

STATISTICAL THERMODYNAMIC ANALYSIS OF COMPLEX FORMATION IN SALT MELTS

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The report will present the results of theoretical calculations of dissociation equilibria for anion complexes of the $(MX_4)^{2-} = M^{2+} + 4X^-$ type in halogenide melts based on MX_2 . A simplified model of a mixture of charged hard spheres of differing diameters is considered, when only electrostatic interactions and the final dimensions of ions are taken into account, and the contribution of the complexes to the thermodynamics of the melt is additionally contributed by its energy of formation. Such a model is a natural starting point for this problem and sheds light on the mechanism of the spontaneous (in the thermodynamic sense) appearance of charged complex groupings. The core of the problem is a system of equations of equilibrium, which contains both the law of effective masses and the equation of state, which allows one to self-consistently calculate the equilibrium concentration of complexes and the density of the melt. By the example of approximation of the diameter of a complex as a tripled diameter of simple ions, it is shown that this can lead to a significant overestimation of the effects of the change in the molar volume when considering its temperature dependence. Allowance for the overlap of atoms within the complex allows us to describe a smoother change in volume with temperature. A generalization of the developed model to the case of binary melts of multivalent metal halides with alkali metal halides is carried out. Examples of typical concentration dependencies of complexes from the composition of these binary melts and thermodynamic characteristics are given. In conclusion, problems and prospects for describing real salt melts containing two- and three-valence cations are discussed. This work was supported by Russian Foundation for Basic Research 18-03-00606