

On the Statistical Basis of the Theory of Electrolytes

Otto Halpern

Citation: *J. Chem. Phys.* **2**, 85 (1934); doi: 10.1063/1.1749425

View online: <http://dx.doi.org/10.1063/1.1749425>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v2/i2>

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

Top downloads: http://jcp.aip.org/features/most_downloaded

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

ADVERTISEMENT



Goodfellow
metals • ceramics • polymers • composites
70,000 products
450 different materials
small quantities **fast**

www.goodfellowusa.com

On the Statistical Basis of the Theory of Electrolytes

OTTO HALPERN, *Physics Department, New York University, University Heights*

(Received December 14, 1933)

In the following paper the author investigates how far the various statistical-thermodynamic methods hitherto proposed are suitable for application to strong electrolytes. The significance of the ionic radius is, in many instances, far more important than has hitherto been assumed. When the influence of the ionic radius is negligible conditions are derived from dimensional considerations which considerably restrict the functional form of the free energy. Furthermore, proceeding from conditions of integrability, thermodynamics appreciably limits the number of possible expressions for the ionic potential. The disregarding of

these limitations has been responsible for certain paradoxes in the literature on this subject. A new fluctuation formula for the electric potential of the ions is derived and conclusions are drawn from it as to the correctness of existing theories. In connection with this last a deduction proposed by Fowler is reviewed. Kramers' theory of electrolytes is tested with respect to its agreement with the theorems here developed. Finally, a review of the statistical and thermodynamical basis of Bjerrum's theory of ionic association is presented.

1. INTRODUCTORY REMARKS

UNEXPECTED progress has been made in the theory of strong electrolytes in the course of the decade since Debye's theory was first put forward. Whereas (assuming the correctness of Debye's deduction for the mean ionic potential) the thermodynamic part was practically disposed of, Debye's conception of the ionic cloud, on the other hand, gave rise to the discovery and interpretation of a number of effects in the field of conductivity. The knowledge thus gained must be regarded as an addition of permanent value to this field.

The basis for this development is provided by Debye's method of calculating the mean ionic potential. That this method does not follow directly from the recognized laws of statistics but must, on the contrary, first be justified by means of statistical principles, has already been emphasized by so many authors that it is hardly necessary to go further into this point at present. The matter lies about as follows: because of the repeatedly observed agreement in the field of dilute aqueous solutions between Debye's theory and experiment a great variety of methods has been tried to vindicate this agreement in theory. The efforts made in this direction are essentially divisible into three groups. To the first of these belong the investigations carried out by Fowler¹ and

Kramers² which proceeded from the rigorous phase integral of Gibbs' canonical ensemble and from this aimed at obtaining Debye's formulas. The second group contains first and foremost an important inquiry by Gronwall, La Mer and Sandved³ who proceed from the same differential equation as Debye but aim at putting it from the start on a stricter mathematical basis by calculating the higher approximations, a procedure which would be unfeasible on principle if the ionic radius were disregarded. Finally, the third group is composed of an investigation by Bjerrum⁴ and of subsequent work following the program outlined in it. In this were introduced, by way of completing Debye's mode of approach, the conceptions of ionic association which are to be explained below.

The result of these investigations as given by the authors themselves, can in its main features be summed up as follows: A concentration can always be found below which the Debye theory retains its validity as a limiting law. For higher concentrations deviations from Debye's limiting law enter which vary according to the different authors. In this connection the Debye limiting law is defined by the statement that the excess

¹ H. A. Kramers, *Proc. Amst. Akad. Sci.* **30**, 145 (1927).

³ T. H. Gronwall, V. K. La Mer and K. Sandved, *Phys. Zeits.* **29**, 358 (1928).

⁴ N. Bjerrum, *Copenhagen Akad. Inst. fys. Medd.* **7**, 9 (1926).

¹ R. H. Fowler, *Statistical Mechanics*, Chapters 8 and 13.

free energy of an ionic solution is given by the formula

$$F = -\sum_i N_i \epsilon_i^2 \kappa / 3D, \quad (1)$$

$$\kappa = (4\pi \sum_i N_i \epsilon_i^2 / DkTV)^{1/2}.$$

The symbols entering into this formula require no further explanation.

It is the purpose of the present investigation to test in the first place the correctness of these results, secondly to show how far it is possible to draw from general properties (conditions of dimension and integrability, etc.) conclusions which must be valid for all theories without exception, and finally to test the validity of certain corollaries of the theory with the aid of general thermodynamic conditions.

