

Stability of Anionic Complexes in Halide Melts of Bivalent Metals

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Abstract—The effect of volume variation at the possible dissociation equilibria of $(MX_4)^{2-}$ anionic complexes in halide melts of bivalent metals are analyzed in terms of the mean-sphere approximation (MSA) of the statistical theory. Within the framework of the simplified model of charged hard spheres of different diameters and valences, the complete system of equilibrium equations is obtained, i.e., equations of the law of mass action and equations of state. This system makes possible self-correlated calculations of both the equilibrium concentration of autocomplexes and the melt density. It is shown that the simplest approximation of the complex diameter as the treble diameter of simple ions overestimates the effects of volume variations when considering dissociation. Taking into account the superposition of spheres makes it possible to describe the smoother volume variations with the temperature.

Keywords: chemical equilibrium, nonideal systems, dissociation of complexes, ionic liquids, anionic complexes, law of mass action, equations of state

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INTRODUCTION

Quite recently 50 years passed since the publication of a study [1] in which a model of the autocomplex structure of molten halides was put forward. When analyzing the spectroscopic, thermodynamic, and transport properties of fused salts, Smirnov et al. [2–5] arrived at the conclusion that many peculiarities in the temperature and concentration dependences of the aforementioned properties can be understood if one assumes the existence of anionic complexes $(MX_n)^{m-}$. These ideas played an important role in understanding the structure of fused salts and provided noticeable progress in studying physicochemical properties. During the subsequent half-century, the school of M.V. Smirnov accumulated and interpreted vast experimental data on physicochemical properties of fused halides of alkali, alkali-earth, and rare-earth metals and also of their various mixtures. The analogous ideas were also voiced in the 70s when analyzing EPR spectra of fused salts [6].

However, as regards its theory, the autocomplex model (and the general model of complexation in fused salts) is insufficiently elaborated so far. Attention was focused on the internal energy of autocomplexes which was calculated to be compared with the standard enthalpy of the melt. This approach made it possible to follow the changes in calorific properties when passing from one salt to another in the series of halides of alkali, alkali-earth metals, etc. For the typical dis-

cussion of calculations of the internal energy of autocomplexes in terms of the conventional model pair potential, followed by calculation of pair bondings of the nearest neighbors within the preset geometry, see [7]. It should be stressed that the concentration of autocomplexes was assumed to be maximum possible. As a result, the calculations of the autocomplex concentration in salt melts were beyond the scopes of studies by Smirnov and its followers.

In cycles of studies [8–10], the problem of complex formation in binary liquid mixtures of salts of multivalent metals with alkali-metal halides (AMH) was developed further as regards statistics and thermodynamics. For example, for binary salt systems of calcium chloride with AMH [8] the existence of the tetrahedral complex $(CaCl_4)^{2-}$ in chemical equilibrium with free calcium cations and chlorine anions was assumed. The complex as a whole was characterized by the radius of a sphere circumscribed about tetrahedron, while the statistical-mechanical part of the problem was reduced to the model of charged hard spheres with different diameters. The authors derived the law of mass action (LMA) and then calculated the complex concentration in the melt. True enough, this calculation did not involve the estimation of various contributions into the free energy of autocomplex associated with its internal degrees of freedom (vibrational and rotational), which were ignored. It was assumed that the main contribution to the equilibrium

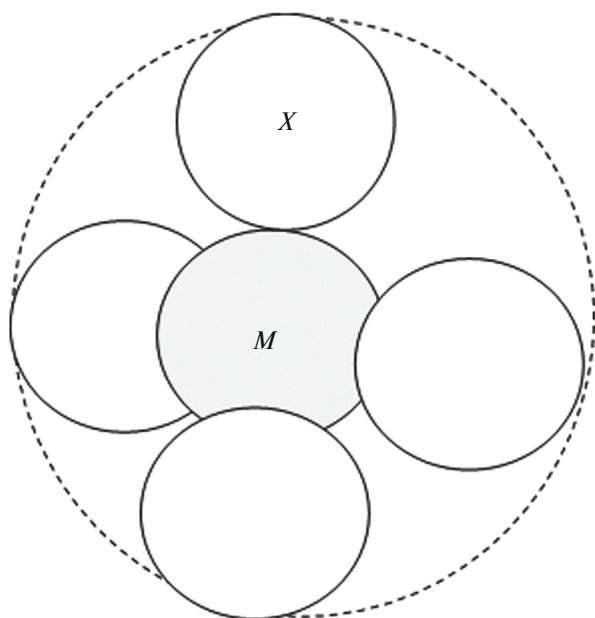


Fig. 1. Geometrical model of autocomplexes $(MX_4)^{2-}$.

constants was made by the dissociation energy determined by coulomb interaction. It is important that the above authors noted the necessity of taking into account the electrostatic interaction of all ions (simple and complex) in the salt melt when calculating the chemical equilibrium.

