<table>
<thead>
<tr>
<th>Title</th>
<th>Relationship between Enthalpy of Mixing and Excess Entropy in Liquid Binary Alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Tanaka, Toshihiro; Gokcen, N.A.; Morita, Z.</td>
</tr>
<tr>
<td>Citation</td>
<td>Zeitschrift für Metallkunde. 81(1) P.49–P.54</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1990</td>
</tr>
<tr>
<td>Text Version</td>
<td>publisher</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/11094/26529">http://hdl.handle.net/11094/26529</a></td>
</tr>
<tr>
<td>DOI</td>
<td></td>
</tr>
<tr>
<td>rights</td>
<td>©Carl Hanser Verlag, München</td>
</tr>
</tbody>
</table>
Relationship Between Enthalpy of Mixing and Excess Entropy in Liquid Binary Alloys

Toshihiro Tanaka*, N. A. Gokcen**, and Z. Morita*

(*Department of Materials Science and Processing, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan, and **Albany Research Center, Bureau of Mines, 1450 Queen Avenue SW, Albany, Oregon 97321-2196, U.S.A.)

A thermodynamic solution model for liquid binary alloys has been derived on the basis of free volume theory. This model can evaluate the excess entropy of mixing from the enthalpy of mixing in liquid binary alloys. The calculated values of excess entropy, excess Gibbs energy and activities of the elements are in good agreement with the experimental data of various alloy systems. It is shown from this model that the relationship between enthalpy of mixing and excess entropy in liquid binary alloys is dependent upon temperature.

Zusammenhang zwischen Mischungsenthalpien und Überschußentropien in flüssigen binären Legierungen


1 Introduction

A significant amount of research on the thermodynamic properties in liquid alloys has been carried out experimentally and also theoretically. Recently, several empirical attempts1) 8) have been made to correlate the enthalpy of mixing $\Delta H_{\text{mix}}$ and excess entropy $\Delta S_{\text{ex}}$ in liquid binary alloys. For example, Kubaschewski1) has obtained the following relationship between partial enthalpy $\Delta H^x$ and partial entropy $\Delta S^x$ of solute elements in dilute solutions.

$$\Delta H^x_{\text{mix}} = 3400 \Delta S^x$$  (1)

Lupis7) has also proposed the following similar relationship:

$$\Delta H^x_{\text{mix}} = r \Delta S^x$$  (2)

In this equation, $r$ is constant and a value of 3000 ± 1000 K for this parameter has been proposed for ordinary metallic solutions. However, Lupis suggested that $r$ is not always constant for all types of alloys and it might be dependent upon the nature of the elements involved in the alloy. Figure 1 shows a plot of maximum values of $\Delta H_{\text{mix}}$ against $\Delta S_{\text{ex}}$ at the same composition. The values of $\Delta H_{\text{mix}}$ and $\Delta S_{\text{ex}}$ are taken from the compilation by Kubaschewski and Acock9). As shown in this figure, the relationship between $\Delta H_{\text{mix}}$ and $\Delta S_{\text{ex}}$ seems to be dependent upon temperature. Kubaschewski1) considered boiling points of component metals, $T_{b, A}$ and $T_{b, B}$, as one of the physical properties of constituents in alloys and obtained another empirical relationship as follows:

$$\Delta S_{\text{ex}} = 0.64 \Delta H_{\text{mix}} / (T_{b, A} + T_{b, B})$$  (3)

On the other hand, Williams5) considered contributions of the configuration and the vibration of atoms in alloys for excess entropy to explain the relationship between $\Delta H_{\text{mix}}$ and $\Delta S_{\text{ex}}$. The coefficients of each contribution, however, were determined by parameter-fitting method with experimental values. Therefore, the physical meanings of each term are not clear, and the physical properties of elements involved in alloy systems have not been adequately taken into account.

The purpose of this work is to derive a thermodynamic model to evaluate the excess entropy and enthalpy of mixing based on the configuration and vibration of atoms in alloys from the free volume theory9) and the first approximation of regular solution model10). On the basis of the model, the relationship between enthalpy of mixing and excess entropy in liquid binary alloys is discussed together with the physical properties of each element in alloys.

