

The stationary Soret effect in electrolytes is described here in terms of unbalance distribution functions.

A characteristic feature of the Soret effect in several electrolytes is the experimentally discovered [1] sign reversal of molecular separation at certain mean temperature and concentration levels. Known theories of heat-mass transfer phenomena in electrolytes [2, 3, 4] based on the Debye-Hückel model do not explain this reversal. This is so, apparently, because the Debye-Hückel model does not adequately describe phenomena where ion-solvent interparticle interactions must be accounted for. An attempt will be made here to theoretically evaluate the Soret effect in electrolytes with due consideration given to such interactions.

An electrolyte will be understood to comprise a system of monotype dipole particles (solvent molecules) and  $M$  types of charged particles (ions). In such a system, obviously, there occur three kinds of interaction: ion-ion, ion-solvent, and solvent-solvent. The interaction potential of  $k$ -th type and  $i$ -th type particles will be denoted by  $\Phi_{ki}(\mathbf{q}, \mathbf{q}')$ , where  $\mathbf{q}$  and  $\mathbf{q}'$  are the coordinate vectors of these particles; the mixture components will be denoted by Latin-letter subscripts, with subscript 0 denoting the solvent. The ion interaction will be described by the Debye-Hückel potential. The interaction between solvent molecules consists of intermittent van der Waals forces  $\chi_{00}$  and dipole-dipole interactions. The latter will be considered in terms of a potential averaged over rotational degrees of freedom [5]. As a result, we have

$$\Phi_{00}(\mathbf{q}, \mathbf{q}') = \chi_{00}(|\mathbf{q} - \mathbf{q}'|) - \frac{2\mu_0^4}{3kT(\mathbf{q})|\mathbf{q} - \mathbf{q}'|^6}, \quad (1)$$

where  $\mu_0$  is the dipole moment of a solvent molecule,  $k$  is the Boltzmann constant, and  $T(\mathbf{q})$  is the temperature at point  $\mathbf{q}$ . It does not matter here whether the temperature  $T$  is referred to point  $\mathbf{q}$  or  $\mathbf{q}'$ , since expression (1) is, indeed, equal to zero for any points  $\mathbf{q}$  and  $\mathbf{q}'$  whose temperatures  $T(\mathbf{q})$  and  $T(\mathbf{q}')$  are substantially different. In order to further avoid divergent integrals, we introduce a cutoff potential  $\Phi_{k0}$  at certain minimum distances  $\lambda_{k0}$  ( $k=0, 1, 2, \dots, M$ ). For  $k \neq 0$  these distances are determined essentially by the solvation of ions in the solvent [6]. The solvent molecules not bonded to ions cannot approach an ion within the radius of the solvation shell and, since there are many more such molecules than bonded ones, hence the mean  $\lambda_{k0}$  distances ( $k \neq 0$ ) are of the order of the solvation radius and this radius, in turn, is larger than the distances at which substantial intermittent forces can appear. Therefore, these forces may be disregarded and thus

$$\Phi_{k0}(\mathbf{q}, \mathbf{q}') = \begin{cases} -\frac{z_k^2 e^2 \mu_0^2}{3kT(\mathbf{q})|\mathbf{q} - \mathbf{q}'|^4} & \text{for } |\mathbf{q} - \mathbf{q}'| > \lambda_{k0}, \\ \infty & \text{for } |\mathbf{q} - \mathbf{q}'| \leq \lambda_{k0}, \end{cases} \quad (2)$$

where  $z_k$  is the valence of the  $k$ -th ion and  $e$  is the charge of an electron,  $k \neq 0$ .