2. DIMENSIONAL CONSIDERATIONS AND THERMODYNAMIC CONDITIONS OF INTEGRABILITY

We shall consider a solution composed of various ions of charge ϵ_i . The number of ions of the i -th group will be denoted by N_i , the total number of all ions by N , the total volume of the solution by V , the dielectric constant by D and the radii of the ions of the i -th kind by a_i . The difficulty inherent in the use of the macroscopic dielectric constant for the treatment of the microscopic forces between the ions has already been emphasized by several authors and will not be gone into here, since we are merely able to recognize its existence but not to overcome it.

Between the ions act the Coulomb forces and repelling forces of the van der Waals type, which prevent the uniting of two opposite charges. We have already partially taken these forces into account by the introduction of ionic radii. The electrical potential energy of two ions of the i -th and k -th kinds is then

$$\epsilon_i \epsilon_k / Dr_{ik},$$

in which r_{ik} denotes the instantaneous distance between the two ions. For the purpose of the following considerations we shall assume the ions to be consecutively numbered from 1 to N , and the i -th ion to have the charge ϵ_i . There are then, accordingly, groups of N_i ions present which all have one and the same charge ϵ_i , although it is not necessarily to be assumed that any two ions in the solution have the same charge. The total excess free energy of the ionic solution, insofar as

it is due to the forces between the ions, is then known to be given by Gibbs' phase integral

$$e^{-(F/kT)} V^N = \int dx_1 \cdots dz_N e^{-E/kT}. \quad (2)$$

In E both the Coulomb and the van der Waals forces are to be included. If the potential energy of the van der Waals forces (short range forces) be put down as E_W , then E equals

$$E = E_C + E_W = E_W + \frac{1}{2} \sum \sum \epsilon_i \epsilon_k / Dr_{ik}. \quad (3)$$

In this expression for the potential energy the proper electric energy $\epsilon_i^2/2Da_i$ of each ion is omitted as being an uninteresting constant. If E be written in the form

$$E = E_W + \frac{1}{2} \sum \epsilon_i \psi_i, \quad (4)$$

then

$$\psi_i = \sum_k \epsilon_k / Dr_{ik} \quad (5)$$

denotes the instantaneous potential produced by all other ions at the position of the i -th ion.

In any electrostatic system the relation⁵

$$\psi_i = \partial E_C / \partial \epsilon_i \quad (6)$$

which follows directly from (3) and (5) is valid. The mean value of the potential $\bar{\psi}_i$ then results on taking the statistical mean value of the expression $\partial E_C / \partial \epsilon_i$. This statistical mean value is obtained by differentiating both sides of (2) with respect to ϵ_i . Thus

$$\frac{\bar{\psi}_i}{\partial \epsilon_i} = \frac{\partial F}{\partial \epsilon_i} = \frac{\int dx_1 \cdots dz_N (\partial E_C / \partial \epsilon_i) e^{(F - E_W - E_C)/kT}}{V^N}. \quad (7)$$

From this follows at once by a second differentiation the fundamental relation

$$\partial \bar{\psi}_i / \partial \epsilon_k = \partial \bar{\psi}_k / \partial \epsilon_i. \quad (8)^*$$

In the absence of van der Waals forces (vanishing ionic radius) the phase integral clearly diverges, since all ions of opposite sign simply neutralize each other. A finite ionic radius (presence of van der Waals forces) is thus of decisive

⁵ The method employed at this point and subsequently is closely connected with that used in an earlier investigation. Cf. Gross and Halpern, *Phys. Zeits.* **26**, 403 (1925).

* All differentiations with respect to ϵ_i are, of course, carried out at constant temperature; the resulting relations for $\bar{\psi}$ therefore refer to *isothermal* properties of the ionic potentials.

importance for the statistical problem. *There is therefore no concentration at which the value of the free energy is independent of the ionic radius (i.e., of the magnitude of the van der Waals forces). It is merely possible, as shown by experiment, to find cases in which, for a given range of values of the ionic radius, the free energy is not appreciably dependent on the actual value of this ionic radius.* In such cases we can write, as an approximation

$$\bar{E} = \bar{E}_C = \frac{1}{2} \sum_i \epsilon_i \psi_i \quad (3a)$$

and thus obtain by means of (7) the relation

$$\bar{E} = F - kT(\partial F / \partial(kT)) = \frac{1}{2} \sum_i (\partial F / \partial \epsilon_i) \epsilon_i \quad (9)$$

or, by a simple transformation ($\eta_i = \epsilon_i^2$),

$$F = kT \frac{\partial F}{\partial(kT)} + \sum_i \eta_i \frac{\partial F}{\partial \eta_i} \quad (10)$$

The solution of this Eulerian partial differential equation is

$$F = kTG(\eta_i/kT), \quad (11)$$

in which G signifies an arbitrary function of the N arguments η_i/kT . G must have the dimension 0; since η_i/kT is of the dimension of a length, G can only be made dimensionless by the introduction of the factor V^{-1} , so that Eq. (11) takes the form

$$F = kTG(\eta_i/kTV^{1/3}). \quad (12)$$

This dimensional equation previously has been obtained by O. Klein⁶ using a statistical method.

