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Thermodynamic Relationship between Enthalpy of Mixing and Excess Entropy in Solid Solutions of Binary Alloys

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Thermodynamic relationships between enthalpy of mixing and excess entropy, and partial enthalpy of solution and partial excess entropy in solid solutions of binary alloys have been derived based on the free volume theory. Using the above relations, excess entropy and excess Gibbs energy of solid solutions in Ag–Au, Ag–Pd and Au–Pd binary alloys have been calculated from enthalpy of mixing, and compared with the literature values.

Zusammenhang zwischen Mischungsenthalpie und Überschußentropie bei binären Legierungen


1 Introduction

Some empirical relationships have been reported [1 to 9] for partial enthalpy of solution and partial excess entropy in dilute solid solutions as well as dilute liquid solutions of binary alloys. In previous work [10 to 17], we derived thermodynamic relationships between enthalpy of mixing and excess entropy in liquid binary alloys, partial enthalpy of solution and partial excess entropy in liquid dilute binary alloys, and enthalpy interaction parameter and entropy interaction parameter in liquid dilute ternary alloys on the basis of the free volume solution model. Based on those relationships, we found that the partial excess entropy of solute elements in liquid dilute binary alloys stems from the free volume of the elements, i.e., displacement of the elements from their equilibrium positions. The purpose of this work is to extend the above free volume solution model to solid solutions of binary alloys and to derive thermodynamic relationships between enthalpy of mixing and excess entropy in solid solutions of binary alloys, and partial enthalpy of solution and partial excess entropy of solute element in dilute solid solutions of binary alloys.

2 Thermodynamic Equations

Based on the free volume solution model [16] and the first approximation of regular solutions considering atom configuration in solutions [18], the excess Gibbs energy $G^E$, the enthalpy of mixing $\Delta H_{\text{mix}}$ and the excess entropy $S^E$ in an A–B binary alloy can be expressed as follows:

$$G^E = \Delta H_{\text{mix}} - T \cdot S^E$$

$$\Delta H_{\text{mix}} = \Omega_{\text{AB}} X_A X_B (1 - X_A X_B \cdot \frac{\Omega_{\text{AB}}}{R T})$$

$$S^E = S^E_{\text{CONF}} + S^E_{\text{VIB}}$$

$$S^E_{\text{CONF}} = -X_A^2 X_B^2 \frac{\Omega_{\text{AB}}^2}{2 RT^2}$$

$$S^E_{\text{VIB}} = \frac{3}{2} X_A X_B \left[ \frac{(L_{\text{AA}} - L_{\text{BB}})^2}{L_{\text{AA}} L_{\text{BB}}} + \frac{4 U_{\text{AA}} U_{\text{BB}} - 2 \Omega_{\text{AB}} (U_{\text{AA}} + U_{\text{BB}}) - (U_{\text{AA}} + U_{\text{BB}})^2}{2 U_{\text{AA}} U_{\text{BB}}} \right]$$

where $X_A$ and $X_B$ are mole fractions of components A and B; $R$ is the gas constant, $T$ is the temperature in K and $\Omega_{\text{AB}}$ is the interaction parameter.

$L_{XX}$ (XX = AA or BB) is the distance which the interatomic potential energy $\Psi(r)$ extends in a cell of atom X in pure metal X as shown in Fig. 1. $U_{XX}$ (XX = AA or BB) is the depth of the potential energy in a cell of atom X in pure metal X as shown in Fig. 1. In addition, the above model gives us the following equations [16] for the partial enthalpy of solution $H_B$ and the partial excess entropy $S^E_B$ of solute element B in an infinitely dilute solution of A–B binary alloy

$$H_B = \Omega_{\text{AB}}$$

$$S^E_B = S^E_{B,\text{CONF}} + S^E_{B,\text{VIB}}$$
when each atom vibrates harmonically in its cell, which is made by its nearest-neighbor atoms

\[ U_{XX} = \left( -2\pi^2 L_{XX}^2 M_X v_X^2 \right) \cdot N_0 \cdot 10^{-7} \]  

(14)

where \( M_X \) (g \cdot mol\(^{-1}\)) is the atomic weight of element X. \( N_0 \) is the Avogadro number. Since the unit of the quantity \(-2\pi^2 L_{XX}^2 M_X v_X^2 / N_0\) in the parentheses in Eq. (14) is erg \cdot atom\(^{-1}\), \( U_{XX}/J \cdot \text{mol}^{-1} \) is obtained [16] by multiplying \( N_0 \cdot 10^{-7} \) to \(-2\pi^2 L_{XX}^2 M_X v_X^2 / N_0\). \( L_{XX} \) is expressed as follows [16, 19]

\[ L_{XX} = a_X \left( \frac{2/3 V_X}{N_0} \right)^{1/3} \]  

(15)

where \( V_X \) (cm\(^3\) \cdot mol\(^{-1}\)) is the molar volume of element X. \( a_X \) in Eq. (15) is a parameter [19] determining the distance which the interatomic potential energy extends in a cell of atom X in pure metal X against the average interatomic distance \((2/3 V_X/N_0)^{1/3}\). The value of \( a_X \) is approximately equal to 0.51 ± 1/2 for liquid metals [19].

