}$  is evidently equal to  ${}^{ik}\overline{\psi_i(q; q, q_k)}$ , that is the value of (22) when  $q' = q_i = q$ . Moreover it is clear that this latter potential must depend only on the relative coordinates  $|q - q_k|$  of the ions  $i$  and  $k$  (except in the surface region of the solution). It therefore remains unaltered by an interchange of the coordinates of  $i$  and  $k$ , or by a shift of their center of gravity.

$${}^{ik}\overline{\psi_i(q; q, q_k)} = {}^{ik}\overline{\psi_i(q_i; q_i, q')}, \quad |q - q_k| = |q' - q_i|, \quad (23)$$

so that one may write

$${}^{ik}\overline{\psi_i(q)} = \frac{\int \cdots \int \psi_i(q_i) e^{-\beta [V_{N-1} + V_k(q')]} dv_1 \cdots dv_{N-2}}{\int \cdots \int e^{-\beta [V_{N-1} + V_k(q')]} dv_1 \cdots dv_{N-2}}, \quad (24)$$

subject to the condition that  $|q' - q_i| = |q - q_k|$ . We shall have occasion to use both of the alternative expressions (21) and (24) in discussing the properties of  ${}^{ik}\overline{\psi_i(q)}$ .

We may integrate Eq. (20) at once to obtain

$$\zeta_{ki} = \zeta_{ki}^0 e^{-\beta \int_0^{e_i} [{}^{ik}\overline{\psi_i(q)} - {}^k\overline{\psi_i(q_i)}] de_i}, \quad (25)$$

$$\zeta_{ki}^0 = \frac{v \int \cdots \int e^{-\beta [V_{N-1} + u_i(q)]} dv_1 \cdots dv_{N-2}}{\int \cdots \int e^{-\beta [V_{N-1} + u_i(q_i)]} dv_1 \cdots dv_{N-1}} = \frac{\int \cdots \int e^{-\beta [V_{N-1} + u_i(q)]} dv_1 \cdots dv_{N-1}}{\int \cdots \int e^{-\beta [V_{N-1} + u_i(q_i)]} dv_1 \cdots dv_{N-1}}. \quad (26)$$

In the second equality (26), the  $v$  factor has simply been written as an integration over  $q_i$ . This can be done since the integrand  $e^{-\beta [V_{N-1} + u_i(q)]}$  is independent of  $q_i$ , the running coordinates of the  $i$  ion having been replaced by  $q$ . It may be noted that  $\zeta_{ki}^0$  is formally the mean value, when  $e_i = 0$ , of the following function

$$\zeta_i^0 = e^{-\beta [u_i(q) - u_i(q_i)]}; \quad \zeta_{ki}^0 = {}^k\overline{\zeta_i^0}|_{e_i=0}. \quad (27)$$

Substitution of (25) in Eq. (15) yields

$$\nabla^2 {}^k\overline{\psi(q)} = -\frac{4\pi}{D} \sum_i c_i e_i \zeta_{ki}^0 e^{-\beta \int_0^{e_i} [{}^{ik}\overline{\psi_i(q)} - {}^k\overline{\psi_i(q_i)}] de_i}. \quad (28)$$

This is an exact form of the Poisson equation for the mean potential  ${}^k\overline{\psi(q)}$ . We note that each of the  $\zeta_{ki}^0$  contains a factor  $e^{-\beta u_{ki}(q - q_k)}$ . When  $|q - q_k|$  becomes small, van der Waals repulsion makes  $u_{ki}(q - q_k)$  positively infinite and each  $\zeta_{ki}^0$  vanishes. Thus "inside" the ion  $k$ , the right-hand side of

Eq. (28) vanishes, and it becomes Laplace's equation. Outside of the ion  $k$ , the  $\zeta_{ki}^\circ$  are effectively unity except for a small term depending upon van der Waals forces. Without going into the details of the calculation, which would divert us from our main purpose, we may state that  $\zeta_{ki}^\circ$  is approximately given by<sup>9</sup>

$$\zeta_{ki}^\circ = 1 - 2 \sum_j B_{ij} C_j (\zeta_{kj} - 1) + \dots, \quad (29)$$

where the  $B_{ij}$  have the same form as the second virial coefficients of an imperfect gas, and  $C_j$  is the bulk concentration of the ion type  $j$ . If van der Waals forces of the attractive type are ignored and the ions are treated as rigid spheres, one may write

$$B_{ij} = (2\pi/3) a_{ij}^3, \quad (30)$$

where  $a_{ij}$  is the mean diameter of ions of types  $i$  and  $j$ .

We are chiefly interested in the properties of the mean potentials  ${}^{ik}\overline{\psi_i(q)}$  and  ${}^k\overline{\psi_i(q)}$ . By means of the following identity, we can relate  ${}^{ik}\overline{\psi_i(q)}$  to its values  ${}^{ik}\overline{\psi_i(q)}|_{e_i=0}$  and  ${}^{ik}\overline{\psi_i(q)}|_{e_k=0}$ , when the charges on the ions  $i$  and  $k$  are, respectively, zero.

<sup>9</sup> The function  $\zeta_{ki}^\circ - 1$  has the form

$$\zeta_{ki}^\circ - 1 = \frac{\int \dots \int e^{-\beta V_{N-1}} [e^{-\beta u_i(q)} - e^{-\beta u_i(q_i)}] dv_1 \dots dv_{N-1}}{\int \dots \int e^{-\beta [V_{N-1} + u_i(q_i)]} dv_1 \dots dv_{N-1}}.$$

Making use of the identity

$$e^{-\beta u_i(q)} - e^{-\beta u_i(q_i)} = (e^{-\beta u_i(q)} - 1) - (e^{-\beta u_i(q_i)} - 1)$$

we may write

$$\begin{aligned} \zeta_{ki}^\circ - 1 &= \frac{\int \dots \int e^{-\beta V_{N-1}} [e^{-\beta u_i(q)} - 1] dv_1 \dots dv_{N-1}}{\int \dots \int e^{-\beta [V_{N-1} + u_i(q_i)]} dv_1 \dots dv_{N-1}} \\ &\quad - \frac{\int \dots \int e^{-\beta V_{N-1}} [e^{-\beta u_i(q_i)} - 1] dv_1 \dots dv_{N-1}}{\int \dots \int e^{-\beta [V_{N-1} + u_i(q_i)]} dv_1 \dots dv_{N-1}}. \end{aligned}$$