These dimensional considerations may, however, be carried considerably further: As is readily seen from (3), E is a symmetrical function of the ϵ_i . This symmetry must accordingly also be valid for F . We may therefore add to (12) the further condition that G depends symmetrically upon the arguments η_i .

Further, as long as we ignore surface phenomena, the free energy, as always in thermodynamics, must be proportional to the total number of the ions, so that the N_i enter in the expression for

F only in the form $N_i f(N_i/V)$. For the following considerations it is of decisive importance to observe that F does not contain the number N_i of ions of the i -th class explicitly but only through the fact that precisely N_i ions have all the same charge ϵ_i . We thus obtain a further limitation, since F has to be of the form

$$F = \sum_i \frac{\eta_i}{V^{1/3}} H_i \left(\frac{\eta_i}{kTV^{1/3}} \right) \equiv \sum_i N_i \eta_i K \left(\frac{N_i}{V} \right), \quad (13)$$

$$H_i = H_k \quad (\text{on account of symmetry!}).$$

This limitation might appear at first sight to be of subsidiary importance, but this is by no means the case.⁷

It must once more be emphasized that all considerations which disregard the ionic radius can not be of general validity but are only justified when it is known that the ionic radius lies within a certain range and that the results are practically independent of its actual value.

3. APPLICATIONS OF THE RELATIONS (8) AND (13)

Let it be first assumed, as is done in the investigations of a number of authors, that F is only a function of the ionic strength. This is defined by the expression

$$F = \sum_i N_i \epsilon_i^2 f(\sum_i N_i \epsilon_i^2), \quad (14)$$

$$\sum_i N_i \epsilon_i^2 = \text{ionic strength.}$$

This assumption is permissible, since according

⁷ One might cast doubt upon the correctness of this argument by referring to the fact that perhaps the number N enters into the expression for the free energy not only by the number of the charge carriers but also through the volume V which is available to all the particles. This, however, is not the case: Let us assume that the N_i enter in some way into the expression for F not only through the ϵ_i but also through V . Let us then compare the excess free energies of two solutions, one containing N ions and the other M additional ions carrying infinitesimally small charges (in the limiting case the charge 0). The excess free energies must then obviously be equal since the ions with the charge 0 can have no effect. They would be unequal however if V were to contain the number of ions as a factor. It must be borne in mind that we are here dealing only with excess free energies as defined above. Failure to notice this fact is responsible for a conflicting result obtained by Kramers (cf. §5 of this note) which therefore must be held to be invalid.

⁶ O. Klein, Medd. fr. K. Vet. Nobelinst. 5 (1919). A derivation of this same equation given by P. van Rysselberghe, J. Chem. Phys. 1, 205 (1933), with the aid of the virial theorem can not be regarded as satisfactory, since in the derivation (Cf., e.g., the transition from (12) to (14) and from (21) to (23)) quantities are treated as independent where as they are actually dependent on the variable of differentiation.

to it F becomes a symmetrical function of ϵ_i^2 . In order to give (14) the form (13) we write

$$F = \frac{\sum_i N_i \epsilon_i^2}{V^{\frac{1}{2}}} H \left(\frac{\sum_i N_i \epsilon_i^2}{kTV^{\frac{1}{2}}} \right). \quad (15)$$

It will be seen at once that (15) satisfies the condition (13), only when F is of the form⁸

$$F = C \sum_i (N_i \epsilon_i^2 / D) (\sum_i N_i \epsilon_i^2 / DkTV)^{\frac{1}{2}}. \quad (16)$$

$C = \text{pure number.}$

From general dimensional considerations therefore we obtain the following result: *Assuming that the free energy is a function merely of the ionic strength and assuming further that the ionic radius lies in a range in which its influence may be disregarded, then a limiting law for the free energy is always valid and this law can differ from that of Debye only by a numerical factor.*

