

A New Approach to the Evaluation of Thermodynamic Properties of Nonideal Solid Solutions by the Molecular Dynamics Method: A Mixing Model of Alkali Halide Solid Solution

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We present a new approach to evaluating the intracrystalline thermodynamic properties of solid solutions by combining the molecular dynamics (MD) method and a chemical thermodynamic approach. The coordination type of ions in alkali halide solid solutions $(A, B)X$ is classified into 7 types X_n ($n = 0-6$) for halide ions and into 13 types A_n ($n = 0-12$) and B_n ($n = 0-12$) for cations, depending on the kind and the coordination number of the nearest cation. Entropy of mixing for a nonideal solid solution was formulated by using the configurational entropy of coordination types. The equilibrium concentration of coordination types is expressed by equilibrium reactions among coordination types. The equilibrium constants in the solid solution of the system NaCl–KCl were then calculated by the MD method and the excess free energies of mixing were obtained by calculation. The asymmetric nature of the solvus curve of the system NaCl–KCl is well demonstrated and the temperature of the apex of the solvus agrees well with experimental data. © 2000

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Key Words: molecular dynamics method; thermodynamics; alkali halide; solid solution; solvus.

INTRODUCTION

Thermodynamic modeling of solid solutions, which was proposed by Guggenheim (1), has been developed by many authors. Margules-type expansion for the excess thermodynamic properties of the system NaCl–KCl by Thompson and Waldbaum (2) and the quasi-chemical approximation by Green (3) of the same system laid the ground for the later works. Theoretical modeling of multicomponent solid solutions has been achieved by Anderson and Lindsley (4) and Helffrich and Wood (5).

In view of the structural and thermodynamic points, Davies and Navrotsky (6) studied a wide variety of structural types and showed that deviations from ideal mixing in a number of isostructural binary solid solutions can be

parameterized and correlated quantitatively using regular and subregular thermodynamic mixing models.

Recent advances in the molecular dynamics method (MD) have made it possible to obtain information about thermodynamic and physical properties of inorganic compounds first hand. Akamatsu *et al.* (7) applied the MD to the solid solutions in the system NaCl–KCl. They obtained a smooth positive asymmetric curve of enthalpy of mixing at 900 K under 0.1 MPa. They used an ideal mixing model for the cation distribution and the configuration was maintained throughout the calculations. Their report stimulated this study, which attempts the simulation of a nonideal solid solution on the atomic scale, to gain insight into the factors responsible for the thermodynamic properties. We know, however, that the equilibrium distribution of cations at low temperatures will never be attained by the MD in such a short time. Kikuchi (8) indicated that the distribution pattern of halide ions in a binary NaCl-type solid solution $(A, B)X$ is described by seven types of anion-centered octahedra, $XA_{6-n}B_n$ ($n = 0-6$), where n is the number of the surrounding cation B . The lattice energy is expressed by the sum $\sum P_n U_n$ where P_n is the probability of an anion-centered octahedron and U_n is the interatomic potential.

FORMULATION

Classification of Coordination Types

For ionic compounds, the interatomic potential (U_{ij}) is expressed in a conventional form (9) as

$$U_{ij} = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j) \exp \frac{a_i + a_j - r_{ij}}{b_i + b_j} + \frac{c_i c_j}{r_{ij}^6}, \quad [1]$$

where the terms on the right side represent the Coulomb energy, repulsive potential, and van der Waals attraction, respectively. The r_{ij} is the distance between two ions i and j . The z_i, z_j are the valences, f_0 is an arbitrarily chosen constant to adjust the dimension, a_i, a_j are the ionic radii, $b_i,$

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b_j are the hardness parameters, and c_i, c_j are the parameters related to van der Waals attraction.

The halide ion X of $(A,B)X$ in a binary NaCl-type solid solution is coordinated by six cations, A and/or B . For such a central anion \mathbf{X}_i , Eq. [1] indicates that the first term is independent of the nature of the surrounding cation, if we use the nominal valences, but the second term strongly reflects the nature of cation A or B . It means that the interatomic potential \mathbf{U}_i of \mathbf{X}_i depends on the number of the different coordinated cations. It is therefore useful to classify the halide ions into seven coordination types according to the combination of coordinated cations,

$$A_6(\mathbf{X}_0), A_5B(\mathbf{X}_1), A_4B_2(\mathbf{X}_2), A_3B_3(\mathbf{X}_3), A_2B_4(\mathbf{X}_4), \\ AB_5(\mathbf{X}_5), B_6(\mathbf{X}_6),$$

where the symbols in parentheses are the abbreviations of the coordination type of \mathbf{X} . Similarly, the cations in the structure are distinguished by 13 coordination types. They are $\mathbf{A}_0, \mathbf{A}_1, \dots, \mathbf{A}_{12}$ and $\mathbf{B}_0, \mathbf{B}_1, \dots, \mathbf{B}_{12}$ where the subscript is the number of the other kind of cation. Similar expressions will be used in this paper.