Now  $U_i(q) = \sum_{j=1, \neq i}^N u_{ij}(q_j - q)$ , where the potentials,  $u_{ij}(q_j - q)$ , of the short range forces are effectively zero unless the distance  $|\mathbf{r}_j - \mathbf{r}|$  is very small, of the order of a molecular diameter. Thus  $e^{-\beta u_i(q)} - 1$  is zero unless at least one distance  $|\mathbf{r}_j - \mathbf{r}|$  is of the order of a molecular diameter. Likewise  $e^{-\beta u_i(q_i)} - 1$  is zero unless at least one interionic distance  $|\mathbf{r}_j - \mathbf{r}_i|$  is of the order of a molecular diameter. Thus each of the two parts of  $\zeta_{ki}^\circ - 1$  must at least contain the ionic concentration  $C$  to a power not lower than the first, and we may state at once  $\zeta_{ki}^\circ - 1 = O(C)$  that is,  $\zeta_{ki}^\circ - 1$  is of negligible order if we neglect terms involving the first power of the concentration. However, we can go farther than that. Thus we may write

$$e^{-\beta u_i(q)} = \prod_{j=1, \neq i}^N e^{-\beta u_{ij}(q_j - q)} = \prod_{j=1, \neq i}^N [1 + (e^{-\beta u_{ij}} - 1)].$$

Expansion of the continued product gives as a first approximation

$$e^{-\beta u_i(q)} = 1 + \sum_{j=1, \neq i}^N (e^{-\beta u_{ij}} - 1) + \dots$$

Now consider an integral of the form

$$\int f(q_i) [e^{-\beta u_{ij}(q)} - 1] dv_j.$$

Since  $(e^{-\beta u_{ij}(q)} - 1)$  is zero except when  $q_j$  is in the immediate neighborhood of  $q$ , we may write approximately

$$\begin{aligned} \int f(q_j) [e^{-\beta u_{ij}(q)} - 1] dv_j &= -2B_{ij} f(q), \\ B_{ij} &= \frac{1}{2} \int (1 - e^{-\beta u_{ij}}) dv_j. \end{aligned}$$

This is a rough but adequate approximation when  $f(q_j)$  does not vary rapidly over the small region, in which  $u_{ij}(q_j - q)$  is effectively different from zero. It amounts to replacing  $f(q_j)$  in this region by its value at the center  $q = q_j$ . Making this approximation, the function  $\zeta_{ki}^\circ - 1$  becomes with the neglect of terms in  $C^2$ ,

$$\begin{aligned} \zeta_{ki}^\circ - 1 &= -2 \sum_j C_j B_{ij} (\zeta_{kj}' - 1), \\ \zeta_{kj}' &= \frac{\int \dots \int e^{-\beta [V_{N-2} + V_j(q)]} dv_1 \dots dv_{N-2}}{\int \dots \int e^{-\beta V_{N-1}} dv_1 \dots dv_{N-1}}. \end{aligned}$$

Thus  $\zeta_{kj}'$  differs from  $\zeta_{kj}$ , simply by the removal of the single ion  $i$ . This removal can produce a change in  $\zeta_{kj}$  only of the order of  $\zeta_{kj}/N_i$ , so that effectively  $\zeta_{kj}' = \zeta_{kj}$ .



$$\overline{\psi_i(q)}^{ik} = \overline{\psi_i(q)}^{ik}|_{e_i=0} + \overline{\psi_i(q)}^{ik}|_{e_k=0} - \overline{\psi_i(q)}^{ik}|_{e_i=0, e_k=0} + \int_0^{e_i} \int_0^{e_k} \frac{\partial^2 \overline{\psi_i(q)}^{ik}}{\partial e_i \partial e_k} de_i de_k. \quad (31)$$

When the charge  $e_i$  is zero, we have from Eq. (22)

$$\overline{\psi_i(q)}^{ik}|_{e_i=0} = \frac{\int \dots \int \psi_i(q) e^{-\beta[V_{N-1}+u_i(q)]} dv_1 \dots dv_{N-2}}{\int \dots \int e^{-\beta[V_{N-1}+u_i(q)]} dv_1 \dots dv_{N-2}}. \quad (32)$$

Both numerator and denominator of (32) may be multiplied by  $v$ , and since both integrands are independent of  $q_i$ , all  $q_i$ 's having been replaced by  $q$ , the  $v$  factors may be expressed as integrations over the running coordinates  $q_i$ .

$$\overline{\psi_i(q)}^{ik}|_{e_i=0} = \frac{\int \dots \int \psi_i(q) e^{-\beta[V_{N-1}+u_i(q)]} dv_1 \dots dv_{N-1}}{\int \dots \int e^{-\beta[V_{N-1}+u_i(q)]} dv_1 \dots dv_{N-1}}. \quad (33)$$

In this expression both  $q_k$  and  $q$  are of course held fixed during the integrations. With the aid of (2), (27) and (33) we find

$$\overline{\psi_i(q)}^{ik}|_{e_i=0} = \frac{\overline{\psi_i(q)\zeta_i^0}|_{e_i=0}}{\zeta_{ki}^0} = \overline{\psi_i(q)}^{ik}|_{e_i=0} + \frac{\overline{\psi_i(q)\zeta_i^0}|_{e_i=0} - \overline{\psi_i(q)}^{ik}|_{e_i=0} \frac{\overline{\zeta_i^0}|_{e_i=0}}{\zeta_{ki}^0}}{\zeta_{ki}^0}. \quad (34)$$

The second term in expression (34) depends primarily upon van der Waals forces and is approximately given by

$$\frac{\overline{\psi_i(q)\zeta_i^0}|_{e_i=0} - \overline{\psi_i(q)}^{ik}|_{e_i=0} \frac{\overline{\zeta_i^0}|_{e_i=0}}{\zeta_{ki}^0}}{\zeta_{ki}^0} = -2 \sum_j B_{ij} C_j \zeta_{kj} \left[ \frac{3}{2} \frac{e_j}{Da_{ij}} + \frac{\overline{\psi_{ij}(q)}^{jk}|_{e_i=0} - \overline{\psi_{ij}(q)}^{jk}|_{e_i=0}}{\zeta_{ij}^0} \right] \quad (35)$$

where the various symbols have the same meaning as in Eq. (29).<sup>9</sup>

Starting from Eq. (24) instead of from (22), we obtain in a similar manner the following expression for  $\overline{\psi_i(q)}^{ik}|_{e_k=0}$

$$\overline{\psi_i(q)}^{ik}|_{e_k=0} = \overline{\psi_i(q)}^{ik}|_{e_k=0} + \frac{\overline{\psi_i(q)\zeta_k^0(q')|_{e_k=0}} - \overline{\psi_i(q)}^{ik}|_{e_k=0} \frac{\overline{\zeta_k^0(q')|_{e_k=0}}}{\zeta_{ki}^0}}{\zeta_{ki}^0} \quad |q' - q_i| = |q - q_k|. \quad (36)$$

As in (34), the second term of (36) is small, and depends primarily upon van der Waals forces.