A similar conclusion can be drawn in a related case. Suppose it is known, for example, that the mean potential $\bar{\psi}_i$ is of the form $\bar{\psi}_i = \epsilon_i f_i$, in which f_i denotes any symmetrical function of the η_i (possibly with the omission of the variable η_i). The condition (8) then leads to the relation

$$\epsilon_i \partial f_i / \partial \epsilon_k = \epsilon_k \partial f_k / \partial \epsilon_i. \quad (17)$$

This can only hold true when f_i contains the ϵ_i in the combination

$$f_i = f_k = f(\sum_i \epsilon_i^2). \quad (18)$$

For, in this case,

$$2\epsilon_i \epsilon_k f' = 2\epsilon_k \epsilon_i f', \quad (19)$$

in which the prime denotes differentiation with respect to the argument ($\sum \epsilon_i^2$). From this point on the argument runs as above.

A considerable number of proposed theoretical formulae do *not* satisfy the general conditions here given or do so only in special cases obtained by artificial restrictions on the parameters, restrictions for which no physical reasons whatsoever can be assigned. Thus, for example, the expression previously given by Debye for the mean potential of an ion, as a function of the ionic radius,

$$\bar{\psi}_i = -\epsilon_i \kappa / D(1 + \kappa a_i),$$

⁸ It follows from (2) and (3) that E and therefore F contain the ϵ only in the combination ϵ^2/D .

is only in agreement with (8) if $a_i = a_k$ be valid. The same argument applies to the more consistent method of integration of Debye's differential equation given by Gronwall, La Mer and Sandved, although it becomes clear, when the higher approximations are taken into consideration, that *even in the case of equal radii* the condition (8) is in general not fulfilled, *unless all the ions carry the same charge*. Thus, for example, Gronwall, La Mer and Sandved obtain for the potential of an ion originating from a uni-divalent electrolyte the expression

$$\bar{\psi}_i = \sum_m^{\infty} (\epsilon_i^{2m-1} / a_i^m) \varphi_m, \quad (20)$$

in which $\varphi_m(\epsilon_i^2)$ denotes a symmetrical function which is of no importance for our further deductions. It will be seen at once that (20) no longer satisfies the condition (8) in higher approximations, since if we write $\bar{\psi}_i$ in the form

$$\bar{\psi}_i = \sum_m^{\infty} \psi_i^{(m)}$$

the relation

$$\partial \psi_i^{(m)} / \partial \epsilon_k = \partial \psi_k^{(m)} / \partial \epsilon_i$$

is no longer valid for $m > 1$. In this connection it must be emphasized that the calculation according to Gronwall, La Mer and Sandved is more consistent and that it alone gives a justification of Debye's method of calculation. The fact that the thermodynamic integrability conditions can not be satisfied points to serious inherent weaknesses of the theory which only accidentally do not become manifest in the first approximation (with ionic radii equal). All theoretical attempts to treat the case of unequal ionic radii on the basis of the Debye theory, have, so far as the author knows, led to formulas which fail to satisfy the integrability condition (8).

For practical purposes this limitation has been of no great importance, since ionic radii have been introduced, at least in aqueous solutions, only for the purpose of correction, and differences between individual ionic radii lie outside the range of accuracy of the theory. But it must be observed, in order to appreciate the argument, that the equality of the ionic radii enforced by thermodynamics is in fact a physically absurd limitation.

A paradox emphasized in the paper by Gronwall, La Mer and Sandved⁹ quoted above also finds its explanation in this manner. If we wish to calculate the free energy of an ionic solution from the given potentials $\bar{\psi}_i$, it is necessary on account of (7) to carry out the integration of the following system of N partial differential equations for the one unknown quantity F

$$\partial F / \partial \epsilon_i = \bar{\psi}_i \quad (21)$$

$$(i = 1, 2 \cdots N).$$

Since for $\epsilon_i = 0$ the free energy is equal to 0, we can in every case take $\epsilon_i = 0$ as the lower limit of integration. The upper limit of integration is given of course by $\epsilon_i = \epsilon_i$. Since we are here dealing with N independent variables it is possible to carry out the integration in any number of ways. The Eqs. (21) and (8) invariably lead to the same result, since it is clear that (8) expresses the necessary and sufficient conditions for the integrability of (21). If (8) is not fulfilled then this is no longer the case. Gronwall, La Mer and Sandved carried out the integration by causing (at least for symmetrical electrolytes of uniform ionic radius) all ionic charges to increase at an equal rate so that during the process of integration all ions had the same charge at any one time. These authors thus maintained, during the integration process, equality of all charges concerned, a condition on which the fulfillment of (8) had been shown to depend. Their result differs from that obtained by H. Mueller, since the latter carried out a different method of integration. He began by causing the charge of the k -th ion to increase from 0 to ϵ_k , while the charges of the other ions were kept constant. During this process there were thus present in the solution ions "of different valencies," so that the integrability conditions (8) were not fulfilled; the deviation of his result from that of Gronwall, La Mer and Sandved, in whose work the integrability condition was (artificially) fulfilled, is thus readily explained.¹⁰

⁹ Gronwall, La Mer and Sandved, *Phys. Zeits.* **29**, 367 (1928).

