Physics. — *Investigations on the free energy of a mixture of ions.* By H. A. KRAMERS. (Communicated by Prof. P. EHRENFEST).

I. Statement of the problem. Main results.

In 1923 DEBYE and HUECKEL [1]) published a simple and elegant method of calculating the influence of the electrostatic forces acting between the ions in the solution of an electrolyte. They arrived at the result that the free energy ζ of a solution is decreased on account of the electrostatic forces by an amount which, for sufficiently small concentrations, can be represented by:

$$\triangle \zeta = - \sum_i \frac{N_i z_i^2 \varepsilon^2 \varkappa}{3} \frac{1}{D} \frac{1}{1 + \varkappa a_i}. \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

In this formula $N_1 \ldots N_s$ denote the numbers in which ions of the kind $1, \ldots i, \ldots s$ are present in the solution; while $z_i \varepsilon$ is the charge (ε = elementary quantum of electricity) and a_i an "effective" radius belonging to an ion of the ith kind. D is the dielectric constant of the solvent and finally, $\varkappa$ is a quantity of the dimensions of a reciprocal length, defined by:

$$\varkappa^2 = \frac{4\pi \varepsilon^2}{Dk T} \sum_i n_i z_i^2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this formula T is the absolute temperature, k BOLTZMANN's constant and n_i the number of ions of the kind i per cm³.

Imagining the ions as spheres of radius a_i plunged in a continuous medium of dielectric constant D, we can, by means of the methods of statistical mechanics, establish an exact expression for $\triangle \zeta$ in the form of a definite integral in which the integration has to be extended over the coordinates of every ion in the solution [2]):

$$V^N e^{-\frac{\triangle \zeta}{kT}} = \int \ldots \int e^{-\frac{E}{kT}} dx_1 \, dy_1 \, dz_1 \ldots dz_N \quad . \quad . \quad . \quad . \quad (3)$$

Here E denotes the electrostatical energy (if D depends on temperature, the electrostatical *free* energy) of a given configuration of the ions in the solution:

$$E = \frac{1}{D} \sum \sum \frac{\varepsilon_k \, \varepsilon_l}{r_{kl}} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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[1]) Phys. Zs. **24**, 185, 1923.

[2]) Comp. W. GIBBS, Principles in statistical mechanics, p. 33, form. 92, and Chapter XIV.

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ε_k and ε_l denote the charges of the k'^{th} and l'^{th} ion, while r_{kl} is the distance between these ions. The integration variables $x_1, \ldots z_N$ in (3) are the cartesian coordinates of the ions, and the integration has to be extended over all possible configurations in the total volume V. The fact that E is a homogeneous function of the coordinates of the degree -1 involves (at any rate if the influence of radii of the ions may be neglected) that the value of $\triangle \zeta / T$ for a mol of the solved substance depends on the temperature T and on the concentration $n = \Sigma n_i$ in the form of a function of n/T^3. [1])

The explicit calculation of $\triangle \zeta$ by means of (3) meets with mathematical difficulties, mainly due to the fact that the ordinary method, development in decreasing powers of T, does not give a series the first terms of which suffice. In the case where the ionic radii are very small, the terms of that series become very large, although a simple consideration shows [2]) that for sufficiently small concentrations $\triangle \zeta$ converges asymptotically to a function which does not depend on these radii. This property is clearly expressed in the formula (1) of DEBYE and HUECKEL. If we take the radii exactly equal to zero, however, the integral (3) diverges; the model involves in that case that the positive and negative ions will, in the state of equilibrium, be groupwise associated.

Starting from formulae equivalent to (3), MILNER, in 1912, tried by long numerical calculations to find the values of $\triangle \zeta$ for very small ionic radii. He introduced several approximations which were difficult to control, and as regards their practical applicability his results fall short of DEBYE's and HUECKEL's [3]) elegant formulae.

DEBYE and HUECKEL do not start from the integral (3) but they apply an ingenuous artifice. They consider the statistical distribution of the ions surrounding a definite ion I and establish a partial differential equation which the mean potential at a distance r from I must obey. This method, however, could only give a first approximation. One might especially suspect that for not too small concentrations the distribution in the nearest neighbourhood of I is not accounted for with sufficient exactness.

In the next chapter we shall, starting from the methods of statistical mechanics, try to determine the influence of the electrostatic forces as far as it does not depend on the ionic radii, i.e. for small radii. For small concentrations we refind the expression of DEBYE and HUECKEL. For larger concentrations, however, we find peculiar deviations. Thus our formulae seem to show that *a state of statistical distribution of the ions which is independent of the atomic radii* and which is established

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[1]) O. KLEIN, Medd. fr. K. Vet. Nobelinstitut, **5**, 1919. See also p. 148 of this article.