The potential  $\overline{\psi_i(q)}^{ik}|_{e_i=0, e_k=0}$  is of course zero if all ions are of equal size, that is if all  $u_{ki}$  have the same form. If the sizes are unequal  $\overline{\psi_i(q)}^{ik}|_{e_i=0, e_k=0}$  will consist of a small term proportional to the concentration, arising from a statistical double layer on the surface of the ion  $i$ .

Differentiation of Eq. (21) leads to the following expression for  $\partial^2 \overline{\psi_i(q)}^{ik} / \partial e_i \partial e_k$

$$\frac{\partial^2 \overline{\psi_i(q)}^{ik}}{\partial e_i \partial e_k} = \beta^2 [\psi_k(q_k) - \overline{\psi_k(q_k)}] [\psi_i(q) - \overline{\psi_i(q)}]^2. \quad (37)$$

This derivative is thus a fluctuation of the third order.

Combining (34), (36) and (37), we obtain, remembering that quantities with the subscript,  $e_i=0$ , are independent of  $e_i$

$$\int_0^{e_i} [\overline{\psi_i(q)} - \overline{\psi_i(q_i)}] d\epsilon_i = e_i \overline{\psi_i(q)}|_{\epsilon_i=0} + \int_0^{e_i} [\overline{\psi_i(q_i)}|_{\epsilon_k=0} - \overline{\psi_i(q_i)}] d\epsilon_i + \varphi_{ki}(q), \quad (38)$$

$$\begin{aligned} \text{where } \varphi_{ki}(q) = & \int_0^{e_i} \int_0^{e_i} \int_0^{e_k} \beta^2 [\overline{\psi_k(q_k)} - \overline{\psi_k(q_k)}] [\overline{\psi_i(q)} - \overline{\psi_i(q)}]^2 d\epsilon_i d\epsilon_i d\epsilon_k \\ & + e_i \left[ \frac{\overline{\psi_i(q)} \overline{\zeta_i^\circ(q)}|_{\epsilon_i=0} - \overline{\psi_i(q)}|_{\epsilon_i=0} \overline{\zeta_i^\circ(q')}|_{\epsilon_i=0}}{\overline{\zeta_i^\circ(q)}|_{\epsilon_i=0}} - \overline{\psi_i(q)}|_{\epsilon_i=0, \epsilon_k=0} \right] \\ & + \int_0^{e_i} \left[ \frac{\overline{\psi_i(q_i)} \overline{\zeta_k^\circ(q')}|_{\epsilon_k=0} - \overline{\psi_i(q_i)}|_{\epsilon_k=0} \overline{\zeta_k^\circ(q')}|_{\epsilon_k=0}}{\overline{\zeta_k^\circ(q')}|_{\epsilon_k=0}} \right] d\epsilon_i. \quad (39) \end{aligned}$$

It is readily seen that the mean potential  $\overline{\psi_i(q)}|_{\epsilon_i=0}$  differs from  $\overline{\psi(q)}$  by a quantity of order  $\overline{\psi(q)}/N_i$  where  $N_i$  is the number of ions of the  $i$ th type. In an averaging process in which only the  $k$  ion is held fixed, all ions of the  $i$ th type are equivalent. Thus the discharge of a single  $i$  ion would alter the potential only by a quantity of negligible order  $(1/N_i)$ . (The discharge of a single ion of course destroys the electrical neutrality of the solution but in a completely trivial manner.) For the same reason  $\overline{\psi_i(q_i)}|_{\epsilon_k=0}$  can be identified with  $\overline{\psi_i(q_i)}$ . Since by Eq. (11) this latter potential is equal to  $\overline{\psi_i}$ , we may identify  $\overline{\psi_i(q_i)}|_{\epsilon_k=0}$  with  $\overline{\psi_i}$ . Further it is clear that  $\overline{\psi_i(q_i)}$  also differs from  $\overline{\psi_i}$  by a quantity of negligible order. The fixed ion  $k$  can influence the potential and distribution in the neighborhood of a particular ion  $i$ , only when that ion is in a region around  $k$ , having a volume,  $\omega$ , of molecular order of magnitude. But the ratio of the probability that an ion  $i$  will be in this small volume to the probability that it will be elsewhere in the solution is roughly  $\omega/v$ , or a quantity of negligible order. Since  $\overline{\psi_i(q_i)}|_{\epsilon_k=0}$  and  $\overline{\psi_i(q_i)}$  are both effectively equal to  $\overline{\psi_i}$  the second term of (38) vanishes. Further, since  $\overline{\psi_i(q)}|_{\epsilon_i=0}$  is effectively equal to  $\overline{\psi(q)}$ , we may write

$$\int_0^{e_i} [\overline{\psi_i(q)} - \overline{\psi_i(q_i)}] d\epsilon_i = e_i \overline{\psi(q)} + \varphi_{ki}(q). \quad (40)$$

This relation is exact to quantities of order  $1/N$ , where  $N$  is the total number of ions. When relation (40) is introduced into Eq. (28), the mean Poisson equation becomes

$$\nabla^2 \overline{\psi(q)} = -\frac{4\pi}{D} \sum_i c_i e_i \overline{\zeta_{ki}^\circ} e^{-\beta[\epsilon_i \overline{\psi(q)} + \varphi_{ki}(q)]}. \quad (41)$$