¹⁰ The significance of the integrability condition and its use to explain the charge paradox has already formed the subject of a communication previously made, as a preliminary statement, by the present author. Cf. *Phys. Rev.* **43**, 495 (1933).

4. FLUCTUATIONS OF POTENTIAL

Debye's methods of calculation, which have proved successful in so many instances, consist, as is well known, in determining the distribution of the charge in the vicinity of a particular ion by combining the Poisson equation with a somewhat free analog of the e -theorem of Boltzmann.

$$\Delta \bar{\psi} = -\epsilon \pi \rho / D = -(\epsilon \pi / D) \sum \rho_0^{(i)} e^{-\epsilon_i \bar{\psi} / kT}. \quad (22)$$

This use of the Boltzmann theorem urgently requires justification by strict statistical principles. If the potential, which also occurs as argument of the exponential function, were determined solely by the particular ion, then this application would be justified. In the case with which we are here concerned it is precisely the contributions of the other ions to this potential which are of decisive importance and for these the simple formulation of the Boltzmann theorem here introduced is not valid. These objections were already raised some time ago by a number of authors and the investigations of Kramers and Fowler, mentioned in the introduction to this paper, aimed primarily at dealing therewith.

As to the magnitude of the error introduced by the use of the Boltzmann theorem, no theoretical statement has hitherto been possible although some information on this point can be obtained with the aid of a strictly valid fluctuation formula for the potential. For this purpose we proceed from the relations (2), (4), (6) and (7) which are strictly valid even in the case of the presence of van der Waals forces, and obtain by differentiation of (7) with respect to ϵ_i the relation

$$V^N \frac{\partial \bar{\psi}_i}{\partial \epsilon_i} = \int dx_1 \cdots dz_N \frac{\partial}{\partial \epsilon_i} \left\{ \frac{\partial E_C}{\partial \epsilon_i} e^{(F - EW - EC) / kT} \right\}. \quad (23)$$

The expression on the right, however, becomes simplified in view of (Cf. (6) and (7))

$$\partial^2 E_C / \partial \epsilon_i^2 = 0, \quad \partial F / \partial \epsilon_i = \bar{\psi}_i$$

to

$$V_N \frac{\partial \bar{\psi}_i}{\partial \epsilon_i} = \frac{1}{kT} \int dx_1 \cdots dz_N e^{(F - EW - EC) / kT} \times (\psi_i \bar{\psi}_i - \psi_i^2) = V^N (1/kT) (\bar{\psi}_i^2 - \bar{\psi}_i^2). \quad (24)$$

In this connection, as is once more emphasized, ψ_i is merely the potential produced by the other

ions at the position of the i -th ion. For the quantitative evaluation of this fluctuation formula it is necessary to know the expression for $\partial\bar{\psi}_i/\partial\epsilon_i$. For our purposes it is perfectly sufficient to regard it as empirically given, by osmotic or activity measurements. Then, as a close approximation, we have in dilute solutions

$$\partial\bar{\psi}_i/\partial\epsilon_i = \bar{\psi}_i/\epsilon_i$$

and therefore

$$\bar{\psi}_i^2 - \bar{\psi}_i^2 = -(kT/\epsilon_i)\bar{\psi}_i. \quad (25)$$

Now Debye's theory has hitherto been applied to aqueous solutions practically only for such ranges in which

$$\epsilon_i\bar{\psi}_i/kT \ll 1. \quad (26)$$

Indeed the estimates to be discussed later, as to the range of validity of the Debye formulas, furnished as a necessary limitation precisely the relation (26). In this case, however, we see from the *strictly valid* fluctuation formula that the potential produced by all other ions exhibits fluctuations which are very great compared with its mean value. Moreover this ratio—and this is perhaps the most important point in the present analysis—is made not better but worse when we pass over to smaller concentrations. For then $\bar{\psi}_i^2$ approaches 0 as N/V , but $\bar{\psi}_i^2$ only as $(N/V)^{1/2}$. If possible at all, it is thus only at higher concentrations that the use of the mean value of ψ in (22) can to some extent be justified; but then the van der Waals forces must be explicitly taken into account.