[2]) S. R. MILNER, Phil. Mag. **23**, 551, 1912, and especially N. BJERRUM, Copenhagen Academy, Mat. fys. Medd. **7**, 9.

[3]) Compare what MILNER himself states about it in NONHEBEL and HARTLEY, Phil. Mag. **7** 2, 586, 1926.

if from the random distribution at very small concentrations we pass to larger concentrations *can only be realised below a certain maximum concentration*. For an electrolyte of the KCl type in water at 15° C. this concentrations corresponds to about 0,03 mol. KCl per litre. The consequences of this seem to be 1. that, conforming with DEBYE's and HUECKEL's results, a description of the phenomena in which the radii are neglected, is only possible at extremely small concentrations, and 2. that is useless, for higher concentrations, to apply DEBYE's and HUECKEL's [1]) formulae as a correction factor.

II. *Calculation of the free energy.*

As our starting point we choose a canonical ensemble of a more general type than that on which (3) was based. A sample of the latter was specified by definite positions of the centres of the N ions in the volume V, each ion carrying its corresponding charge. Our generalized ensemble, however, will be such that, for a given configuration of the centres of the N ions, the charge on the kth ion may still assume any value of which the charge of an arbitrary ion in the solution is capable. The chance that an arbitrary ion belongs to the kind i is expressed by the fraction N_i/N. We will therefore allow N^N samples of our ensemble to correspond with a given configuration of the ions in the volume under consideration, in such a way that for given charges of the ions $1, 2, \ldots k-1, \ k+1, \ldots N$, there will be N_i samples in which the kth ion carries the charge $z^i \varepsilon$, i taking the values $1, \ldots s$. Our ensemble forms thus a part of the so-called grand-ensemble introduced by GIBBS [2]), namely that part for which the number of ions in V just equals N.

If now we proceed to calculate mean values in our generalised ensemble we must remember that the integrals over all possible configurations of the N ions will diverge if the radii are taken infinitely small. This difficulty may be met in two ways. We may in the first place assume the radii to be finite (method A). In that case the extension over which the variabeles $x_1, \ldots z_N$ are to be integrated will depend on the charges attributed to the ions. Formally all configurations of the centres of the N ions are permissible if we add to the energy expression (4) a function which becomes infinite if the centres of two ions with charges ε_i and ε_j are nearer to each other than $a_i + a_j$. Only if all the radii a_i were equal it would be permissible for all samples of the ensemble, to integrate over the same extension in the $x_1 \ldots z_N$ space.

In the second place (method B) we might apply a less physical treatment, not comparing the ions to solid spheres, but modifying the

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[1]) For the literature compare F. HUECKEL, Zur Theorie der Elektrolyte, Ergebnisse der exakten Naturwissenschaften III, 1925.

[2]) Principles in statistical mechanics, Ch. XV. See especially p. 190. The quantities μ_i of GIBBS are in our terminology equal to $kT \log N_i/N$.

expression (4) in another way. This may be done so that the integrals representing the mean values over all configurations no longer diverge but that at the same time the property of the energy to be a homogeneous function of the coordinates of the degree -1 is preserved. For this purpose we may choose for the energy function:

$$E' = \frac{1}{D} \, \Sigma \, \Sigma \, \varepsilon_k \, \varepsilon_l \, g_{kl} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where g_{kl} is equal to

$$g_{kl} = \frac{1}{r_{kl}} (1 - e^{-\lambda h_{kl}}), \qquad h^2 = \frac{r_{kl}^2}{4 R_{kl}^2} = \frac{(x_k - x_l)^2 + (y_k - y_l)^2 + (z_k - z_l)^2}{(x_k + x_l)^2 + (y_k + y_l)^2 + (z_k + z_l)^2} \quad (6)$$

If the origin of the system of coordinates is taken somewhere outside the vessel so that R_{kl} is always of the order of magnitude of the linear dimensions of the vessel ($d \leqq V^{1/3}$), λ can always be taken so large that the energy expression (5) practically coincides for all configurations with (4). Deviations will only occur if $\lambda \dfrac{r_{kl}}{d}$ is of the order 1 or smaller. As the mean distance of two neighbouring ions is of the order $dn^{-1/3}$ we need only take λ of the order $n^{1/3}$ or $n^{2/3}$ [1]).

