



Fig. 3. Temperature dependence of the rate of exchange i .

SUMMARY

1. A study has been made of the rate of exchange of elements between two liquid phases (lithium in amalgam and potassium in aqueous KCl solution) at various temperatures and amalgam concentrations.
2. The rate of exchange of elements increases linearly with amalgam concentration when the latter is varied from 0.1 to 0.7 equiv. litre⁻¹.
3. Since the activation energy determined in this work is close to that for the viscous flow of mercury, the rate-determining stage of the exchange of elements in our experiments was probably transport of material in the interior of the drop.
4. The rate of electrochemical exchange is greater than the rate of transport of material under the conditions of our experiments, its lower limit being 5 A cm⁻² when the amalgam concentration is 0.7 equiv. litre⁻¹.

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where $D \approx 10^{-5}$ cm² sec⁻¹ is the diffusion coefficient of lithium in the amalgam, $N_A = 0.3$ equiv. litre⁻¹ the concentration of the amalgam, $t = 0.033$ sec the time taken by the drop to traverse a layer of solution 20 mm thick, and F is the Faraday. Eqn. (5) then yields $i_{\text{tr}} \approx 0.3$ A cm⁻². The measured current densities i in experiments 7-12 (Table 4) proved to be much greater than i_{tr} , which means that mixing in the drop is much more intense than would be accounted for by diffusion. According to Levich⁵, mixing in the amalgam drop takes place under the influence of surface forces balanced out by viscous forces in the interior of the drop. The temperature variation of the rate of exchange of elements determined in our experiments makes it possible to find the activation energy of the process determining the rate of exchange. Assuming that in our experiments the rate of exchange is determined by the transport of material in the drop by viscous flow, we can calculate the appropriate activation energy. The dependence of the rate of material transport by diffusion or viscous flow on the activation energy and temperature is given by the following equation:

$$i_{\text{tr}} = Ae^{-E/RT}, \quad (6)$$

where E is the activation energy and A a constant. From the plots of $\ln i$ against $1/T$ for various values of h , the mean activation energy is found to be $E = 1.1 \pm 0.2$ kcal $\times$ mole⁻¹. Since the activation energy of viscous flow is the same as that of diffusion in a liquid⁷, the value of E obtained can be regarded as the activation energy of diffusion as well. Probably our value of E does not differ appreciably from the corresponding energy for pure mercury because the concentration of the amalgams in our experiments was small. According to Shishido⁶ the activation energy of self-diffusion in mercury is $1.00-0.97$ kcal $\times$ mole⁻¹, i.e. close to our value. Hence it follows that the values of i found in our experiments characterise transport processes in the amalgam, and therefore the actual rate of exchange, which occurs in the reaction zone, is greater than our values.

An increase in the current density i with decrease in the thickness of the solution layer h (Tables 2-4) may be explained by the fact that in our experiments the entrainment of aqueous solution by the drop was not completely eliminated. Thus with decrease in h the contribution of the process in the entrained liquid increased, resulting in an increase of i .

THE STATIC THEORY OF SOLUTIONS OF STRONG ELECTROLYTES

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Development of a theory of concentrated electrolyte solutions is of great practical interest in view of the important role which these solutions play in experimental physico-chemical investigations. The lack of a consistent theory of concentrated electrolyte solutions is to be explained both by the mathematical difficulties involved in the solution of this problem and by the absence of sufficiently reliable experimental data on the nature of short-range ionic interactions. Other aspects of this problem relate to the effect of the solvent on the thermodynamic properties of the system.

One of the first attempts to set up a quantitative theory of solutions of strong electrolytes was made by Debye and Hückel¹. However, experimental studies showed that the applicability of this theory is limited to very low concentrations^{2-5†}.

† For a number of electrolytes deviations from the Debye-Hückel theory were observed even in the "Debye concentration range".

Attempts to extend the theory to somewhat higher concentrations were later made by a number of other workers⁶⁻¹⁴. Gronwall *et al.* gave an analytical solution of the complete Poisson-Boltzmann equation⁶. However, the solutions thus obtained are not self-consistent. Another attempt to set up a theory of concentrated electrolyte solutions was made by Bjerrum⁷, who started from the concept of ion association. This idea was further developed by Fuoss and Kraus and Fuoss⁸.

Guggenheim⁹ tried to allow for the "specific interaction" of ions in connection with the present problem. A statistically consistent approach to the calculation of thermodynamic properties of electrolyte solutions was made by Bogolyubov^{15†}, who developed the method of correlation functions for the solution of statistical equilibrium problems, which was free from the fundamental deficiencies characteristic of the Debye-Hückel method. An analogous procedure was also developed by Born and Green¹⁶. The statistical Born-Green-Bogolyubov method is based on an examination of distribution functions describing the probability that complexes of 1, 2, 3, etc. species are located at given positions, and on setting up for the complete set of the corresponding correlation functions of a system of integrodifferential equations, which can sometimes be solved by successive asymptotic expansions in powers of a small parameter.