Mixing Model of an Ideal Solid Solution

The distribution of cations A, B in an ideal solid solution should be statistically random. The probability of finding a halide ion coordination type $[\mathbf{X}_n]$ will give a binominal distribution against the fractions of two kinds of cation, x_A, x_B ,

$$[\mathbf{X}_n] = ({}_6C_n)x_A^{6-n}x_B^n, \quad [2]$$

where $n = 0-6$, $({}_6C_n)$ is the combination number, and $x_A + x_B = 1$.

They are $[\mathbf{X}_0] = x_A^6$, $[\mathbf{X}_1] = 6x_A^5x_B$, $[\mathbf{X}_2] = 15x_A^4x_B^2$, $[\mathbf{X}_3] = 20x_A^3x_B^3$, $[\mathbf{X}_4] = 15x_A^2x_B^4$, $[\mathbf{X}_5] = 6x_Ax_B^5$, and $[\mathbf{X}_6] = x_B^6$. The relation $\Sigma[\mathbf{X}_n] = 1$ is given by substituting $x_B = 1 - x_A$ into the above equations.

The configurational entropy for 1 mol of a coordination type \mathbf{X}_n can be expressed as

$$S_n^X = \mathbf{R} \ln ({}_6C_n) \quad [3]$$

or $S_0^X = 0$, $S_1^X = \mathbf{R} \ln 6$, $S_2^X = \mathbf{R} \ln 15$, $S_3^X = \mathbf{R} \ln 20$, $S_4^X = \mathbf{R} \ln 15$, $S_5^X = \mathbf{R} \ln 6$, and $S_6^X = 0$, where \mathbf{R} is the gas constant. The entropy of mixing for these seven types of octahedron can be expressed as

$$S^{\text{mix}, Xn} = -\mathbf{R} \Sigma[\mathbf{X}_n] \ln [\mathbf{X}_n]. \quad [4]$$

Since the same cation in the structure is present six times in Eqs. [3] and [4], the overall entropy of mixing per

mole becomes

$$S^{\text{mix}} = (1/6)\mathbf{R}(\Sigma[\mathbf{X}_n]S_n^X - \Sigma[\mathbf{X}_n] \ln [\mathbf{X}_n]). \quad [5]$$

Substituting $[\mathbf{X}_n]$ and S_n^X into Eq. [5] by Eqs. [2] and [3], one obtains the well-known equation

$$S^{\text{mix}} = -\mathbf{R}(x_A \ln x_A + x_B \ln x_B). \quad [6]$$

Similar relations are found in cation coordination types \mathbf{A}_n and \mathbf{B}_n . The probability (or concentration) of \mathbf{A}_n and \mathbf{B}_n being present in the structure becomes

$$[\mathbf{A}_n] = ({}_{13}C_n)x_A^{13-n}x_B^n \quad (n = 0-12), \quad [7]$$

$$[\mathbf{B}_n] = ({}_{13}C_n)x_A^n x_B^{13-n} \quad (n = 0-12). \quad [8]$$

The configurational entropies are

$$S_n^A = \mathbf{R} \ln ({}_{13}C_n) \quad (n = 0-12), \quad [9]$$

$$S_n^B = \mathbf{R} \ln ({}_{13}C_n) \quad (n = 0-12), \quad [10]$$

and the overall entropy of mixing is expressed also by

$$S^{\text{mix}} = (1/13)\mathbf{R}(\Sigma[\mathbf{A}_n]S_n^A + \Sigma[\mathbf{B}_n]S_n^B - \Sigma[\mathbf{A}_n] \ln [\mathbf{A}_n] \\ - \Sigma[\mathbf{B}_n] \ln [\mathbf{B}_n]). \quad [11]$$

Mixing Model of a Nonideal Solid Solution

It may be expected that the concentration of coordination types $\mathbf{X}_n, \mathbf{A}_n$ and \mathbf{B}_n in nonideal solution deviates from that in the ideal solution. It may also be expected that the entropy of mixing of such solid solutions will be smaller than that of the ideal solid solutions. The following procedure makes it possible to create a mixing model of a nonideal solid solution.