Let us analyze the single-particle distribution functions in the  $F_i^{(k)}(\mathbf{q}, \mathbf{p})$  system [7]. They are time-independent, since a steady state is assumed. In an infinite volume with different local temperatures the dependence of these functions on the coordinates can be related to their dependence on temperature alone. Therefore, we will seek  $F_i^{(k)}$  as functions of temperature and momentum, i.e., for the time being we will depart from the physical significance of temperature as a macroscopic quantity and will instead treat it in

Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 21, No. 1, pp. 152-160, July, 1971. Original article submitted July 8, 1970.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

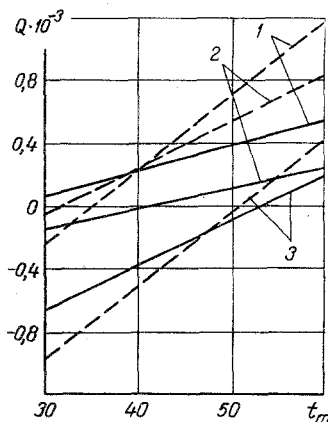


Fig. 1. Experimental data obtained by K. F. Alexander [1] on the transfer heat of molecular separation  $Q$  (J/mole) as a function of the mean temperature  $t_m$  ( $^{\circ}\text{C}$ ), compared with theoretical calculations according to formulas (26) and (28).

The theoretical data are shown by solid lines, the experimental data are shown by dashed lines: LiCl (1), LiBr (2), LiI (3).

The respective ion-solvent and solvent-solvent correlation functions can also be broken down into equilibrium and unbalance components. The unbalance components will be assumed of the same order as  $f^{(k)}_1(q)$ . This is, obviously, not always true. For example, it is known not to be the case at very low temperatures. We will consider here, however, the electrolyte temperature to be about  $T=300^{\circ}\text{K}$ . We insert (3) and (4) into the first Bogolyubov equation [7]. We then equate terms of like powers in  $\nabla T$  disregarding the highest-power term. We insert potentials (1), (2) and the Debye-Hückel potential into the resulting expressions. With the condition of electroneutrality applied to the total system, we separate in the equations their integral and differential parts. For  $Z^{(k)}$  we write the series:

$$Z^{(k)}(T, p^2) = \sum_{n=0}^{\infty} \Psi_n^{(k)}(T) (p^2)^n. \quad (5)$$

We then set up the matrix equation

$$\frac{\partial \Psi^{(k)}}{\partial T} = P^{(k)} \Psi + \lambda^{(k)}. \quad (6)$$

Here  $\Psi^{(k)}$  and  $\lambda^{(k)}$  are infinite-dimensional vectors with components  $\Psi_n^{(k)}$ ,  $-\delta_{0n}\omega^{(k)}$  respectively ( $n=0, 1, 2, \dots$ ),  $\delta_{in}$  are Kronecker deltas, and  $P^{(k)}$  is a matrix with components:

$$P_{ni}^{(k)}(T) = \left( \frac{3}{2T} - \frac{\alpha_k}{kT^3} \right) \delta_{ni} - \frac{\delta_{n-1,i}}{2m_k k T^2} + \frac{2m_k \alpha_k (n+1) \delta_{n+1,i}}{T^2}. \quad (7)$$

The symbol  $\omega^{(k)}(T)$  represents:

$$\omega^{(k)}(T) = \sum_{i=0}^M \frac{n_i}{kT} \cdot \frac{\partial}{\partial T} \times \int \Phi_{hi}(q, q') (2\pi m_i k T)^{-3/2} Z^{(i)} \exp\left(-\frac{p^2}{2m_i k T}\right) dq' dp. \quad (8)$$

terms of some potential field. We assume that  $F_1^{(k)}$  can be expanded into a power series in the temperature gradient. The first term will, obviously, be the equilibrium function. Owing to the system isotropy and by virtue of the covariance principle, the second significant term will be of the second order in  $\nabla T$ . The higher-order terms will be disregarded. The temperature gradient is assumed uniform. Insofar as the volume is infinite, the system may be considered homogeneous under equilibrium conditions. Based on all this we write

