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Thermodynamics of Binary Mixed Crystals in the Sub-quasi-chemical/Debye Approximation

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A new statistical model for the description of the thermodynamic properties of binary mixed crystals is discussed. The model is based on an asymmetrical analogue of the quasi-chemical approximation and the Debye model of a solid. With two interchange-energy parameters and two interchange-Debye-temperature parameters, all important thermodynamic functions, at constant volume, of the binary mixed crystal can be calculated as a function of temperature and composition. The binary system $\{(1-x)\mathrm{NaI} + x\mathrm{KI}\}$ (s) is used for illustration of the model. © 1995 Academic Press, Inc.

INTRODUCTION

If two crystalline substances have the same morphology and their molecules are of not too different size and chemical nature, then binary mixed crystals can be formed. In the literature several statistical thermodynamic mixing models applicable to binary mixed crystals are known. In the simplest models, such as the regular, the subregular, the quasi-regular, and the quasi-sub-regular mixing models, the different particles A and B are assumed to be distributed randomly over the lattice sites. The more sophisticated mixing models, such as the quasi-chemical and the modified quasi-chemical mixing models, take into account deviations from random mixing. However, in all these mixing models the effect of thermal vibrations is not (explicitly) considered. The central atoms theory by Lupis and Elliott (1), originally developed for binary mixtures of fused metals, deals with the effect of thermal vibrations by means of the free-volume theory leading to the Einstein approximation; see also the recent work of Tanaka *et al.* (2–4). For a detailed discussion of these models, the reader is referred to the monograph by Guggenheim (5), the textbook by Lupis (6), and in the case of the modified quasi-chemical model, to Pelton and Blander (7).

In our opinion, any realistic model that describes the thermodynamic mixing behavior of solids should be an integrated approach simultaneously taking into account local ordering and thermal vibrations. In addition the model should lead to excess thermodynamic functions that can have a certain degree of asymmetry. The mixing model that will be described below is based on an asymmetrical analogue of the quasi-chemical approximation, which we shall refer to as the sub-quasi-chemical approximation, and the Debye theory of a solid.

SUB-QUASI-CHEMICAL/DEBYE APPROXIMATION

Average Surroundings

Consider a three-dimensional lattice with N lattice sites and coordination number z. It is assumed that there are no vacancies and that the lattice is completely filled with N_A particles A and N_B particles B. In a lattice with coordination number z each particle forms z pairs, hence, the total number of pairs is given by $\frac{1}{2}zN$

$$\tfrac{1}{2}zN = \tfrac{1}{2}z[N_A + N_B],$$

or equivalently

$$\begin{aligned}\tfrac{1}{2}zN &= \{N_{AA} + \tfrac{1}{2}N_{AB}\} + \{N_{BB} + \tfrac{1}{2}N_{AB}\},\\ &= N_{AA} + N_{BB} + N_{AB},\end{aligned} \quad [1]$$

where N_{AA}, N_{BB}, and N_{AB} are the numbers of AA, BB, and AB pairs, respectively. From [1] follows, for the number of AA and BB pairs,

$$N_{AA} = \tfrac{1}{2}[zN_A - N_{AB}] \text{ and } N_{BB} = \tfrac{1}{2}[zN_B - N_{AB}]. \quad [2]$$

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The mean fraction of atoms A around another atom A in a binary mixed crystal of A and B, α_{AA}, is given by

$$\alpha_{AA} = \frac{N_{AA}}{N_{AA} + \frac{1}{2}N_{AB}} = 1 - \frac{N_{AB}}{zN_A}, \quad [3]$$

which is simply the ratio of the total number of AA interactions and the total number of pair interactions in which an A atom is present as the central atom. Note that we write $\frac{1}{2}N_{AB}$ and not N_{AB} implying that we distinguish between AB and BA. Analogously, we may define the fractions α_{BB}, α_{AB}, and α_{BA} where the first character in the subscript refers to the central atom and the second character to the surroundings of that central atom. It can be shown that $\alpha_{AA} + \alpha_{AB} = 1$, $\alpha_{BB} + \alpha_{BA} = 1$, and $\alpha_{AB} + \alpha_{BA} = N_{AB}/N^*_{AB}$ where the asterisk denotes a random distribution of molecules A and B over the lattice sites. One might say that the α's are the average local mole fractions.