The higher fluctuations of ψ_i , ψ_i^3 , etc., can be determined in an analogous manner; since, however, they do not lead to further restricting conditions, they will not here be explicitly given.*

5. REMARKS ON THE INVESTIGATIONS BY KRAMERS AND FOWLER

The result arrived at in the preceding paragraphs conflicts with a relation deduced by Fowler also from statistical mechanics, according to which it would appear that at sufficiently low concentrations, Debye's method of combining

* Similar applications of the fluctuation-formulae can be made to the problem of electric and magnetic polarizability (Clausius-Mosotti relation and Lorentz's inner field). Cf. a preliminary note of the present author, *Phys. Rev.* **40**, 134 (1932).

the Poisson equation and the Boltzmann theorem was correct. Fowler¹ derives the following relation:

$$\epsilon_m \Delta \psi_i + 4\pi \bar{\rho} \epsilon_m / D = -\frac{1}{kT} \left\{ \sum_{xyz} \left[\left(\frac{\partial W}{\partial x} \right)^2 - \left(\frac{\partial W_m}{\partial x} \right)^2 \right] \right\}. \quad (27)$$

The left side of this equation requires no further explanation; for the exact meaning of the density $\bar{\rho}$ here introduced, reference should be made to Fowler's own arguments. W denotes the energy which the m -th ion situated at the point x, y, z assumes, under the influence of the particular ion and of all other ions, $\sum (\partial W / \partial x)^2$ the square of the gradient of this energy, and W_m the mean value of W . In Debye's theory the right side of (27) is made equal to 0. This is permissible according to Fowler, provided the terms on the right side are small compared with those on the left side. He shows by explicit calculation that $\sum_{xyz} (\partial W_m / \partial x)^2 / kT$ is, in fact, sufficiently small when

$$\epsilon_m \bar{\psi}_i / kT \ll 1$$

holds. This implies that in Fowler's opinion we may, in fact, make the right-hand side equal to 0, at very low concentrations.

In this connection, however, it has not been taken into consideration that $(\partial W / \partial x)^2$ in view of

$$\left(\frac{\partial W}{\partial x} - \frac{\partial W_m}{\partial x} \right)^2 = \left(\frac{\partial W}{\partial x} \right)^2 - \left(\frac{\partial W_m}{\partial x} \right)^2 > 0$$

is invariably greater than $(\partial W_m / \partial x)^2$ and in the present case even becomes of a higher order of magnitude. This can be demonstrated in the following manner. $\partial W / \partial x$ denotes the instantaneous force exerted in the x -direction upon a charge ϵ_m at the point x, y, z . The mean value of the expression

$$(1/kT\epsilon_m^2) \sum_{xyz} (\partial W / \partial x)^2$$

is thus equal to the mean of the square of the field strength at the point occupied by the charge. The order of magnitude of this quantity $(\bar{E})^2$ can be calculated from the general relation

$$A = (DV/8\pi)(\bar{E})^2, \quad (28)$$

in which A denotes the free electric energy of the solution. This free electric energy contains as

largest term the proper energy of the ions which for spherical ions is approximately given by

$$A = \sum N_i \epsilon_i^2 / 2Da. \quad (29)$$

We thus obtain

$$\begin{aligned} \frac{1}{kT} \sum \left(\frac{\partial W}{\partial x} \right)^2 &= \frac{\epsilon_m^2}{kT} (\vec{E})^2 = \frac{8\pi \epsilon_m^2 A}{DVkT} \\ &= \frac{8\pi \epsilon_m^2}{DkTV} \sum \frac{N_i \epsilon_i^2}{2Da} = \kappa^2 \frac{\epsilon_m^2}{2aD}. \end{aligned} \quad (30)$$

The other terms in the free electric energy A , due to the interaction of the ions, will be disregarded in this connection, since we have already shown in the preceding paragraph that they are of an appreciable order of magnitude. At all events, provided the concentrations concerned are not too high, the following holds:¹¹

$$|\kappa^2 \epsilon_m \bar{\psi}| = \epsilon_m^2 \kappa^3 / D \ll 1/kT \sum_{xyz} \overline{(\partial W / \partial x)^2} = \epsilon_m^2 \kappa^2 / 2aD \quad (31)$$

for all $\kappa \ll 1/a$. This shows again that it is not justifiable to make the right side equal to 0 and that going to lower concentrations by no means improves matters.