In view of the difficulties involved in finding the binary distribution function for systems with coulombic interaction, Tolmachev and Tyablinov¹⁹ attempted to improve the convergence of the binary function for small r and Bazarov²¹ calculated this function for a rigid sphere model. Somewhat earlier Bazarov made a qualitative allowance for the repulsive forces on the basis of a "smoothed" interaction potential of the type $e_a e_b (1 - e^{-\alpha r})/D_0 r$, which also eliminates the divergence of $F_{ab}(r)$ at zero r 's.

It must be emphasised that, because of the complexity of ionic interactions in solutions, the formulations proposed by the above workers for the interionic interaction potential cannot be regarded as sufficiently satisfactory. Indeed, although at large distances the effect of interionic interaction is determined mainly by coulombic forces,

$$\Phi_{ab}(r) \rightarrow e_a e_b / D_0 r$$

(D_0 is the dielectric constant valid for two ions sufficiently far apart when their binary interaction is being estimated), at small distances, together with purely repulsive and coulombic forces, quantum-mechanical dispersion forces and forces of other types also play a substantial part. Short-range interaction in solutions is also considerably complicated by the effect of ionic solvation, so that an exact solution must allow for the microscopic structure of the solvent.

Another deficiency of a number of studies on the theory of electrolyte solutions is the fact that the non-additivity of thermodynamic functions of the given systems with respect to coulombic and short-range forces (see for example Ref.9) has been ignored.

† Kramers¹⁷ and Fowler¹⁸ also dealt with the statistical basis of the Debye-Hückel theory, starting from the general expression for the partition function.

§ This form of the potential is unsatisfactory apparently even as a qualitative device since with small r it leads to attractive and not repulsive forces for charges of the same sign.

In the present work explicit thermodynamic functions of the system are sought, on the basis of an interionic potential of a fairly general type, with a correlation term reflecting the non-additivity of the system with respect to coulombic and "specific" interaction of ions in solution. Introduction of an appropriate method for the approximation of the correlation functions makes it also possible to derive and express in a general form the fundamental equations of the association theory directly from general statistical postulates.

Moderately Concentrated Electrolyte Solutions

Consider an electrolyte solution occupying a macroscopic volume V . When the concentration of ions is moderate, then, as in the Debye-Hückel theory, we can regard the solvent, to a given approximation, as a continuous medium with dielectric constant D_0 , which in general depends on the distance r between the species and on a number of other factors.

For the sake of generality we shall also suppose that the system contain ions, which as regards their charge belong to $M \geq 2$ different classes, and that as a whole it is electrically neutral:

$$\sum_{(1 \leq a \leq M)} N_a e_a = 0, \quad (1)$$

where N_a is the total number of species of the given type with charge $e_a = e z_a$ (z_a is the electrovalence of the ion). The potential energy of the system with $N = \sum_{1 \leq a \leq M} N_a$ ions

can be written in the following form:

$$U_N(q_1, \dots, q_N) = \sum_{a,b} \Phi_{ab}(|q_1 - q_b|), \quad (2)$$

where $\Phi_{ab}(|q - q'|)$ is the energy of interaction of a pair of ions located at points $q = \{q^\alpha\}$ and $q' = \{q'^\alpha\}$, with $\alpha = 1, 2, 3$. The summation in Eqn.(2) is made over all the different pairs of ions constituting the system.

Starting from the Gibbs canonical distribution factor,

$$D_N(q_1, \dots, q_N) = Q_N^{-1} \exp\left\{-\frac{1}{\theta} U_N(q_1, \dots, q_N)\right\} \quad (3)$$

and introducing the sequence of distribution functions $F_{a_1, \dots, a_s}$ in terms of the relations

$$F_{a_1, \dots, a_s}(q_1, \dots, q_s) = V^s \int \dots \int D_N(q_1, \dots, q_N) dq_{s+1} \dots dq_N, \quad (4)$$

we obtain in asymptotic approximation ($N \rightarrow \infty$, $V \rightarrow \infty$, $N/V = 1/\nu < \infty$) the following systems of equations relating the distribution functions of different orders:

$$\begin{aligned} \frac{\partial F_{a_1, \dots, a_s}}{\partial q_1^\alpha} + \frac{1}{\theta} \frac{\partial \Phi_{a_1, \dots, a_s}}{\partial q_1^\alpha} F_{a_1, \dots, a_s} + \\ + \frac{1}{\theta \nu} \sum_{(1 \leq a_{s+1} \leq M)} \frac{\partial \Phi_{a_1, \dots, a_{s+1}}(|q_1 - q_{s+1}|)}{\partial q_1^\alpha} F_{a_1, \dots, a_{s+1}} dq_{s+1} = 0, \quad (5) \end{aligned}$$

where $\Phi_{a_1, \dots, a_s}(q_1, \dots, q_s)$ represents the potential energy of an isolated complex of s ions of $a_1, \dots, a_s$ -th classes respectively.