\( v_X \) in Eq. (14) can be expressed in Eq. (16) when the harmonic oscillation is assumed [19] for an atom in its cell

\[ v_X = 2.8 \cdot 10^{12} \beta_X \left( \frac{T_{m,X}}{M_X (V_X)^{2/3}} \right)^{1/2} \]  

(16)

where \( \beta_X \) is a coefficient converting the solid state frequency to that in the liquid at the melting point [16, 19]. The values of \( \beta_X \) for various elements were obtained from the experimental data on surface tension of pure liquid metals. When the values of \( \beta_X \) are not available, it can be set approximately to 0.5 of the pure liquid metals [16, 19].

Substituting Eqs. (15) and (16) into Eq. (14), we obtain

\[ U_{XX} = -2\pi^2 \left( \frac{a_X}{N_0} \right)^{1/3} \frac{1}{2} M_X \left[ \frac{2.8 \cdot 10^{12} \beta_X T_{m,X}}{M_X (V_X)^{2/3}} \right]^{1/2} \frac{1}{N_0} \cdot N_0 \cdot 10^{-7} \]

\[ = -2\pi^2 \left( \frac{2/3 V_X}{N_0} \right)^{2/3} (2.8 \cdot 10^{12})^2 \cdot 10^{-7} \left( a_X \right)^2 \left( \beta_X \right)^2 T_{m,X} \]

\[ = K \left( a_X \right)^2 \left( \beta_X \right)^2 T_{m,X} \]  

(17)

where \( K = -2\pi^2 \left( \frac{2/3 V_X}{N_0} \right)^{2/3} (2.8 \cdot 10^{12})^2 \cdot 10^{-7} = -2740 \)  

(18)

For liquid metals \( a_X = 1/2 \), then

\[ U_{XX}^l = -685 \left( \beta_X \right)^2 T_{m,X} / J \cdot \text{mol}^{-1} \]  

(19)

For solid metals, \( \beta_X = 1 \) but the values of \( a_X \) for solid metals are not available. Therefore,

\[ U_{XX}^s = -2740 \left( a_X \right)^2 T_{m,X} / J \cdot \text{mol}^{-1} \]  

(20)
However, from Eq. (13),
\[
U_{XX} - U_{XX}^S = -685(\beta_X)^2 T_{m,X} + 2740(\alpha_X)^2 T_{m,X} = 17.6 T_{m,X} / \text{mol}^{-1} \tag{21}
\]
Thus, the following equation for \( U_{XX}^S \) is obtained from Eqs. (19) to (21)
\[
U_{XX}^S = -\{685(\beta_X)^2 + 17.6\} T_{m,X} / \text{mol}^{-1} \tag{22}
\]
The value of \( \alpha_X \) for solid metal X is determined from Eqs. (20) and (22) as follows
\[
\alpha_X = \left(\frac{685(\beta_X)^2 + 17.6}{2740}\right)^{1/2} \tag{23}
\]
When we set \( \beta_X = 0.5 \), we obtain \( \alpha_X = 0.263 \). Schematic diagram for \( U_{XX}^S \) and \( U_{XX} \) with \( T_{m,X} = 1000 \), \( \beta_X = 0.5 \) and \( \alpha_X = 0.263 \) is shown in Fig. 2. From this figure, \( U_{XX}^S \) has a deeper and narrower potential well than \( U_{XX} \). This means that atoms in solid state can move freely in smaller region around their equilibrium position than those in liquid state. In other words, atoms in solid state have smaller free volume than those in liquid state.