This equation is statistically exact, since only quantities of negligible order of magnitude,  $0(1/N)$ , have been neglected in its derivation. From now on, we shall begin to make approximations. Suppose we assume the ions to be rigid spheres and neglect van der Waals forces of the attractive type. Let  $a_k$  be the mean distance of closest approach of the other ions to ion  $k$ . The primary effect of van der Waals forces is to make the  $\zeta_{ki}^\circ$  vanish inside the sphere  $a_k$ . If secondary effects of van der Waals forces in  $\zeta_{ki}^\circ$  and in  $\varphi_{ki}$  are ignored, Eq. (41) becomes:<sup>10</sup>

<sup>10</sup> The simplification of (41) when the ions are assumed to have different sizes is more elaborate, but offers no difficulty. Except for the fluctuation terms, the equations are identical with those employed by Scatchard in the treatment of this case. (G. Scatchard, Phys. Zeits. 33, 22 (1932).)

$$\begin{aligned}\nabla^2 \overline{\psi(q)} &= -\frac{4\pi}{D} \sum_i c_i e_i e^{-\beta [e_i \overline{\psi(q)} + \varphi_{ki}(q)]}; & |\mathbf{r} - \mathbf{r}_k| > a_k \\ &= 0; & |\mathbf{r} - \mathbf{r}_k| \leq a_k;\end{aligned}\quad (42)$$

$$\varphi_{ki}(q) = \beta^2 \int_0^{e_i} \int_0^{e_i} \int_0^{e_k} \overline{[\psi_k(q_k) - \overline{\psi_k(q_k)}][\psi_i(q) - \overline{\psi_i(q)}]^2} de_i de_i de_k.$$

If the fluctuation terms  $\varphi_{ki}$  are neglected, Eq. (42) reduces to the fundamental equation of the Debye-Hückel theory.

$$\begin{aligned}\nabla^2 \overline{\psi(q)} &= -\frac{4\pi}{D} \sum_i c_i e_i e^{-\beta e_i \overline{\psi(q)}}; & |\mathbf{r} - \mathbf{r}_k| > a_k \\ &= 0; & |\mathbf{r} - \mathbf{r}_k| \leq a_k.\end{aligned}\quad (43)$$

The nature of this approximation becomes clearer when the fluctuation (37) is expressed in terms of  $\overline{\psi_k(q_k)}$ , the mean potential in the ion  $k$ , when the ion  $i$  is held fixed at the point  $q$ . We recall that

$$\overline{\psi_k(q_k)} = \frac{\int \cdots \int \psi_k(q_k) e^{-\beta [V_{N-1} + V_i(q)]} dv_1 \cdots dv_{N-2}}{\int \cdots \int e^{-\beta [V_{N-1} + V_i(q)]} dv_1 \cdots dv_{N-2}}. \quad (44)$$

By differentiation of (44), we find

$$\overline{[\psi_k(q_k) - \overline{\psi_k(q_k)}][\psi_i(q) - \overline{\psi_i(q)}]^2} = \frac{1}{\beta^2} \frac{\partial^2 \overline{\psi_k(q_k)}}{\partial e_i^2}. \quad (45)$$

Suppose that  $\overline{\psi_k(q_k)}$  is expanded in a Taylor's series of the form

$$\overline{\psi_k(q_k)} = \overline{\psi_k(q_k)}|_{e_i=0} + e_i \left[ \frac{\partial \overline{\psi_k(q_k)}}{\partial e_i} \right]_{e_i=0} + \sum_{n=2}^{\infty} \frac{e_i^n}{n!} \left[ \frac{\partial^n \overline{\psi_k(q_k)}}{\partial e_i^n} \right]_{e_i=0}. \quad (46)$$

If it is a sufficient approximation to neglect all but the first two terms of the expansion (46), the fluctuation (45) and also the integrated fluctuation  $\varphi_{ki}$  vanish. Thus, we see that the neglect of the fluctuation terms is equivalent to assuming that  $\overline{\psi_k(q_k)}$  can be approximated by a linear function of the charge,  $e_i$ , on the ion  $i$ . When the point  $q$ , at which the ion  $i$  is situated, is at a large distance from the ion  $k$ , we should expect this to be a rather good approximation. Moreover, aside from the neglect of certain secondary effects of van der Waals forces, it is the only approximation involved in the derivation of the Debye-Hückel Eq. (43) from statistical mechanics. This is a rather striking fact, for the opinion was generally held that the neglect of the local influence of the ion  $i$ , when situated at  $q$ , on the potential and distribution in the neighborhood of the ion  $k$ , was only one of the defects of the Debye theory. However, it appears that not even this factor is entirely neglected.

It is interesting to remark that  $\varphi_{ki}$  depends entirely upon the screening influence of the statistical space charge on the interaction of the ions  $i$  and  $k$ , and therefore vanishes at zero ionic concentration. Thus we may write

$$\begin{aligned}\lim_{c=0} \overline{\psi_k(q_k)} &= \frac{e_i}{Dr}; & r = |\mathbf{r} - \mathbf{r}_k| \\ \lim_{c=0} \frac{\partial^2 \overline{\psi_k(q_k)}}{\partial e_i^2} &= 0\end{aligned}\quad (47)$$

and therefore by Eqs. (42) and (45)

$$\lim_{c=0} \varphi_{ki} = 0. \quad (48)$$

The potential  $\overline{\psi(q)}$ , on the other hand, approaches  $e_k/Dr$ , so that

$$\lim_{c=0} \varphi_{ki}(q) / \overline{\psi(q)} = 0. \quad (49)$$

Eq. (49) suggests that we might use solutions of the Debye-Hückel Eq. (43) to obtain a first approximation to  $\overline{\psi_k(q_k)}$ , which we require to

obtain an estimate of  $\varphi_{ki}$ . When the distance  $|\mathbf{r}-\mathbf{r}_k|$  between the fixed ions  $i$  and  $k$  is large, we should expect to obtain a fair approximation to  ${}^{ik}\overline{\psi_k(q_k)}$  by writing

$${}^{ik}\overline{\psi_k(q_k)} = {}^k\overline{\psi_k(q_k)} + {}^i\overline{\psi(q_k)}|_{q_i=q}. \quad (50)$$

This approximation involves the assumption that the statistical space charges around the ions  $i$  and  $k$  are additive, in other words that they overlap without mutual interference. More exactly, it can be shown to be equivalent to neglecting a fourth order fluctuation of the form

$$[{}^{ik}\overline{\psi_k(q_k)} - {}^k\overline{\psi_k(q_k)}] {}^i\overline{\psi(q_k)}|_{q_i=q}^2$$

in the derivative,  $\partial^2 {}^{ik}\overline{\psi_k(q_k)}/\partial e_i^2$ .