We will now replace the expression (3) for $\triangle \zeta$ by the mean value over our generalised ensemble:

$$V^N \, e^{-\frac{\triangle \zeta}{kT}} = \int \ldots \int N^{-N} \, \Sigma \, e^{-\frac{E'}{kT}} \, dx_1 \ldots dz_N \quad . \quad . \quad . \quad (7)$$

Here Σ denotes the summation over the N^N samples corresponding to a given configuration. The considerations of KLEIN cited above will now hold exactly if the method B is assumed, whereas they will hold approximately if A is applied. In fact if every coordinate is multiplied by an arbitrary factor f, and if, at the same time, the temperature is chosen f times smaller, the value of the exponent in (7) does not change. From this it follows that, by the introduction of the factor f, the value of integral has been multiplied by f^{3N} since the volume of the vessel has become f^3 times as large. If we remember, moreover, that for N sufficiently large and for a given concentration n ($=$ number of ions in unit volume) the integral in (7) will depend on N only in the form of an Nth power (this holds exactly with method A, but approximately with method B), we see that (7) can be written in the form:

$$e^{-\frac{\triangle \zeta}{kT}} = [\varphi \, (n^{1/3}/T)]^N \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The deduction shows that this result under all circumstances stands as an approximation, which can be applied only as far as a statistical

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[1]) The occurrence in (5) of R_{kl}, the distance of the geometrical centre of two ions from the origin, means that this centre is attracted towards, or repelled from, the origin. Only for a pair of ions which lie very near to each other ($r_{kl} \leqq R_{kl}/\lambda$) and which for small concentrations are very rare, will these forces have a perceptible influence.

distribution of the ions exists, which does not depend on the ionic radii.

We will now transform the integrand in (7).

We consider the expression (5) for E' as a quadratic function of the N variables $\varepsilon_1, \varepsilon_2 \ldots \varepsilon_N$, and we imagine this function to be given the canonical form by a so-called "transformation of principal axes":

$$E' = \frac{1}{D} \, \Sigma \, \Sigma \, \varepsilon_k \, \varepsilon_l \, g_{kl} = {}^1/_2 \sum_1^N b_m y_m^2 \; . \quad . \quad . \quad . \quad (9)$$

The quantities b_m are the roots of the following equation of the Nth degree:

$$\triangle \, (b) = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$\triangle$ being a determinant $|\triangle_{kl}|$ of the order N, the diagonal terms of which are equal to b whereas the other terms are given by $\triangle_{kl} = -g_{kl/D}$. Let the relation between the ε's and the y's be represented by:

$$y_m = \Sigma \, \gamma_{mk} \, \varepsilon_k \, , \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

the coefficients γ_{mk} obeying the well known conditions of orthogonality:

$$\Sigma_k \, \gamma_{mk}^2 = 1. \qquad \Sigma_k \, \gamma_{mk} \gamma_{m'k} = 0 \quad . \quad . \quad . \quad . \quad (12)$$

The b's as well as the γ's depend only on the ionic configuration. The summation in the integrand in (7) has now become a summation over the different values which the y's can assume as a consequence of the different discrete ε_k-values in our ensemble. This summation, however, can be written in the form of an integral if we may assume that all quantites γ_{mk} are small compared with unity, an assumption which will be fulfilled, independent of the concentration, for the large majority of possible configurations. In that case the quantities y can practically assume all values between $-\infty$ and $+\infty$, and the probability that y lies between y_m and $y_m + dy_m$ will be given by a GAUSS error function. The mean value of y_m is equal to zero since the mean value of ε_k is equal to zero, due to the condition of neutrality $\Sigma N_i z_i = 0$. For the mean value of y_m^2 we find, using (12),

$$\overline{y_m^2} = \Sigma \, \gamma_{mk}^2 \, \overline{\varepsilon_k^2} = \varepsilon^2 \, (\Sigma \, \gamma_{mk}^2) \cdot \left(\Sigma_i \frac{N_i}{N} z_i^2 \right) = \varepsilon^2 \, \Sigma_i \frac{N_i}{N} z_i^2 = \eta$$

where η is an abbreviation. From (12) follows furthermore that the different y's are statistically independent.

$$\overline{y_m y_{m'}} = \Sigma \, \gamma_{mk} \gamma_{m'k} \cdot \overline{\varepsilon_k^2} = \eta \, \Sigma \, \gamma_{mk} \gamma_{m'k} = 0$$