Approximating the purely repulsive forces in terms of rigid spheres, it is convenient to adopt the following scheme for the calculation of the interionic potential $\Phi_{ab}(r)$:

$$\begin{aligned} \Phi_{ab}(r) = +\infty, \quad r < r_0; \quad \Phi_{ab}(r) = U_{ab}, \quad r_0 < r < r_s; \\ \Phi_{ab}(r) = e^2 z_a z_b / D_0 r, \quad r > r_s, \quad (6) \end{aligned}$$

where r_0 is the radius of the ion and r_s the radius of the solvation shell. The function $U_{ab}(r)$ defines the interaction of ions in the intermediate region between regions where purely "repulsive" and purely coulombic forces operate.

Eqn. (6) for $\Phi_{ab}(r)$ can also be put in the form

$$\Phi_{ab}(r) = \begin{cases} 0, & r < r_0, \\ e^2 z_a z_b / D_0 r, & r > r_0, \end{cases} \quad \Phi'_{ab}(r) = \begin{cases} +\infty, & r < r_0, \\ U_{ab}(r), & r_0 < r < r_s, \\ 0, & r > r_s. \end{cases} \quad (7)$$

or

$$\Phi_{ab}(r) = \Psi_{ab}^{(k)}(r) + \Psi'_{ab}(r), \quad (8)$$

$$\Psi_{ab}^{(k)}(r) = \begin{cases} +\infty, & r < r_0, \\ e^2 z_a z_b / D_0 r, & r > r_0, \end{cases} \quad \Psi'_{ab}(r) = \begin{cases} 0, & r < r_0, \\ U_{ab}(r), & r_0 < r < r_s, \\ 0, & r > r_s, \end{cases}$$

where

$$U'_{ab} = U_{ab} - e^2 z_a z_b / D_0 r.$$

We shall examine first the representation of potential (6) in form (8) and solve the problem concerning the behaviour of this system, which is characterised by the binary potential $\Psi_{ab}^{(k)}(r)$. The corresponding system of correlation functions will be denoted by $F_{a_1 \dots a_s}^{(k)}$, ..., a_s . The initial system of equations then takes the form

$$\frac{\partial F_{a_1 \dots a_s}^{(k)}}{\partial q_1^2} + \frac{1}{\theta} \frac{\partial \Psi_{a_1 \dots a_s}^{(k)}}{\partial q_1^2} F_{a_1 \dots a_s}^{(k)} +$$

$$+ \frac{1}{\theta v} \sum_{(1 < a_{s+1} < M)} n_{a_{s+1}} \frac{\partial \Psi_{a_1 \dots a_{s+1}}^{(k)}(|q_1 - q_{s+1}|)}{\partial q_1^2} F_{a_1 \dots a_{s+1}}^{(k)} dq_{s+1} = 0. \quad (9)$$

We now make use of the expansion in powers of the dimensionless parameter $\epsilon = v/r_d^3$, where v is the specific volume and r_d the characteristic length, which is a function of temperature and solution concentration:

$$r_d^{-3} = \frac{4\pi e^2}{D_0 \theta v} \sum_{(a)} n_a z_a^2, \quad n_a = N_a / N.$$

In view of the specific features of the potential $\Psi_{ab}^{(k)}$, the usual form of power expansion is inapplicable and it is convenient to employ a somewhat different method for the approximation of the correlation functions. For this purpose, we shall estimate the order of magnitude of the second and third terms in Eqn. (9) for large and small distances between the species. Using in the estimates for large [? (Ed. of Translation)] distances the Debye-Hückel approximation, i.e. the following expression in terms of the correlation functions:

$$F_{ab}^{(k)} = 1 - \frac{e^2 z_a z_b}{D_0 \theta r} e^{-r/r_d}, \quad (9')$$

we can show that for small distances ($r < r_s$) the integral term in Eqn. (9) becomes small compared with the second term. This means that in this region the dependence of the binary function on distance is determined mainly by the Boltzmann factor:

$$F_{ab}^{(k)}(r) = \begin{cases} 0, & r < r_0, \\ \exp\left\{-\frac{e^2 z_a z_b}{D_0 \theta r}\right\}, & r_0 < r < r_s. \end{cases}$$

