Measurement of Activity of Gallium in Liquid Ga–In–Bi Alloys Using Stabilized Zirconia as the Solid Electrolyte

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EMF of galvanic cells with stabilized zirconia solid electrolyte was measured to determine the activity of gallium in liquid Ga–In–Bi alloys in the temperature range from 1050 to 1200 K along three pseudobinary lines of (InₓBi₁₋ₓ)Ga where y = 0.25, 0.50 and 0.75. A mixture of Ga and Ga₂O₃ was used as the reference electrode. The activity curves of Ga show positive deviations from ideality in the whole composition range. Iso-activity curves at 1073 K in the ternary Ga–In–Bi alloys were derived by combining the results of this study with activity data for Ga–In and Ga–Bi alloys. The iso-activity curves display small waves, and have concave curvatures in the Ga-rich region at lower temperatures. Using Darken’s equation, data for two binary systems Ga–In and Ga–Bi, and ternary data determined in this study, ΔG⁰ at 1073 K was derived. The results are compared with those from the general model calculation proposed by Chou.

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1. Introduction

Many studies have been carried out on alloy systems related to semiconducting and soldering materials which are of interest from both the scientific and technological points of view. An accurate knowledge of the thermodynamic properties and phase diagrams of these systems is essential. Some of the binary systems have been studied extensively, but the experimental data for ternary and/or multi-component systems are not always adequate. The present study is performed in the course of our program of experimental thermodynamic studies of liquid gallium alloys at high temperatures by use of an emf method¹¹ to determine the activity of gallium in the liquid Ga–In–Bi alloys.

Activities of gallium in the liquid Ga–In¹–⁹ and Ga–Bi¹,¹⁰,¹¹ alloys show moderately positive deviations from Raoult’s law for both systems at high temperatures. Klinedinst et al.⁵ applied the emf method with zirconia solid electrolyte to Ga–In system for the first time to determined the gallium activity. The results are in reasonably agreement with those by another investigators¹–⁹ with some scatter in higher gallium concentration range. Macut et al.² obtained higher values by multiple Knudsen-cell effusion technique even at higher temperatures.

For Ga–Bi alloys Yatsenko and Danilin¹⁰ reported the values of small positive deviations from ideality and of irregular concentration dependence. Predel et al.¹³ determined the gallium activity of very large positive deviations from Raoult’s law at 583 K based on their calorimetric study and phase diagram. We reported the activity values of moderately positive deviation from ideality at 1073 K¹¹ from emf method with zirconia solid electrolyte.

For ternary Ga–In–Bi alloys there seem no thermodynamic data hitherto.

The purpose of this study is to determine the activity of gallium in liquid Ga–In–Bi alloys by use of the emf method with stabilized zirconia as solid electrolyte in the whole composition range by choosing the compositions along the three pseudobinary lines of InₓBi₁₋ₓ–Ga in the temperature range of 1000–1200 K. The reference electrode used was Ga, Ga₂O₃.

2. Experimental

2.1 Materials

The alloys used in this study were prepared from high-purity materials (Ga: 99.9999 mass % purity from Sumitomo Chemicals Co., Ltd.; In and Bi: more than 99.999% from Mitsubishi Materials Co., Ltd.). Ga₂O₃ powder added to the alloy electrode and reference electrode in a mass ratio about 1:9 was of 99.99% purity from Mitsubishi Materials Co., Ltd. Zirconia solid electrolyte crucibles (0.92ZrO₂ + 0.08Y₂O₃, OD 8 mm, ID 5 mm and length 50 mm) were produced by coprecipitation method in Nippon Chemical Industrial Co., Ltd.

2.2 Experimental apparatus and procedures

The experimental equipment and procedure used in this study are quite similar to the previous one¹¹ for Ga–Sb–M (M = In, Bi, Te, Ge, Sn) alloys. Improved parts of the cell apparatus are as follows: A chromel-alumel thermocouple was put into a long silica-sheath which was settled by the cell, in order to decrease the attack by the possible vapor from the electrode. Another protecting silica tube covered the zirconia electrolyte and a smaller silica tube the bottom of which peeped into the electrolyte. In the smaller tube a tungsten wire was settled as a lead to the alloy electrode. And the smaller tube had a hole at the upper part near the glass cap for evacuation above the alloy electrode. At the upper end of the small silica tube, a rubber stopper was applied for evacuation of the reaction tube and guidance of a tungsten lead wire.

The alloy elements, weighed to give mixtures with desired concentrations, were placed in an alumina crucible placed in T-shaped alumina tube which was settled in the thermocouple.
compositions, and Ga₂O₃ powder were put in a zirconia crucible with a tungsten lead wire (ϕ0.5 mm), and the crucible was settled in the reference electrode (Ga, Ga₂O₃) put in an alumina crucible in which another tungsten wire was settled as a lead wire.

