CALCULATION OF THERMODYNAMIC PROPERTIES AND OF LIQUIDUS LINE POSITIONS FOR Na–K ALLOYS

K. Yu. Shunyaev and V. L. Lisin

Institute of Metallurgy, Ural's Division of Russian Academy of Sciences, 101 Amundsen Str. Ekaterinburg 620016, Russia

Abstract

A model of an ideal associated solution, containing self-associates of different sizes and shapes, was considered. Calculations of the thermodynamic properties of mixing of Na–K liquid alloys and of liquidus line positions were carried out. Possible modifications of the model are discussed.

Keywords: associated solution, binary eutectic alloys, liquidus line, Na–K, thermodynamic properties

Introduction

One of the models which has been successfully applied for a long time to the description of the behaviour of the thermodynamic properties of mixing is a model of an ideal associated solution. General theory predicts the possibility of existence of complexes of different sizes and stoichiometry, including self-associates, in liquids [1]. However, one usually bears in mind only from one to three associates of minimum size and single atoms of initial components when making the calculations. In the model considered this is caused by the necessity of reasonable restriction of the model parameters that are equilibrium constants of formation of associates from initial components of solution [2, 3]. We have proposed one version of an ideal associated solution model [4–7] which takes into account complexes of different sizes and shapes. We used the pair approximation for nearest neighbours when calculating the enthalpies of associates, but did not consider the differences in sizes of different complexes and associates for the configurational entropy, as in the usual model of an ideal associated solution [1]. It was shown that such an approach allows the number of model parameters to be minimized and also allows values of the parameters to be obtained from the melting temperatures of stable compounds. Thereby, one can avoid the traditional procedures of model-parameter fitting and perform essentially non-empirical calculations.

Model

Let us consider the $A_c B_{1-c}$ binary system, containing components that are insoluble in the solid phase, but which form solutions with complete solubility in the liquid phase. Let it be an ideal solution of $A_{n,i}$ and $B_{n,i}$ associates (n – number of atoms in the complex, i – number of pairs of nearest neighbours in the complex). If one accepts that the energy of the complex is defined as the sum of the energies of the pairs of nearest neighbours and is limited only by configurational contributions to entropy, then the molar fractions of complexes will correlate with each other by the following expressions [6]:

$$x_{A_{n,i}} = K_{A_{n,i}} x_{A_1}^n = \exp\left(\frac{\alpha_A i}{kT}\right) x_{A_1}^n = t_A^i x_{A_1}^n$$

$$x_{B_{n,i}} = K_{B_{n,i}} x_{B_1}^n = \exp\left(\frac{\alpha_B i}{kT}\right) x_{B_1}^n = t_B^i x_{B_1}^n$$

(1)

where $x_{A_{n,i}}$; $x_{B_{n,i}}$; x_{A_1}; x_{B_1}; are the molar fractions of $A_{n,I}$, $B_{n,i}$ complexes and of A_1, B_1 single atoms respectively, α_A and α_B are the bonding energies of AA and BB pairs of nearest neighbours taken with the inverse sign, $K_{A_{n,i}}$; $K_{B_{n,i}}$ are the corresponding equilibrium constants; $t_A = \exp(\alpha_A/kT)$; $t_B = \exp(\alpha_B/kT)$.

Then the system of balanced equations for determination of the concentrations of single atoms and of associates in solution will be:

$$\sum_{n=1}^{\infty}\sum_{i=n-1}^{m_n} x_{A_{n,i}} + \sum_{n=1}^{\infty}\sum_{i=n-1}^{m_n} x_{B_{n,i}} = 1$$

$$c = \frac{\displaystyle\sum_{n=1}^{\infty}\sum_{i=n-1}^{m_n} n x_{A_{n,i}}}{\displaystyle\sum_{n=1}^{\infty}\sum_{i=n-1}^{m_n} n x_{A_{n,i}} + \sum_{n=1}^{\infty}\sum_{i=n-1}^{m_n} n x_{B_{n,i}}}$$

(2)

If the associates in the melt are expected to have different configurations, then i obviously changes from $n-1$, corresponding to a linear chain, to a certain number m_n. If one assumes that such an associate has the local geometry of the corresponding component, this number can be found for small n [6, 7]. Since the rows in (2) quickly reconverge, it is sufficient to define the $m_n(n)$ dependency at up to $n \sim 10$–15 for making the calculations. Now the system (2) can be solved numerically under known α_A and α_B. It is possible also to approximate the $m_n(n)$ dependency by a suitable function. This does not lead to a loss of accuracy but allows the sums in the balance equations and in expressions for thermodynamic characteristics of mixing to be expressed by analytical relations [7].