In the following formulations, $\mathbf{X}_n, \mathbf{A}_n$, and \mathbf{B}_n are treated as chemical species since they are chemically different and energetically discrete. Under equilibrium conditions, the coordination types \mathbf{X}_n will be equilibrated to each other,

$$5\mathbf{X}_0 + \mathbf{X}_6 = 6\mathbf{X}_1 \quad [12]$$

$$4\mathbf{X}_0 + 2\mathbf{X}_6 = 6\mathbf{X}_2 \quad [13]$$

$$3\mathbf{X}_0 + 3\mathbf{X}_6 = 6\mathbf{X}_3 \quad [14]$$

$$2\mathbf{X}_0 + 4\mathbf{X}_6 = 6\mathbf{X}_4 \quad [15]$$

$$\mathbf{X}_0 + 5\mathbf{X}_6 = 6\mathbf{X}_5. \quad [16]$$

Applying the mass action law to them, we have

$$K_1^X [\mathbf{X}_0]^5 [\mathbf{X}_6] = [\mathbf{X}_1]^6 \quad [17]$$

$$K_2^X [\mathbf{X}_0]^4 [\mathbf{X}_6]^2 = [\mathbf{X}_2]^6 \quad [18]$$

$$K_3^X [\mathbf{X}_0]^3 [\mathbf{X}_6]^3 = [\mathbf{X}_3]^6 \quad [19]$$

$$K_4^X [\mathbf{X}_0]^2 [\mathbf{X}_6]^4 = [\mathbf{X}_4]^6 \quad [20]$$

$$K_5^X [\mathbf{X}_0] [\mathbf{X}_6]^5 = [\mathbf{X}_5]^6. \quad [21]$$

From the definition

$$[\mathbf{X}_0] + [\mathbf{X}_1] + [\mathbf{X}_2] + [\mathbf{X}_3] + [\mathbf{X}_4] + [\mathbf{X}_5] + [\mathbf{X}_6] = 1 \quad [22]$$

and from the mass balance, it follows that

$$[\mathbf{X}_1] + 2[\mathbf{X}_2] + 3[\mathbf{X}_3] + 4[\mathbf{X}_4] + 5[\mathbf{X}_5] + 6[\mathbf{X}_6] = 6x_B, \quad [23]$$

where $6x_B$ of the right side comes from the coordination number.

It is thus possible to evaluate all the concentrations from Eqs. [17]–[23] if the equilibrium constants are known.

The formulations for cations are similar to the above. The elementary reactions are

$$(12 - n)\mathbf{A}_0 + n\mathbf{A}_{12} = 12\mathbf{A}_n \quad (n = 1-11) \quad [24]$$

$$(12 - n)\mathbf{B}_0 + n\mathbf{B}_{12} = 12\mathbf{B}_n \quad (n = 1-11) \quad [25]$$

and the possible site change reactions between \mathbf{A} and \mathbf{B} can be expressed as

$$\mathbf{A}_0 + \mathbf{B}_0 = \mathbf{A}_{12} + \mathbf{B}_{12}. \quad [26]$$

Applying mass action law to them, we have

$$K_n^A [\mathbf{A}_0]^{12-n} [\mathbf{A}_{12}]^n = [\mathbf{A}_n]^{12} \quad (n = 1-11) \quad [27]$$

$$K_n^B [\mathbf{B}_0]^{12-n} [\mathbf{B}_{12}]^n = [\mathbf{B}_n]^{12} \quad (n = 1-11) \quad [28]$$

$$K^{AB} [\mathbf{A}_0][\mathbf{B}_0] = [\mathbf{A}_{12}][\mathbf{B}_{12}] \quad [29]$$

and from the mass balance,

$$\Sigma[\mathbf{A}_n] = x_A \quad (n = 0-12) \quad [30]$$

$$\Sigma[\mathbf{B}_n] = x_B \quad (n = 0-12). \quad [31]$$

Because the total number of coordinated B ions to the central A ions is equal to that of A ions to the central B ions,

$$\Sigma n[\mathbf{A}_n] = \Sigma n[\mathbf{B}_n] \quad (n = 1-12). \quad [32]$$

Equations [27] and [28] include 11 individual equations, respectively. Therefore, 26 equations are described for 26 unknown concentrations.