It is well known that even in dilute solutions of strong electrolytes, one must return to the principle of the free-energy minimum as regards the number of particles involved in the reaction [11]. As a result, the LMA takes its most general form with the activity coefficient that should be calculated with regard to electrostatic interactions of all particles involved in the reaction. Generalizing the classical notations on complex formation in fused salts, it is necessary to take into account also the specifics of dissociative equilibria in the ionic medium with electrostatic interaction and also the finite size of ions (excluded volume). The important deviation of the considered problem on the chemical equilibrium in fused salts from that in dilute solutions of strong electrolytes consists in the fact that here one has to find the minimum of free energy of Gibbs, rather than of Helmholtz, because the equilibrium mole volume of the melt or its average density are not constant. Indeed, in dilute solutions, the equilibrium volume is preset by the conditions of the problem, i.e., by the initial volume of solvent. On the other hand, for a salt melt, any change in the concentration of free ions and complexes, i.e., a shift of dissociation equilibrium in any direction, inevitably induces changes in the average density or volume of the system. Thus, the average density should be self-correlated with the concentration of autocomplexes at the fixed external pressure and temperature, i.e., by using

the equation of state too. As a result, the calculation of the concentration of autocomplexes inevitably becomes a self-correlated problem on solving the system of LMA equations and melt's equation of state.

The preliminary estimates in terms of the simplified model of a salt melt which uses the complete theory of Debye–Hückel for the electrostatic part of free energy and the van der Waals approach for the contribution of excluded-volume forces have shown that a temperature region exists above which the complexes become unstable [12, 13]. On our opinion, this result reflects the fact that the decrease in the electric energy of the ionic melt formed by particles with the minimum size always prevents the formation of larger complex anions due to the increase in the mean field formed by the ionic atmosphere. Moreover, the work on formation of a larger cavity in liquid (against the forces of excluded volume) also considerably increases when large particles are formed. However, the reason for applying the Debye–Hückel model to the problem on chemical equilibrium in a salt melt apparently was to carry out qualitative and rather rough analysis of the problem of complexation. The next step in the development of the statistical theory of autocomplexes is to take into account the discrete nature of the ionic atmosphere. This can be achieved within the framework of the mean-sphere approximation (MSA) by self-correlated calculations of the packing factor of simple and complex ions in salt melt at the fixed temperature and pressure.

Thus, this study is aimed at analyzing the thermodynamics of complex formation in halide melts of bivalent metals based on the simplified model of charged hard spheres (with anions and cations of the equal diameter), which takes into account the effects of volume variation upon shifts of chemical equilibrium at dissociation of composite complex anions. The effect of superposition of atoms inside the complex on the position of chemical equilibrium is also discussed on the qualitative level.

THEORY

Model

Now, we try to formulate the model for melts of salts such as $M_{1/3}^{2+}/X_{2/3}^-$ (for convenience, the original chemical formula MX_2 is transformed per one atom). We assume that the following chemical reaction to form the composite (complex or autocomplex) anion can occur:

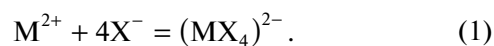


Figure 1 shows the geometrical model of such complex.

The number of atoms in such system $N = N_M^0 + N_X^0$, where $N_M^0 = 1/3 N_X^0$.

We can write the ratios between numbers of free ions and autocomplexes based on the laws of conservation. From the condition of material balance, it follows that $N_M = N_M^0 - N_C$; $N_X = N_X^0 - 4N_C$. Hence, the total number of atoms is $N = N_M + N_X + 5N_C$.

Next, taking into account the condition of electro-neutrality $(+2)N_M + (-1)N_X + (-2)N_C = 0$, we obtain $N_M = 1/3 N - N_C$ and $N_X = 2/3 N - 4N_C$. The number of particles $N_P = N - 4N_C$ is smaller than the number of atoms.

Let us express the mole fractions in the ternary system of simple ions and complexes through a single independent variable, i.e., the concentration of auto-complex groups: $n_C \equiv N_C/N_P$. Then, the mole fractions of cations and anions are equal to $n_M = 1/3(1 + n_C)$. The value that characterizes the average number of atoms per particle is $\chi \equiv N/N_P = 1 + 4n_C$.

Free Energy

It is evident that the main difficulty in developing the theory of fused salts prone to complexation is the explicit consideration of sizes and charges of simple and complex ions in the system. The simplest model that allows taking into account both the repulsion of ions at small distances and the coulomb interaction is the model of a liquid with charged hard spheres of different diameters and electric valences. Then, the Helmholtz free energy of such liquid can be represented as the sum of ideal, hard-sphere, and coulomb terms

$$F = F_{id} + F_{hs} + F_q. \quad (2)$$

To perform clear analysis of the consequences of this theory, we assume for simplicity that the sizes of free cations and anions coincide $d_M = d_X = d$ and the size of autocomplex $d_C = 3d$ is determined by the diameter of the sphere circumscribed about this molecular formation inside which the mass centers of cation and anion are localized at the minimum possible distance d .

Now we estimate the dimensionless density of atoms as $\rho = d^3 N/V$, where V is the volume occupied by the system.

Ideal contribution. Let us use the well-known formula for the mixture of polyatomic gases [14]:

$$F_{id} = -kT \sum_i N_i \ln Z_i, \quad (3)$$

where $Z_i = Z_i^{el} Z_i^{vib} Z_i^{rot} Z_i^{tr}$ is the molecular-statistical integral which we represent as the product of partial statistical integrals describing the various degrees of freedom (electronic, vibrational, rotational, and translational, respectively).