Average Interchange Energies

At infinite dilution the partial interchange energies ω_{AB} and ω_{BA} are given by

$$\omega_{AB} = u_{AB} - u_{AA} \quad \text{and} \quad \omega_{BA} = u_{BA} - u_{BB}, \quad [4]$$

implying that the difference in energy between breaking an AA interaction (with pair interaction energy u_{AA}) and forming an AB interaction (with pair interaction energy u_{AB}) is equal to ω_{AB} and analogously for ω_{BA}. In the subregular solution model—a random distribution of A and B over the lattice sites despite of the nonzero interchange energies—this leads to the following composition dependence of the interchange energy (8),

$$\omega(x) = (1 - x)\omega_{BA} + x\omega_{AB}, \quad [5]$$

where ω_{AB} and ω_{BA} are constants. This interchange energy multiplied by the total number of AB interactions $N^*_{AB} = zNx(1 - x)$ is the energy of mixing

$$U^E(x) = zNx(1 - x)[(1 - x)\omega_{BA} + x\omega_{AB}]. \quad [6]$$

In the sub-quasi-chemical approximation, N^*_{AB} should be replaced by N_{AB}. Second, the partial interchange energies ω_{AB} and ω_{BA} are no longer considered constants and they are to be replaced by the average partial interchange energies ω_A and ω_B given by

$$\omega_A = \alpha_{AB}\omega_{AB} + \alpha_{AA}\omega_{BA}, \quad [7]$$

$$\omega_B = \alpha_{BA}\omega_{BA} + \alpha_{BB}\omega_{AB}. \quad [8]$$

Consequently, the average interchange energy may then be expressed as

$$\omega(T, x) = (1 - x)\omega_B + x\omega_A, \quad [9]$$

and the energy of mixing of the binary mixed crystal becomes

$$U^E(T, x) = N_{AB}\omega(T, x). \quad [10]$$

It is easily verified that Eq. [10] reduces to Eq. [6] in the case of random mixing.

In the quasi-chemical theory (1) the free energy of mixing can be written as

$$\Delta_{mix}A(T, x) = -kT \ln \left(g \exp\left[-\frac{N_{AB}\omega}{kT}\right]\right), \quad [11]$$

where g, the (approximate) number of configurations, is given by

$$g = \frac{[N_A + N_B]!}{N_A!N_B!} \frac{N^*_{AA}!N^*_{BB}![N^*_{AB}/2]![N^*_{AB}/2]!}{N_{AA}!N_{BB}![N_{AB}/2]![N_{AB}/2]!}, \quad [12]$$

and ω is defined as

$$\omega \equiv u_{AB} - \tfrac{1}{2}(u_{AA} + u_{BB}). \quad [13]$$

In the sub-quasi-chemical approximation ω in Eq. [11] is replaced by $\omega(T, x)$ of Eq. [9].

Average Debye Temperatures

The Debye cut-off frequency of an atom A entirely surrounded by other atoms A is denoted by $\nu_{D,AA}$ or expressed as the Debye characteristic temperature $\Theta_{D,AA} = h\nu_{D,AA}/k$. For the Debye temperature of an atom A entirely surrounded by atoms B we use the notation $\Theta_{D,AB}$. Analogously we have $\Theta_{D,BB}$ and $\Theta_{D,BA}$. The average Debye temperature of an atom A in a mixture of A and B may now be approximated by

$$\Theta_{D,A} = \alpha_{AA}\Theta_{D,AA} + \alpha_{AB}\Theta_{D,AB}, \quad [14]$$

and for an atom B in a mixture of A and B

$$\Theta_{D,B} = \alpha_{BB}\Theta_{D,BB} + \alpha_{BA}\Theta_{D,BA}. \quad [15]$$

After the introduction of these assumptions and notations the Debye partition function of the binary ideally mixed crystal ($\Theta_{D,AB} = \Theta_{D,AA}$, $\Theta_{D,BA} = \Theta_{D,BB}$) and the Debye partition function of the mixed crystal can be calculated easily.