In this approximation, we have, since the derivatives of  ${}^k\overline{\psi_k(q_k)}$  with respect to  $e_i$  are of negligible magnitude  $O(1/N_i)$

$$\frac{\partial^2 {}^{ik}\overline{\psi_k(q_k)}}{\partial e_i^2} = \frac{\partial^2 {}^i\overline{\psi(q_k)}|_{q_i=q}}{\partial e_i^2}. \quad (51)$$

Now  ${}^i\overline{\psi(q_k)}|_{q_i=q}$ , equal to  ${}^i\overline{\psi(|\mathbf{r}-\mathbf{r}_k|)}$ , satisfies an equation of the type (42). Let us try as an approximation, the Gronwall-La Mer-Sandved<sup>11</sup> solution of the Debye-Hückel Eq. (43).

$${}^i\overline{\psi(q_k)}|_{q_i=q} = \sum_{m=1}^{\infty} (-\beta)^{m-1} \left( \frac{e_i}{Da_i} \right)^m \psi_m(a_i, r), \quad (52)$$

$$r = |\mathbf{r}-\mathbf{r}_k|,$$

where the  $\psi_m$  (in the Gronwall-La Mer notation  $\epsilon^{m-1}\psi_m$ ) are symmetrical functions of the ionic charges,  $e_1 \cdots e_N$ ; and their derivatives with respect to the charge  $e_i$  of any single ion are quantities of negligible order of magnitude. From Eqs. (42), (45), (51) and (52), we obtain the following estimate of the integrated fluctuation  $\varphi_{ki}$ .

$$\varphi_{ki}(r) = e_k \sum_{m=2}^{\infty} (-\beta)^{m-1} \left( \frac{e_i}{Da_i} \right)^m \psi_m(a_i, r). \quad (53)$$

No claim is made that this estimate is exact, but it probably is of the right order of magnitude. We see that it does not involve the initial Debye

approximation ( $m=1$ ) at all, but only the Gronwall-La Mer correction terms  $m \geq 2$ . Since the  $\varphi_{ki}(r)$  of Eq. (53) are not exact, it would not be worth while to employ them in the tedious integration of Eq. (42). However, without detailed calculation, it is easily seen that they cannot influence the initial Debye approximation to  ${}^k\overline{\psi(q)}$ , although they may make contributions comparable with, but probably somewhat smaller than the Gronwall-La Mer correction terms. We should expect their contributions to be small under the same conditions that the Gronwall-La Mer terms are small, namely when

$$e_k e_i / Dr k T \ll 1 \text{ for all } e_i. \quad (54)$$

At distances from the ion  $k$ , such that the above condition (54) is satisfied, the initial Debye approximations to  ${}^k\overline{\psi(q)}$  and to  ${}^k\overline{\rho(q)}$  should be adequate and the Poisson Eq. (42) should reduce effectively to the linear equation of the Debye-Hückel theory.

$$\left. \begin{aligned} \nabla^2 {}^k\overline{\psi(q)} - \kappa^2 {}^k\overline{\psi(q)} &= 0, \quad \kappa^2 = \frac{4\pi}{DkT} \sum_i c_i e_i^2, \\ r > r_0; \quad \frac{e_k e_i}{Dr_0 k T_i} &\ll 1. \end{aligned} \right\} \quad (55)$$

If it happens that the ions are so large that the following condition is fulfilled

$$e_k e_i / Da_k k T \ll 1 \text{ for all } e_i. \quad (56)$$

Eq. (55) would be a good approximation in the entire region outside the boundary sphere  $a_k$ , as assumed in the original formulation of the Debye-Hückel theory. These statements cannot be regarded as rigorously established without an exact calculation of the fluctuation terms, but the present estimate of the  $\varphi_{ki}$  seems reliable enough to make them convincing.

The exact determination of the fluctuation terms,  $\varphi_{ki}$  is very difficult, and no convenient means of calculation has yet been devised. However, it seems worth while to outline a possible method of successive approximation. If the mean potential  ${}^{ik}\overline{\psi_k(q_k)}$  is known,  $\varphi_{ki}$  may be calculated from its second derivative with respect to  $e_i$ . Now

$${}^{ik}\overline{\psi_k(q_k)} = {}^{ik}\overline{\psi_k(q_k; q, q_k)}, \quad (57)$$

<sup>11</sup> Gronwall, La Mer and Sandved, Phys. Zeits. 29, 358 (1928).

where  $\overline{ik\psi(q_k; q, q_k)}$  is the value of the mean potential  $\overline{ik\psi(q'; q_i, q_k)}$  given by Eq. (22) when  $q' = q_k$  and  $q_i = q$ . By the same methods employed in the derivation of Eq. (28), it may be shown that  $\overline{ik\psi(q', q_i, q_k)}$  satisfies the following Poisson equation:

$$(\nabla')^2 \overline{ik\psi(q'; q_i, q_k)} = -\frac{4\pi}{D} \sum_i c_i e_i \int_0^\infty \overline{ik\psi(q'; q_i, q_k)} \times e^{-\beta \int_0^{\psi_i(q')} \overline{ik\psi(q'; q_i, q_k)} d\psi_i} d\psi_i. \quad (58)$$

The exact solution of this equation would require the knowledge of fluctuation terms depending on a mean potential  $\overline{ik\psi}$ , which may be shown to satisfy a Poisson equation similar to (58). By setting up a series of Poisson equations for  $\overline{1\psi}, \overline{2\psi}, \dots, \overline{n\psi}$  in which 1, 2,  $\dots$ ,  $n$  ions are, respectively, held fixed during the averaging process, and neglecting fluctuation terms in the equation for  $\overline{n\psi}$ , one could presumably obtain any desired degree of approximation by making  $n$  large enough. To obtain an exact solution, one would have to set up a system of Poisson equations for  $N-1$  mean potentials,  $\overline{1\psi}, \dots, \overline{N-1\psi}$  and solve them simultaneously. However, when  $n$  becomes of the same order of magnitude as  $N$ , one can no longer make the simplifications in the statistical charge density that are possible for small  $n$ , and one has a set of simultaneous integro-differential equations, which are virtually impossible to solve.