Evaluation of Equilibrium Constants

The above equilibrium constants are calculated from the interatomic potential by the form $K = \exp(-\Delta G/nRT)$. For example, the ΔG for Equation [12] is written as

$$\Delta G_1^X = 6(\mathbf{U}_1^X - \mathbf{TS}_1^X) - (5\mathbf{U}_0^X + \mathbf{U}_6^X), \quad [33]$$

where \mathbf{U}_0^X , \mathbf{U}_1^X , and \mathbf{U}_6^X are the internal energies, which are equal to the interatomic potentials obtained by the MD at a given mole fraction of x_B . Since the excess volume of mixing is generally small, contribution of the term $\mathbf{P}\Delta V$ can be neglected.

Excess Free Energy of Mixing

The concentrations of \mathbf{X}_n are calculated by the Newton–Raphson method using Eqs. [17]–[23]. The concentrations of \mathbf{A}_n and \mathbf{B}_n were calculated by a Monte Carlo method using Eqs. [27]–[32]. The excess enthalpy of mixing is expressed by

$$\Delta H = (1/2)\{\Sigma[\mathbf{X}_n]\mathbf{U}_n^X + \Sigma[\mathbf{A}_n]\mathbf{U}_n^A + \Sigma[\mathbf{B}_n]\mathbf{U}_n^B\} - (x_A\mathbf{U}^A + x_B\mathbf{U}^B), \quad [34]$$

where \mathbf{U}^A and \mathbf{U}^B are the internal energies of the end member A and B , respectively. The excess free energy of mixing is expressed by

$$\Delta G = \Delta H - (1/2)\mathbf{RT}\{(1/6)(\Sigma[\mathbf{X}_n]\mathbf{S}_n^X - \Sigma[\mathbf{X}_n] \ln [\mathbf{X}_n]) + (1/13)(\Sigma[\mathbf{A}_n]\mathbf{S}_n^A + \Sigma[\mathbf{B}_n]\mathbf{S}_n^B - \Sigma[\mathbf{A}_n] \ln [\mathbf{A}_n] - \Sigma[\mathbf{B}_n] \ln [\mathbf{B}_n])\}. \quad [35]$$

The above equation is based on the assumption that all coordination types are distributed at random in the structure.

APPLICATION TO THE NaCl–KCl SYSTEM

Interatomic Potential of Coordination Type

The structural model for $(\text{Na}_{1-x}\text{K}_x)\text{Cl}$ was prepared and the average potential for each of the coordination types, \mathbf{X}_n , \mathbf{A}_n , \mathbf{B}_n were obtained by the MD at 300°C under

TABLE 1
Energy Parameters Used for MD Calculations

	Effective charge	Repulsive parameters		Parameter c (kJ/mol) ^{1/2}
		a/nm	b/nm	
Na	0.668	0.1259	0.008	0.006
K	0.702	0.1563	0.008	0.024
Cl	—	0.1950	0.009	0.173

Note. $f_0 = 4.184$. The effective charge of Cl is equal to $-(q_{Na}n_{Na} + q_{K}n_{K})/(n_{Na} + n_{K})$, where q_{Na} , q_{K} are the effective charges of Na and K and n_{Na} , n_{K} are the number of Na and K in the basic cell.

atmospheric pressure. The program of the MD was newly written in Fortran. The basic cell consists of 256 Cl atoms and 256 cations, which are randomly distributed. Effective charges for metal ions were calculated from the electronegativity data of Pauling and calculated as $1 - \exp\{-1/4(x_M - x_{Cl})^2\}$, where x_M is the electronegativity of the metal ion and x_{Cl} is that of Cl. The effective charge of Cl^- was determined so as to neutralize the entire charge of the structure. The values c_i , c_j were calculated from the ionization energy and the ionic polarizability (9). The repulsive parameters were determined so as to reproduce the lattice constant of the end members, NaCl and KCl. The energy parameters used are listed in Table 1. The calculation was performed with 1 fs of the step time up to 4000 steps.