The chance that y_m lies between y_m and $y_m + dy_m$ $(m = 1, 2 \ldots N)$ therefore equal to

$$(2 \, \pi \, \eta)^{-N/2} \, exp \left[- \frac{\Sigma y_m^2}{2\eta} \right] dy_1 \ldots dy_N \quad . \quad . \quad . \quad (13)$$

and the integrand in (7) can be calculated as follows:

$$N^{-N} \Sigma\, e^{-E'/kT} = (2\pi\eta)^{-N/2} \int \ldots \int dy_1 \ldots dy_N \cdot exp\left[-\tfrac{1}{2} \Sigma \left(\frac{1}{\eta} + \frac{b_m}{kT} \right) y_m^2 \right] =$$

$$= \left[\prod_1^N \left(1 + \frac{\eta}{kT} b_m \right) \right]^{-1/2} = \left[\left(\frac{-\eta}{kT} \right)^N \triangle \left(-\frac{kT}{\eta} \right) \right]^{-1/2} = A^{-1/2} \ . \ . \ (14)$$

Here $\triangle$ denotes, just as in (10), the Nth degree polynomial the roots of which are the b's and we see that A is an abbreviation for

$$A = \begin{vmatrix} 1 & ag_{12} & ag_{13} \ldots & ag_{1N} \\ ag_{21} & 1 & ag_{23} \ldots & ag_{2N} \\ & \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ ag_{N1} & \cdot \quad \cdot \quad \cdot \quad \cdot \quad 1 \end{vmatrix} \quad . \quad . \quad . \quad . \quad (15)$$

where g_{kl}, according to what has been said with reference to (6), is practically everywhere equal to $1/r_{kl}$. The quantity a stands as an abbreviation

$$a = \frac{\eta}{DkT} = \frac{\varepsilon^2}{DkTN} \Sigma N_i z_1^2 = \frac{\varkappa^2}{4\pi n} \quad . \quad . \quad . \quad . \quad (16)$$

The quantity a is independent of the concentration n and has the dimensions of a length[1]). It is related in the way stated with DEBIJE's $\varkappa^2$ which is directly proportional to the concentration.

Before we proceed, some remarks must be made as regards the approximation tacitly involved in the results (14) and (15). In the first place it will be seen that the integration over a y-coordinate y_m is only permissible as long as $1 + b_{m/kT}$ is positive. Now b_m will often be negative, so that for every configuration T may always be so small that the mentioned quantity becomes negative. In that case the integration over y_m from $-\infty$ to $+\infty$ would lead to on infinitely large value. In order to meet this difficulty, we might extend the integration from $-M$ to $+M$, these quantities being the extreme values which y_m can assume, i.e. $M = \varepsilon_{max} \sqrt{N}$ where ε_{max} is the maximum ionic charge present. We will however content ourselves here with stating that $A^{-1/2}$ would, for a given configuration, exactly represent the mean value of $e^{-E'/kT}$ in our generalised ensemble if the possible values of ε_k for an ion were not limited to the discrete values $z_1\varepsilon, \ldots z_s\varepsilon$ but if ε_k could assume all values from $-\infty$ to $+\infty$, the chance for ε_k to lie between ε_k and $\varepsilon_k + d\varepsilon_k$ being proportional to $exp\left[-\varepsilon^2{}_k/2_{\eta}\right] d\varepsilon_k$. That this holds for a continuous range of values a, including $a = 0$, for which A is positive, is easily verified, for instance by on one side developing $A^{-1/2}$ in a series of powers of a, and by on the other side developing $e^{-E'/kT}$ in a series of negative powers of T and

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[1]) At $T = 300°$ Kelvin, $D = 80$, and for a binary electrolyte with $z_1 = z_2 = 1$, we have $\varkappa = 6,9 \cdot 10^{-8}$ cm.

averaging over all possible ε_k values. The two series will coincide exacly provided the ε_k are not distributed discretely but continuously in the way just mentioned.

A closer investigation of the approximation involved in (14) would of course be very desirable; in the final result this approximation involves the neglect of terms essentially depending on the ionic radii and in the quantities $\overline{\varepsilon_k{}^3}$, $\overline{\varepsilon_k{}^4}$, etc. We will, therefore, not enter upon this question here.

By means of the value of the integrand in (7), given by (14) and (15), we find for the decrease of the free energy due to the interionic forces:

$$\triangle \zeta = - kT \, log \, \overline{A^{-1/2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where the bar denotes that the mean value has to be taken over all configurations of the ions in the volume under consideration. Now, if (17) is to have a thermodynamical meaning, the relative fluctuations of A must be exceedingly small on account of the large number of ions. We may therefore replace $\overline{A^{-1/2}}$ by $\overline{A}^{-1/2}$.