The solution of Eq. (58) for  $\overline{ik\psi(q'; q_i, q_k)}$  is difficult, even in the Debye-Hückel approximation corresponding to (43), since two ionic centers are involved. A solution of this equation in the initial Debye approximation corresponding to Eq. (55) has been obtained by Scatchard and Kirkwood.<sup>12</sup> Using their approximation to  $\overline{ik\psi(q_k)}$ , we find that  $\varphi_{ki}$  vanishes. A solution of the complete Debye-Hückel equation for two ionic centers by the Gronwall-La Mer method has never been carried out, but it is quite certain that it would lead to a value of  $\varphi_{ki}$  of the same form and magnitude as Eq. (53).

It may be objected that, since we have based our calculation of the  $\varphi_{ki}$  upon solutions of a Poisson equation in which similar fluctuation terms were neglected, we have not definitely

shown that they cannot be large. The final answer to this question must await an exact calculation of the  $\varphi_{ki}$  by some independent method. We have shown, however, that the Debye-Hückel Eq. (42) is statistically consistent with values of the fluctuation terms of the magnitude of the Gronwall-La Mer terms, and we believe to have presented convincing, if not conclusive evidence that they cannot influence the initial Debye approximation.

#### IV.

The significance of the Gronwall-La Mer terms remains somewhat ambiguous, due to the fact that the fluctuation terms may make contributions to  $\overline{k\psi(q)}$  of comparable although somewhat smaller magnitude. Moreover, even if the  $\varphi_{ki}$  were known with exactness, the integration of Eq. (42) would be complicated and tedious. It therefore seems very desirable to employ the method of Bjerrum<sup>13</sup> or one similar to it in the treatment of ions of small size and high valence, for which the initial Debye approximation is inadequate. The essential feature of Bjerrum's method consists in neglecting the screening effect of other ions on the interaction of an ion pair,  $k$  and  $i$ , when the two ions are close together. Bjerrum also makes use of a special hypothesis concerning ionic association, which, though intuitively attractive, is in some respects arbitrary. We shall outline an alternative treatment here, which utilizes Bjerrum's screening approximation, but not his association hypothesis. The method leads to a result which is almost identical with that of Bjerrum at low ionic strengths, but which is somewhat different at higher ionic strengths. Although Bjerrum's special hypothesis concerning association is not employed, ionic association in the classical sense involving a continuum of molecular species without sharply graded dissociation energies, is still implicitly taken into account. The method is proposed as an alternative and not necessarily as a substitute for Bjerrum's treatment, for the latter may give better results under conditions favoring a sharply graded binary association of the ions.

The potential  $\overline{k\psi_k(r)}$  at a distance  $r$  from the

<sup>12</sup> Scatchard and Kirkwood, Phys. Zeits. 33, 297 (1932).

<sup>13</sup> N. Bjerrum, Kgl. Dan. Vid. Sels. VII, 9 (1926).

ion  $k$ , can be expressed in terms of the spherically symmetric charge density,  ${}^k\overline{\rho(r)}$ , in the following manner

$${}^k\overline{\psi_k(r)} = \frac{4\pi}{Dr} \int_0^r \xi^2 {}^k\overline{\rho(\xi)} d\xi + \frac{4\pi}{D} \int_r^\infty \xi {}^k\overline{\rho(\xi)} d\xi. \quad (59)$$

Because of the van der Waals forces of the repulsive type,  ${}^k\overline{\rho(\xi)}$  vanishes in the neighborhood of  $\xi=0$ , so that the above expression converges. The value of the potential at the center of the ion  $k$  is therefore

$${}^k\overline{\psi_k} = \frac{4\pi}{D} \int_0^\infty \xi {}^k\overline{\rho(\xi)} d\xi. \quad (60)$$

Further,  ${}^k\overline{\rho(\xi)}$  must satisfy the following normalization condition

$$4\pi \int_0^\infty \xi^2 {}^k\overline{\rho(\xi)} d\xi = -e_k. \quad (61)$$

This condition is imposed by the electrical neutrality of the solution as a whole. That it is satisfied by the exact charge density,  ${}^k\overline{\rho(q)}$  of Eq. (14) is easily verified by direct integration of the  $\zeta_{ki}$ . When the ions are treated as rigid spheres of diameter  $a$ , the charge density  ${}^k\overline{\rho(\xi)}$  vanishes when  $\xi \leq a$ . In this case, the boundary conditions, requiring  ${}^k\overline{\psi(q)}$  and the normal component of its gradient to be equal on the two sides of the boundary sphere  $a$ , are automatically fulfilled, when Eqs. (60) and (61) are satisfied. However, these equations are more general than the simple boundary conditions, for they hold even when the ions do not have sharp boundaries.

Let us suppose that  $r_0$  is some distance, beyond which condition (54) is satisfied. Outside of the sphere  $r_0$ , the Debye linear equation may be employed to obtain  ${}^k\overline{\psi(r)}$  and  ${}^k\overline{\rho(r)}$

$$\left. \begin{aligned} \nabla^2 {}^k\overline{\psi(r)} - \kappa^2 {}^k\overline{\psi(r)} &= 0, \\ {}^k\overline{\psi(r)} &= A \frac{e^{-\kappa r}}{r}, \\ {}^k\overline{\rho(r)} &= -\frac{D\kappa^2 A}{4\pi} \frac{e^{-\kappa r}}{r}, \end{aligned} \right\} r > r_0, \quad (62)$$

where the solution,  $e^{+\kappa r}/r$  is excluded since it would make  ${}^k\overline{\psi(r)}$  infinite as  $r$  tends to infinity, a physically impossible situation. With the aid of

