Liquidus Curves of Eutectic NaK and NaCs Systems

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The Conformal Solution and Flory's expressions for the free energy of mixing ΔG_M of a binary liquid alloy have been modified by using a form for the enthalpy of mixing ΔH_M which incorporates the concentration dependence given by Miedema's semiempirical model. This model emphasizes the importance of the atomic cell-surface area concentration in evaluating ΔH_M. The modified forms of ΔG_M have been used to construct the liquidus curves of NaCs and NaK.

1. Introduction

It is well known [1] that the liquidus curves (at constant pressure) of a binary mixture in which the components are completely miscible in the liquid state but immiscible in the solid state can be described by the equation

$$\ln(x_i \gamma_i) = \int_{T_i^0}^{T} \frac{L_{i0}}{R T^2} \, dT \quad (i = 1, 2), \tag{1}$$

where x_i and γ_i are the mole fraction and the activity coefficient, respectively, and L_{i0} and T_i^0 are respectively the heat of fusion at the temperature T and the melting point of the pure component i. To integrate (1), the dependence of L_{i0} on T must be taken into account, and this can be done using Kirchhoff's equation

$$L_{i0}(T) - L_{i0}(T_i^0) = -\int_{T_i^0}^{T} (C_{p,i}^L - C_{p,i}^S) \, dT, \tag{2}$$

where $C_{p,i}^L$ and $C_{p,i}^S$ are the heat capacities at constant pressure of the pure component i in the liquid and solid states, respectively. The difference $\Delta C_{p,i}^0 = C_{p,i}^L - C_{p,i}^S$ is generally assumed to be constant in the temperature range of interest, so that (1) becomes

$$-\ln(x_i \gamma_i) = \frac{L_{i0}(T_i^0)}{R}\left(\frac{1}{T} - \frac{1}{T_i^0}\right) + \frac{\Delta C_{p,i}^0}{R}\left(\ln\frac{T_i^0}{T} + 1 - \frac{T_i^0}{T}\right). \tag{3}$$

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In order to apply (3) to a particular system it is necessary to know an expression for the activity coefficients taken from a theory of mixtures. For example, Bhatia and March [2] have applied the *Conformal Solution model* (*C*) (or the regular solution model in the zeroth approximation [3]) to explain the liquidus curves of the NaK alloy. In this theory the free energy of mixing has the expression

$$\Delta G_M = R T (x_1 \ln x_1 + x_2 \ln x_2) + w x_1 x_2, \tag{4}$$

w being the interchange energy parameter and R the gas constant. Then the activity coefficients are

$$\ln \gamma_1 = (w/RT) x_2^2, \quad \ln \gamma_2 = (w/RT) x_1^2. \tag{5}$$

In their work on NaK Bhatia and March used the value $(w/R) = 421.3\ \mathrm{K}^{-1}$, which they obtained by fitting the conformal solution structure factors [4] to experimental data of McAlister and Turner [5].

For the NaCs system, in which the regular solution model fails because the atomic volumes of the components differ widely, Bhatia and March [6] have used *Flory's model* (*F*) [7]. In this model the free energy of mixing has the form

$$\Delta G_M = R T (x_1 \ln \varphi_1 + x_2 \ln \varphi_2) + w x_1 \varphi_2, \tag{6}$$

where φ_1 and φ_2 are concentrations by volume

$$\varphi_1 = \frac{x_1 V_1}{x_1 V_1 + x_2 V_2}, \quad \varphi_2 = \frac{x_2 V_2}{x_1 V_1 + x_2 V_2}, \tag{7}$$

V_1 and V_2 being the atomic volumes of the two components. By appropiate differentiation of (6),