Let us introduce a special notation for the characteristic sums for the purpose of simplification:

$$S_{1L} = \sum_{n=1}^{\infty} \sum_{i=n-1}^{m_n} x_{L_{n,i}} = \sum_{n=1}^{\infty} \sum_{i=n-1}^{m_n} x_{L_1}^n t_L^i$$

$$S_{2L} = \sum_{n=1}^{\infty} \sum_{i=n-1}^{m_n} n x_{L_{n,i}} = \sum_{n=1}^{\infty} \sum_{i=n-1}^{m_n} n x_{L_1}^n t_L^i$$

$$S_{3L} = \sum_{n=1}^{\infty} \sum_{i=n-1}^{m_n} i x_{L_{n,i}} = \sum_{n=1}^{\infty} \sum_{i=n-1}^{m_n} i x_{L_1}^n t_L^i \qquad (3)$$

$$S_{4L} = \sum_{n=1}^{\infty} \sum_{i=n-1}^{m_n} n^2 x_{L_{n,i}} = \sum_{n=1}^{\infty} \sum_{i=n-1}^{m_n} n^2 x_{L_1}^n t_L^i$$

Here L denotes the A or B kind of atom.

Now the balance equation system (2) is

$$S_{1A} + S_{1B} = 1$$
$$c(S_{2A} + S_{2B}) = S_{2A} \qquad (4)$$

Thermodynamic characteristics of mixing look as follows:

$$\Delta G^M = RT(c \ln a_A + (1-c) \ln a_B) = RT \left(c \ln \frac{x_{A_1}}{x_{A_0}} + (1-c) \ln \frac{x_{B_1}}{x_{B_0}} \right) \qquad (5)$$

$$\Delta H^M = -\frac{\alpha_A S_{3A} + \alpha_B S_{3B}}{S_{2A} + S_{2B}} + c \alpha_A \frac{S_{3A0}}{S_{2A0}} + (1-c) \alpha_B \frac{S_{3B0}}{S_{2B0}}$$

Here ΔG^M, ΔH^M are the free energy of mixing and enthalpy of mixing respectively, a_A and a_B are the activities of the A and B components. The zero symbol in the sum means that the corresponding sum is calculated at the considered temperature for the pure component in the liquid phase. One can also easily express the long-wave limit of the concentration-concentration partial structural factor, which is known [8] to be defined by the second derivative of free energy, as:

$$S_{cc}(0) = RT \left(\frac{\partial \Delta G}{\partial c^2} \right)_{T,p,n}^{-1} = \frac{c^2 S_{4B} + (1-c)^2 S_{4A}}{S_{2A} + S_{2B}} \qquad (6)$$

To calculate thermodynamic properties using the above-mentioned expressions, it is necessary to know the values of the energy parameters, α_A and α_B. As was shown in [6–7], it is possible to calculate these parameters from the equality of the free energies of the liquid and solid phases at the melting temperatures of the components of the solution, considering an associate of infinite size as a crystal. Therefore, one can express the energy parameters in terms of the melting temperatures of the components. For structures with dense packing (FCC, HPC) $\alpha_L = 0.177 RT_L$, where T_L is the melting temperature of the L component. Results for a BCC-lattice are slightly different, taking into account, in particular, such circumstances as that the difference in distances to the first and to the second neighbours is not as great in this lattice.
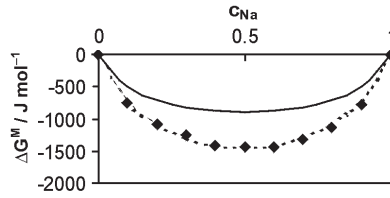
Fig. 1 Gibbs free energy of mixing of Na–K liquid alloys at $T=384$ K.
Solid line – model calculation taking into account only self-associates,
dashed line – calculation with provision for mixed associates, rhombic dots –
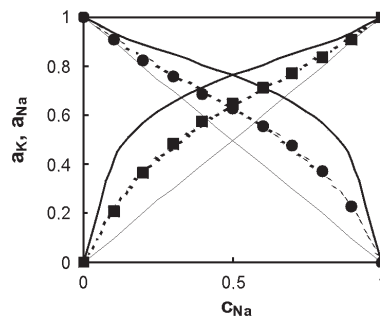experimental data [10]

Fig. 2 Activities of components of Na–K liquid alloys at $T=384$ K. Solid and dashed
lines are the same as in Fig. 1. Dark circles and dark squares – K and Na experi-
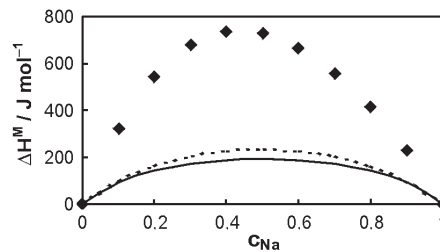mental activities, respectively [10]

Fig. 3 Enthalpy of mixing of Na–K liquid alloys at $T=384$ K. Solid and dashed lines
are the same as in Fig. 1. Rhombic dots – experimental data [10]