An example of potential data for $(Na_{0.5}K_{0.5})Cl$ is listed in Table 2. It is shown that the average potential of the Cl ion decreases linearly with an increasing number of coordinated

TABLE 2
Coordination Types and the Average Interatomic Potentials of the Solid Solution $(Na_{0.5}K_{0.5})Cl$ Calculated by MD at 300°C Under Atmospheric Pressure

Coordination type	Number	Potential (kJ/mol)	Coordination type	Number	Potential (kJ/mol)
X_0	1	-320.55	A_8	14	-361.52
X_1	25	-333.35	A_9	9	-358.05
X_2	56	-344.55	B_2	2	-270.60
X_3	93	-355.68	B_3	9	-283.67
X_4	58	-369.84	B_4	13	-294.00
X_5	18	-385.99	B_5	21	-299.36
X_6	5	-398.13	B_6	24	-311.19
A_3	5	-406.91	B_7	25	-321.58
A_4	14	-397.40	B_8	22	-329.31
A_5	18	-390.19	B_9	10	-341.27
A_6	36	-380.53	B_{10}	1	-348.17
A_7	32	-369.54	B_{11}	1	-358.12

Note. Symbols for Na, K, and Cl are represented by A, B, and X, respectively.

K ion, and the average potentials of cations have a linear relation to the number of the other coordinated cations. Hereafter, symbols for Na, K, and Cl will be represented also by A, B, and X, respectively, for convenience. It will be noted that the extreme coordination types such as A_0 , B_0 , A_{12} , B_{12} , etc., are absent in Table 2, indicating that the cell size was not large enough to represent the exact ratio of these coordination types. For example, the A_{12} type cannot be generated in the cell at the composition ($x_B = 0.1$). Many "artificial" cells, which contain an extreme coordination type artificially assigned in the cell, were prepared to obtain the potential for the extreme type. The potential data of the cell for the composition ($x_B = 0.14$), including one A_{12} type, are shown in Fig. 1. It is shown that the linear relation between the potential value of A_n and n is maintained, even in these cases.

Since the potential value of a coordination type depends on the composition, more than 40 sets of structural models were prepared. The resulting excess internal energies of all sets are shown in Fig. 2. Attempts to change parameters in Eq. [1] and to give nominal charges for ions gave almost the same results, suggesting that the excess energy of mixing is not sensitive to these parameters.

The dependence on composition of the interatomic potential of X_n is seen in the high degree of correlation in least-squares fits. All the coordination types ($n = 0-6$) have a correlation coefficient $r > 0.98$. Similarly, cation coordination types A_n , B_n also give lines with $r > 0.99$. As the changes in potential by n at a constant composition can be linear as shown in Fig. 1, the data were regressed linearly on both composition and n . The changes in ΔH and ΔG at

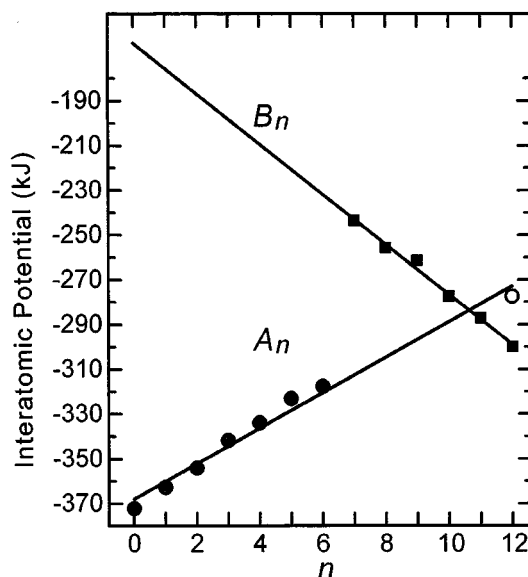


FIG. 1. Change of the average interatomic potential of A_n and B_n in the solid solution at $x_B = 0.14$ of the system NaCl-KCl. The open circle represents the potential of A_{12} , which was artificially assigned in the cell.

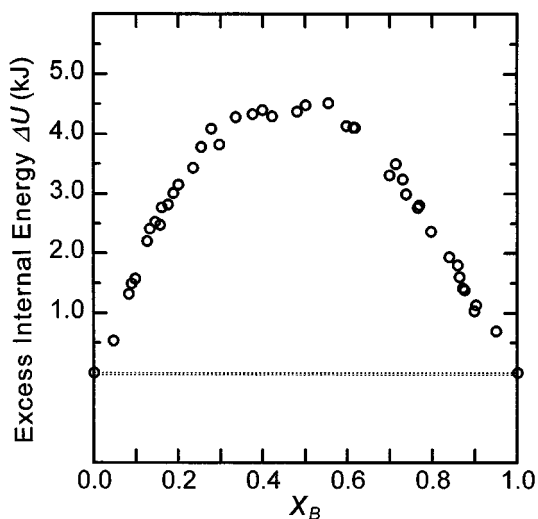


FIG. 2. Excess internal energies (ΔU) obtained by MD at 300°C under atmospheric pressure as a function of mole fraction x_B . Plots for $x_B = 0.1, 0.2, \dots, 0.9$ are the original basic cell and the others are the “artificial” cell mentioned in the text, showing no difference in results.