Kramers has attempted to evaluate the Gibbs phase integral directly by a very ingenious method. Unfortunately the assumptions and omissions made in the course of the integration can hardly be estimated in their effect on the final result. We shall, therefore, not enter into a discussion of the various details and shall content ourselves with drawing attention to only two points of general significance. As the result of his calculations, Kramers obtains for the free energy an expression of the form

$$F = - \sum_i N_i \epsilon_i^2 (\kappa / 3D + C\kappa^2 + \dots). \quad (32)$$

As will be seen, the free energy is here only a function of κ and therefore of the ionic strength;

¹¹ It will be seen from (30) that $\sum (\partial W / \partial x)^2$ is proportional to κ^2 while all the terms on the left side of (27) are proportional to κ^3 . L. Onsager in a lecture given before the American Chemical Society in Washington, 1933, has pointed out that the consideration of the van der Waals forces would reduce the fluctuation terms. But this could not make the right side of (27) of smaller order of magnitude (proportional to κ^4 , as Fowler supposed). It follows from the general fluctuation-formula (25) that at low concentrations the fluctuation terms always become dominant as compared with the retained average values.

in spite of this other terms occur in (32) besides those giving the limiting law (1). This is contradictory to the rigorous dimensional considerations previously given (Cf. in particular footnote after (13) and §3), so that for this reason, if for no other, the formula for the free energy can not be correct.

The second important point is to be found in the way in which the ionic radius (the van der Waals forces) is treated. Kramers himself emphasizes the fact that the phase integral is divergent for infinitely small ionic radius. Nevertheless he expresses the opinion that it is always possible to find a concentration at which the value of the free energy is independent of the ionic radius. This can not be admitted. Since the integral becomes infinite for $a = 0$ there can never be a concentration at which it is independent of the value of the ionic radius. As explained above, we can only hope to make the free energy independent of the particular value selected for the ionic radius if this value is contained in a range fixed from the outset. Experiment seems to indicate that this is possible in the case of aqueous solutions or other solutions of sufficiently high dielectric constant. The universal existence of a limiting law can not, however, be admitted. This statement may be illustrated by a simple estimate obtained from Gronwall, La Mer and Sandved's integration of Debye's equation. Let us consider an electrolyte in a solution of low dielectric constant (f.i. dioxane $D \sim 2$). Now Gronwall, La Mer and Sandved¹² give an expression for the activity coefficient from which the regions of concentration can easily be estimated in which the terms containing the ionic radius may be disregarded in the expression for the free energy, in comparison with the limiting term. The condition for this can be reformulated as follows:

$$1 \gg \sum_{m=1}^{\infty} \frac{\kappa a}{(2m-1)(2m+2)!} \left(\frac{\epsilon^2}{DkTa} \right)^{2m}. \quad (33)$$

The sum

$$\sum_{m=1}^{\infty} \frac{\kappa a}{(2m-1)(2m+2)!} \left(\frac{\epsilon^2}{DkTa} \right)^{2m}$$

can easily be calculated for sufficiently large

¹² Gronwall, La Mer and Sandved, Phys. Zeits. **29**, 376 (1928), formula 69.

values of $\epsilon^2/DkTa$. An asymptotical expression is thus obtained

$$\Sigma = \frac{1}{2} \left(\frac{DkTa}{\epsilon^2} \right)^3 e^{\epsilon^2/DkTa}. \quad (34)$$

For a reasonable value of the ionic radius

$$a \sim 5.10^8 \text{ cm}$$

there results the condition

$$\kappa \ll (1/2a)(\epsilon^2/DkTa)^3 e^{-\epsilon^2/DkTa} \quad (35)$$

or for the ionic concentration in mols p. lit.

$$c \ll 10^{-30}.$$

As will be seen, there can be no question of a valid limiting law for any reasonable concentrations. At the same time, of course, the method adopted by Gronwall, La Mer and Sandved though strictly consistent in itself is nevertheless subject to the objections, given in §3 and §4. For such low concentrations only the fluctuation term in (25) is decisive, the application of the Boltzmann theorem therefore is *even for approximation purposes*, completely illusory.

The result of these arguments can perhaps be summed up as follows: Contrary to general opinion, it is impossible by a reduction of concentration always to reach a region in which the limiting law holds. While the Debye theory as extended by Gronwall, La Mer and Sandved permits to do so, though for media of low dielectric constant only at concentrations without physical interest the consideration of the fluctuation terms excludes this possibility. There would be nothing like a limiting law in water either if the ionic dimensions happened to be, let us say, one-fiftieth of their actual value.