2 Derivation of Thermodynamic Equations

In this work, the relationship between the enthalpy of mixing $\Delta H_{\text{mix}}$ and the excess entropy $\Delta S_{\text{ex}}$ is discussed on the

![Fig. 1. Relationship between enthalpy of mixing and excess entropy in liquid binary alloys.](image-url)
basis of the free volume theory advanced by Shimoji and Niwa. Assuming that an atom vibrates harmonically in its cell surrounded by the nearest-neighbour particles, the partition functions for pure liquid A and B, $Q_{AA}$ and $Q_{BB}$, are given by the following equations.

$$Q_{AA} = \frac{V_A^N}{V_B^N} \cdot \exp \left(-\frac{E_A}{kT}\right) = \left(-\frac{nR_A^2 kT/U_A}{N_A}\right)^{3/2} \cdot \exp \left(-\frac{N_A \cdot U_{AA}}{2kT}\right)$$  \hspace{1cm} (4)

$$Q_{BB} = \frac{V_B^N}{V_B^N} \cdot \exp \left(-\frac{E_B}{kT}\right) = \left(-\frac{nR_B^2 kT/U_B}{N_B}\right)^{3/2} \cdot \exp \left(-\frac{N_B \cdot U_{BB}}{2kT}\right)$$  \hspace{1cm} (5)

$V_A, V_B$: free volumes of A and B atoms in pure liquid.

$R_A, R_B$: distances which interatomic potential extends in cells of pure liquid A and B respectively, as shown in Fig. 2.

$U_A, U_B$: depth of potential energy in cells of pure liquid A and B respectively, as shown in Fig. 2.

$u_{AA}, u_{BB}$: energies of A - A and B - B pairs, respectively.

$Z$: coordination number.

$N_A, N_B$: number of A and B atoms.

$k$: Boltzmann constant.

$T$: temperature in K.

Partition function of A - B binary alloy is

$$Q = g \cdot \left(-\frac{nR_A^2 kT/U_A}{N_A}\right)^{3/2} \cdot \left(-\frac{nR_B^2 kT/U_B}{N_B}\right)^{3/2} \cdot \exp \left(-\frac{(N_A \cdot U_{AA} + N_B \cdot U_{BB})}{2kT}\right)$$  \hspace{1cm} (6)

$g$: degeneracy factor.

$R_A, R_B$: distances which interatomic potential of A and B atoms extend in cells of A - B binary alloy.

$U_A, U_B$: depth of potential energy of A and B atoms in cell of A - B binary alloy.

The energy $E = (N_A \cdot U_{AA} + N_B \cdot U_{BB})/2$ of A - B binary alloy in Eq. (6) can be expressed in terms of pair interaction energy of A - A, B - B and A - B, namely, $u_{AA}, u_{BB}$ and $u_{AB}$ as follows:

$$E = N_A \cdot U_{AA}/2 + N_B \cdot U_{BB}/2 + N_{AB} \cdot U_{AB}/2$$  \hspace{1cm} (7)

$N_{AB}$: number of A - B pairs.

$$\Omega_{AB} = Z \cdot (u_{AB} - 1/2 \cdot (u_{AA} + u_{BB}))$$; exchange energy \hspace{1cm} (8)

For condensed systems and at ordinary pressure levels, the Gibbs energy may be assumed to be equivalent to the Helmholtz energy, because their difference, the term PV, is usually negligible. Thus, for all practical purposes\textsuperscript{9},

$$G_{AA} \sim F_{AA} = -kT \ln Q_{AA}$$  \hspace{1cm} (9)

$$G_{BB} \sim F_{BB} = -kT \ln Q_{BB}$$  \hspace{1cm} (10)

From the above equations, the change in Gibbs energy of mixing, $\Delta G_{\text{mix}}$, is

$$\Delta G_{\text{mix}} = G - (G_{AA} + G_{BB})$$

$$= N_{AB} \cdot \Omega_{AB}/2 - kT \ln g$$

$$-kT \cdot 3/2 \cdot [N_A \ln (-nR_A^2 kT/U_A) + N_B \ln (-nR_B^2 kT/U_B)]$$

$$+ N_{AB} \ln \left(\frac{-nR_{AB}^2 kT/\Omega_{AB}}{-nR_A^2 kT/U_{AA}}\right) + N_{AB} \ln \left(\frac{-nR_{AB}^2 kT/\Omega_{AB}}{-nR_B^2 kT/U_{BB}}\right)$$ \hspace{1cm} (12)

Next, the enthalpy and entropy terms in the A - B binary alloy will be derived separately.