Debye Partition Function of a Binary Mixed Crystal

The logarithm of the Debye partition function is given by

$$\ln Q_D = -9N\left(\frac{T}{\Theta_D}\right)^3 \int_0^{y_D}\left[\frac{y}{2} + \ln(1 - \exp[-y])\right] y^2\, dy, \quad [16]$$

where $y = h\nu/kT$ and $y_D = h\nu_D/kT$. For a binary mechanical mixture as well as for a binary ideally mixed crystal of A and B we may write

$$\ln Q_D^{id}(T, x) = \ln Q_{D,AA} + \ln Q_{D,BB}, \quad [17]$$

where $\ln Q_{D,AA}$ and $\ln Q_{D,BB}$ are the Debye partition functions of pure A and B, and N of Eq. [16] is replaced by N_A and N_B, respectively. The Debye partition functions of atoms A and B in the binary nonideally mixed crystal are denoted by $\ln Q_{D,A}$ and $\ln Q_{D,B}$, respectively. These are functions of $\Theta_{D,A}$ and $\Theta_{D,B}$ given by Eqs. [14] and [15]. Analogous to Eq. [17] we write for the binary nonideally mixed crystal

$$\ln Q_D^{mc}(T, x) = \ln Q_{D,A} + \ln Q_{D,B}, \quad [18]$$

and the vibrational excess free energy we write as

$$\Delta_{mix}A^{vib}(T, x) = A^{E,vib}(T, x) = -kT \ln \frac{Q_D^{mc}(T, x)}{Q_D^{id}(T, x)}. \quad [19]$$

Total Partition Function of Mixing and Its Maximization

The partition functions of the sub-quasi-chemical approximation and the Debye partition function on mixing may be combined leading to

$$\begin{aligned}\Delta_{mix}A(T, x) &= -kT \ln Q_{mix} \\ &= -kT \ln\left\{\frac{Q_D^{mc}(T, x)}{Q_D^{id}(T, x)} \sum_{N_{AB}} g \exp\left[-\frac{N_{AB}\omega(T, x)}{kT}\right]\right\},\end{aligned} \quad [20]$$

where the sum may be replaced by its maximum term (which is equivalent to minimizing $\Delta_{mix}A(T, x)$)

$$\partial\left(\frac{Q_D^{mc}(T, x)}{Q_D^{id}(T, x)} g \exp\left[-\frac{N_{AB}\omega(T, x)}{kT}\right]\right)\Big/\partial N_{AB} = 0,$$

or

$$\partial\left(\ln g + \ln \frac{Q_D^{mc}(T, x)}{Q_D^{id}(T, x)} - \frac{N_{AB}\omega(T, x)}{kT}\right)\Big/\partial N_{AB} = 0, \quad [21]$$

leading to

$$\tfrac{1}{2}\ln(N_{AA}) + \tfrac{1}{2}\ln(N_{BB}) - \ln(\tfrac{1}{2}N_{AB}) + \frac{\partial}{\partial N_{AB}}\left[\ln\left(\frac{Q_D^{mc}(T, x)}{Q_D^{id}(T, x)}\right) - \frac{N_{AB}\omega(T, x)}{kT}\right] = 0. \quad [22]$$

An analytical solution of Eq. [22] is not available and numerical methods have to be used to solve the equation. After numerically solving Eq. [22] for the equilibrium number of AB interactions $\bar{N}_{AB}$, we may write the free energy of mixing in the sub-quasi-chemical/Debye approximation as

$$\Delta_{mix}\bar{A}(T, x) = -kT \ln\left(\bar{g}\,\frac{\bar{Q}_D^{mc}(T, x)}{\bar{Q}_D^{id}(T, x)} \exp\left[-\frac{\bar{N}_{AB}\bar{\omega}(T, x)}{kT}\right]\right), \quad [23]$$

where $\bar{g}$ is given by [12]. For the excess free energy and the excess entropy can be written

$$\bar{A}^E(T, x) = \Delta_{mix}\bar{A}(T, x) - RT\{(1 - x)\ln(1 - x) + x \ln x\} \quad [24]$$

and

$$\bar{S}^E(T, x) = \frac{\bar{U}^E(T, x) - \bar{A}^E(T, x)}{T}, \quad [25]$$

respectively, where $\bar{U}^E(T, x)$ is given by Eq. [10].