$$F_1^{(k)} = (2\pi m_k k T)^{-3/2} \exp\left(-\frac{p^2}{2m_k k T}\right) + f^{(k)}(T, p) \quad (k=0, 1, \dots, M), \quad (3)$$

where  $m_k$  is the mass of a  $k$ -th type particle,  $p$  is the momentum,  $f^{(k)}$  is the sought second-order function of  $\nabla T$ . Binary distribution functions are represented by a sum of correlation functions and products between single-particle functions. The overall system is electrically neutral. Locally this electroneutrality will be maintained, we assume, if  $\text{grad } T$  is so small that the integrals  $\int F_1^{(k)} dp$  are linear functions of the local temperature. This condition is stipulated as a basis for disregarding the ion-ion correlation functions. With a stationary elemental Soret effect all hydrodynamic velocities vanish:

$$\int p F_1^{(k)}(q, p) dp = 0.$$

This condition is satisfied for any  $q$  when  $F_1^{(k)} = F_1^{(k)}(q, p^2)$ . It follows from (3), then, that  $f^{(k)} = f^{(k)}(T, p^2)$ . Introducing unknown functions  $Z^{(k)}(T, p^2)$ , we have

$$f^{(k)}(T, p^2) = (2\pi m_k k T)^{-3/2} Z^{(k)}(T, p^2) \exp\left(-\frac{p^2}{2m_k k T}\right). \quad (4)$$

We have also made the following designations here:

$$\alpha_k = \begin{cases} \frac{4\pi\mu_0^4}{3k} \left( \sum_{i=1}^M \frac{\tilde{n}_i z_i^2 e^2}{\lambda_{i0}} + \frac{2\tilde{n}_0 \mu_0^2}{3\lambda_{00}^3} \right) & \text{for } k=0, \\ \frac{4\pi\tilde{n}_0 z_k^2 e^2 \mu_0^2}{3k\lambda_{k0}} & \text{for } k \neq 0. \end{cases} \quad (9)$$

As long as matrix  $P^{(k)}(T)$  is commutative with matrix  $P^{(k)}(T')$ , solving Eq. (6) becomes much easier. The procedure by which a solution is obtained will not be shown here, so as not to digress from the main point of this analysis. We only note that the method required here has been outlined in [8], using the properties of exponential operators [9] and generalized Kronecker deltas [10]. One also considers here that the values of  $2m_k \alpha_k / T$  are of the  $10^{-32}$ – $10^{-36}$  orders of magnitude, i.e., all but the zeroth-power terms are disregarded. As a result we have

$$\Psi_n^{(k)} = T^{3/2} \exp\left(\frac{\alpha_k}{kT^2}\right) \sum_i \left\{ \frac{A_i^{(k)}}{(n-i)! (2m_k kT)^{n-i}} - \frac{(-1)^i}{(2m_k k)^n T^{n-i} (n-i)! i!} \int \frac{\omega^{(k)}(T)}{T^{i+3/2}} \exp\left(-\frac{\alpha_k}{kT^2}\right) dT \right\}, \quad (10)$$

where  $A_i^{(k)}$  are constants found from the normalization criterion for functions (3). It can be shown that in our case the normalization criterion may be written as  $\Psi_n^{(k)}(T_m) = 0$ , with  $T_m$  denoting some mean-over-the-volume temperature. Since  $\nabla T$  has already been assumed uniform, hence for relatively small temperature drops across the volume one may let  $T_m \approx (T_{\min} + T_{\max})/2$ . We can find the constants  $A_i^{(k)}$  from our normalization criterion, if

$$\sum_i \frac{(-1)^{n-i} Q^{n-i}}{(n-i)! (i-1)!} = \delta_{ni} \quad (11)$$

is satisfied for any arbitrary  $Q$ . Then (10) becomes

$$\Psi_n^{(k)} = \frac{T^{3/2} \exp\left(-\frac{\alpha_k}{kT^2}\right)}{(2m_k kT)^n} \times \sum_i \frac{(-1)^i T^i}{(n-i)! i!} \int_T^{T_m} \frac{\omega^{(k)}(\xi)}{\xi^{i+3/2}} \exp\left(-\frac{\alpha_k}{k\xi^2}\right) d\xi. \quad (12)$$