On the other hand, when r is large, Bogolyubov's formula for $F_{ab}^{(k)}$ is correct:

$$F_{ab}^{(k)} = 1 - \frac{e^2 z_a z_b}{D_0 \theta r} e^{-r/r_d}. \quad (9'')$$

It follows from Eqns. (9') and (9'') that the expressions for $F_{ab}^{(k)}$ for large and small distances are directly interconvertible in the intermediate region, where

$$\exp(-r/r_d) \approx 1,$$

$$\exp\left(-\frac{e^2 z_a z_b}{D_0 \theta r}\right) \approx 1 - \frac{e^2 z_a z_b}{D_0 \theta r}.$$

We must also note that Eqns. (9') and (9'') can be combined by means, for example, of an interpolation formula of the following type†:

$$F_{ab}^{(k)}(r) = \begin{cases} 0, & r < r_0, \\ \exp\left\{-\frac{e^2 z_a z_b}{D_0 \theta r} e^{-r/r_d}\right\}, & r > r_0. \end{cases} \quad (10)$$

Transition to the corresponding potential $\Phi_{ab} = \Psi_{ab}^{(k)} + \Psi'_{ab}$ may be effected by Bogolyubov's method by introducing a system of approximations in terms of correlations²¹. Using this method, the following expansion for the energy of the system can be obtained in the present case:

$$\Delta F = -\theta \ln Q \quad (Q = \text{configurational integral}),$$

$$\Delta F = \Delta F(\Psi^k) - \frac{\theta}{2} \sum_{a,b} \frac{N_a N_b}{v^2} \int f_{ab}(q, q') F_{ab}^{(k)}(q, q') dq dq' + \dots \quad (11)$$

where $F_{ab}^{(k)}$ is the correlation function defined by Eqn. (10), and $f_{ab}(q, q')$ has the following form:

$$f_{ab}(q, q') = \exp\left\{-\frac{1}{\theta} \Psi'_{ab}(|q - q'|)\right\} - 1. \quad (12)$$

Using for the free energy of the system $\Delta F(\Psi^k)$, derived from the potential $\Psi_{ab}^{(k)}(r)$, the general statistical formula²² and introducing explicit expressions for $f_{ab}(q, q')$ and $F_{ab}^{(k)}(q, q')$, we finally obtain

$$\Delta F = N \frac{2\pi e^2}{v D_0} \sum_{a,b} n_a n_b z_a z_b \int_0^\infty \int_0^\infty \left[\exp\left\{-\frac{e^2 z_a z_b}{D_0 \theta r} e^{-r/r_d}\right\} - 1 \right] r dr d\tau -$$

$$- N \frac{2\pi}{v} \theta \sum_{a,b} n_a n_b \int_0^\infty \left[\exp\left\{-\frac{1}{\theta} \Psi'_{ab}(r)\right\} - 1 \right] \exp\left\{-\frac{e^2 z_a z_b}{D_0 \theta} \frac{e^{-r/r_d}}{r}\right\} r^2 dr. \quad (13)$$

If allowance is made for the fact that

$$\Psi'_{ab}(r) = \begin{cases} 0, & r > r_s, \\ U_{a,b}(r) - e^2 z_a z_b / D_0 r, & r_0 < r < r_s, \end{cases}$$

and that in the range $r_0 < r < r_s$

$$e^{-r/r_d} \approx 1, \quad (14)$$

the above result can be simplified:

$$\Delta F = N \frac{2\pi e^2}{v D_0} \sum_{a,b} n_a n_b z_a z_b \int_0^\infty \int_0^\infty \left[\exp\left\{-\frac{e^2 z_a z_b}{D_0 \theta r} e^{-r/r_d}\right\} - 1 \right] r dr d\tau -$$

$$- N \frac{2\pi}{v} \theta \sum_{a,b} n_a n_b \int_{r_0}^{r_s} \left[\exp\left(-\frac{1}{\theta} U_{ab}(r)\right) - \exp\left\{-\frac{e^2 z_a z_b}{D_0 \theta} \frac{e^{-r/r_d}}{r}\right\} \right] r^2 dr.$$

We shall now examine certain special cases.

If the effect of ion solvation is ignored, i.e.,

$$U_{ab}(r) = e^2 z_a z_b / D_0 r,$$

and the ionic radii are sufficiently large,

$$r_0 \gg \max_{(a,b)} \left| \frac{e^2 z_a z_b}{D_0 \theta} \right|, \quad (15)$$

then the second term disappears and the integrand in the

† This formula was derived in a different way by Tolmachev and Tyablinov¹⁹. However, the above derivation shows that it must be regarded as merely an interpolation formula.

first term may be expanded in series. In this case we obtain the result of the Debye-Hückel theory:

$$\Delta F_D = -\frac{N\theta}{12\pi} \frac{v}{r_d^3} \left(1 - \frac{3}{4} \frac{r_0}{r_d} + \dots\right). \quad (16)$$