6. BJERRUM'S IONIC ASSOCIATION

In the method proposed by Bjerrum for the calculation of the free energy with the aid of "ionic association" the following essential points of view stand out. Whereas Debye characterizes the interaction between a particular ion and the other ions by the introduction of the concept of an ionic cloud in which the charge is continuously distributed with variable density, Bjerrum attempts to take account of the atomistic concentration of the charge, by considering the isolated

interaction between two ions. He thus subdivides the neighborhood of each ion into two parts; in a region close to the ion he determines the probability of finding another ion while outside a certain radius R Debye's method is employed. Bjerrum himself has already pointed out that this division, and the choice of the radius R contains arbitrary elements. If a pair of ions is located within the radius R , this pair is regarded as a "molecule" and is not to be considered as contributing anything to the ionic atmosphere.

This method is mathematically completely analogous to another which for decades has been used to calculate the equation of state of gases in the presence of van der Waals forces.¹⁸ The physical justification of this procedure was given by the fact that the intramolecular forces concerned decreased with a high power of the distance. Precisely for this reason the method breaks down for Coulomb forces. Bjerrum's calculation of the ionic association also differs in two points, to its disadvantage, from the determination of the van der Waals correction: The sphere of action of two atoms within which they can be regarded as united to a "molecule," is actually independent of the temperature, whereas according to Bjerrum we find it given by the expression

$$R = \epsilon_i \epsilon_k / 2DkT. \quad (36)$$

The dependence on T in (36) can not be avoided since the dependence on D is quite essential and according to statistical mechanics (Cf. (2) and (3)) the excess free energy divided by kT is only a function of the expression

$$\epsilon_i \epsilon_k / DkT.$$

In Bjerrum's case this has the troublesome consequence that the Helmholtz equation, which connects energy and free energy, is no longer valid.

To prove this we refer to Bjerrum's formula for the excess free energy f of a pair of ions forming a molecule

$$e^{-(f/kT)} (4\pi R^3/3) = \int_a^R 4\pi r^2 dr e^{-(\epsilon_i \epsilon_k / DkTr)} \quad (37)$$

$$(a \ll R).$$

Differentiation of (37) with respect to T leads to

¹⁸ Cf. R. H. Fowler, *Statistical Mechanics*, Chapter 9. See also further references.

$$e^{-(f/kT)} \frac{4\pi R^3}{3} \left(\frac{f}{kT^2} - \frac{1}{kT} \frac{\partial f}{\partial T} + \frac{3}{R} \frac{\partial R}{\partial T} \right) \\ = \int_a^R (4\pi r \epsilon_i \epsilon_k / DkT^2) e^{-(\epsilon_i \epsilon_k / DkTr)} dr \\ + 4\pi R^2 e^{-(\epsilon_i \epsilon_k / DkTR)} (\partial R / \partial T) \quad (38)$$

or after a slight transformation, denoting by \bar{u} the average excess energy of the ion pair, to

$$f - T(\partial f / \partial T) = \bar{u} + 3kT(1 - e^{[f - (\epsilon_i \epsilon_k / DR)] / kT}) \\ (\partial R / \partial T = -R/T). \quad (39)$$

The additional term

$$3kT(1 - e^{[f - (\epsilon_i \epsilon_k / DR)] / kT})$$

is, in general, not small but of the same order of magnitude as \bar{u} .

The second point which leads to difficulties in quantitative applications is the question how the "proper-volume" of the "molecules" is to be taken into account. Ions spaced at a distance smaller than R are to be regarded as "associated." For solutions of small dielectric constant and

particularly for multivalent ions, R assumes very large values, precisely on account of the long range of the Coulomb forces. Thus, for example, for univalent electrolytes in dioxane, at room temperature, R takes the value 1.4×10^{-6} cm. The volume correction in the expression for the free energy of the non-associated ions which can easily be made in the case of van der Waals forces can no longer be carried out in this instance.¹⁴ It will also be impossible, in general, except for infinitesimally small analytic concentrations, to state to which of the other ions a particular ion belongs. The difficulty involved in the fact that the forces in electrolytes are long range forces can not be overcome by the application of a method capable of furnishing valid results for short range forces only.

To his colleague, Professor Doermann, the author wishes to express his thanks for revision of the manuscript.

¹⁴ The argument given here will be applied in a discussion of electrical conductivity in media of small dielectric constant (Cf. Gross and Halpern, this Journal, to be published).