We approximate the electronic part by the Boltzmann probability of the nondegenerate ground state

$$Z_i^{el} \approx e^{-E_i^0/kT} + \dots$$

The translational part is written conventionally as

$$Z_i^{tr} = \frac{eV}{N_i \lambda_i^3}, \quad \text{where } \lambda_i = \left(\frac{2\pi\hbar^2}{m_i kT} \right)^{1/2}$$

is the thermal wavelength, V is the volume occupied by the system, \hbar and k are the constants of Plank and Boltzmann, respectively, m_i are masses of particles, e is the Napierian base.

Vibration and rotation are possible only for auto-complexes and make a weaker pre-exponential (power) contribution to the dependence of its concentration on the temperature: $Z_c^{vib} \approx \frac{1}{1 - e^{-\hbar\omega/kT}}$,

$$Z_i^{rot} \approx \frac{(2kT)^{3/2} (\pi I_1 I_2 I_3)^{1/2}}{\sigma \hbar^3}, \quad \text{where } \omega \text{ is the frequency of}$$

valence oscillations in the complex, $I \equiv I_1 = I_2 = I_3$ are the moments of inertia along principal axes (for tetrahedron, $I = 16m_X a$), σ is the symmetry number (for tetrahedron, $\sigma = 12$), m_X is the halide ion mass. Furthermore, for simplicity, we used the Einstein model with the only frequency of normal vibrations, because the vibrational degrees of freedom make insignificant, i.e., pre-exponential, contribution to the temperature dependence of concentration of auto-complexes for problem under consideration.

It is convenient to pass to the change in free energy by reckoning the ideal contribution of energy from the ground-state energy of free simple cation and anion in the absence of complexes and defining the dissociation energy as the difference between the corresponding ground electron terms of ions and autocomplex

$$\begin{aligned} \Delta F_{id} = & -E_d N_C \\ & + kT \left\{ N_M \ln \left(\frac{N_M \lambda_M^3}{V} \right) + N_X \ln \left(\frac{N_X \lambda_X^3}{V} \right) \right. \\ & \left. + N_C \ln \left(\frac{N_C \lambda_C^3 Z_C^{vib} Z_C^{rot}}{V} \right) - N_P \right\}, \end{aligned} \quad (4)$$

where $E_d = E_M^0 + 4E_X^0 - E_C^0$, $E_d > 0$ is the energy of dissociation or formation of complexes $(MX_4)^{2-}$.

Hard-sphere contribution to the free energy. To assess the contribution of repulsive forces at small distances upon the interaction of particles, we can use the approximation of the statistical theory of liquids. This approximation is based on the solution of Lebowitz of the system of equations of Percus–Yewick for a mixture of hard spheres with different diameters [15], namely, the approximation of Mansoori–Carnahan–Starling (MCS) [16] which is one of the best approximations as compared with the Monte-Carlo and

molecular-dynamics computer simulations. For our case, the free energy is as follows:

$$F_{\text{hs}} = -\frac{3}{2}NkT[1 - y_1 + y_2 + y_3] + \frac{3y_2 + 2y_3}{1 - \eta} + \frac{3}{2} \frac{1 - y_1 - y_2 - \frac{1}{3}y_3}{(1 - \eta)^2} + (y_3 - 1) \ln(1 - \eta). \quad (5)$$

We designate

$$\eta = \frac{\pi\rho}{6\chi}(n_M + n_X + 27n_C) = \frac{\pi\rho}{6(1 + 4n_C)} \left(\frac{(1 + n_C)}{3} + \frac{2(1 - 2n_C)}{3} + 27n_C \right)$$

—the total packing factor, $y_1 = \frac{d_X + d_C}{\sqrt{d_X d_C}}(\omega_{MC} + \omega_{XC})$,

$$y_2 = \frac{a_2 \sqrt{d_X d_C}}{a_3}(\omega_{MC} + \omega_{XC}), \quad y_3 = 1/\chi(n_M + n_X + 9n_C)^3 \times (n_M + n_X + 27n_C)^{-2}.$$

Indices M, X, and C mark the values pertaining to cations, anions, and complexes, respectively.

Here,

$$a_i = n_M(d_M)^i + n_X(d_X)^i + n_C(d_C)^i,$$

$$\omega_{MC} = \frac{n_M n_C}{\chi} \frac{(d_M - d_C)^2 \sqrt{d_M d_C}}{d^3} (n_M + n_X + 27n_C)^{-1} = \frac{n_C(1 + n_C)}{3(1 + 4n_C)} \frac{(d_M - d_C)^2 \sqrt{d_M d_C}}{d^3} \times \left(\frac{(1 + n_C)}{3} + \frac{2(1 - 2n_C)}{3} + 27n_C \right)^{-1},$$

$$\omega_{XC} = \frac{n_X n_C}{\chi} \frac{(d_X - d_C)^2 \sqrt{d_X d_C}}{d^3} (n_M + n_X + 27n_C)^{-1} = \frac{2n_C(1 - 2n_C)}{3(1 + 4n_C)} \frac{(d_X - d_C)^2 \sqrt{d_X d_C}}{d^3} \times \left(\frac{(1 + n_C)}{3} + \frac{2(1 - 2n_C)}{3} + 27n_C \right)^{-1}.$$