This proposed approach for the calculation of energy parameters also allows the calculation of phase diagrams within the framework of the model of the liquid considered. In the simplest case, that is in the absence of mutual solubility of components in the solid phase, such calculation does not require any additional assumptions. For instance, the accounting expression for the branch of the liquidus line adjacent to the A component (T_{LA}) is:

$$-0.5\alpha_A z_A = RT_{LA} \ln x_{A_l} \tag{7}$$

where z_A is the coordination number of the A component in the solid state.
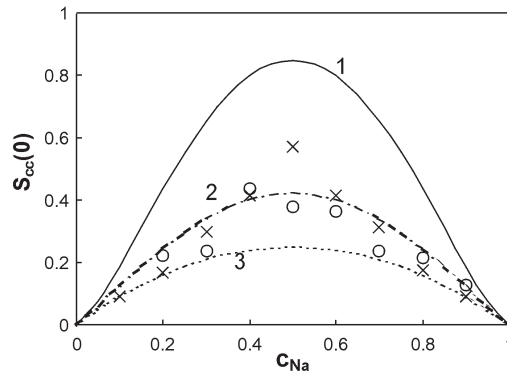
Fig. 4 Long-wave limit of concentration-concentration partial structural factor of Na–K liquid alloys at $T=384$ K. Solid line 1 – model calculation taking into account only self-associates; dashed line 2 – calculation with provision for mixed associates, dashed line 3 – calculation using the ideal solution model; light circles, crosses – experimental data [11]
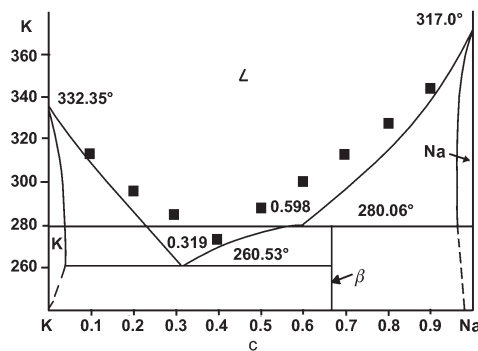

Fig. 5 Liquidus curve for the Na–K system [10] (squares – theoretical calculations)

Analysis shows that the model correctly describes the particularities of the thermodynamic characteristics for the majority of eutectic systems, namely positive deviations from ideal behaviour of component activities and of enthalpies of mixing, and a decrease of melting temperature when adding the second component [6, 7]. However, quantitative agreement with experiment is not achieved because of the crudeness of the model in use. It was proposed in [9] to modify the model, taking into account the possibility of existence of associates of mixed composition in liquids. Such modernization does not revise significantly the structure of the accounting expressions, but only gives rise to additional terms, corresponding to mixed associates. Besides this, an additional energy parameter appears, characterizing the bonding energy of the AB pair. This parameter happens to be used as a parameter of fitting.

Results and discussion

The Na–K system belongs to the systems of eutectic type [10]. The components are completely soluble in the liquid phase, but are practically insoluble in the solid state. The thermodynamic characteristics of mixing are practically symmetrical with respect to an equiatomic composition. The results of calculations within the proposed model are shown in Figs 1–4 (solid curves) and in Fig. 5 (squares). From comparison with experiment, it is seen that the model satisfactorily reproduces the behaviour of the concentrational dependencies of the considered characteristics, particularly taking into account the absence of fitting parameters. At the same time, no strictly quantitative agreement is observed. This is probably due to the fairly crude model's basic assumption on the exclusive presence of self-associates in the melt. Indeed, when the probable presence of mixed associates with various stoichiometry in the liquid phase is added into consideration, the agreement with experiment is much better for all the characteristics, except for the enthalpy of mixing (dashed lines in Figs 1–4). The absence of good agreement for the enthalpy of mixing is caused in this case, not by model's disadvantages, but by the use of assumptions that facilitate the mathematical procedures but greatly reduce the values of the enthalpy of mixing by themselves [5]. The proposed model clearly demonstrates the importance of consideration of self-association effects when calculating eutectic systems and alloys characteristics. It allows calculations of both the thermodynamic properties of mixing and of phase diagrams to be carried out using one and the same base.

* * *

References

1 I. Prigogine and R. Defay, Chemical Thermodynamics, Longmans Green and Co., London, 1954.
2 K. Wasai and K. Mukai, J. Jap. Inst. Metals, 46 (1982) 266.
3 A. G. Morachevsky, A. G. Mokrievich and E. A. Mayorova, J. Appl. Chem., 66 (1993) 1441 (in Russian).
4 N. C. Tkachev, K. Yu. Shunyaev and A. N. Men, Phys. Chem. Liquids, 15 (1986) 271.
5 K. Yu. Shunyaev, N. C. Tkachev and A. N. Men, Melts, 2 (1990) 360.
6 N. C. Tkachev, K. Yu. Shunyaev, A. N. Men and N. A. Vatolin, Doklady Akademii Nauk, 302 (1988) 153 (in Russian).
7 K. Yu. Shunyaev and N. A. Vatolin, Doklady Akademii Nauk, 332 (1993) 167 (in Russian).
8 A. B. Bhatia and D. E. Thornton, Phys. Rev. B, 2 (1970) 3004.
9 K. Yu. Shunyaev and V. A. Krashaninin, Metalli, No. 4 (1991) 82 (in Russian).
10 R. Hultgren, P. Desai, D. Hawkins, M. Gleiser and K. Kelley, Selected Values of the Thermodynamic Properties of Binary Alloys, ASM. Metal Park, Ohio 1973.
11 B. P. Alblas and W. van der Lugt, J. Phys. F, 10 (1980) 531.