If condition (15) does not hold, then

$$\Delta F = N \frac{2\pi e^2}{D_0 v} \sum_{a,b} n_a n_b z_a z_b \int_0^{\infty} \left[\exp \left\{ -\frac{v e^2 z_a z_b}{D_0 \theta r} e^{-r/r_d} \right\} - 1 \right] r dr. \quad (17)$$

As shown by Tolmachev and Tyablinov¹⁹, this expression allows for the effect of ion pairs. Retaining only terms in v/r_d (raised to the first power only), we obtain the following expression for a uni-univalent electrolyte:

$$\Delta F = -\frac{1}{2} N \theta \alpha \left(1 - \frac{v}{4\pi r_d^3}\right) - \frac{N \theta v}{12\pi r_d^3}, \quad (18)$$

$$\alpha = \frac{1}{2v} \int_0^q \exp(e^2/D_0 \theta r) 4\pi r^2 dr, \quad q = \max \left| \frac{e^2 z_a z_b}{D_0 \theta} \right|.$$

This expression for ΔF is the same as that obtained by Bjerrum⁷ who assumed however that the binary interaction potential is throughout of purely coulombic character, whereas the above result is much more general, since it allows at the same time for the effect of ion solvation.

It is also noteworthy that, when condition (15) holds, we can, by retaining only the first term in the series expansion of the exponential in the first integral of Eqn.(17), obtain Guggenheim's result⁹ for ΔF , which provides the theoretical basis for the empirical expression defining the activity coefficient proposed by Brønsted:

$$\log f = A\sqrt{c} + \beta_1 c, \quad (19)$$

where c is the concentration.

If the universal function of the system ΔF is known, we can, for a given $U_{ab}(r)$, find the equation of state, the activity coefficients, the integral heats of dilution, and other thermochemical characteristics. On the other hand, relations of the type of (14) make it possible in principle to estimate the order of magnitude of $U_{ab}(r)$ from experimental data on activity coefficients and other thermodynamic properties of the system.

Some Further Improvements

To determine more exactly the behaviour of $F_{ab}(r)$ at small r ($r < r_0$), we shall now examine the representation of the corresponding potential $\Phi_{ab}(r)$ in form (7). Since $\Phi_{ab}^{(k)}(r)$ can be converted to $\Phi_{ab}(r)$ by the method described above (a system of approximations in terms of correlations), it is necessary to examine first a system of species interacting with each other, the interaction being determined by a binary potential:

$$\Phi_{ab}^{(k)}(r) = \begin{cases} 0, & r < r_a, \\ \frac{e^2 z_a z_b}{D_0 r}, & r > r_a. \end{cases} \quad (20)$$

As before, the distribution functions of such a system are defined by the set of equations (9), where, however, $\Psi^{(k)}$ must be replaced by $\Phi^{(k)}$, as defined in Eqn.(20).

By extending Tolmachev and Tyablinov's method¹⁹ to the present case, we can show that the binary correlation function $F_{ab}^{(k)}(r)$, corresponding to potential (20), is defined in

this case, up to terms with the Debye dimensionless parameter $\epsilon = v/r_d^3$ (raised to the first power only), by the integral equation

$$\ln F_{ab}^{(k)}(q, q') + \frac{1}{\theta} \sum_{(c)} n_c \int \Phi_{ac}^{(k)}(q, q') \ln F_{cb}^{(k)}(q', q') dq' = -\frac{1}{\theta} \Phi_{ab}^{(k)}(q, q'). \quad (21)$$

This can be solved, for example, by the method of three-dimensional Fourier integrals:

$$F_{ab}^{(k)}(z) = \exp \{-G_{ab}(r)\}, \quad (22)$$

where

$$G_{ab}(r) = \frac{2e^2 r_a r_b}{\pi \theta D_0 k^2} \frac{r}{r} \int_0^{\infty} \frac{k \cos r_a k \sin r_b k}{k^2 + \frac{\pi^2}{r^2} \cos r_a k} dk. \quad (23)$$

If, in particular, we assume here that $r_a = 0$, then it is readily seen from Eqn.(23) that when r is large, $F_{ab}^{(k)}(r)$ becomes the Bogolyubov distribution function:

$$\Delta F(\Phi^{(k)}) = -\frac{2\pi N e^2 T}{V D_0} \int \frac{dT}{T^2} \sum_{a,b} n_a n_b z_a z_b e^{-G_{ab}(r)} r dr. \quad (24)$$

In the general case the free energy of the system ΔF , due to interionic interaction, is defined by an expansion of the type

$$\Delta F = \Delta F(\Phi^{(k)}) + \frac{2\pi \theta}{3V} r_0^3 \sum_{a,b} N_a N_b - \frac{2\pi \theta}{V} \sum_{a,b} N_a N_b \int_{r_0}^{r_a} \exp[-G_{ab}(r)] \left\{ \exp \left[-\frac{U_{ab}(r)}{\theta} \right] - 1 \right\} r^2 dr + \dots \quad (25)$$

where the missing terms correspond to approximations of a higher order, in terms of correlations and in terms of the dimensionless Debye parameter v/r_d^3 for the function $F_{ab}^{(k)}(r)$. The function $G_{ab}(r)$ in Eqn.(25) is defined by Eqn.(23), and $U_{ab}(r)$ is an arbitrary function characterising the interionic interaction potential in the region $r_0 < r < r_a$.