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the following expressions for the activity coefficients are obtained:

$$\ln \gamma_1 = \ln \frac{1}{x_1 + x_2 r} + \frac{x_2 (r-1)}{x_1 + x_2 r} + \frac{(w/RT)\, x_2^2 r^2}{(x_1 + x_2 r)^2},$$
$$\ln \gamma_2 = \ln \frac{r}{x_1 + x_2 r} + \frac{x_1 (1-r)}{x_1 + x_2 r} + \frac{(w/RT)\, x_1^2 r}{(x_1 + x_2 r)^2}, \quad (8)$$

where $r = V_2/V_1$. By introducing these expressions in (3), Bhatia and March [6] obtained fairly good agreement with the experimental liquidus curve of Kim and Letcher [8]. The value of w used in their calculation was $(w/R) = 436.6\ \mathrm{K}^{-1}$, which gives the best fit of Flory's theory to the experimental EFM data of Ichikawa et al. [9, 10].

2. Modified Conformal and Flory Models

The factor w appears in the enthalpy of mixing ΔH_M of (4) and (6). This factor is then multiplied by a function $F(x_1, x_2)$ controlling the concentration dependency of ΔH_M. $F(x_1, x_2)$ is given as the product of x_1 times x_2 (in (4)) or times φ_2 (in (6)). But the success of the semiempirical theory of heats of mixing developed by Miedema and coworkers [11] suggests that $F(x_1, x_2)$ is of the form

$$F(x_1, x_2) = x_1 \xi_2, \quad (9)$$

where ξ_2 is the atomic cell surface area concentration

$$\xi_2 = \frac{x_2 V_2^{2/3}}{x_1 V_1^{2/3} + x_2 V_2^{2/3}}. \quad (10)$$

Using (9) in the enthalpy of mixing and leaving the entropy of mixing unmodified one obtains the expressions

$$\Delta G_M = RT (x_1 \ln x_1 + x_2 \ln x_2) + w x_1 \xi_2, \quad (11)$$
$$\Delta G_M = RT (x_1 \ln \varphi_1 + x_2 \ln \varphi_2) + w x_1 \xi_2, \quad (12)$$

which are the modified forms of (4) and (6), respectively. Expressions (11) and (12) will be called here the *Modified Conformal* (MC) and *Modified Flory* (MF) forms of ΔG_M, respectively. These two models have been applied by Alonso and coworkers [12, 13] in the study of the concentration fluctuations of simple alloys. In addition Gallego et al. [14, 15] have shown that ΔG_M (MF) appears in a natural way within the framework of Kehiaian's theory of mixtures [16], which is a version of Guggenheim's quasi-lattice theory [3] in terms of contact surface interactions. It then appears natural to apply the MC and MF models to construct the liquidus curves of NaCs and NaK because Bhatia and March [2] have shown that there is a close relationship between the slope of the liquidus curve and the concentration fluctuations. From (11) the activity coefficients may be found to be given by

$$\ln \gamma_1 = (w/RT)\, \xi_2^2, \quad \ln \gamma_2 = (w/RT)\, \xi_1^2. \quad (13)$$

On the other hand, from (12) one obtains

$$\ln \gamma_1 = \ln \frac{1}{x_1 + x_2 r} + \frac{x_2 (r-1)}{x_1 + x_2 r} + \frac{(w/RT)\, x_2^2 (r^{2/3})^2}{(x_1 + x_2 r^{2/3})^2},$$
$$\ln \gamma_2 = \ln \frac{r}{x_1 + x_2 r} + \frac{x_1 (1-r)}{x_1 + x_2 r} + \frac{(w/RT)\, x_1^2 r^{2/3}}{(x_1 + x_2 r^{2/3})^2}. \quad (14)$$

Using the appropriate expressions for $\ln \gamma_1$ and $\ln \gamma_2$ in (3), the liquidus curves are readily constructed. The input data for the pure components are shown in Table 1.

Table 1. Thermodynamic properties of the pure components, used as input data in the calculations: T^0 (melting point), L_0 (heat of fusion), ΔC_p^0 (change of heat capacity by melting).

Metal	T^0(K) [a]	L_0/RT^0 [b]	$(\Delta C_p^0)/R$
Na	371.0	0.86	0.06 [c]
K	336.35	0.86	0.16 [c]
Cs	301.55	0.87	0.17 [d]

[a] Reference [17]. [b] L_0 from [18]. [c] Reference [2]. [d] From [18] and [19].