2.1 Enthalpy Term

From Eq. (12),

$$\Delta H_{\text{mix}} = \Delta H_{\text{ex}} = N_{AB} \cdot \Omega_{AB}/Z$$  \hspace{1cm} (13)

As regards the configuration of atoms in alloys, short range order is taken into account on the basis of the first approximation to the regular solutions proposed by one of the authors\textsuperscript{10}. According to this model, $N_{AB}$ is given by the following equation for dilute solutions:

$$N_{AB} = Z \cdot N_A x_A x_B (1 - x_A x_B \Omega_{AB}/kT)$$  \hspace{1cm} (14)

$N_O$: Avogadro's number

$x_A, x_B$: mole fractions of A and B, respectively.

Consequently, the enthalpy of mixing per mole $\Delta H_{\text{mix}} = \Delta H_{\text{mix}}/N_O$ can be given by the following equation:

$$\Delta H_{\text{mix}} = \Omega_{AB} x_A x_B (1 - x_A x_B \Omega_{AB}/kT)$$  \hspace{1cm} (15)

2.2 Entropy Term

The entropy arising from configuration of atoms in alloys $\Delta S_{\text{conf}} = -k \ln g$ consists of the following two terms:

$$\Delta S_{\text{conf}} = -k \ln g$$

$$= \Delta S_{\text{conf}}^{\text{ideal}} + \Delta S_{\text{conf}}^{\text{ex}}$$  \hspace{1cm} (16)

In this equation, $\Delta S_{\text{conf}}^{\text{ideal}}$ is the ideal entropy of mixing.

$$\Delta S_{\text{conf}}^{\text{ideal}} = -k \ln (x_A \ln x_A + x_B \ln x_B)$$  \hspace{1cm} (17)

For excess entropy arising from configuration of atoms in alloys, the following equation based on the first approximation to the regular solutions\textsuperscript{10} was also adopted

$$\Delta S_{\text{conf}}^{\text{ex}} = -x_A^2 x_B^2 \Omega_{AB}^2/2 \cdot kT$$  \hspace{1cm} (18)

Excess entropy arising from vibration of atoms $\Delta S_{\text{vib}}^{\text{ex}}$ can be derived from Eq. (12), i.e.,

$$\Delta S_{\text{vib}}^{\text{ex}} = 3/2 \cdot kN_O \{2x_A \ln (R_A/R_{AA}) + 2x_B \ln (R_B/R_{BB}) + x_A \ln (U_{AA}/U_A) + x_B \ln (U_{BB}/U_B)\}$$  \hspace{1cm} (19)

In order to evaluate $\Delta S_{\text{vib}}^{\text{ex}}$ in the above equation, it is necessary to have information on $R_A, R_B, U_A$ and $U_B$ in A - B binary alloy. In this work, the simplest relations were adopted from Shimoji and Niwa, i.e., the random distribution of atoms is assumed with the following equations:

---

Fig. 2. Interatomic potential in a cell.
\[ U_A = x_A U_{AA} + x_A U_{AB}, U_B = x_B U_{BB} + x_A U_{AB} \]  
(20)

\[ U_{AB} = Z \cdot \Omega_{AB} \]

\[ R_A = 1/2 \{ R_{AA} + (x_A R_{RA} + x_B R_{RB}) \} \]

\[ R_B = 1/2 \{ R_{BB} + (x_A R_{RA} + x_B R_{RB}) \} \]

(21)

(22)

Finally, the excess entropy for vibration of atoms per mole, \( \Delta S_{EE}^{\text{B}} \), is given by

\[ \Delta S_{EE}^{\text{B}} = 3/2 \cdot k \cdot x_A x_B [(R_{AA} - R_{BB})^2/R_{AA} R_{BB}] \]

\[ + (2U_{AA} U_{BB} - U_{AB} (U_{AA} + U_{BB})) \]

\[ \Omega_{AB} (U_{AA} + U_{BB})/2 \]

(23)

(24)

Consequently,

\[ \Delta S_{EE}^{\text{B}} = 3/2 \cdot k \cdot x_A x_B [(R_{AA} - R_{BB})^2/R_{AA} R_{BB}] \]

\[ + (4U_{AA} U_{BB} - 2\Omega_{AB} (U_{AA} + U_{BB})) \]

\[ - (U_{AA} + U_{BB})^2/2U_{AB} \]

(25)

In the preceding equations, all the quantities except \( \Omega_{AB} \) belong to the pure elements. Thus, if the value of \( \Omega_{AB} \) can be obtained from the enthalpy of mixing \( \Delta H_{\text{mix}} \), then \( \Delta S_{EE}^{\text{B}} \) can be calculated from Eq. (25). It is obvious from Eqs. (14), (15) and (25) that \( \Delta H_{\text{mix}} \) is related to \( \Delta S_{EE}^{\text{B}} \) through \( \Omega_{AB} \).