The model described above may be used the other way around, to derive the parameters $\Theta_{D,AB}$, $\Theta_{D,BA}$, ω_{AB}, and ω_{BA} from experimental region-of-demixing data. In order to do these calculations we developed the computer program SQUAD (9), which is discussed briefly, together with the SQUAD analysis of a number of binary systems in Ref. (10), and will be discussed in more detail in a subsequent paper (11).

Although the sub-quasi-chemical/Debye model is particularly suitable for the description of simple binary mixed crystals of the substitutional type, it can also be applied to simple binary salt systems with a common ion. In that case, the influence of the common-ion sublattice on the mixing behavior is not considered explicitly. However, the ω and Θ parameters obtained by means of an analysis of region-of-demixing data for these systems incorporate the effect of the common-ion sublattice.

Here, we will give as an example the results for the analysis of the binary system sodium iodide + potassium iodide as depicted in Figs. 1–5. The experimental region-of-demixing data as measured by Chanh (13) are plotted together with the SQUAD analysis of these data in Fig. 1.

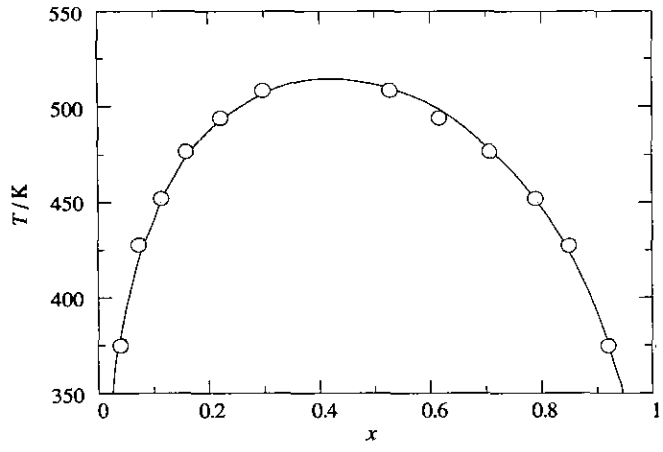

FIG. 1. SQUAD analysis of the region of demixing of $\{(1 - x)$NaI (A) + xKI (B)$\}$ (s). $\Theta_{D,AA} = 164$ K and $\Theta_{D,BB} = 131$ K (12), $\omega_{AB} = 998$ J · mole^{-1} $\omega_{BA} = 1169$ J · mole^{-1} $\Theta_{D,AB} = 146.4$ K and $\Theta_{D,BA} = 123.3$ K. The dots represent the experimental data as measured by Chanh (13).

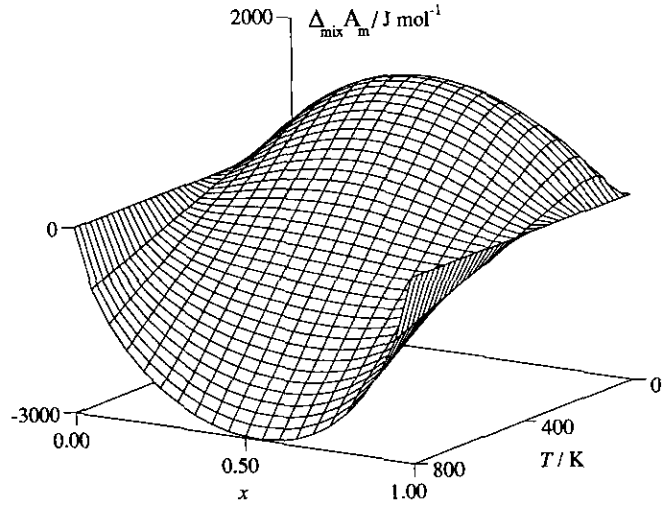

FIG. 2. Free energy of mixing function of $\{(1 - x)$NaI + xKI$\}$ (s).