Depending on the conditions, an explicit expression for $\Delta F(\Phi^{(k)})$ in Eqn.(25) may be obtained either by introducing an equivalent reversible charging process or by integrating the expression for the electrostatic part of the interaction energy $E(\Phi^{(k)})$ with respect to temperature (Gibbs-Helmholtz integral):

$$\Delta F(\Phi^{(k)}) = -T \int \frac{E(\Phi^{(k)})}{T^2} dT. \quad (26)$$

For example, if r_a can be regarded as a function of temperature only, it is more convenient to introduce a reversible charging process, when an explicit expression for $\Delta F(\Phi^{(k)})$ is found from the relation

$$\Delta F(\Phi^{(k)}) = N \frac{2\pi e^2}{D_0 v} \sum_{a,b} n_a n_b z_a z_b \int_0^1 \int_0^1 \left\{ \exp[-\tilde{G}_{ab}(r; \tau)] - 1 \right\} r dr d\tau, \quad (27)$$

where

$$\tilde{G}_{ab}(r; \tau) = \frac{2e^2 r_a r_b}{\pi \theta D_0} \frac{r}{r} \int_0^{\infty} \frac{k \cos r_a k \sin rk}{k^2 + \frac{\pi^2}{r^2} \cos r_a k} dk, \quad (28)$$

whereas calculation of $\Delta F(\Phi^{(k)})$ from the Gibbs-Helmholtz relation leads to the following result:

$$\Delta F(\Phi^{(k)}) = -\frac{2\pi N e^2 T}{v D_0} \int \frac{dT}{T^2} \sum_{a,b} n_a n_b z_a z_b e^{-G_{ab}(r)} r dr. \quad (29)$$

In the integration of $E(\Phi^{(k)})$ with respect to T it is necessary to take into account the possible temperature dependence of the parameter r_a .

It should be noted that in the general case the above integrals are not employed in a finite form. In the limiting

case of very dilute solutions the following relation (symmetrical binary electrolyte) is obtained for $\Delta F(\Phi^R)$:

$$\Delta F(\Phi^R) = -\frac{2\pi\epsilon^2}{3D_0} N z^2 \left(1 + \frac{3}{20} r_s^2 \kappa^2 + \dots\right), \quad (30)$$

which passes into the limiting Debye-Hückel equation when $r_s = 0$. If the difference between the real potential $\Phi_{ab}(r)$ and the coulombic potential is disregarded in the region $r_0 < r < r_s$ (model of completely rigid spheres), then assuming that $r_s = r_0$ throughout and expanding $\exp[-G_{ab}(r)]$ in series, we obtain from Eqns.(25)–(30) the following expression for dilute solutions:

$$\Delta F = -\frac{2\pi\epsilon^2}{3D_0} \left(1 + \frac{3}{20} r_0^2 \kappa^2 + \dots\right) + \frac{2\pi\epsilon^2}{3V} r_0^2 \sum_{a,b} N_a N_b, \quad (31)$$

which is identical with Bazarov's result²¹.

Further analysis of the above results and the calculation of activity coefficients, integral heats of dilution, and other thermochemical characteristics of solutions of strong electrolytes are described in another paper.

Calculation of the Heat of Dilution

On the basis of the above results, it is possible to calculate the thermodynamic characteristics of a system, such as activity coefficients, integral heats of dilution, etc. From the definition of the total heat of dilution†, we have

$$\Delta H = T^2 \frac{\partial}{\partial T} \left(\frac{\Delta F}{T} \right), \quad (32)$$

where the derivatives are obtained at constant N and p , i.e.,

$$\Delta H = T^2 \left[\frac{\partial}{\partial T} + \frac{\partial D}{\partial T} \frac{\partial}{\partial D} + \frac{\partial V}{\partial T} \frac{\partial}{\partial V} + \frac{\partial r_0}{\partial T} \frac{\partial}{\partial r_0} + \frac{\partial r_s}{\partial T} \frac{\partial}{\partial r_s} + \frac{\partial q}{\partial T} \frac{\partial}{\partial q} \right] \left(\frac{\Delta F}{T} \right). \quad (33)$$