Coulomb contribution to the free energy in the mean-sphere approximation. The contribution of electrostatic interactions of simple and complex ions to the Helmholtz free energy can be taken as Blum's solution of the problem of charged hard spheres with arbitrary diameters and valences in the mean-sphere approximation [17–19]:

$$F_q = -\frac{e^2}{\varepsilon} \left[\sum_i N_i \frac{z_i^2 \Gamma}{1 + \Gamma d_i} + \frac{\pi \Omega V P_n^2}{2\Delta} \right], \quad (6)$$

where

$$\Omega = 1 - \frac{\pi\rho}{2\Delta\chi} \left(\frac{n_M}{(1 + \Gamma d)} + \frac{n_X}{(1 + \Gamma d)} + \frac{27n_C}{(1 + 3\Gamma d)} \right) = 1 - \frac{\pi\rho}{2\Delta(1 + 4n_C)} \times \left(\frac{1 + n_C}{3(1 + \Gamma d)} + \frac{2(1 - 2n_C)}{3(1 + \Gamma d)} + \frac{27n_C}{(1 + 3\Gamma d)} \right),$$

$$P_n = 1 - \frac{\rho}{\Omega\chi} \left(\frac{n_M z_M}{(1 + \Gamma d)} + \frac{n_X z_X}{3(1 + \Gamma d)} + \frac{3n_C z_C}{(1 + 3\Gamma d)} \right) = 1 - \frac{\rho}{\Omega(1 + 4n_C)} \times \left(\frac{(1 + n_C) z_M}{3(1 + \Gamma d)} + \frac{2(1 - 2n_C) z_X}{3(1 + \Gamma d)} + \frac{3n_C z_C}{(1 + 3\Gamma d)} \right),$$

z_i are valences, Γ is the reciprocal Blum length that describes the characteristic scale of attenuation of charge oscillations about the central ion, which must be determined by the coupling equation

$$\Gamma^2 = \frac{2e^2 \pi\rho}{2kT\varepsilon d\chi} (n_M X_M^2 + n_X X_X^2 + n_C X_C^2),$$

$$X_M = \frac{z_M - \frac{\pi d^2}{2\Delta} P_n}{1 + \Gamma d}, \quad X_X = \frac{z_X - \frac{\pi d^2}{2\Delta} P_n}{1 + \Gamma d},$$

$$X_C = \frac{z_C - \frac{\pi(3d)^2}{2\Delta} P_n}{1 + \Gamma d}.$$

Assessment of the Dissociation Energy of Complex

In principle, the dissociation energy of a complex can be calculated by the quantum chemistry methods. However, within the scopes of this study, we can use simple and illustrative approximations. First, for the sake of simplicity, we assume that the complex anion $(MX_4)^{2-}$ has the tetrahedral configuration. Second, if we assume that the chemical bond inside the complex is predominantly ionic, then the binding energy of the pair of nearest neighbors cation-anion within the complex is evidently equal to $z_M e^2 / \varepsilon d$. The dissociation energy in the nearest neighbors approximation is $E_d^0 = 8e^2 / \varepsilon d$, because the $(MX_4)^{2-}$ complex has four such pairs. This method of calculating the dissociation free energy seems to give the reasonable estimate of its upper limit. To roughly assess its lower limit, we can consider also the contribution to the dissociation energy due to the coulomb repulsion of ligands in the second coordination sphere. For a $(MX_4)^{2-}$ complex, the number of such pairs is six and the distance between them can be easily found from the geometry

of tetrahedron, because the height of the pyramid built based on the vertices localized in the mass centers of anions is $3d/2$; hence, its edge is $\frac{3\sqrt{3}}{2\sqrt{2}}d$. We have

$$E_d = 4e^2/\epsilon d \left(1 - \frac{\sqrt{2}}{\sqrt{3}}\right) \approx 0.736e^2/\epsilon d.$$

It is evident that dissociation energy can be sufficiently high, reaching the values of the order of magnitude of several tens of eV. In the below calculations, we use these estimates as the upper (the nearest neighbors) and the lower (the second coordination sphere) limits of its range, when considering the dissociation energy as a parameter of the theory.