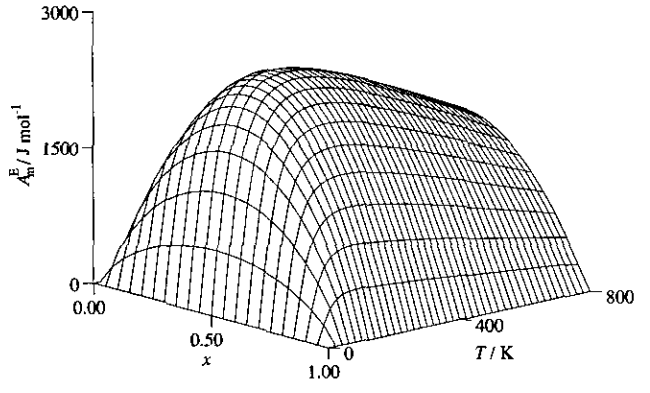

FIG. 3. Excess free energy function of $\{(1 - x)$NaI + xKI$\}$ (s).

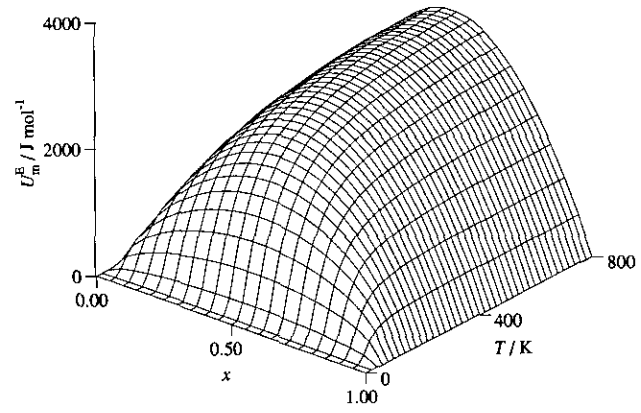

FIG. 4. Excess energy function of $\{(1 - x)$NaI + xKI$\}$ (s).

For the fit as depicted in Fig. 1 the following interchange parameters were used: $\omega_{AB} = 998$ J · mole^{-1}, $\omega_{BA} = 1169$ J · mole^{-1}, $\Theta_{D,AB} = 146.4$ K, and $\Theta_{D,BA} = 123.3$ K. For the coordination number we used $z = 12$, i.e., the coordination number of the sublattice in which substitution takes place. The free energy of mixing for this system is depicted as a function of temperature and composition in Fig. 2. At lower temperatures the system is demixed in two phases and the binodal compositions are given by the common tangent at the free energy of mixing curve at the specified temperature. At temperatures above approximately 515 K the free energy of mixing is convex downward in the entire composition range and a continuous series of binary mixed crystals is formed. The excess free energy is depicted as a function of temperature and composition in Fig. 3. At 0 K the system is completely demixed in the pure substances resulting in a zero excess free energy. With increasing temperature the excess free energy rises rapidly toward a maximum and eventually drops off almost linearly with temperature. The excess energy is plotted as a function of temperature and compo-

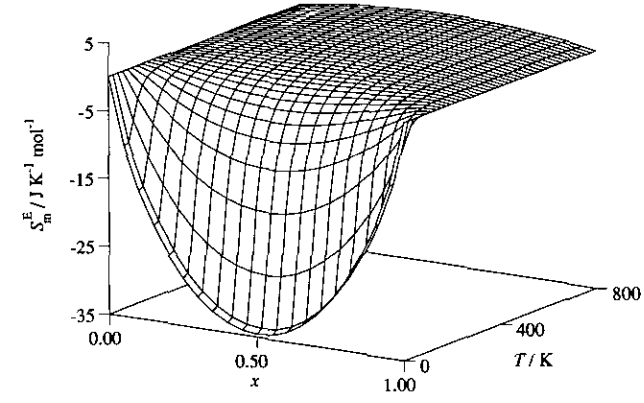

FIG. 5. Excess entropy functions of $\{(1 - x)$NaI + xKI$\}$ (s).

sition in Fig. 4. With increasing temperature the excess energy increases until a random distribution of A and B over the lattice sites is reached, i.e., to the subregular approximation. Finally, in Fig. 5, the excess entropy as a function of temperature and composition is shown. At lower temperatures the excess entropy is mainly a configurational excess entropy, determined by the nonrandomness of the mixture. At more elevated temperatures the effect of thermal vibrations is of major importance leading to a positive excess entropy in the entire composition range.

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