3. Results

The calculated liquidus curves are compared with the experimental ones in Figs. 1 and 2. Figure 1 shows that the MF model is inferior to Flory's model in the NaCs alloy. The parameter w has been varied to obtain a good fit to the experimental liquidus curve. The two theoretical curves correspond to (w/R) (F) $= 421.3\ \mathrm{K}^{-1}$, (w/R) (MF) $= 536.2\ \mathrm{K}^{-1}$. These values agree with values obtained by using the same models to fit other thermodynamic properties [6, 13]. Since the same form for the entropy of mixing is used in both models (see (6) and (12)), the results of Fig. 1 suggest that the

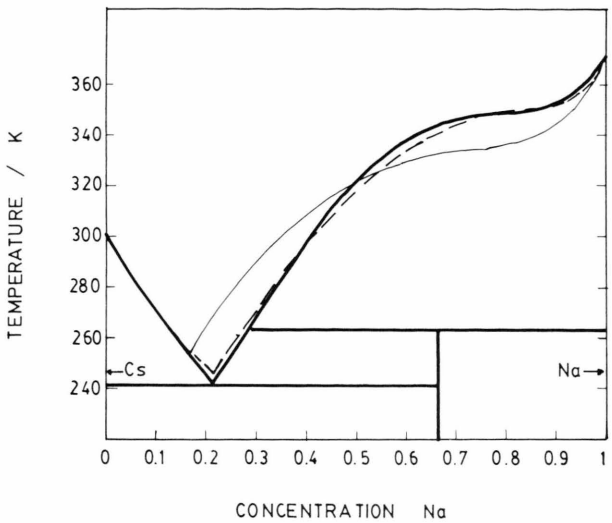

Fig. 1. Experimental [17] and calculated liquidus curves of NaCs. ---- F, —— MF.

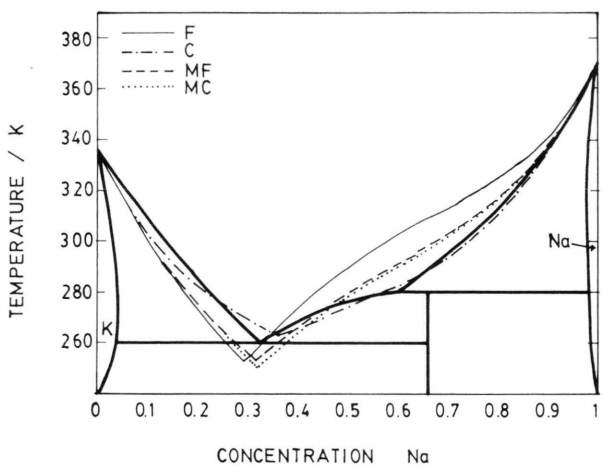

Fig. 2. Experimental [17] and calculated liquidus curves on NaK.

factor controlling the concentration dependence of ΔH_M in NaCs is well described by $x_1 \varphi_2$, rather than by $x_1 \xi_2$. Support for this interpretation is obtained by comparing the ratio α of the heats of solution,

$$\alpha = \frac{\Delta H_S \text{ (Cs in Na)}}{\Delta H_S \text{ (Na in Cs)}}, \tag{15}$$

where

$$\Delta H_S \text{ (Cs in Na)} = \lim_{x_2 \to 0} \frac{\Delta H_M (x_1, x_2)}{x_1 x_2}, \tag{16}$$

$$\Delta H_S \text{ (Na in Cs)} = \lim_{x_1 \to 0} \frac{\Delta H_M (x_1, x_2)}{x_1 x_2}. \tag{17}$$

Here $x_1 = x_{Na}$, $x_2 = x_{Cs}$. α is a measure of the asymmetry of $\Delta H_M (x_1, x_2)$. Thus, in the MF model

$$\alpha \text{ (MF)} = (V_{Cs}/V_{Na})^{2/3}. \tag{18}$$

On the other hand

$$\alpha \text{ (F)} = V_{Cs}/V_{Na}. \tag{19}$$

Using experimental volumes one finds α (MF) = 2.08 and α (F) = 3.03. The value of α obtained from the experimental heats of mixing measured by Yokokawa and Kleppa [20] is $\alpha = 3.57$, which favours the result of α (F). This suggests that the function controlling the concentration dependence of ΔH_M in Miedema's theory is susceptible of improvement in some alloys.