Conditions of Chemical Equilibrium at Complex Formation

To derive the equations describing the conditions of equilibrium in the system, allowing for the reaction of complex formation at the constant pressure (P_0) and temperature, it is necessary to find the minimum of the Gibbs free energy

$$\Delta G(V, N_C, T) \equiv \Delta F_{id}(V, N_C, T) + F_{hs}(V, N_C, T) + F_q(V, N_C, T) + P_0V. \quad (7)$$

In the case under consideration, the following two independent variables are responsible for the position of minimum: the mean atomic density and the concentration of autocomplexes. By equating the free-energy derivatives with respect to these variables to zero, we obtain the complete conditions of equilibrium in the system under consideration with chemical reaction (1):

$$\begin{cases} \left(\frac{\partial \Delta G}{\partial N_C}\right)_{V,T} = 0 & \text{(LMA)} \\ \left(\frac{\partial \Delta G}{\partial V}\right)_{N_C,T} = 0 & \text{(EOS)} \end{cases}. \quad (8)$$

The first equation in system (8) represents the law of mass action and can be reduced as follows:

$$\frac{n_C(1+4n_C)^4}{(1+n_C)(1-2n_C)^4} = K_0 \exp\left(\frac{E_d}{kT}\right) \gamma, \quad (9)$$

where $K_0 = \frac{2^4 \lambda^3 \lambda_M^{12} \lambda_X^{12} Z_C^{vib} Z_C^{rot}}{3^5 \lambda_C^3 d^{12}} \rho^4$, γ is the mean activity coefficient which, for the model of charged hard spheres, is the product of the hard-sphere and coulomb parts

$$\gamma = \gamma_q \gamma_{hs}. \quad (10)$$

In the case of complexation reaction under consideration,

$$\gamma_q = \exp\left[\frac{\mu_M^q + 4\mu_X^q - \mu_C^q}{kT}\right]. \quad (11)$$

In the MSA approximation of the model of charged hard spheres (Blum's solution), the contribution of the coulomb interaction for the i th type of particles can be written as follows:

$$\begin{aligned} \mu_i^q &= \frac{e^2}{3ed_i} [4z_i^2 - 2z_i X_i (1 + \Gamma d_i) \\ &+ X_i^2 (1 + \Gamma d_i) (\Gamma d_i - 2)]. \end{aligned} \quad (12)$$

The hard-sphere term in the formula for the mean activity coefficient γ_{hs} is totally analogous to that in Eqs. (11), (12) with substitution of index "hs" for index "q." The expressions for the contributions of hard-sphere interaction to the chemical potentials of simple and composite ions can be written as follows:

$$\begin{aligned} \mu_M^{hs} = \mu_X^{hs} &= kT \left[\left(3 \frac{a_2^2}{a_3^2} - 2 \frac{a_2^3}{a_3^3} - 1 \right) \ln \Delta + \frac{\pi \rho}{2\Delta} \right. \\ &\times \left. \left(\frac{a_2 + a_1}{\chi} + \frac{\pi \rho a_2 a_1}{6\Delta \chi^2} + \frac{a_2^2}{a_3 \Delta \chi^2} - \frac{a_2^3}{3a_3^2 \Delta \chi^2} + \frac{\pi \rho a_2^3}{9a_3 \Delta^2 \chi^2} - \frac{1}{3} \left(\frac{a_2^3}{a_3^3 \chi} - 1 \right) \right) \right], \end{aligned}$$

$$\begin{aligned} \mu_C^{hs} &= kT \left[\left(27 \frac{a_2^2}{a_3^2} - 54 \frac{a_2^3}{a_3^3} - 1 \right) \ln \Delta \right. \\ &- \frac{3\pi \rho}{2\Delta} \left(\frac{a_2 + 3a_1}{\chi} + \frac{3\pi \rho a_2 a_1}{2\Delta \chi^2} \right. \\ &\left. \left. + \frac{3a_2^2}{a_3 \Delta \chi^2} - \frac{3a_2^3}{a_3^2 \Delta \chi^2} + \frac{\pi \rho a_2^3}{a_3 \Delta^2 \chi^2} - \frac{1}{2} \left(\frac{a_2^3}{a_3^3 \chi} - 1 \right) \right) \right], \\ a_i &= n_M (d_M)^i + n_X (d_X)^i + n_C (d_C)^i. \end{aligned}$$

The second equation in system (8) is the equation of state (EOS), i.e., relates the density with external pressure and temperature:

$$\begin{aligned} \frac{P_0 d^3}{NkT} \equiv p_0 &= \frac{p_{id} + p_{hs} + p_q}{\chi}, \quad (13) \\ p_{id} + p_{hs} &\equiv -d^3 (N_p kT)^{-1} \left(\frac{\partial (\Delta F_{id} + \Delta F_{hs})}{\partial V} \right)_{N_C, T} \\ &= \frac{\eta + (1-3y_1)\eta^2 + (1-3y_2)\eta^3 - y_3 \eta^4}{\frac{1}{6} \pi a_3 (1-\eta)^3}, \\ p_q &\equiv -d^3 (N_p kT)^{-1} \left(\frac{\partial \Delta F_q}{\partial V} \right)_{N_C, T} = -\frac{\Gamma^3}{3\pi} - \frac{\pi e^2}{2kT\epsilon d} \left(\frac{P_n}{\Delta} \right)^2. \end{aligned}$$

