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V. I. Kuz' min, V. K. Prokhorenko, O. Ya. Samoilov, and I. Z. Fisher

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Abstract

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V. I. Kuz' min, V. K. Prokhorenko, O. Ya. Samoilov, and I. Z. Fisher

On the Temperature Dependence of the Coordination Numbers of Particles in Liquid Solutions

(Presented by Academician I. I. Chernyaev on 21 VI 1961)

One of the basic characteristics of the structure of a liquid is the average coordination number of its particles. The close connection of the coordination number with the thermal (above all, translational) motion of liquid particles has already been noted more than once ([1–3]). This connection is clearly manifested in the high level of fluctuations of coordination numbers ([4,5]). Of great interest is the question of the temperature dependence of coordination numbers. This dependence acquires special significance in the case of liquid solutions, since changes in the coordination number with temperature that are different for particles of different kinds lead to a substantial rearrangement of the structure of the solution as the temperature changes: a regrouping of particles occurs, as a result of which the content in the solution of solvent particles that do not enter the nearest environment of solute particles ("free" solvent) changes.

Let us have a binary solution consisting of particles of kind a (solvent) and kind b (solute). The change in the content of free solvent in the solution with changing temperature is connected with the quantity

$$\delta_b = \left(\frac{\partial Z_{ba}}{\partial T}\right)_p - \left(\frac{\partial Z_{aa}}{\partial T}\right)_p, \tag{1}$$

where Z_{ba} is the average number of particles a surrounding a particle b in the solution, and Z_{aa} is the same quantity for solvent particles.

The indicated rearrangement of the structure is very important, in particular, for aqueous electrolyte solutions. Precisely for this reason, a number of properties of such solutions depend in many respects on the difference between the temperature changes of the coordination numbers of ions in aqueous solutions (the average numbers of water molecules constituting the immediate environment of a given ion in the solution) and the temperature change of the coordination

Fig. 1

Figure 1: Fig. 1

number of molecules in water. In work ([6]), using a thermochemical method, the temperature changes of the coordination numbers of a number of monatomic ions in dilute aqueous solutions were determined. It was established that the dependence of the corresponding quantities δ_i on the crystallochemical radius of the ion r_i is, on the whole, represented by a curve with a maximum at $r_i > r_{H_2O}$, where r_{H_2O}—the "radius" of the water molecule—is taken approximately equal to 1.38 Å.

It is of interest to determine the quantities δ_b for model liquid solutions. Let the solution be a collection of a large number of spheres of diameter D_a, forming a "liquid," to which a small number of spheres of diameter D_b has been added. The coordination number Z_{ba} is equal to

$$Z_{ba} = 2\lambda \int_0^{\rho_{\min}^{ba}} g_{ba}(\rho)\rho^2 d\rho, \tag{2}$$

where $\lambda = 2\pi D_a^3/v$ is the dimensionless density of the system; $g_{ba}(\rho)$ is the radial distribution function for a pair of particles b and a; $\rho_{\min}^{ba}$ is the dimensionless distance from the origin to the first minimum of the integrand

expressions. Z_{aa} is expressed analogously. The functions $g_{ba}(\rho)$ and $g_{aa}(\rho)$ were found in the form of segments of power series in λ, by solving Bogolyubov' s integral equations (7) for these functions in the case of a system of spheres. Thus, it was assumed that $g_{ba}(\rho) = 0$ for $\rho < (1+\varepsilon)/2$, and

$$g_{ba}(\rho) = 1 + \lambda g_{ba}^{(1)}(\rho) + \lambda^2 g_{ba}^{(2)}(\rho) + \cdots \tag{3}$$

for $\rho > (1+\varepsilon)/2$. The functions $g_{ba}^{(1)}$ and $g_{ba}^{(2)}$ depend on the concentration of the solution n and on the ratio of the particle diameters $\varepsilon = D_b/D_a$. The function $g_{aa}(\rho)$ is obtained from (3) at $\varepsilon = 1$. The series (3) were truncated by us at the terms written out, but it can be shown that even at not small values of λ this does not lead to substantial errors (although the whole calculation is then only qualitatively correct). From (2) one can directly determine $(\partial Z_{ba}/\partial\lambda)$ and $(\partial Z_{aa}/\partial\lambda)$, and for the system of hard spheres these quantities turn out to be independent of temperature. The derivatives of interest to us, $(\partial Z_{ba}/\partial T)_p$ and $(\partial Z_{aa}/\partial T)_p$, can be found from the relation

$$\left(\frac{\partial Z_{ba}}{\partial T}\right)_p = \frac{\partial Z_{ba}}{\partial \lambda}\left(\frac{\partial \lambda}{\partial T}\right)_p \tag{4}$$

Fig. 1

Fig. 2

Figure 2: Fig. 2

with the aid of the equation of state of the system of spheres (7)

$$\frac{2\pi D_a^3}{kT}\, p = \lambda \left\{ 1 + \frac{1}{3}\lambda g_{aa}(1, \lambda) \right\}, \tag{5}$$

where for a dilute solution we have put $n \to 0$.

Similar calculations were carried out by us at $\lambda = 5$, which approximately corresponds to the density of a real aqueous solution, for 7 values of ε: 0.5; 0.75; 1.00; 1.25; 1.5; 1.75; and 2.00. The results of the calculations are presented in Fig. 1 for the quantity $T\delta_b$ according to (1) as a function of ε. For comparison, Fig. 2 gives the quantities δ_i for monatomic ions found in work (6). The obvious correspondence between the results of calculations for the system of spheres and the experimental results for aqueous electrolyte solutions is important in connection with elucidating the nature of the dependence $\delta_i(r_i)$ for these solutions, in particular the question of the extent to which the dependence $\delta_i(r_i)$ is determined by the specific interaction of ions and water molecules and to what extent it is determined by the ratio of the sizes of the solution particles (6).

Fig. 2

Belorussian State University
named after V. I. Lenin

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.

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