A general expression for $\overline{A}$ is derived in the following way. We denote the determinant (15) which refers to N ions in the volume V by A_N, while a determinant which is constructed in an analogous way but which refers to only $N-1$ ions in the same volume, will be called A_{N-1}. We may write:

$$\overline{A_N} = a^N \begin{vmatrix} 1/_a & g_{12} & g_{13} \cdots \\ g_{21} & 1/_a & g_{23} \cdots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Differentiating with respect to a and remembering that the mean values of the subdeterminants of the diagonal terms in (18) are all equal we find:

$$\frac{\partial \overline{A_N}}{\partial a} = \frac{N}{a} \overline{A_N} - a \frac{N}{a^2} \overline{A_{N-1}} = \frac{N}{a} (\overline{A_N} - \overline{A_{N-1}}) \quad . \quad . \quad . \quad (19)$$

Considering $\overline{A_N}$ as a function of the continuous variable N and writing as an approximation

$$\overline{A_N} - \overline{A_{N-1}} = \frac{\partial \overline{A}}{\partial N} \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

(19) will assume the form:

$$a \frac{\partial \overline{A}}{\partial a} = N \frac{\partial \overline{A}}{\partial N}$$

From this we conclude at once that $\overline{A}$, for a given volume V, depends on N in the form of a function of aN:

$$\overline{A} = \psi (aN, V) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

We compare this result with (8) the right hand term of which equals $\overline{A}^{-1/2}$. As T is inversely proportional to α, and n equal to N/V, we find:

$$\overline{A} = \psi\,(\alpha N, V) = \left[\omega\left(\frac{\alpha^3 N}{V}\right)\right]^N \quad . \quad . \quad . \quad . \quad . \quad (22)$$

This functional relation is only satisfied by:

$$\overline{A} = exp\,[-\,2\,K\,(\alpha N)^{3/2}\,V^{-1/2}] = exp\,[-\,2\,K\alpha^{3/2}\,n^{1/2}\,N] \quad . \quad (23)$$

From the relation

$$\triangle \zeta = {}^1/_2\,kT\,log\,\overline{A} \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

it follows then that $\triangle \zeta$ has precisely the form which formula (1) of DEBYE and HUECKEL assumes for infinitely small radii.

Before calculating the constant K in (23) we will first investigate what becomes of $\overline{A}$ if we do not introduce the approximation (20). In fact follows from (23) that for larger concentrations the ratio between $\overline{A}_N$ and $\overline{A}_{N-1}$ will deviate more and more from unity, so that (20) is no longer permissible. For the sake of simplicity we will in the following calculation assume $V = 1$, i.e. $n = N$, so that we may write:

$$\overline{A}_n = [\omega\,(\alpha^3\,n)]^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

For $\overline{A}_n - \overline{A}_{n-1}$ we get then, using (25):

$$\overline{A}_n - \overline{A}_{n-1} = [\omega\,(\alpha^3\,n)]^n - [\omega\,(\alpha^3\,(n-1))]^{n-1} =$$

$$= [\omega\,(\alpha^3\,n)]^{n-1}\left[\omega - \left(1 - \alpha^3\,\frac{\omega'}{\omega}\right)^{n-1}\right] = [\omega\,(\alpha^3\,n)]^{n-1}\left[\omega - e^{-\alpha^3 n\,\omega'/\omega}\right].$$

Here ω' denotes the differential coefficient $\dfrac{d\omega}{dx}$ of ω with respect to the argument

$$x = \alpha^3\,n \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

The approximations which have been introduced are quite in conformity with the spirit of statistical mechanics and are certainly legitimate if the number of ions is sufficiently large [1].

Equation (19) now assumes the form:

$$\frac{\partial \overline{A}_n}{\partial \alpha} = n\,\omega^{n-1} \,.\, 3\,\alpha^2\,n\,\omega' = \frac{n}{\alpha}\,\omega^{n-1}\,(\omega - e^{-\alpha^3 n\,\omega'/\omega}\,).$$

This leads to the following differential equation for ω:

$$3\,x\,\omega' = \omega - e^{-x\,\omega'/\omega} \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

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[1] Mr. ORNSTEIN had informed me that, in his dissertation (Leyden, 1908) analogous transformations were successfully applied in the theory of the equation of state.

The exact solution of this equation can be represented by means of a parameter t:

$$\omega = e^t (1 + 3t)^{-1} \qquad K^2 x = t^2 (1 + 3t)^{-3} \quad . \quad . \quad . \quad (28)$$

where K is a constant of integration.

For small t values we find:

$$\omega = \bar{A}^{1/n} = 1 - 2K\sqrt{x} \text{ or } \bar{A}^{1/n} = 1 - 2Ka^{3/2}n^{1/2} . \quad . \quad (29)$$

Thus K is the same constant as that entering in (23).