In this work, we correlate the depth of potential energy in each cell of pure elements, \( U_{AA} \) and \( U_{BB} \) in Eq. (25), with other physical quantities. If an atom vibrates harmonically in its cell of a pure element, then the free volumes \( \nu_{AA} \) and \( \nu_{BB} \) are expressed by

\[ \nu_{AA} = -(n_{AA}^2 kT/\Omega_{AA})^{3/2} \]

(26)

\[ \nu_{BB} = -(n_{BB}^2 kT/\Omega_{BB})^{3/2} \]

(27)

On the other hand, the free volumes \( \nu_{AA} \) and \( \nu_{BB} \) can also be given by the following equations (11):

\[ \nu_{AA} = (kT/2\pi n_{AA}^2)^{3/2} \]

(28)

\[ \nu_{BB} = (kT/2\pi n_{BB}^2)^{3/2} \]

(29)

\( M_{AA} \) and \( M_{BB} \): atomic weights of A and B.

\( \nu_{AA} \) and \( \nu_{BB} \): frequencies of A and B in pure liquid.

From Eqs. (26) to (29)

\[ U_{AA} = -2n_{AA}^2 R_{AA} M_{AA} \nu_{AA} \]

(30)

\[ U_{BB} = -2n_{BB}^2 R_{BB} M_{BB} \nu_{BB} \]

(31)

Substitution of Eqs. (30) and (31) into Eq. (25) gives

\[ \Delta S_{EE}^{\text{B}} = 3/2 \cdot k \cdot x_A x_B [(R_{AA} - R_{BB})^2/R_{AA} R_{BB}] + 2 \]

\[ \Omega_{AB} (R_{AA} M_{AA} \nu_{AA}^2 + R_{BB} M_{BB} \nu_{BB}^2) \]

\[ - 2n_{AA}^2 R_{AA} M_{AA} M_{BB} \nu_{AA}^2 \nu_{BB} \]

\[ - 2n_{BB}^2 R_{BB} M_{AA} M_{BB} \nu_{AA} \nu_{BB} \]

(32)

From the foregoing equation, \( \Delta S_{EE}^{\text{B}} \) can be calculated from \( \Omega_{AB} \) obtained from \( \Delta H_{\text{mix}} \) when the values of \( R_{AA}, R_{BB}, M_{AA}, M_{BB}, \nu_{AA} \) and \( \nu_{BB} \) are known. \( M_{AA} \) and \( M_{BB} \) are the atomic weights and \( R_{AA} \) and \( R_{BB} \), the distances in the cells for the potential energy and assumed to be half of the nearest-neighbour distance, \( r_{AA} \) and \( r_{BB} \), thus, \( R_{AA} = 1/2r_{AA} \) and \( R_{BB} = 1/2r_{BB} \). The values of \( \Omega_{AA} \) and \( \Omega_{BB} \) can be obtained from molar volumes of pure elements \( V_A \) and \( V_B \) in the following way if a close-packed structure can be assumed in liquid metal.

\[ \Omega_{AA} = (2l^2 V_A/N_A)^{1/3} \]

(33)

\[ \Omega_{BB} = (2l^2 V_B/N_B)^{1/3} \]

(34)

Values of \( \Omega_{AA} \) and \( \Omega_{BB} \) can be obtained from the following revised Lindemann's equations (12) if frequency at temperature 7°C is assumed to be equal to that at the melting point of each pure element.

\[ \Omega_{AA} = 2.8 \cdot 10^2 \beta_A (T_{m,A}/M_{AA} V_A^{2/3})^{1/2} \]

(35)

\[ \Omega_{BB} = 2.8 \cdot 10^2 \beta_B (T_{m,B}/M_{BB} V_B^{2/3})^{1/2} \]

(36)

\( T_{m,A} \) and \( T_{m,B} \): melting points of pure elements A and B. \( \beta_A \) and \( \beta_B \): correction coefficients to transform the frequency in solid into that in liquid at the melting point.