300°C vs composition are shown in Fig. 3; they were calculated by using these regression lines and by Eqs. [34] and [35]. It is noted that the potential for the apex of ΔH obtained by Eq. [34] is 1.9 kJ lower than that obtained by MD (cf. Fig. 2). It is also noted that the substitution of $[X_n]$, $[A_n]$, and $[B_n]$ in Eq. [34] by the ideal concentration, which is given by Eqs. [2], [7], and [8], gives the same curves as those of Fig. 3. The result is derived from the assumption that the interatomic potential at a constant composition is linearly related to the increasing number of n . It causes the

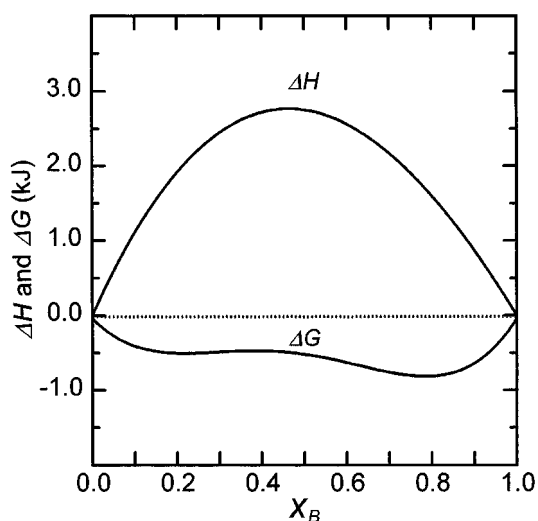


FIG. 3. Change of ΔH and ΔG as a function of composition for (Na,K)Cl at 300°C under atmospheric pressure.

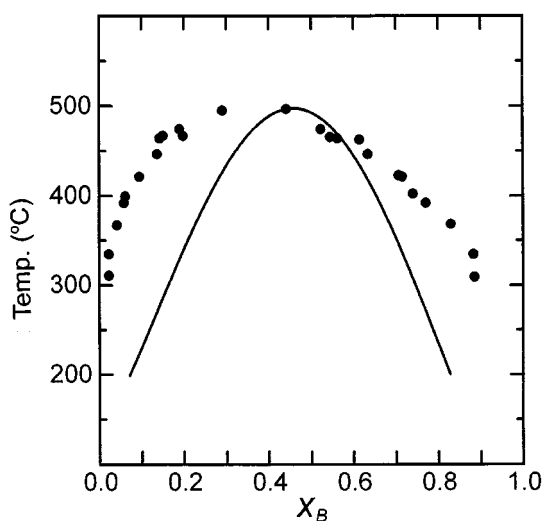


FIG. 4. Calculated solvus curve of the system NaCl-KCl under atmospheric pressure based on ΔH at 300°C. Dots are the experimental data collected by Green (1970).

ΔU of the reactions, Eqs. [12]–[16], [24], and [25], to be zero and the ΔG to become merely a function of the configurational entropy and the temperature. For this reason, it is estimated from the linear relationship of n that the cation distribution in solid solution of (Na,K)Cl is ideal.

The change in ΔG as a function of temperature and composition was calculated by using the ΔH at 300°C and the ΔS for the ideal mixing. The calculated solvus curve is shown in Fig. 4. The asymmetric nature of the solvus curve is demonstrated and the temperature of the apex agrees well with the experimental data (3). The sharper feature of the calculated solvus may be caused by incorrectness of given parameters for MD or due to the assumption that ΔH at temperatures higher than 300°C is the same as that calculated at 300°C.

CONCLUSIONS

We have shown that the solvus curve of a solid solution in the system NaCl-KCl can be estimated from the lattice constants of both end members, NaCl and KCl, without using any further experimental data. The present approach uses classification of coordination types and the subsequent formulation to evaluate thermodynamic quantities for a nonideal solid solution. It can be applied to any kind of solid solution with different types of structure. Intracrystalline chemical equilibrium relations at comparably low temperatures can be estimated by the combination of the conventional MD method and the chemical thermodynamic approach.

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