In order to find the functions  $\omega^{(k)}(T)$ , we first determine  $\omega^{(k)}(T_m)$ . For this we take the momentum integral outside the differentiation and summation signs. Then, from (5), (8), (11), and (12) we will obtain

$$\omega^{(k)}(T_m) + \sum_{l=0}^M \frac{\tilde{n}_l}{kT_m} \left[ \int \Phi_{kl}(q, q') dq' \right]_{T=T_m} \omega^{(l)}(T_m) = 0. \quad (13)$$

By means of the Debye potential this can be reduced to a matrix equation:

$$A\omega(T_m) + \frac{\omega(T_m)}{\sum_{n=1}^M z_n a_n} + \frac{b}{\sum_{n=1}^M z_n a_n} = 0, \quad (14)$$

where  $\omega(T_m)$ ,  $z$ ,  $a$ , and  $b$  are  $M$ -dimensional vectors with the components  $\omega^{(k)}(T_m)$ ,  $z_k$ ,  $4\pi\tilde{n}_k z_k e^2 / \epsilon \kappa^2 kT_m$ , and  $4\pi\tilde{n}_0 z_k^2 e^2 \mu_0^2 \omega^{(0)}(T_m) / 3k^2 T_m^2 \lambda_{k0}$  respectively ( $k = 1, 2, \dots, M$ ). Here  $A$  is a matrix with components

$$A_{ki} = \frac{z_k a_i}{\sum_l z_l a_l} \quad (15)$$

and  $\kappa$  is the inverse Debye radius:

$$\kappa^2 = \frac{4\pi e^2}{\epsilon(T_m) kT} \sum_{i=1}^M \tilde{n}_i z_i^2, \quad (16)$$

with  $\epsilon$  denoting the dielectric permittivity of the electrolyte (which, according to our premise, depends on the mean temperature).

Equation (14) can be solved, considering that  $A$  is a projection matrix, i.e., that  $A^2 = A$  and that its trace is equal unity. One must also know here the form of matrix  $S$ :

$$S_{ki} = -z_M \delta_{ki} (k, i \neq M), S_{kM} = z_k (k \neq M), S_{Mi} = a_i,$$

with the aid of which matrix  $A$  is reduced to diagonal form. The solution is

$$\omega^{(k)}(T_m) = \frac{4\pi \tilde{n}_0 \mu_0^2 e^2}{3k^2 T_m^2} \omega^{(0)}(T_m) \left\{ \frac{z_k^2}{\lambda_{k0}} - \frac{z_k \sum_i \frac{\tilde{n}_i z_i^3}{\lambda_{i0}}}{2 \sum_i \tilde{n}_i z_i^2} \right\} (k \neq 0). \quad (17)$$

Next, one can see from (13) and (17) that  $\omega^{(0)}(T_m)$  is arbitrary. In order to determine the functions  $\omega^{(k)}(T)$ , we will expand (12) into a power series in  $T^{-1/2} - T_m^{-1/2}$  and will retain only the first-order term (this is a very small quantity for most real electrolytes). We can obtain a series expansion in the vicinity of point  $T_m^{-1/2}$  as well as in the vicinity of  $T^{-1/2}$ . Equating both series, we have

$$\omega^{(k)}(T) = \left( \frac{T_m}{T} \right)^{3/2} \omega^{(k)}(T_m). \quad (18)$$