Since Lindemann's equation gives the frequency at the melting point in solid, coefficients \( \beta_A \) and \( \beta_B \) are necessary to obtain the frequency in liquid state. To a good approximation, \( \beta \) can be set to 0.5 for elements (12) having no data for \( \beta \).

As mentioned above, if the value of \( \Omega_{AB} \) can be estimated by any method, e.g. Miedema's semi-empirical rules (13), all the thermodynamic quantities can be calculated from the preceding equations. However, we focus on the relationship between \( \Delta H_{\text{mix}} \) and \( \Delta S_{EE}^{\text{B}} \) (\( \Delta S_{EE}^{\text{CONF}} + \Delta S_{EE}^{\text{VIB}} \)) in this work and the obtain \( \Omega_{AB} \) from measured values of \( \Delta H_{\text{mix}} \). Thus, from Eq. (15), \( \Omega_{AB} \) can be expressed as

\[ \Omega_{AB} = kT \{ 1 - (1 + 4\Delta H_{\text{mix}}/kT)^{1/2} \} \]

(37)

In Eq. (37), the value of \( \Omega_{AB} \) can be obtained from measured values of \( \Delta H_{\text{mix}} \) at each composition. Then, \( \Delta S_{EE}^{\text{CONF}} \) and \( \Delta S_{EE}^{\text{VIB}} \) can be calculated from Eqs. (32) to (37). Furthermore, excess Gibb's energy \( \Delta G_{E} \) and activity of element X, \( a_x \), may also be evaluated. However, \( \Omega_{AB} \) for alloys with \( \Delta H_{\text{mix}} > 0 \) can be obtained from

\[ 1 > 4 \cdot \Delta H_{\text{mix}}/kT \]

(38)

Therefore, for these alloys, the configuration of atoms is assumed to be random and the calculation of \( \Delta S_{EE}^{\text{B}} \) and \( \Delta G_{E} \) is carried out by the following equations:

\[ \Delta S_{EE}^{\text{B}} = \Delta S_{EE}^{\text{CONF}} + \Delta S_{EE}^{\text{VIB}} \]

\[ \Delta S_{EE}^{\text{CONF}} = 0 \]

\[ \Delta G_{E} = \Delta H_{\text{mix}} - T \Delta S_{EE}^{\text{VIB}} \]

(39)

(40)

(41)

3 Calculation of \( \Delta S_{EE}^{\text{B}}, \Delta G_{E} \) and \( a_x \) in Liquid Binary Alloys and Discussion on Validity of the Present Model

In this section, \( \Delta S_{EE}^{\text{B}}, \Delta G_{E} \) and \( a_x \) in various liquid binary alloys were calculated from measured values of \( \Delta H_{\text{mix}} \) on the basis of the present thermodynamic model and then the validity of this model is discussed.

Table 1 shows physical quantities of several elements needed for calculation of \( \Delta S_{EE}^{\text{B}} \). For \( \Delta H_{\text{mix}} \) values selected by Hultgren et al. (14) were adopted. Measured values of \( \Delta S_{EE}^{\text{B}}, \Delta G_{E} \) and \( a_x \) presented in Hultgren et al. were also used for comparison with the calculated results in this work.

As an example, the calculated results for \( \Delta S_{EE}^{\text{B}}, \Delta G_{E} \) and \( a_x \) in liquid binary Ag-Zn system are shown in Table 2. First, the
values of $\Omega_{a_{2}b_{2}}$ were calculated from $\Delta H_{\text{MIX}}$ at each composition in Hultgren et al. with Eq. (37). Then, using Eqs. (15) and (32) to (37), $\Delta S^{E_{x}}$ was evaluated from $\Omega_{a_{2}b_{2}}$ and other quantities shown in Table 1. Further, $\Delta G^{E_{x}}$ and $\beta_x$ were also calculated. Figure 3a shows a comparison of the calculated results for $\Delta S^{E_{x}}$, $\Delta G^{E_{x}}$ and $\beta_x$ with the experimental data for this system. As is obvious from this figure, the calculated results are in good agreement with the experimental data. In the same way, $\Delta S^{E_{x}}$, $\Delta G^{E_{x}}$ and $\beta_x$ in other liquid binary alloys were calculated and the results are shown in Figs. 3b to p together with the experimental values. It is obvious from these figures that the calculated and experimental values are in good agreement in various alloys. Especially, for alloys which show $\Delta H_{\text{MIX}} > 0$, it seems to be sufficient to consider the vibrational contribution to $\Delta S^{E_{x}}$. On the other hand, some of the alloys indicating large negative values of $\Delta H_{\text{MIX}}$ show strange activity curves in the high solute concentration region. Thus, more strict equations for short range order configuration of atoms have to be used for these alloys.