Eqs. (62) and (14), the relations (60) and (61) become

$$\begin{aligned} {}^k\overline{\psi_k} &= \frac{1}{D} \sum_i c_i e_i K_{ki} - \kappa A e^{-\kappa r_0}, \\ -e_k &= \sum_i c_i e_i G_{ki} - DA(1 + \kappa r_0) e^{-\kappa r_0}, \end{aligned} \quad (63)$$

$$K_{ki} = 4\pi \int_0^{r_0} \xi \zeta_{ki}(\xi) d\xi,$$

$$G_{ki} = 4\pi \int_0^{r_0} \xi^2 \zeta_{ki}(\xi) d\xi.$$

Eliminating  $A$  from these two equations, and making use of Eq. (11), we obtain<sup>14</sup>

$$\overline{\psi_k} = -\frac{1}{D} [e_k + \sum_i c_i e_i G_{ki}] \frac{\kappa}{1 + \kappa r_0} + \frac{1}{D} \sum_i c_i e_i K_{ki}. \quad (64)$$

At small concentrations the  $\zeta_{ki}$  become independent of the ionic strength, and the above expression approaches the limiting law of the Debye-Hückel theory. If the mean diameter of the ions is such that condition (55) is fulfilled, we may take  $r_0 = a_k$ , and the integrals  $G_{ki}$  and  $K_{ki}$  vanish. We are then left with the initial Debye approximation to  $\psi_k$ . When (55) is not satisfied, we may obtain approximate expressions for the integrals  $K_{ki}$  and  $G_{ki}$  by neglecting the influence of screening on the functions  $\zeta_{ki}$  when  $r$  is less than  $r_0$ . When screening is neglected, we may write

$$\begin{aligned} {}^k\overline{\psi(r)} &= e_k / Dr; & {}^{ik}\overline{\psi_k(q_k)} &= e_i / Dr; \\ \partial^2 {}^{ik}\overline{\psi_k(q_k)} / \partial e_i^2 &= 0; & r &\leq r_0. \end{aligned} \quad (65)$$

Thus the neglect of screening causes the fluctuation (45) to vanish, and we have

$$\varphi_{ki}(r) = 0; \quad r \leq r_0. \quad (66)$$

For simplicity, we assume that the molecules are rigid spheres and neglect attractive van der Waals forces. If we denote the mean diameter of the ion  $k$  and an ion of the type  $i$  by  $a_{ki}$ , and remember that  $\zeta_{ki}$  must vanish when  $r \leq a_{ki}$ , we may write

$$\begin{aligned} \zeta_{ki} &= e^{-\beta e_i e_k / Dr}; & a_{ki} < r \leq r_0 \\ &= 0; & r \leq a_{ki} \end{aligned} \quad (67)$$

<sup>14</sup> It should be remarked that  $\sum_i e_i c_i G_{ki}$  and  $\sum_i e_i c_i K_{ki}$  are opposite in sign to  $e_k$ , since the integrals  $G_{ki}$  and  $K_{ki}$  are much greater when  $e_i$  is opposite in sign to  $e_k$  than when of the same sign.

and the integrals  $K_{ki}$  and  $G_{ki}$  become

$$\begin{aligned} K_{ki} &= 4\pi \int_{a_{ki}}^{r_0} \xi e^{-\beta e_i e_k / D \xi} d\xi, \\ G_{ki} &= 4\pi \int_{a_{ki}}^{r_0} \xi^2 e^{-\beta e_i e_k / D \xi} d\xi. \end{aligned} \quad (68)$$

Except for the fact that condition (54) must be satisfied, the distance  $r_0$ , within which screening is neglected, is somewhat arbitrary. It may be chosen in the manner which Bjerrum proposes, or perhaps by some more convenient criterion. As in Bjerrum's theory, the integrals  $K_{ki}$  and  $G_{ki}$  are fortunately very insensitive to its value. However, we must certainly require that  $r_0$  be less than  $1/\kappa$ , for the neglect of screening to a distance comparable with  $1/\kappa$  would be a rather drastic approximation.

When screening is neglected in the calculation of  $K_{ki}$  and  $G_{ki}$ , the approximate  $\bar{\psi}_k$  no longer satisfies the condition of integrability (4). However, if  $r_0$  is treated as independent of the ionic charges, the integrability condition is satisfied up to terms in  $\kappa^3$ . Bjerrum circumvents this difficulty by means of his association hypothesis, but does not overcome it. In fact it would be somewhat fortuitous if any approximate  $\bar{\psi}_k$  exactly satisfied the integrability condition, unless the method of approximation was specifically chosen with that purpose in mind.

Approximate expressions for the logarithm of the activity coefficient of the ion  $k$  may be obtained from Eqs. (64) and (68) with the aid of either the Debye or the Güntelberg-Müller charging process. They differ very little from the corresponding expressions of Bjerrum at low ionic strength. We hope to develop the method more fully at a later time, choosing, if possible, better approximations to the integrals  $K_{ki}$  and  $G_{ki}$ , which are consistent with the condition of integrability.

We recall that Bjerrum's treatment leads to numerical values of activity coefficients, which differ very little from those obtained from the Gronwall-La Mer-Sandved potential, when the latter converges sufficiently rapidly. Since Eq. (64) leads to essentially the same result as the Bjerrum method, when screening is neglected,

we have indirect evidence that the Gronwall-La Mer-Sandved potential is probably a fairly good approximation in spite of the neglect of fluctuation terms. In other words, the neglect of all screening effects at small distances, of which the fluctuation terms are a part, leads to a result which differs but little from that of Gronwall and La Mer, who neglected only fluctuation terms. This suggests the conclusion that all screening effects, including fluctuations, are unimportant at small distances, in comparison with the large constant term  $e_k/Dr$  in both the mean potential and the potential of the mean force.

## V.

It seems worth while to discuss briefly the relation of the general theory of fluctuations to the properties of electrolyte solutions, since it has occasionally been the source of some misunderstanding. Suppose that  $Y$  is some additive property of a macroscopic system consisting of  $N$  microscopic systems, for example molecules or ions. If  $y_k$  is the contribution of the microscopic system  $k$  to  $Y$ , we may write

$$Y = \sum_{k=1}^N y_k, \quad \bar{Y} = \sum_{k=1}^N \bar{y}_k, \quad (69)$$

since the averaging process is a linear operation. The same equality does not hold for the mean square fluctuations  $(Y - \bar{Y})^2$  and  $\sum_{k=1}^N (\bar{y}_k - \bar{y}_k)^2$ , which in general are not only unequal but of entirely different orders of magnitude. We say that  $Y$  is a normal property of the macroscopic system (sensibly constant to external observation, with the value  $\bar{Y}$ ) when  $(Y - \bar{Y})^2$  is very small relative to  $\bar{Y}^2$ . This in no way implies that  $(y_k - \bar{y}_k)^2$  must be small relative to  $\bar{y}_k^2$ . In general, this is not the case, nor would we expect it to be, for a single molecule or a small number of molecules does not have normal properties in the thermodynamic sense. However, the fact that  $(y_k - \bar{y}_k)^2$  may be of the same or greater magnitude as  $\bar{y}_k^2$ , in no way invalidates Eq. (69).  $\bar{Y}$  is still the sum of the  $\bar{y}_k$ , and  $Y$  is a normal property if  $(Y - \bar{Y})^2 / \bar{Y}^2$  is small. In fact, unless  $(y_k - \bar{y}_k)^2$  happens to be specifically employed in the calculation of  $\bar{y}_k$ , its value is quite irrelevant.