It remains to find  $\omega^{(0)}(T_m)$ . Let us say we have produced in the system such a small temperature gradient that (12) becomes a linear function of  $T$ . Then (3), (4), (5), and (12) will yield

$$F_1^{(k)} = (2\pi m_k k T)^{-3/2} \{1 + \omega^{(k)}(T_m)(T_m - T)\} \exp\left(-\frac{p^2}{2m_k k T}\right), \quad (19)$$

i.e., we have a quasiequilibrium state. The expression inside the large brackets is now a unitary distribution function with respect to the coordinates and it satisfies the Bogolyubov equation which relates it to binary functions [7, 11]. For the time being, let us now digress from the model and consider an ion gas in some continuous medium, as is done in the Debye-Hückel theory. One may then disregard all but the ion distribution functions. The partial ion pressure in the system may be represented by binary distribution functions and then, with the aid of the Bogolyubov equation, this partial pressure may be related to unitary functions. Considering the condition of electroneutrality in the system, we will then obtain from (17) and (19):

$$\omega^{(0)}(T_m) = -\frac{3kT_m^2}{4\pi \tilde{n}_0 \mu_0^2 e^2 \sum_{i=1}^M \frac{\tilde{n}_i z_i^2}{\lambda_{i0}}} \left[ \frac{\partial^2 p_{\text{ion}}}{\partial T^2} \right]_{T=T_m}, \quad (20)$$

where  $p_{\text{ion}}$  is the partial ion pressure. We use here the approximate equation of state for ions in a plasma or in an electrolyte [12]:

$$p_{\text{ion}} = \sum_{i=1}^M \tilde{n}_i k T - \frac{\kappa^3}{24\pi} k T. \quad (21)$$

It follows from (16), (20), and (21) that

$$\omega^{(0)}(T_m) = \frac{3k^2 T_m \kappa^3}{128\pi^2 \tilde{n}_0 \mu_0^2 e^2 \sum_i \frac{\tilde{n}_i z_i^2}{\lambda_{i0}}}. \quad (22)$$

From the very beginning we have imposed the condition of local electroneutrality on a state of the (19) kind and, therefore, with the condition of total electroneutrality we can show that  $\lambda_{k0} \sim z_k^2$ .

Obviously,  $\lambda_{k0}$  must also be proportional to the Debye radius: as the radius increases, the solvent molecules must remain at a farther distance away from the ions. We will introduce a dimensionless constant  $A$  which depends on the properties of the solvent and

$$\lambda_{k0} = A \frac{z_k^2}{\kappa}. \quad (23)$$

The Soret coefficient will be found from the continuity equation, in our case  $\text{div } \mathbf{J}_k = 0$ . For this purpose, the diffusion current density  $\mathbf{J}_k$  must be expressed in terms of distribution functions. After the resulting expression has been reduced to a matrix equation of the (14) kind, the projection matrix of its solution and the fact that  $\sum_k c_k = 1$  will help us to obtain

$$\frac{\text{grad } c_k}{\text{grad } T} = \frac{\sum_{i=0}^M m_i c_i}{\sum_{i=0}^M \tilde{c}_i \int p_1 F_1^{(i)} dp} \quad (24)$$

$$\times \left\{ \frac{\tilde{c}_k}{m_k} \int p_1 \frac{\partial F_1^{(k)}}{\partial T} dp - c_k \sum_{k=0}^M \frac{\tilde{c}_i}{m_i} \int p_1 \frac{\partial F_1^{(i)}}{\partial T} dp \right\},$$

where  $c_k$  and  $\tilde{c}_k$  are the local and the mean concentration of the  $k$ -th component (in fractions of the total number of particles) and  $p_1$  is one of the momentum components. The Soret coefficient is by definition:

$$s = -\frac{1}{c(1-c)} \cdot \frac{\text{grad } c}{\text{grad } T} = \frac{1}{c(1-c)} \cdot \frac{\text{grad } c_0}{\text{grad } T}, \quad (25)$$