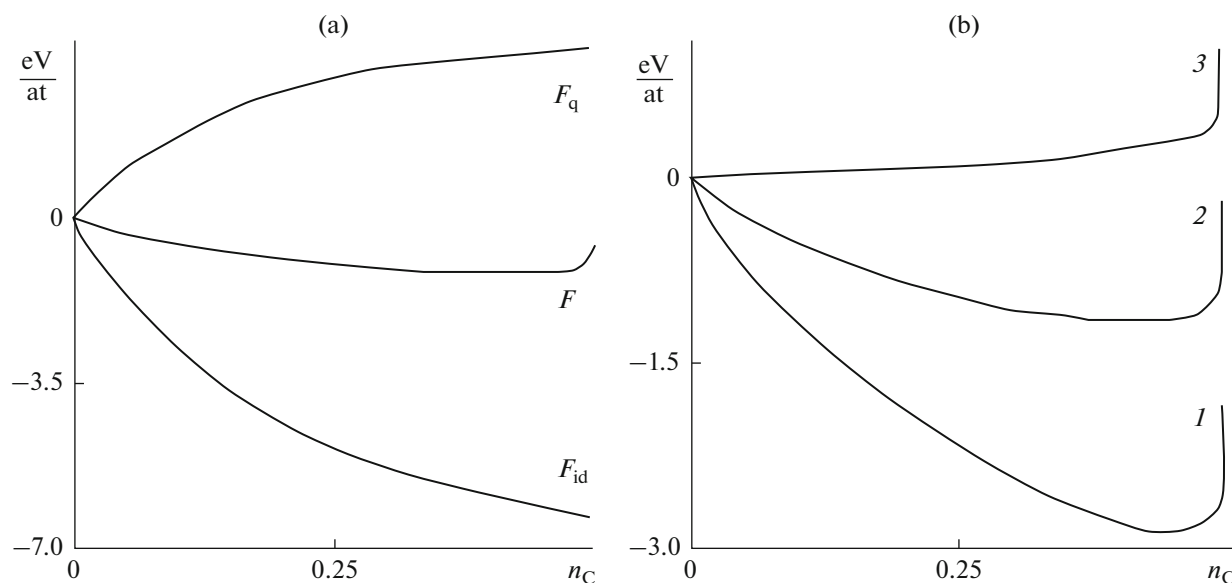


Fig. 2. (a) Typical dependences of different contributions to free energy on the concentration of autocomplexes at the fixed temperature (3500°C) and pressure ($0.6241 \times 10^{-6} \text{ eV/\AA}^3$ corresponds to atmospheric pressure); (b) concentration dependence of the free energy at different temperatures kT/E_d : (1) 0.015; (2) 0.017; (3) 0.019.

Note that the so complicated method of calculating the chemical equilibrium is associated with a very simple reason. Any change in the volume at the constant pressure and temperature inevitably shifts the chemical equilibrium and, vice versa, any change in the concentration of complexes affects the volume. As a result, the mean atomic density must be considered as a significant and peer variable in the problem on chemical equilibrium.

Furthermore, when calculating the pressure in systems with chemical reactions (the variable number of particles), one has to recalculate each contribution to the initial number of atoms.

RESULTS AND DISCUSSION

System of equations (8) was solved by the Newton–Raphson method with initial values determined analytically as the low-temperature asymptotics. In calculations, we used the following model parameters: the frequency of normal valence vibrations $\omega = 2\pi c\nu$, where c is the velocity of light, $\nu = 200 \text{ cm}^{-1}$. For the $(MX_4)^{2-}$ autocomplex, the ion masses corresponded to the case of calcium chloride; in our case, the moment of inertia was $5.35 \times 10^{-37} \text{ g cm}^2$.

Figure 2a shows the results of calculations of different contributions to the free energy as a function of the autocomplex concentration at the constant temperature. To better understand, we also plotted the variation of contributions to the free energy corresponding to the zero concentration of autocomplexes. The presence of the free energy minimum at the nonzero con-

centration is evident. The ideal contribution is the main factor favoring the formation of autocomplexes. This contribution provides a decrease in the free energy at relatively low concentration values. The coulomb interaction of simple and composite ions in the reaction mixture prevents the formation of autocomplexes. The variation of this contribution lies in the positive region and increases with the increase in concentration.

Figure 2b shows the concentration dependences of the free energy at different temperatures. It is seen that as the temperature increases, the dependences change their form. Moreover, the free energy increases and passes to the positive region at temperatures at which autocomplexes are absent.

Figure 3a shows the results of calculations of the autocomplex concentration for several values of dissociation energy which varies as a parameter in this theory. It is seen that the region of characteristic values, in which the autocomplex concentration considerably differs from zero is shifted to relatively low temperatures (about $\frac{kT}{E_d} \sim 10^{-2}$). This means that the chemical equilibrium with respect to formation of autocomplexes is substantially shifted to the left, i.e., towards dissociation, if we consider the ideal case which ignores the coulomb interaction of simple and compound ions. The lower the dissociation energy, the narrower the temperature range of the existence of autocomplex groups. Moreover, when the dissociation energies become too low, the concentration of auto-