After the cell was assembled in the homogeneous temperature region in the reaction tube settled in the vertical type electric-resistance furnace, the reaction tube was evacuated and then filled with purified argon gas. This operation was two or three times repeated. After that the temperature was raised to a desired value. Immediately after the cell temperature became constant, the alloy electrode was stirred by the tungsten lead wire to shorten the equilibrium time required and emf measurement started. The cell temperature was raised and lowered, alternatively, and controlled to ±1 K at each temperature with a thermo-controller (Thermo-Iet, Eiko Electric Co. Ltd., TPC-A202C2) and a Pt–13Rh2Pt thermocouple. The emfs of the cell and the cell temperature were measured with a digital voltmeter (Multi-Logging Meter AD-5311, A&D Co. Ltd.) with a printer.

3. Results

The emfs of cell I for the ternary alloys were measured.

\[-W, \text{ Ga, Ga}_2\text{O}_3|\text{ZrO}_2(+\text{Y}_2\text{O}_3)|\text{Ga–In–Bi}(l)\]

\[\text{Ga}_2\text{O}_3, W(+)\]  

(I)

The compositions of the ternary alloys are chosen for pseudobinary systems of \((\text{In},\text{Bi}_{1−y})_{x=0 \sim 0.25}\), where \(y = 0.25, 0.50, 0.75; x = 0.1, 0.3, 0.5, 0.70\) and 0.9. After the cell temperature reached desired one, the cell emfs were measured and printed out. Normally the stable equilibrium emf was obtained in 1 to 5 h, depending on the alloy composition and temperature for the first time, and after that it took a very short period of time to get stable emf of the cell at the new temperatures.

Experimental emf data for Ga–In–Bi ternary alloys are shown in Figs. 1(a)–(c) for 15 different compositions. Different symbols corresponding to each alloy composition show that they are obtained from different experimental runs, and they show the reproducibility of the experimental data. As all the data points distribute around a linear line for each composition, the relations between emf \((E/\text{mV})\) and temperature \((T/K)\) are obtained by least squares regression analysis, and are listed in Table 1.

Using the data shown in Table 1, activities of Ga \(a_{\text{Ga}}\) in the alloys are calculated from eq. (I).

\[-3EF = RT \ln a_{\text{Ga}} = \Delta G_{\text{Ga}}\]  

(1)

where \(F\): the Faraday constant, \(R\): the gas constant and \(\Delta G_{\text{Ga}}/\text{Jmol}^{-1}\): partial molar Gibbs energy of mixing of Ga. Uncertainty limits in the activity values can be easily derived from those in the emf values. The activity values are shown in Table 2 at each temperature for three pseudobinary systems, some of which are derived by extrapolation of \(E\) vs \(T\) relations to lower or higher temperature range.

Figure 2 shows the concentration dependence of the gallium activity along the pseudobinary systems \((\text{In},\text{Bi}_{1−y})\)–Ga (\(y = 0.25, 0.5, 0.75\)) with those of the binary systems of Ga–In[1,12] and Ga–Bi.[1,12] In the whole concentration range, activity of Ga shows moderately positive deviations from ide-
Table 1 Temperature dependence of emf of cell:
\((-\text{Ga}, \text{Ga}_2\text{O}_3\text{)}\text{ZrO}_2\text{)(+)}\text{Ga–In–Bi}(\text{i}), \text{Ga}_2\text{O}_3\text{)(+)}.

<table>
<thead>
<tr>
<th>X$_{\text{Ga}}$</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bi$<em>{0.75}$In$</em>{0.25}$)-Ga</td>
<td>0.1</td>
<td>6.2</td>
<td>0.2359</td>
</tr>
<tr>
<td>(Bi$<em>{0.5}$In$</em>{0.5}$)-Ga</td>
<td>0.3</td>
<td>-5.14</td>
<td>0.0249</td>
</tr>
<tr>
<td>(Bi$<em>{0.25}$In$</em>{0.75}$)-Ga</td>
<td>0.5</td>
<td>-3.44</td>
<td>0.0424</td>
</tr>
<tr>
<td>(Bi$<em>{0.5}$In$</em>{0.5}$)-Ga</td>
<td>0.7</td>
<td>-14.2</td>
<td>0.0186</td>
</tr>
<tr>
<td>(Bi$<em>{0.75}$In$</em>{0.25}$)-Ga</td>
<td>0.9</td>
<td>-10.3</td>
<td>0.0115</td>
</tr>
</tbody>
</table>

Table 2 Activity values of gallium in In–Bi–Ga(i) alloys along pseudobinary systems.