where  $\tilde{c} = \sum_{i=1}^M \tilde{n}_i / \tilde{n}$ , with  $\tilde{n}$  denoting the average number of particles per unit volume and  $s$  obviously depending on the location of a given point in space. For simplicity, we compute the Soret coefficient at the points where  $T = T_m$ . It can be shown that in narrow thermal diffusion channels the values of this coefficient are approximately equal to the mean value for a channel. From the stipulated criterion for normalizing the distribution functions, we have  $c_k = \tilde{c}_k$  at all points where  $T = T_m$ . In computing with expression (24) it becomes necessary to resolve the indeterminacy of 0:0, since all integrals are equal to zero here. One should take advantage here of the fact that the ratio of integrals from  $-\infty$  to  $+\infty$  of odd functions may be replaced by the ratio of integrals from 0 to  $+\infty$  of the same functions.

Inasmuch as, for the purpose of further analysis, the dielectric permittivity must be defined in specific terms, we will consider only aqueous electrolytes. For water the Kirkwood formula [13] gives a value of  $\epsilon$  which agrees closely with test data. Of course, strictly speaking, the value of  $\epsilon$  for an electrolyte is not the same as that for water. We will, however, use the Kirkwood formula. Then, considering that  $\tilde{n} \approx N_A \rho_0 / M_0$  (where  $N_A$  is the Avogadro number), we obtain from (3), (4), (5), (12), (17), (18), (22), (23), (24), and (25):

$$s = \frac{m_0(1-\tilde{c}) + \tilde{c} \sum_{i=1}^M m_i \tilde{x}_i}{m_0(1-\tilde{c}) + \tilde{c} m_0^{1/2} \sum_{i=1}^M m_i^{1/2} \tilde{x}_i} \cdot \frac{1}{2T_m} \left\{ 1 - m_0^{1/2} \sum_{i=1}^M \tilde{x}_i m_i^{-1/2} \right. \quad (26)$$

$$\left. \times \left[ 1 - 4.66 \frac{\tilde{c}^{1/2}}{(1-\tilde{c})^{3/2}} \left( \sum_{i=1}^M \tilde{x}_i z_i^2 \right)^{3/2} \right] - \alpha \frac{T_m^2}{(1-\tilde{c})^2} \sum_{i=1}^M \tilde{x}_i z_i^2 \right\},$$

where

$$\alpha = \frac{9k^2 M_0^2 A}{224\pi^2 \mu_0^4 \rho_0^2 N_A^2} \left( \frac{3}{\eta^2 + 2} \right)^2,$$

$\eta$  is the refractive index,  $\tilde{x}_i$  is the fraction of  $i$ -th type ions in the total number of ions. Since  $A$  has not been determined,  $\alpha$  is also undetermined. We will, therefore, proceed on the basis of test data.

It is evident from (15) that, in principle, a mean temperature  $T_{m0}$  such that

$$T_{m0}^2 = \frac{1 + m_0^{1/2} \sum_{i=1}^M \tilde{x}_i m_i^{-1/2} \left[ 4.66 \frac{\tilde{c}^{1/2}}{(1-\tilde{c})^{3/2}} \left( \sum_{i=1}^M \tilde{x}_i z_i^2 \right)^{3/2} - 1 \right]}{\alpha \sum_{i=1}^M \tilde{x}_i z_i^2} (1-\tilde{c})^2 \quad (27)$$

may be reached at which no molecular separation occurs. K. F. Alexander [1] has performed tests on molecular separation in various electrolytes with a 0.05 N concentration. A reversal of the separation sign was detected in several salt solutions. The transfer heat of molecular separation was determined in [1] according to the formula:

$$Q = -sRT_m^2 \left( 1 + \frac{d \ln f}{d \ln c} \right), \quad (28)$$

where R is the gas constant and f is the activity coefficient. A sign reversal in (28) was observed by Alexander in lithium salts. Therefore, the constant  $\alpha$  can be determined according to [1] and (27). When using the data for LiCl, LiBr, and LiI, the values of the constant  $\alpha$  are respectively  $0.13 \cdot 10^{-5}/\text{deg}^2$ ,  $0.9 \cdot 10^{-5}/\text{deg}^2$ , and  $0.2 \cdot 10^{-5}/\text{deg}^2$ . The graphs of  $Q(T_m)$  for these salts shown in Fig. 1 have been plotted according to Eqs. (26) and (28) with  $\alpha = 0.19 \cdot 10^{-5}/\text{deg}^2$ . For comparison, test results are also shown here.