As before, here r_0 is the radius of an unsolvated ion, r_s the radius of the solvation shell, and q the association parameter. Evaluation of ΔH in the general case requires numerical calculations; the expression for ΔH also depends on the particular type of potential of short-range forces. For a z - z -valent electrolyte and low concentrations, the calculation simplifies, since it can be readily shown that in this case the general expression for ΔF yields

$$\Delta F = -\frac{1}{2} N 0 \alpha (1 - v/4\pi r_s^3) - N 0 v/12\pi r_s^3 - N \frac{2\pi}{v} 0 \sum_{a,b} n_{ab} \int_{r_0}^{r_s} \left[\exp \left\{ -\frac{1}{\theta} U_{ab}(r) \right\} - \exp \left\{ -\frac{e^2 r_a r_b}{D_0 r} \right\} \right] r^2 dr. \quad (34)$$

In the third term the components determined by ion pairs of the same sign are small compared with those arising from ion pairs of opposite signs. This term is formally identical with the corresponding expression in Guggenheim's theory⁹. However, it must be emphasised that Guggenheim's result for ΔF does not take into account the influence of long-range (coulombic) forces on the effect of ion pairs, the concentration dependence of the free energy of solvation

also being neglected. The expression for ΔH , corresponding to ΔF as defined in Eqn.(25), may be put in the following form:

$$\Delta H = \Delta H_D + \Delta H_c + \Delta H_p, \quad (35)$$

where ΔH_D is the Debye term, ΔH_c represents Bjerrum's correction, and ΔH_p characterises the influence of short-range forces:

$$\Delta H_D = \frac{e^2 N}{D_0 r_d} \left(1 + \frac{\partial \ln D_0}{\partial \ln T} + \frac{T\phi}{3} \right) \approx A_D V \bar{c},$$

$$\Delta H_p = RT^2 N \times 10^{-3} \left(\phi\beta - \frac{\partial\beta}{\partial T} - \frac{\partial D}{\partial T} \frac{\partial\beta}{\partial D} - \frac{\partial r_0}{\partial T} \frac{\partial\beta}{\partial r_0} - \frac{\partial r_s}{\partial T} \frac{\partial\beta}{\partial r_s} \right) c \approx A_p c,$$

$$\Delta H_c = -\frac{1}{2} N k T^2 \left(\frac{\partial\alpha}{\partial T} + \frac{\partial D}{\partial T} \frac{\partial\alpha}{\partial D} + \frac{\partial V}{\partial T} \frac{\partial\alpha}{\partial V} + \frac{\partial r_0}{\partial T} \frac{\partial\alpha}{\partial r_0} + \frac{\partial q}{\partial T} \frac{\partial\alpha}{\partial q} \right) c \approx A_c c.$$

Here $\phi = (1/V)(\partial V/\partial T)$ is the coefficient of thermal expansion, and α and β are respectively defined by the following formulae:

$$\alpha = \frac{1}{2v} \int_{r_0}^{r_s} \exp(e^2/D_0 r) 4\pi r^2 dr, \quad \beta = \int_{r_0}^{r_s} 4\pi r^2 (e^{-V_s(r)/kT} - e^{e^2 r_a r_b / D_0 r}) r dr. \quad (36)$$

SUMMARY

1. Thermodynamic functions of a system in an explicit form have been sought on the basis of an interionic potential of a fairly general type.
2. The present systematic statistical theory follows directly from Gibbs' distribution for a system of interacting species.
3. Introduction of a general potential, which at large distances approximates to Coulomb's law and at small distances to the potential of short-range forces, makes it possible to extend the theory to concentrations higher than the "Debye concentrations".
4. In particular the theory provides a theoretical basis for the activity coefficient expression given by Brönsted.
5. On the basis of the theory, it is possible to calculate the activity coefficients and heats of dilution of solutions of any structure.

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† This expression is correct provided that the effect of the compressibility of the solution and the pressure dependence of the dielectric constant are neglected.

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ISOMORPHISM OF THE CRYSTALS OF PHOSPHATE COATINGS

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A solution containing the preparation "Mazhef", sodium nitrate, and sodium fluoride was suggested¹ for the cold phosphatising of ferrous and non-ferrous metals, and subsequently investigated in detail²⁻⁴. Although the composition of the phosphatising solution may be similar, the properties of coatings formed on different metals and by different chemical and electrolytic methods are not identical. They differ in structure and in their strength, as well as surface, protective, and other properties². It could be supposed that the variation in the properties of the coatings was due to differences in their chemical and phase constitution associated with variations in the conditions of crystallisation of the insoluble phosphates.