### Table 1

<table>
<thead>
<tr>
<th>Elements</th>
<th>$M_x$</th>
<th>$V_x$</th>
<th>$T_m$</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>107.9</td>
<td>10.27</td>
<td>1234</td>
<td>0.47</td>
</tr>
<tr>
<td>Al</td>
<td>27.0</td>
<td>10.00</td>
<td>993</td>
<td>0.52</td>
</tr>
<tr>
<td>Cd</td>
<td>112.4</td>
<td>13.00</td>
<td>594</td>
<td>0.55</td>
</tr>
<tr>
<td>Cu</td>
<td>63.5</td>
<td>7.11</td>
<td>1356</td>
<td>0.45</td>
</tr>
<tr>
<td>Fe</td>
<td>55.9</td>
<td>7.09</td>
<td>1809</td>
<td>0.49</td>
</tr>
<tr>
<td>Hg</td>
<td>200.6</td>
<td>14.09</td>
<td>234</td>
<td>0.84</td>
</tr>
<tr>
<td>In</td>
<td>114.8</td>
<td>15.73</td>
<td>430</td>
<td>0.68</td>
</tr>
<tr>
<td>K</td>
<td>39.1</td>
<td>45.61</td>
<td>336</td>
<td>0.46</td>
</tr>
<tr>
<td>Mg</td>
<td>24.3</td>
<td>14.00</td>
<td>922</td>
<td>0.45</td>
</tr>
<tr>
<td>Na</td>
<td>22.5</td>
<td>23.79</td>
<td>371</td>
<td>0.49</td>
</tr>
<tr>
<td>Pb</td>
<td>207.2</td>
<td>18.27</td>
<td>600</td>
<td>0.55</td>
</tr>
<tr>
<td>Si</td>
<td>28.1</td>
<td>12.07</td>
<td>1885</td>
<td>0.50</td>
</tr>
<tr>
<td>Ti</td>
<td>204.4</td>
<td>17.22</td>
<td>577</td>
<td>0.56</td>
</tr>
<tr>
<td>Zn</td>
<td>65.4</td>
<td>9.17</td>
<td>693</td>
<td>0.54</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>$X_{\text{Zn}}$</th>
<th>$\Delta H_{\text{MIX}}$ (J/mol)</th>
<th>$\Delta S_{\text{MIX}}$ (J/mol · K)</th>
<th>$\Delta S_{\text{CONF}}$ (J/mol · K)</th>
<th>$\Delta S^{E_{x}}$ (J/mol · K)</th>
<th>$\Delta G^{E_{x}}$ (J/mol)</th>
<th>$\beta_{\text{Zn}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>-3800</td>
<td>-0.53</td>
<td>-0.37</td>
<td>-0.90</td>
<td>-2750</td>
<td>0.02</td>
</tr>
<tr>
<td>0.20</td>
<td>-4810</td>
<td>-0.64</td>
<td>-0.55</td>
<td>-1.19</td>
<td>-3420</td>
<td>0.04</td>
</tr>
<tr>
<td>0.30</td>
<td>-6370</td>
<td>-0.80</td>
<td>-0.34</td>
<td>-1.64</td>
<td>-4440</td>
<td>0.09</td>
</tr>
<tr>
<td>0.40</td>
<td>-7230</td>
<td>-0.88</td>
<td>-1.32</td>
<td>-1.90</td>
<td>-4990</td>
<td>0.17</td>
</tr>
<tr>
<td>0.50</td>
<td>-7300</td>
<td>-0.90</td>
<td>-1.34</td>
<td>-1.94</td>
<td>-5030</td>
<td>0.30</td>
</tr>
<tr>
<td>0.60</td>
<td>-6650</td>
<td>-0.83</td>
<td>-0.38</td>
<td>-1.71</td>
<td>-4550</td>
<td>0.46</td>
</tr>
<tr>
<td>0.70</td>
<td>-5220</td>
<td>-0.70</td>
<td>-0.32</td>
<td>-1.32</td>
<td>-3670</td>
<td>0.62</td>
</tr>
<tr>
<td>0.80</td>
<td>-3500</td>
<td>-0.51</td>
<td>-0.33</td>
<td>-1.84</td>
<td>-2510</td>
<td>0.77</td>
</tr>
<tr>
<td>0.90</td>
<td>-1620</td>
<td>-0.27</td>
<td>-0.39</td>
<td>-1.36</td>
<td>-1200</td>
<td>0.90</td>
</tr>
</tbody>
</table>