3 Calculation of Excess Entropy and Excess Gibbs Energy from Enthalpy of Mixing in Solid Solutions of Binary Alloys based on the Free Volume Solution Model

As some examples of the application of Eqs. (1) to (5) for solid solutions in the above three binary alloys. Since we have paid attention to the relationship between \( \Delta H_{\text{mix}} \) and \( S^E \) at each composition of an alloy including the relationship between \( H_B \) and \( S_B^E \) at an infinitely dilute solution, \( \Omega_{AB} \) has been obtained from \( \Delta H_{\text{mix}} \) at each composition to obtain \( S^E \) and \( G^E \) in Table 2. In other words, although the calculated results in Table 2 show the composition dependence of \( \Omega_{AB} \), we have confirmed here that the relationship between \( \Delta H_{\text{mix}} \) and \( S^E \) in Eqs. (1) to (5) hold at each composition of the above alloys when \( \Omega_{AB} \) has the same composition dependence in the equation of \( \Delta H_{\text{mix}} \) as that of \( S^E \). Figures 3a to c show the

Figs. 3a to c. Comparison of calculated results for excess Gibbs energy and excess entropy in solid solutions of (a) Ag–Au, (b) Ag–Pd, (c) Au–Pd binary alloys. △, ○: Experimental, — : Calculation.
Table 2. Calculated results for excess entropy and excess Gibbs energy with literature values.

\[
\begin{array}{|c|c|c|c|c|c|c|c|c|c|}
\hline
\text{Ag–Au at 800 K} & \text{Ag–Au at 1200 K} & \text{Au–Pd at 1200 K} & \text{X}_{\text{Ag}} & \text{X}_{\text{Au}} & \text{X}_{\text{Pd}} & \text{X}_{\text{Pd}} & \text{X}_{\text{Au}} & \text{X}_{\text{Au}} & \text{X}_{\text{Pd}} & \text{X}_{\text{Pd}} & \text{X}_{\text{Au}} & \text{X}_{\text{Au}} & \text{X}_{\text{Pd}} & \text{X}_{\text{Pd}} \\
\hline
\text{\(U_{\text{AgAu}} = -208443 \text{ J \cdot mol}^{-1}\)} & \text{\(U_{\text{AgPd}} = -208443 \text{ J \cdot mol}^{-1}\)} & \text{\(U_{\text{AuPd}} = -243244 \text{ J \cdot mol}^{-1}\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} & \text{\(T \cdot S^E_{\text{CONF}}(\text{Calc.})\)} \\
\hline
\text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} & \text{J \cdot mol}^{-1} \\
\hline
0.30 & -4046 & -5648 & -7000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 \\
0.40 & -4544 & -6770 & -8000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 & -4000 \\
0.50 & -4648 & -8000 & -10000 & -5000 & -5000 & -5000 & -5000 & -5000 & -5000 & -5000 & -5000 & -5000 & -5000 & -5000 \\
0.60 & -4381 & -10000 & -12000 & -6000 & -6000 & -6000 & -6000 & -6000 & -6000 & -6000 & -6000 & -6000 & -6000 & -6000 \\
0.70 & -3761 & -12766 & -15000 & -7000 & -7000 & -7000 & -7000 & -7000 & -7000 & -7000 & -7000 & -7000 & -7000 & -7000 \\
\hline
\end{array}
\]
\text{\(T \cdot S^E\) (Exp.) \(= \Delta H^E - G^E\) (Exp.) in Ref. [21].}

4 Relationship between Partial Enthalpy of Solution and Partial Excess Entropy of Solute Elements in Infinitely Dilute Solid Solutions of Binary Alloys

From Eqs. (6) to (9), (15) and (22), we have derived the approximate relationship between partial enthalpy of solution \(H_B\) and partial excess entropy \(S^E_B\) of solute element B in an infinitely dilute solid solution of a A–B binary alloy on the basis of the assumption in Eq. (24)

\[
T_{m,A} \approx T_{m,B}, V_A \approx V_B, \beta_A = \beta_B = 0.5
\]

Then,

\[
L_{AA} \approx -189 T_{m,A}, L_{BB} \approx -189 T_{m,B}
\]

Finally,

\[
\tilde{H}_B \approx \frac{15.1}{1/T_{m,A} + 1/T_{m,B}} S^E_B
\]

for solid solutions of binary alloys.

Compared with the following similar relation for liquid binary alloys [16], the difference between the relationship \(\tilde{H}_B\) vs. \(S^E_B\) in solid solutions and that in liquid solutions is

\[
T_{m,A} \approx T_{m,B}, V_A \approx V_B, \beta_A = \beta_B = 0.5
\]
not so large, which corresponds to the empirical results reported by Kubaschewski [3] and Lupis [4]

\[ H_b \approx \frac{13.7}{1/T_{m,A} + 1/T_{m,B}} \]  

(27)

for liquid binary alloys.

5 Concluding Remarks

In the present work, we discussed the thermodynamic relationship between enthalpy of mixing and excess entropy in solid solutions of binary alloys based on the free volume theory. The excess entropy and excess Gibbs energy in some solid solutions were calculated from the enthalpy of mixing using the model obtained here, and compared with the literature values. We also obtained the approximate relationship between the partial enthalpy of solution \( H_X \) and the partial excess entropy \( S_X^{e} \) of solute elements in dilute solid solutions of binary alloys.

Literature


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