For larger values of x, ω changes in a peculiar way. The maximum value which x can take for real values of t (and only such values lead to real ω) correspond with $t = {}^2/_3$, and just for that x value ($K^2 x = {}^4/_{243}$) ω takes its minimum value. For t larger both x and $-\omega$ decrease. To such values, as well as to negative values for t, we shall attach no physical significance. The figures on this page give $-{}^{10}log\,\omega$ as a function
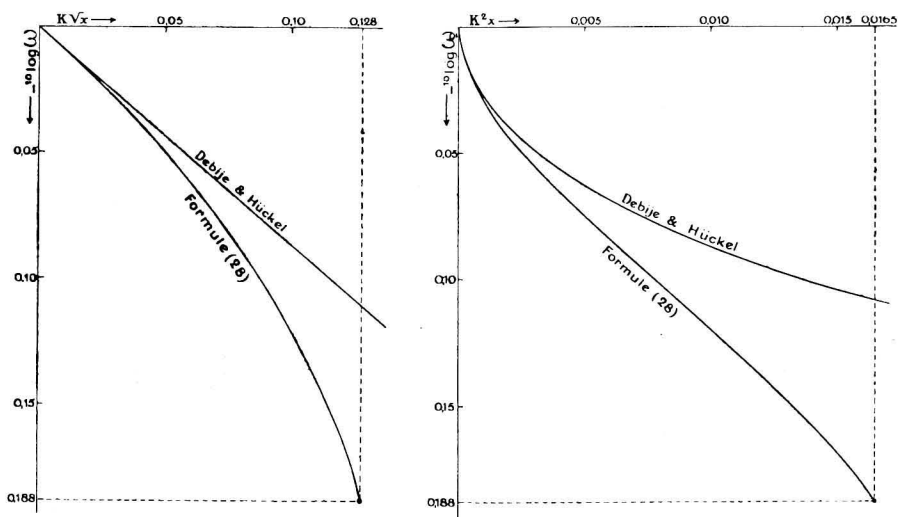
of $\sqrt{x}$ and of x. In both figures also the function $-{}^{10}log\,\omega = 0{,}869\,K\sqrt{x}$ which would correspond to DEBIJE's and HUECKEL's formula has been given.

In order to find the value of the constant K we might simply assume the formula of DEBIJE and HUECKEL to hold for small concentrations. For the sake of uniformity, however, we will start directly from the expression (15) for A, and by means of it compute the function ω in (25) for small concentrations. For simplicity we again put $V = 1$, $N = n$. Let, for a given configuration A_{n-1} represent a determinant analogous to (15), but in which the ion number 1 is disregarded. Then putting:

$$\frac{A_{n-1}}{A_n} = \xi_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

the quantity ξ_1 will be the solution of the following set of linear equations with n unknown quantities $\xi_1, \xi_2, \ldots \xi_n$:

$$\sum_k \xi_k\, b_{k1} = {}^1/_\varkappa \qquad\qquad (a)$$

$$\sum_k \xi_k\, b_{kl} = 0\ (l = 2, 3 \ldots n) \qquad (b) \qquad \cdots \cdots \quad (31)$$

where

$$b_{kl} = \frac{1}{r_{kl}}\,(l \neq k) \qquad b_{kk} = {}^1/_\varkappa .$$

For a configuration where the particles are practically distributed at random, the significance of ξ_1 can be simply illustrated in the case where a is small compared with the mean distance ϱ between neighbouring ions. We imagine n metal spheres distributed at random in the volume $V = 1$. The spheres carry charges $\xi_1, \xi_2 \ldots \xi_n$. The equations (31) then express that the potential at the surface of the first sphere equals ${}^1/_\varkappa$, whereas the potentials at the surface of the other spheres are equal to zero. This may be realized by earthing the spheres $2, 3 \ldots n$. Then ξ_1 is the charge which the first sphere must carry in order to possess a potential ${}^1/_\varkappa$ or, in other words, $\xi_1 a$ is the capacity of the system of conductors just described. The illustration holds only as long as the surface charge on each sphere is equally distributed, and in order that this be so the above mentioned condition $a \langle\langle \varrho$ is necessary.