Let us consider the mean electrostatic energy of the solution<sup>15</sup>

$$\bar{W} = \sum_{k=1}^N \bar{w}_k; \quad \bar{w}_k = \frac{1}{2} e_k \bar{\psi}_k. \quad (70)$$

We may write at once

$$\overline{(w_k - \bar{w}_k)^2} / \bar{w}_k^2 = \overline{(\psi_k - \bar{\psi}_k)^2} / \bar{\psi}_k^2, \quad (71)$$

where  $\overline{(\psi_k - \bar{\psi}_k)^2}$ , which has been calculated by Halpern,<sup>5</sup> is given by

$$\overline{(\psi_k - \bar{\psi}_k)^2} = -kT \partial \bar{\psi}_k / \partial e_k. \quad (72)$$

If the  $\bar{\psi}_k$  is assumed, as a first approximation, to be linear in  $e_k$ , as for example in the Debye limiting law, we have from relations (71) and (72)

$$\overline{(w_k - \bar{w}_k)^2} / \bar{w}_k^2 = -kT / e_k \bar{\psi}_k. \quad (73)$$

In dilute solutions,  $-kT / e_k \bar{\psi}_k$  as estimated from experimental values of the activity coefficient, or from the Debye limiting law, is in general much greater than unity, so that  $\overline{(w_k - \bar{w}_k)^2}$  is usually greater than  $\bar{w}_k^2$ . This fact alone in no way invalidates the Debye limiting law. It should be remarked that if the magnitude of  $\overline{(w_k - \bar{w}_k)^2} / \bar{w}_k^2$  were taken as a criterion for the validity of statistical calculations of the type of Eq. (69), it would invalidate not only the Debye limiting law but also any other limiting law. In fact by a similar line of reasoning one could cast doubt upon the ideal gas law,  $pV = NkT$ , since the fluctuation  $\overline{(\epsilon - \bar{\epsilon})^2}$  in the energy of a single gas molecule is equal to  $\frac{2}{3} \bar{\epsilon}^2$  where  $\bar{\epsilon}$  is the mean energy of a single molecule. Of course, the fluctuation in the total energy of an ideal gas, consisting of  $N$  molecules is such that  $\overline{(E - \bar{E})^2} / \bar{E}^2 = 2 / (3N)$ , or negligible if  $N$  is large, let us say of the order of  $10^{20}$ .

It is easily shown that, while  $\overline{(w_k - \bar{w}_k)^2} / \bar{w}_k^2$  may be large,  $\overline{(W - \bar{W})^2} / \bar{W}^2$  is always negligibly small in solutions of finite volume and finite concentration, amenable to thermodynamic measurement. Thus, it is easily demonstrated that

<sup>15</sup>  $\bar{W}$  is related to the thermodynamic energy of the solution in the following manner:

$$E - E_0 = \bar{W} [1 + (\partial \log D / \partial \log T)_\sigma]$$

where  $E$  is the energy when all ions are fully charged and  $E_0$  is the energy when they are completely discharged.

$$\overline{(W - \bar{W})^2} = -\frac{kT}{2} \left\{ \frac{\partial}{\partial \lambda} \left[ \frac{\bar{W}(\lambda e_1 \cdots \lambda e_N)}{\lambda^2} \right] \right\}_{\lambda=1}. \quad (74)$$

If the mean electrostatic energy  $\bar{W}$  is assumed to be a homogeneous function of degree three in the ionic charges,  $e_1 \cdots e_N$ , as for example, according to the Debye-Hückel limiting law

$$\frac{\bar{W}(\lambda e_1 \cdots \lambda e_N)}{\lambda^2} = \lambda \bar{W},$$

$$\frac{\overline{(W - \bar{W})^2}}{\bar{W}^2} = -\frac{1}{2} \frac{kT}{\bar{W}} \sim \frac{1}{N} \left( \frac{1}{2} \frac{kT}{e_k \bar{\psi}_k} \right). \quad (75)$$

Now  $-kT / 2e_k \bar{\psi}_k$  is of the order of magnitude of  $(-\log \gamma_\pm)^{-1}$ , where  $\gamma_\pm$  is the mean activity coefficient of the ions. Moreover, in all solutions of thermodynamic interest  $(-N \log \gamma_\pm)^{-1}$  is a very small quantity, of an order of magnitude not greater than about  $10^{-10}$  in all solutions of sufficient volume and concentration to be of thermodynamic interest. Thus  $\bar{W}$  is certainly a normal property of electrolyte solutions. Of course, strictly speaking, it ceases to be such at zero electrolyte concentration, but long before mathematically zero concentration is reached both  $\bar{W}$  and  $\overline{(W - \bar{W})^2}$  become too small for thermodynamic observation.

If it were true that a quadratic fluctuation of the type  $\overline{(\psi_k - \bar{\psi}_k)^2}$  had been neglected in the Poisson-Boltzmann equation, there would be an adequate basis for objecting to the Debye limiting law since  $\overline{(\psi_k - \bar{\psi}_k)^2}$  is of the order of  $\kappa$ . It is to be emphasized, however, that no such quadratic fluctuation is neglected, but only the difference between the mean potential and the potential of the mean force. We have shown that this difference may be expressed in terms of a third order fluctuation of the potential, which does not affect the initial Debye approximation to the mean potential and is small at large distances from the central ion. Further, this fluctuation term depends entirely upon the screening action of the statistical space charge and therefore its influence on the distribution function at small distances from the central ion is small compared with that of the Coulomb term,  $e_k / Dr$ , at low ionic concentrations.