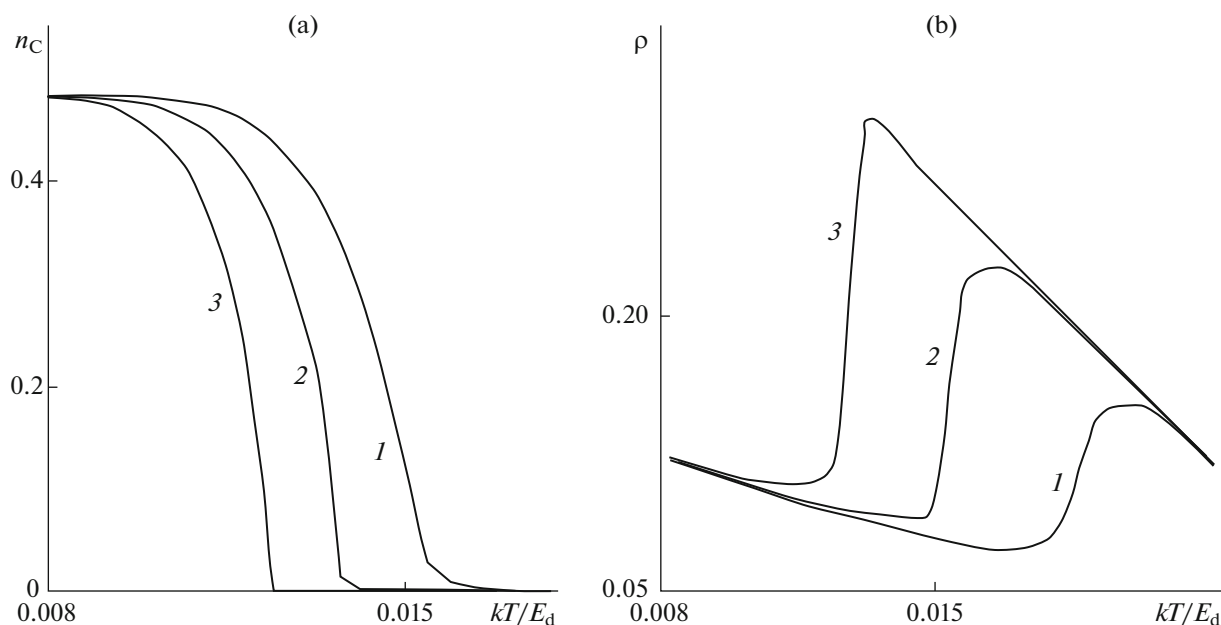


Fig. 3. (a) Calculated temperature dependences of the concentration of $(MX_4)^{2-}$ autocomplexes and (b) calculated temperature dependences of the melt density at different dissociation energies: (1) $E_d = E_d^0$; (2) $0.9E_d^0$; (3) $0.8E_d^0$; (4) $0.7E_d^0$.

complexes is zero throughout the whole reasonable temperature region.

Figure 3b shows the calculated temperature dependences of the atomic density of a bivalent metal halide melt for different values of dissociation energy of $(MX_4)^{2-}$ complexes. It is evident that the temperature dependence of the density has a maximum which shifts in the high temperature direction with the increase in dissociation energy, as the height of this maximum decreases. The curve acquires the standard monotonic form in which the density decreases with the temperature once the temperature of complex formation reaches the marked threshold after which the complexes are totally instable.

We regard these data on the behavior of density as the most interesting consequence of the developed qualitative model.

The dissociation is so active in the narrow temperature interval that a considerable part of free volume earlier contained within the complex is liberated. As a result, the pronounced anomalies appear also in the density plot, which generally contradicts the experiment. Now we try to refine the volume changes in an elementary act of complexation due to superposition of spheres inside the complex in order to analyze qualitatively the possible changes in the dissociation process.

Note that in terms of the spherical model for the autocomplex with the diameter $3d$, its volume is $27v_0$, where $v_0 = \frac{\pi}{6}d^3$ is the volume of unbound cation or anion. $5v_0$ accounts for the volume occupied by the

bivalent-metal cation and four halide anions. Thus, $22v_0$ is the additional volume necessary for the formation of the complex. It is evident that these values are substantially overestimated. The more accurate theory should operate with the factor reflecting the shape of these molecules.

The rigorous consideration of the shape factor of complexes is beyond the scopes of our study. However, we can illustrate qualitatively the possible consequences of rigorous consideration of volume variations within the framework of a spherical model with superposition of spheres within the complex.

Let us circumscribe a regular pyramid in the sphere of radius $3d$ which was used earlier for the description of autocomplex $(MX_4)^{2-}$. We can easily find that its volume is $v_p = 2\sqrt{6}d^3$. Let us determine the sphere (Fig. 4) with the radius such that its volume $v_f = \frac{\pi}{6}d_f^3$ coincides with the pyramid volume $v_f = v_p$. Then, the diameter of the reduced (or effective) sphere describing the autocomplex is $d_f = 2\left(\lambda d + \frac{d}{2}\right)$. Now we can easily find the parameter of superposition (λ) of spherical atoms inside the complex that satisfies such volume cut-off. In our case of the complex anion with the tetrahedral geometry, $\lambda = \frac{\sqrt[3]{2/\pi}\sqrt{6}-1}{2} \approx 0.554$.