The equations (31) may be solved by an artifice quite analogous to that applied by DEBIJE and HUECKEL. Using the terminology of the electrostatic system just described we introduce the mean potential φ existing at a distance r from the first sphere. Further we consider ξ_{kl} as a function of the distance r of the kth to the first sphere. The mean space charge in unit volume is seen to be equal to ξn, and POISSON's formula takes the form:

$$\triangle \varphi = -\,4\,\pi\,\xi\,n . \qquad \cdots \cdots \quad (32)$$

Now, according to (31b), the value of φ is so as just to be compensated by the potential due to the charge ξ_k if from an arbitrary point in space we pass to a point lying on the surface of the kth sphere. We therefore write:

$$\varphi = -\,{}^\xi/_\varkappa \qquad \cdots \cdots \cdots \quad (33)$$

Eliminating ξ from (32) and (33) we arrive at a differential equation for φ quite analogous to that obtained by DEBIJE and HUECKEL:

$$\triangle \varphi - 4\,\pi\,\varphi\,a\,n = 0 \qquad \cdots \cdots \cdots \quad (34)$$

Its solution is:

$$\varphi = \xi_1 \frac{e^{-r\sqrt{4\pi\,\varkappa\,n}}}{r} \qquad \cdots \cdots \cdots \quad (35)$$

We have chosen ξ_1 as constant of integration, since for small r values, φ must behave as ξ_1/r. The charge ξ_1 can now be calculated for instance by replacing in (31a) the summation over the ions $2, 3, \ldots n$ by an integral over the total volume. By means of (33) and (35) we obtain in this way:

$$1/_\alpha = \xi_1/a + 4\pi \int_0^\infty \frac{\xi n}{r} r^2 \, dr = \xi_1/a - 4\pi n\, a \int_0^\infty \varphi r \, dr =$$

$$= \xi_1/a - 4\pi \xi_1 a n \int_0^\infty e^{-r\sqrt{4\pi \alpha n}} \, dr = \xi_1/a - \xi_1 \sqrt{4\pi n a}$$

To the first approximation this gives:

$$\xi_1 = 1 + \sqrt{4\pi a^3 n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

For $4\pi an$ sufficiently small, the value of the integral is mainly determined by a part of space which contains many spheres; this justifies our method of solving ξ_1.

We have now calcutated the right hand side of (30) for a random distribution of ions and for small concentrations. Since under these conditons the left hand side of (30) will be equal to $\overline{A}_{n-1}/\overline{A}_n$ we find, using (25):

$$\overline{A}_{n-1}/\overline{A}_n = \left[\omega\left(a_3\left(n-1\right)\right)\right]^{n-1} \Big/ \left[\omega\left(a_3\, n\right)\right] = 1/_\omega\, e^{-x^3 n^{\omega'}/_\omega} \quad , \quad . \quad (37)$$

Introducing again the abbreviation (26), we find from (30), (36) and (37) the following differential equation for ω:

$$e^{-x^{\omega'}/_\omega} = \omega\left(1 + \sqrt{4\pi x}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Substituing for ω the solution (29) which holds for small x values, we obtain an equation which determines K:

$$e^{-x^{\omega'}/_\omega} = e^{K\sqrt{x}} = 1 + K\sqrt{x} = \omega\left(1 + \sqrt{4\pi x}\right) = 1 - 2K\sqrt{x} + \sqrt{4\pi x}$$

$$K = 1/_3 \sqrt{4\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Going back to the general case of N ions in a volume V we find from (17), (25), (26), (28) and (39):

$$\triangle \zeta = 1/_2\, N k T\, log\ nat\ \omega(x)$$

$$\omega = e^t \left(1 + 3t\right)^{-1} \quad , \quad \frac{4\pi}{9} x = t^2 \left(1 + 3t\right)^{-3} \quad . \quad . \quad . \quad . \quad (40)$$

$$x = a^3\, n = \left(\frac{\varepsilon^2}{D k T n} \Sigma\, n_i z_i^2\right)^3 n$$

To the first approximation the following formulae hold $(x \ll 1)$:

$$\left.\begin{aligned}
\omega &= 1 - \tfrac{2}{3}\sqrt{4\pi x} - \tfrac{5}{18}\, 4\pi x \ldots \\
-\log \omega &= \tfrac{2}{3}\sqrt{4\pi x} + \tfrac{1}{2}\, 4\pi x \ldots \\
\triangle \zeta &= - \Sigma \frac{N_i\, z_i^2\, \varepsilon^2\, \varkappa}{3}\frac{\varkappa}{D} - \ldots
\end{aligned}\right\} \quad \ldots \ldots \text{(41)}$$

The last expression coincides exactly with DEBYE's and HUECKEL's formula (1) in the limiting case of small ionic radic.

III. *Discussion of results.*

By means of (40) we will first calculate some important thermodynamical quantities.