Figure 2 presents the results for NaK. The most successful fit is obtained with the Conformal Solution model ($w/R = 429.0$ K^{-1}). Since the C and MC models only differ in the form of the enthalpy of mixing, let us compare their respective values of the ratio $\alpha = (\Delta H_S \text{ (K in Na)})/(\Delta H_S \text{ (Na in K)})$. One then finds $\alpha \text{ (MC)} = (V_K/V_{Na})^{2/3} = 1.57$, and α (C) = 1 ($\Delta H (x_1, x_2)$ is symmetric in the concentrations in the Conformal Solution model). On the other hand, from experimental values of the enthalpy of mixing [20], $\alpha = 1.61$, in favor of α (MC). This fact indicates that the good agreement with the experimental liquidus curve obtained by the Conformal Solution model is somewhat fortuitous and comes from a compensation of errors in the entropy and enthalpy of mixing. The MF model gives a liquidus curve of similar quality to that of the MC model. This is understandable because V_{Na} and V_K are not too different, and Flory's entropy of mixing is nearly ideal in the case of similar volumes. Finally, Flory's model is the less successful one, due to an inaccurate description of the concentration factor $F(x_1, x_2)$ of the enthalpy of mixing (α (F) = 1.96).

4. Summary and Comments

The expressions for the free energy of mixing of a binary liquid alloy corresponding to a) the Conformal Solution model and b) Flory's model have been modified by introducing a form for the factor $F(x_1, x_2)$ controlling the concentration dependence of ΔH_M suggested by Miedema's theory [11]. This theory emphasizes the importance of atomic cell

surface area concentrations in the evaluation of ΔH_M. The effect of this modification has been tested by constructing the liquidus curves of NaK and NaCs. Flory's model is more successful than its modified counterpart in the case of NaCs. The reason is that $\Delta H_M(x_1, x_2)$ becomes too symmetric in the concentrations in the modified model. In the case of NaK, the two models based on the ideal entropy of mixing, namely, the Conformal Solution model and its modified counterpart, are the more successful ones. In fact, due to a fortuitous cancellation of errors, the Conformal Solution model gives the best results. The use of an expression for the enthalpy of mixing of liquid alloys with the concentration dependence factor $F(x_1, x_2)$ suggested by Miedema's theory can then be useful in the study of the thermodynamic properties of liquid alloys. Although one of the two alloys studied in this paper (NaCs) is not particularly well represented by this concentration factor there is more than enough evidence, from the success of Miedema's theory [11], that $F(x_1, x_2) = x_1 \xi_2$ provides a good overall description of most alloys. Miedema's theory also provides a value for the parameter w in terms of the difference of electronegativity and difference of cell boundary electron density between the two components of the alloy. In this paper, as well as in previous ones [12, 13], rather than using this theoretical value of w, its value has been chosen so as to optimize the fit to the property of interest (the liquidus curves here).

Finally we mention a simplification used in this paper, as well as in previous ones by other authors [2, 6], in constructing the liquidus curves of NaK and NaCs. The simplification consists in neglecting the existence of the solid components Na_2K and Na_2Cs. Below the temperature at which the compound decomposes, the liquid phase is in equilibrium with the compound and not with pure Na. The effect of the compound on the form of the liquidus curve is clearly visible in NaK, but is unimportant in NaCs. The consideration of the compound would complicate the computations. On the other hand, not all the necessary input data pertaining to the compound are known.

Acknowledgements

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