If we take the new diameter for $(MX_4)^{2-}$ autocomplexes and calculate the concentration and the density, it becomes evident that the characteristic region of the

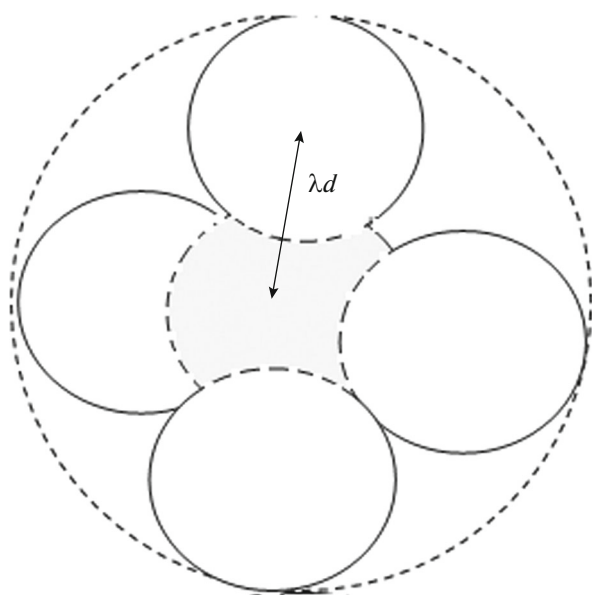


Fig. 4. Geometrical model of $(MX_4)^{2-}$ autocomplexes with regard to superposition.

existence of complexes shifts to the higher temperatures (Fig. 5a). This can be easily explained by the fact that the dissociation energy calculated in terms of the crystal field model with the new distance between centers λd increased. This led to a shift of the temperature interval of complex stability to the higher temperatures.

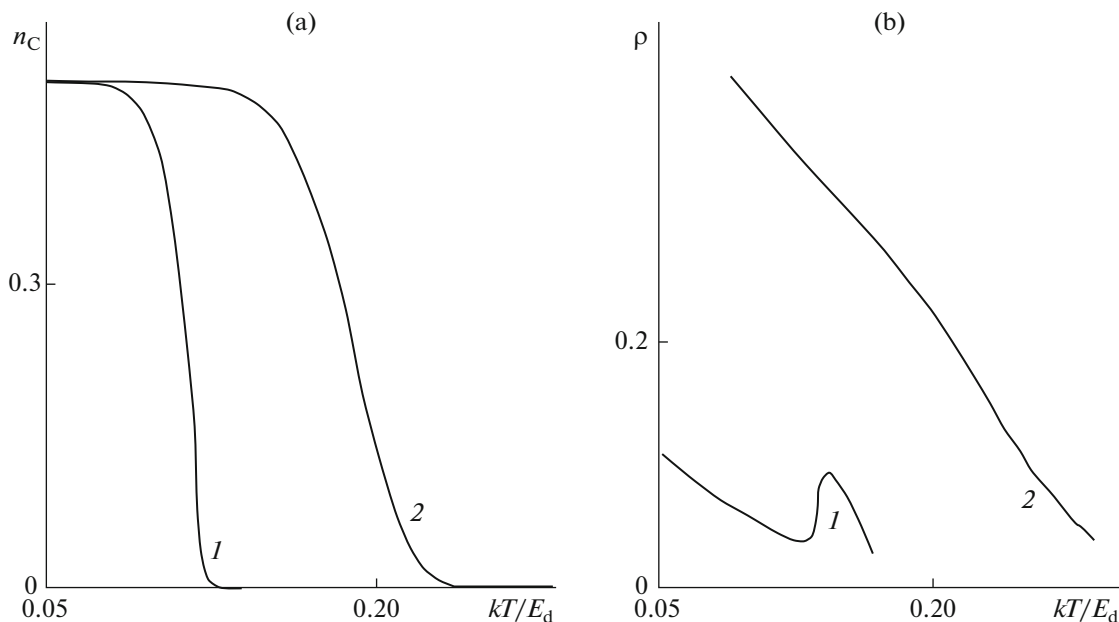


Fig. 5. (a) Calculated temperature dependences of the concentration of $(MX_4)^{2-}$ complexes and (b) calculated temperature dependences in the approximation of the nearest neighbors (1) without and (2) with regard to the superposition of spherical atoms within the complex.

Figure 5b shows that when the geometry of complexes under study is considered rigorously, the anomaly in density curve disappears. The maximum in curve 1 of Fig. 5b is transformed to the monotonic decrease in the density with the increase in the temperature. It is seen that the decrease in the radius of complex leads to the increase in the density at equal temperature. The more rigorous consideration of the autocomplex size results in compacting of the system. Indeed, the size of autocomplexes decreases which means that they occupy the smaller volume.

CONCLUSIONS

(1) The effects of volume variation upon possible dissociation equilibria of anionic complexes $(MX_4)^{2-}$ in halide melts of bivalent metals are considered.

(2) Within the framework of the simplified model of a molten electrolyte as a mixture of charged hard spheres of different diameters and valences, it is shown that the simplest approximation of the diameter of complex as the treble diameter of simple ions leads to substantial overestimation of the effects of volume variation when considering dissociation.

(3) By the example of tetrahedral complexes $(MX_4)^{2-}$ in halide melts MX_2 , it is qualitatively demonstrated that the density variations with the temperature radically change when the autocomplex shape is taken into account.

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