If our results are applied to the other salts in [1], then the values of  $\alpha$  will be somewhat greater. One may attribute this to the fact that, strictly speaking, A in (23) does not depend on the properties of the solvent only, as has been assumed here. Apparently, A depends also on certain properties of the solute which affect the solvation.

It can be seen from Fig. 1 that, regardless of the various assumptions, our results are qualitatively in agreement with experiments [1]. As Alexander has pointed out, his results confirm the Eastman hypothesis concerning the impossibility of a sign reversal in the Soret coefficient. Evidently, as is shown in our analysis, a sign reversal can occur if the ion-solvent interaction forces are taken into account.

#### NOTATION

M	is the number of different types of ions in an electrolyte;
$\Phi_{ki}(q, q')$	is the interaction potential between a k-th type particle at point q and an i-th type particle at point q';
$u_0$	is the dipole moment of a solvent molecule;
T, $T_m$	are the local and mean temperatures, respectively;
$z_k$	is the valence of a k-th type ion;
$m_k$	is the mass of a k-th type particle;
$n_k, \tilde{n}_k$	are the local and mean concentrations, respectively, of a k-th type particle;
$\epsilon$	is the dielectric permittivity;
$\kappa$	is the inverse Debye radius;
$\lambda_{k0}$	is the radius of a solvated k-th type ion;
$J_k$	is the diffusion current density of the k-th component;
s	is the Soret coefficient of molecular separation;
$\rho_0$	is the density of solvent;
$M_0$	is the molecular weight of solvent;
$\tilde{x}_k$	is the average fraction of k-th type ions in total number of ions;
$T_{m0}$	is the mean temperature at which molecular separation ceases;
Q	is the transfer heat of molecular separation.

#### LITERATURE CITED

1. K. F. Alexander, *Zeitschr. Physik. Chem.*, 203, 228 (1954).
2. J. N. Agar, *Structure of Electrolytic Solutions*, New York (1959).
3. E. Helfand and J. G. Kirkwood, *J. Chem. Phys.*, 32, 857 (1960).
4. E. Helfand, R. J. Bearman, and V. S. Vaidhyanathan, *J. Math. Phys.*, 4, 160 (1963).
5. D. Hirschfelder, Ch. Curtiss, and R. Byrd *Molecular Theory of Gases and Liquids* [Russian translation], IL, Moscow (1961).

6. R. Robinson and R. Stokes, *Electrolytic Solutions* [Russian translation], IL, Moscow (1963).
7. N. N. Bogolyubov, *Problems in the Dynamic Theory of Statistical Physics* [in Russian], Gostekhizdat, Moscow (1946).
8. F. R. Gantmakher, *Matrix Theory* [in Russian], Izd. Nauka, Moscow (1967).
9. D. A. Kirzhnits, *Field Methods in Multiparticle Theory* [in Russian], Moscow (1963).
10. A. A. Bogush and F. I. Fedorov, *Dokl. Akad. Nauk BSSR*, 12, 21 (1968).
11. I. Z. Fisher, *Statistical Theory of Liquids* [in Russian], Fizmatgiz, Moscow (1961).
12. R. Balescu, *Statistical Mechanics of Charged Particles* [Russian translation], Izd. Mir, Moscow (1967).
13. G. Froehlich, *Theory of Dielectrics* [Russian translation], IL, Moscow (1960).