For the logarithm of the coefficient of activity $(f_a)_i$ of the ions of the kind i we find:

$$\log (f_a)_i = \frac{1}{kT}\frac{\partial \triangle \zeta}{\partial N_i} = \frac{3}{2}t\left(1 - z_i^2\,\frac{N}{\Sigma N_i\, z_i^2}\right) - \frac{1}{2}\log(1+3t) \quad . \quad . \text{(42)}$$

If only two kinds of ions are present for which $z_1 + z_2 = 0$ (KCl, MgSO$_4$), the first term of the right hand member becomes equal to zero and we find:

$$f_a = \frac{1}{\sqrt{1+3t}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \text{(43)}$$

For the decrease $\triangle p$ and $\triangle \psi$ in the values of the osmotic pressure p and the thermodynamical potential ψ due to the interionic forces we find:

$$\left.\begin{aligned}
\triangle p &= -\frac{\partial \triangle \xi}{\partial V} = \frac{1}{2}\,NkT\,\frac{1}{\omega}\frac{d\omega}{dx}\frac{V}{x} = -\frac{NkT}{2V}t \\
\triangle \psi &= \triangle \zeta + V \triangle p = -\frac{1}{2}\,NkT\,\log(1+3t)
\end{aligned}\right\} \quad . \quad . \quad . \text{(44)}$$

From the first of these formulae we obtain a simple interpretation of the quantity t. Since the osmotic pressure of the ideal solution is equal to $\dfrac{NkT}{V}$, the coefficient with which this expression must be multiplied in order to obtain the osmotic pressure corrected for interionic forces, i.e. the osmotic coefficient f_0, is given by:

$$f_0 = 1 - \frac{t}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \text{(45)}$$

The maximum concentration for which our formulae still have a meaning corresponds, according to what has been said on p. 9, to $t = \tfrac{2}{3}$ and is thus given by:

$$\frac{4\pi}{9}x = \frac{4\pi}{9}a^3 n = \frac{4}{243}$$

For $D = 80$, $T = 300$, a becomes equal to $6,9.10^{-8} \frac{\Sigma N_i z_i^2}{N}$ and we find consequently that the number of gramions in a litre at that concentration is equal to:

$$\frac{1000\, n}{6,06.10^{23}} = 0,059 \left(\frac{N}{\Sigma N_i\, z_i^2} \right)^3 \quad . \quad . \quad . \quad . \quad . \quad (46)$$

For an electrolyte of the KCl type this corresponds to a concentration of 0,03 mol. KCl per litre, for an electrolyte of the $MgSO_4$ type with 0,0005 mol. $MgSO_4$ per litre, etc. For this maximum concentration the osmotic coefficient is always equal to $^2/_3 = 0,67$ whereas the logarithm of the coefficient of activity has become equal to $1 - z_i^2 \frac{\Sigma N_i z_i^2}{N} - \frac{1}{2} \log 3$. For KCl and $MgSO_4$ the coefficient of activity itself has thus become equal to $\frac{1}{\sqrt{3}} = 0,58$.

It is certainly striking that our formulae have a physical meaning only in a relatively small range of concentrations. We might naturally ascribe this to the circumstance that we have neglected the finite dimensions of the ions, although the integral (7) which was our starting point, diverges for infinitely small radii. The mathematical expression for the compromise which has been made is obviously involved in formulae (8) and (14). As mentioned in the text these approximations involve the neglect of terms depending essentially on the ionic radii. The meaning of the peculiar behaviour of the function ω would then be as follows. Considering an isothermal compression of the system where we start from a very big volume V i.e. from very small concentrations, statistical distributions of the ions will, at the beginning of the process, be possible, which are continuously connected with the random distribution at very small concentrations. This might also be expressed by stating that, for sufficiently small concentrations, an "atmosphere of free ions" can exist. At larger concentrations, however, the tendency of ions with opposity charges to "associate" becomes so preponderant (large fluctuations of the quantity A in (15)), that at concentrations larger than our critical concentration, no distribution of ions can exist which is independent of the dimensions of the ions. Obviously this does not yet mean that these dimensions will not play a part even at smaller concentrations (partial „association" of the ions).

It will therefore be clear that a comparison of the theory with the experiments is rather useless so long as the influence of the ionic radii has not been investigated more closely. We hope to return to this question on a later occasion. Meanwhile I think we may conclude already that it is illegitimate, from a theoretical point of view, to treat the state of a mixture of ions, at greater concentrations and without neglecting

the ionic radii, in the way proposed by DEBIJE an HUECKEL. In fact it seems that the considerations of these authors are based too much on the picture of an atmosphere of free ions. The beautiful investigations of BJERRUM (loc. cit. p. 2) point in the same direction. In this work the electrolyte is considered as a mixture of "free" and "associated" ions (not chemical association in the sense of the old theory, of course) and in many cases more plausible values for the ionic radii are found than in DEBIJE's and HUECKEL's theory.