

DETERMINATION OF THE FREE ENERGY OF ASSOCIATION OF Zn^{++} -CATION VACANCY COMPLEXES FROM SOLUBILITY DATA

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The study of the association reaction of Zn^{++} with cation vacancies into complexes in the $NaCl + ZnCl_2$ system is of considerable interest. With the exception of the values for the Gibbs free energy of association .48 eV at 703 °C [1] and .4 eV at 590 °C [2] obtained by means of heterodiffusion measurements in crystals doped with $ZnCl_2$ and $CaCl_2$ respectively, there are no further data on the association of Zn^{++} into complexes. As large elastic deformations of the surrounding lattice of this small ion are expected, no theoretical calculations of the association energy of Zn-complexes were performed to date. It is only assumed that the association energy might reach a fairly high value [3].

As will be shown solubility measurements can be used for the determination of the Gibbs free energy of association in a wide temperature range. This method is advantageous mainly in the case of less soluble divalent admixtures, where the investigation of the association by means of diffusion or conductivity measurements is difficult.

From the simple solubility theory for free divalent admixtures in alkali halides [4] it follows that in the temperature range where the formation of thermal vacancies is negligible the following equation holds good

$$c_f = \exp(S_i/2k) \exp(-H_i/2kT) \quad (1)$$

where c_f stands for the solubility of free divalent admixtures at temperature T , H_i for the enthalpy (heat), S_i for the entropy of solution per molecule, configurational entropy not being included, k for Boltzmann's constant.

The association of admixture ions into complexes increases the total solubility [5], so that in a limited temperature range, as in the case of equation (1), the temperature dependence of the total solubility c_T will be [6]

$$c_T = \exp(S_i/2k) \exp(-H_i/2kT) + \\ + 12 \exp[(S_i - S_a)/k] \exp[-(H_i - H_a)/kT] \quad (2)$$

where S_a stands for the entropy and H_a for the enthalpy of association; in all

the equations the concentrations are expressed in molar fractions and the energies in eV. Equation (2) holds good when we assume the independence of the equilibrium constant K_a of the association reaction

$$K_a = 12 \exp(G_a/kT) = 12 \exp(-S_a/k) \exp(H_a/kT) \quad (3)$$

on admixture concentration, i. e. the validity of the simple Stasiv-Tel'kov association model. The factor 12 in (3) assumes the existence of complexes only in the ground state; $G_a = H_a - TS_a$ is the Gibbs free energy of association.

From equations (1) and (2) there follows another possibility of using the solubility measurements. If both, the temperature dependence of the total solubility c_T and the temperature dependence of the free admixtures solubility c_f are known, we can determine the temperature dependence of the Gibbs free energy of association and also the enthalpy and entropy of association by comparison of c_f and c_T . To this end equation (2) is expressed in a more convenient form

$$c_T = c_f + 12c_f^2 \exp(G_a/kT) \quad (4)$$

or

$$c_T = c_f(1 + c_f K_a). \quad (5)$$

From equation (5) we obtain the equilibrium constant

$$K_a = \left(\frac{c_T}{c_f} - 1 \right) / c_f. \quad (6)$$

Further, by means of equation (3) the heat of association H_a as well as the entropy of association S_a may be determined from the temperature dependence of K_a . The heat of association H_a is determined from the slope and S_a from the abscissa (for $1/T = 0$) of the dependence of $\ln K_a$ on $1/T$. It is possible to determine the Gibbs free energy of association for a given temperature not only from K_a but also directly from the relation

$$G_a = kT \ln \left[\left(\frac{c_T}{c_f} - 1 \right) / 12c_f \right] \quad (7)$$

obtained from equation (4).