### 4 Relationship Between $\Delta H_{\text{MIX}}$ and $\Delta S^{E_{x}}$

As stated above, $\Delta H_{\text{MIX}}$ and $\Delta S^{E_{x}}$ are related to each other by Eqs. (14), (15) and (25). Figure 4 shows the relationship between $\Delta H_{\text{MIX}}$ and $\Delta S^{E_{x}}$ at $x=x_{A}$ obtained by the present calculation. This figure appears to show a temperature dependence of the relationship between $\Delta H_{\text{MIX}}$ and $\Delta S^{E_{x}}$. This temperature dependence can be confirmed by the following treatment. Thus, considering the alloys with small absolute values of $\Omega_{A-B}$ and small differences of atomic weights and nearest-neighbour distances, Eqs. (15), (18) and (32) can be transformed into the following approximate equations:

\[ \Delta H_{\text{MIX}} = x_{A} \Omega_{A-B} \]  
\[ \Delta S^{E_{x}} = 0 \]
\[ \Delta S_{\text{Vib}} = x_A x_B \Omega_{A-B} \left( \frac{1}{T_{m, A}} + \frac{1}{T_{m, B}} \right) \]  

(44)

From the above equations, \( \Delta H_{\text{Mix}} \) and \( \Delta S_{\text{Ex}} \) are related by

\[ \Delta S_{\text{Ex}} \propto \Delta H_{\text{Mix}} \left( \frac{1}{T_{m, A}} + \frac{1}{T_{m, B}} \right) \]  

(45)

Then, Fig. 4 can be reconstructed by using Eq. (45) as shown in Fig. 5, wherein most of the alloys seem to fall onto a linear relation. This means that the relationship between \( \Delta H_{\text{Mix}} \) and \( \Delta S_{\text{Ex}} \) are dependent upon melting points of the components. Thus, the temperature dependence of the empirical relationship shown in Fig. 1 can be explained thermodynamically by the present model.

5 Some Problems in Present Model

The present model is successful in evaluation of some thermodynamic properties of binary alloys. However, the following improvements should be made in the future:

1) A more satisfactory treatment of alloys which show complicated behaviour of thermodynamic properties versus compositions.

2) In alloys showing large negative values of \( \Delta H_{\text{Mix}} \), more appropriate short range order configuration of atoms have to be considered.

3) A better treatment of alloys exhibiting the different signs between \( \Delta H_{\text{Mix}} \) and \( \Delta S_{\text{Ex}} \) is necessary. However, this problem also requires careful experimental investigation. Such alloys are near the origin of \( \Delta H_{\text{Mix}} - \Delta S_{\text{Ex}} \) maps. Therefore, considering the difficulties of thermodynamic experiments, some unreliable experimental values might pose unexpected obstacles in correlating \( \Delta H_{\text{Mix}} \) and \( \Delta S_{\text{Ex}} \).

7 Summary

In this work, a thermodynamic model was derived on the basis of the free volume theory and the first approximation to the regular solutions. The model is capable of evaluating the excess entropy from the enthalpy of mixing of liquid binary alloys. The calculated results were discussed and compared with the experimental data. The results obtained are summarized as follows.

1) Values of \( \Delta S_{\text{Ex}} \) could be estimated from \( \Delta H_{\text{Mix}} \) and the \( \Delta G_{\text{Ex}} \) and \( a_i \) were obtained in various liquid binary alloys. The calculated results for \( \Delta S_{\text{Ex}}, \Delta G_{\text{Ex}} \) and \( a_i \) were in good agreement with the experimental data on various liquid binary alloys.

2) The relationship between \( \Delta H_{\text{Mix}} \) and \( \Delta S_{\text{Ex}} \) was explained by considering configuration and vibration of atoms in alloys on the basis of the present model. It was shown that the relationship between \( \Delta H_{\text{Mix}} \) and \( \Delta S_{\text{Ex}} \) in liquid binary alloys depends on the melting points of component elements.

Literature


6) R. CROMBIE and D. B. DOWNE, Scripta Metall. 6 (1972) 277.