The phase constitution of phosphate coatings has been quite inadequately studied, the literature on this topic being very limited⁵⁻⁸. A study has been made of the chemical and phase constitution of phosphate coatings obtained under optimum operating conditions² on iron, zinc, aluminium, and magnesium by the methods of cold chemical and electrolytic phosphatising in a solution of Mazhef containing activating additives. The spectra were determined by G. S. Karetnikov on an ISP-22 quartz spectrograph with an a.c. arc generator as exciting source. The slit width was 0.05 mm, and the time of exposure on a photographic plate of spectral type was 3–20 sec. The analysis was based on the ultra-violet emission spectra.

The X-ray diffraction phase analysis of the coatings was carried out by the present writer together with I. S. Strel'tsov, using a URS-70k-1 general-purpose X-ray diffraction apparatus and a camera of diameter 90.2 mm with copper radiation (nickel filter). The current was 14–15 mA, the voltage 30–32 kV, the diameter of the specimen 0.6 mm, the exposure time $2\frac{1}{2}$ h, and the conditions of development standard.

EXPERIMENTAL

It was of interest to determine the content of manganese, iron, and zinc in the phosphate coatings and also aluminium and magnesium in the case of coatings on these two metals. Table 1 shows the results of a chemical analysis of the coatings carried out in collaboration with N. A. Kiseleva, while Figs. 1–3 reproduce the spectrograms of the coatings. Fig. 4 gives for comparison the spectrogram of a phosphatising solution containing (per litre) 60 g of Mazhef, 50 g of zinc nitrate, and 4 g of sodium fluoride. The results of the spectroscopic and chemical analyses show that the composition of the coatings is different on different metals and depends on the method of phosphatising. All coatings have a large content of manganese and zinc.

Ions of the metals subjected to phosphatising are present in least amount in coatings obtained by cathodic phosphatising, and in greatest amount in those obtained by a.c. electrolytic phosphatising.

From the analytical results, these phosphate coatings could be expected to contain a series of phosphates: phosphates (all hydrogen replaced by metal) and hydrogen phosphates of manganese, zinc, and iron, and also the phosphates (all hydrogen replaced) of aluminium and magnesium in the case of coatings on these two metals. Table 2 gives data on the interplanar spacings and the intensities of the three strongest lines for some insoluble phosphates of the above metals.

TABLE 1. Chemical composition of coatings obtained by cold phosphatising methods (%)*.

Metal, phosphatising method	Fe	Mn	Zn	Al	Mg	P
Al, chemical	—	6.0	22.4	11.5	—	21.2
Al, cathodic	—	9.0	23.7	3.7	—	17.1
Fe, a.c. electrolytic	5.9	7.0	31.7	—	—	12.6
Fe, chemical	2.2	14.1	30.0	—	—	10.5
Fe, cathodic	1.2	10.1	32.0	—	—	12.0
Mg, chemical	—	19.0	21.6	—	2.3	11.2
Zn, chemical	—	9.2	32.0	—	—	13.0

* Composition of phosphatising solution (in g litre⁻¹): Mazhef 60, zinc nitrate 25–50, sodium fluoride 0.5–8 (depending on the nature of the metal to be phosphatised)².

TABLE 2. Interplanar spacings of the three most intense lines for crystals of various insoluble phosphates^{9,10}.

Compound	Interplanar spacings, Å			Intensities (on 1–100 scale)		
Mn ₃ (PO ₄) ₂	3.28	2.87	2.53	100	75	80
Mn ₃ (PO ₄) ₂ ·3H ₂ O	3.35	2.60	3.01	100	100	80
MnHPO ₄ ·3H ₂ O	3.50	4.75	2.77	100	80	80
FePO ₄	3.47	3.02	4.39	100	40	23
Fe ₃ (PO ₄) ₂ ·8H ₂ O	no data	—	—	—	—	—
FeHPO ₄	ditto	—	—	—	—	—
FePO ₄ ·2H ₂ O	4.36	5.50	3.12	100	80	80
"	3.30	3.65	4.20	100	60	50
Zn ₃ (PO ₄) ₂	3.60	3.07	3.99	100	84	82
Zn ₃ (PO ₄) ₂ ·4H ₂ O	2.84	4.58	1.93	100	75	50
"	2.85	9.10	3.47	100	40	40
Zn ₃ (PO ₄) ₂ ·2H ₂ O	1.81	2.93	3.19	100	40	33
AlPO ₄	3.32	1.38	4.27	100	100	80
"	3.32	1.38	1.82	100	96	86
"	2.18	1.71	1.39	100	100	100
AlPO ₄ ·2H ₂ O	2.72	1.96	2.22	1	2	3
Mg ₃ (PO ₄) ₂	no data	—	—	—	—	—
Mg ₃ (PO ₄) ₂ ·3H ₂ O	3.45	3.05	5.90	100	80	40
Mg ₃ (PO ₄) ₂ ·4H ₂ O	4.10	5.20	3.23	100	80	80