As in case of Zn^{++} in NaCl the temperature dependence of the total solubility [6]

$$c_T = .132 \exp(-.458/kT) \quad (8)$$

as well as the temperature dependence of the free zinc solubility [1]

$$c_f = .17 \exp(-.49/kT) \quad (9)$$

are known, we tried to determine the temperature dependence of the equilibrium constant K_a and the Gibbs free energy of association G_a of zinc in the temperature range of 350—650 °C by means of the method suggested. In this temperature range the relations (8) and (9) are valid and the concentration of the thermal vacancies is negligible. The values K_a and G_a obtained by substituting relations (8) and (9) in equations (6) or (7) are given, together with the respective temperatures, in Table 1. The temperature dependence of the equilibrium constant K_a so obtained is plotted in Fig. 1. From the thus calculated temperature dependence it follows that the heat of association H_a will be very high in case of zinc, i. e. .65 eV and the entropy of association will be 4×10^{-4} eV/deg. That means a value between .3 and .4 eV for the Gibbs free energy of association in the given temperature range.

Table 1

Temperature dependence of the Gibbs free energy of association G_a and of the equilibrium constant K_a of the association reaction for zinc complexes

T [°C]	350	400	450	500	550	600	650
K_a	19500	8700	4040	2060	1110	650	420
G_a [eV]	.40	.38	.36	.34	.32	.30	.29

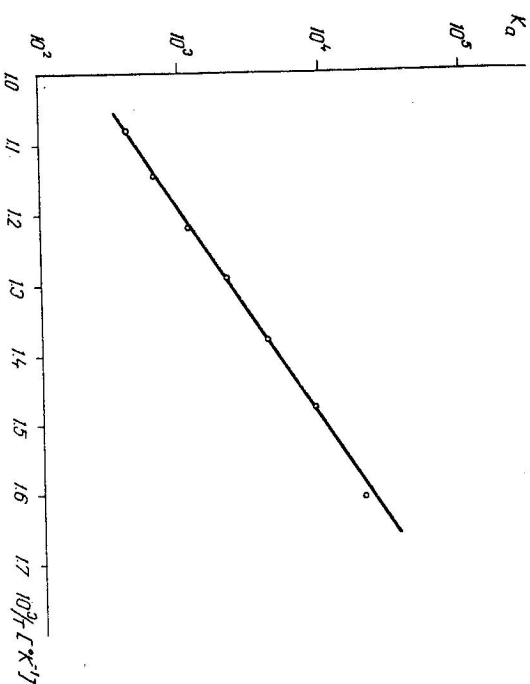


Fig. 1. Temperature dependence of the equilibrium constant K_a of the association reaction for zinc complexes.

The values of the Gibbs free energy of association calculated by this method are lower at high temperatures than those determined from the dependence of the zinc diffusion coefficient on its own concentration [1]. 48 eV at 703 °C or on the concentration of another homogeneously built-in divalent admixture [2]. 48 eV at 590 °C. The strong temperature dependence of the Gibbs free energy of association might be a consequence of the application of the simple association model at higher temperatures, where the zinc solubility and, therefore, the concentration of free defects are considerable.

The accuracy of the association parameters of Zn^{++} determined by the described method should be subject to a special discussion due to the fact that the temperature dependence of the solubility of free zinc [1] used in these calculations is subjected to an error hard to estimate. The necessary c_f values were determined by the extrapolation of two conductivity regions: the admixture and the precipitation regions. If the conductivity values used for the extrapolation are influenced by association, the c_f so determined will be higher than the real c_f and may approach the value of c_r . At any rate, it may be stated that K_a or G_a can be only higher than quoted in Table I, because the real c_f could be only smaller than the measured one given by equation (9) and in consequence the value of $c_r - c_f$ could be only higher than that used in the calculations. Also the fact that no interactions of free defects were taken into account may cause that the real values of G_a and K_a are higher than those quoted in Table I, especially at higher temperatures. The values given in Table I are therefore, no doubt, the lowest possible.

In case of $NaCl + ZnCl_2$ [1] the precipitation and admixture conductivity regions were clearly defined. Therefore it is probable that in the case of this system the calculated values of the association parameters as given in Table I are established with good accuracy for low temperatures at least.

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