<table>
<thead>
<tr>
<th>X$_{\text{Ga}}$</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(In$<em>{0.75}$Bi$</em>{0.25}$)-Ga</td>
<td>1000</td>
</tr>
<tr>
<td>(In$<em>{0.5}$Bi$</em>{0.5}$)-Ga</td>
<td>0.1</td>
</tr>
<tr>
<td>(In$<em>{0.75}$Bi$</em>{0.25}$)-Ga</td>
<td>0.3</td>
</tr>
<tr>
<td>(In$<em>{0.5}$Bi$</em>{0.5}$)-Ga</td>
<td>0.5</td>
</tr>
<tr>
<td>(In$<em>{0.75}$Bi$</em>{0.25}$)-Ga</td>
<td>0.7</td>
</tr>
<tr>
<td>(In$<em>{0.5}$Bi$</em>{0.5}$)-Ga</td>
<td>0.9</td>
</tr>
</tbody>
</table>

4. Discussion

In order to obtain the iso-activity curve of Ga in the liquid Ga–In–Bi alloys, activity data for liquid Ga–In$_{1.12}$ and Ga–Bi$_{1.12}$ alloys are used as the starting and ending points, and the experimental data for the pseudobinary systems of (In$_x$Bi$_{1-x}$)-Ga in this study are used. From the smoothing curves of a$_{\text{Ga}}$ vs X$_{\text{Ga}}$ plots in each binary and pseudobinary system, the alloy compositions corresponding to the activity values of every one tenth were read. The iso-activity curves at 1073 and 1200 K are shown in Figs. 3(a)(b). Each curve is of small wavy type in this system, and have concave curvatures in the Ga rich region at the lower temperature. The shape of the curves at 1200 K is quite similar to those of Ga–Sb–Bi alloys at 1073 K$^3$ in Ga–In–In$_{0.5}$Bi$_{0.5}$ region. From these figures one can draw the activity curves in any directions in the ternary system. One of the utility of this result is calculation of integral values of excess Gibbs free energy of mixing in the ternary alloys. By use of the following Darken’s equation, $\Delta G^\text{XS}$ can be derived from the two binary data of Ga–In and Ga–Bi and ternary data along pseudobinary system of (In$_x$Bi$_{1-x}$)-Ga.

$$\Delta G^\text{XS} = (1 - X_{\text{Ga}}) \int_{0}^{X_{\text{Ga}}} \frac{\Delta G^\text{XS}_{\text{Ga}}}{(1 - X_{\text{Ga}})^2} dX_{\text{Ga}}$$

$$X_{\text{Bi}} \int_{0}^{1} \frac{\Delta G^\text{XS}_{\text{Bi}}}{(1 - X_{\text{Ga}})^2} dX_{\text{Ga}}$$

$$\Delta G^\text{XS}_{\text{In}} \int_{0}^{1} \frac{\Delta G^\text{XS}_{\text{In}}}{(1 - X_{\text{Ga}}^2)} dX_{\text{Ga}}$$

$\Delta G^\text{XS}$-values calculated in this study at 1073 K are shown in Fig. 4 as solid lines.

Recently Chou$^{13}$ proposed a general solution model for predicting ternary thermodynamic properties only from the three related binary systems by use of the selected binary compositions closely located to the ternary itself. (In detail see Ref. 13)). As a result $\Delta G^\text{XS}$ are represented by eq. (3).

$$\Delta G^\text{XS} = \Delta G^\text{XS}_{2x_1x_2} + \Delta G^\text{XS}_{3x_1x_2} + \Delta G^\text{XS}_{3x_2x_3}$$

where $\Delta G^\text{XS}$ are given by:

$$\Delta G^\text{XS}_{1x_1x_2} = \left\{ (x_1 + \xi_1 x_2)(x_1 + (1 - \xi_1) x_2) \right\}$$

$$\Delta G^\text{XS}_{2x_1x_2} = \left\{ (x_1 + \xi_1 x_2)(x_1 + (1 - \xi_1) x_2) \right\}$$

$$\Delta G^\text{XS}_{3x_1x_2} = \left\{ (x_1 + \xi_1 x_2)(x_1 + (1 - \xi_1) x_2) \right\}$$

$$\Delta G^\text{XS}_{3x_2x_3} = \left\{ (x_1 + \xi_1 x_2)(x_1 + (1 - \xi_1) x_2) \right\}$$

(3)
where $x_i$: mole fraction of component $i$ in the ternary system, $X_{(i2)} = x_1 + x_2\xi_{21}; X_{(23)} = x_2 + x_3\xi_{23}; X_{(i3)}$ similarity coefficient, $\Delta G_{ij}^{X}$: excess Gibbs free energy of mixing in the $i-j$ binary system, $\xi_{ij}$: mole fraction of component $i$ in the $i-j$ binary system and the range of $X_{(i2)}$ varies from $x_1$ to $(x_1 + x_3)$. In order to calculate the value of from eq. (3), binary data for Ga–In$^{1,12}$, Ga–B$^{1,12}$ and In–Bi$^{14}$ are fitted to the Redlich-Kister presentation by eqs. (4) and (5).

$$\Delta G_{ij}^{X} = X_i X_j \sum_{i=0}^{n}(X_i - X_j)Y L_{ij}^{(o)}(T)$$

(4)

$$L_{ij}^{(o)}(T) = a_{ij}^{(o)} + b_{ij}^{(o)} T + c_{ij}^{(o)} T^2$$

(5)

From the experimental data for binary systems, $\Delta G_{ij}^{X}$-values were calculated from 1000 to 1200 K at intervals of 50 K, and the fitting parameters shown in Table 3 were obtained. Calculated similarity coefficients for three binaries Ga–In, Ga–Bi and Bi–In are $\xi_{Ga-In} = 0.030821$, $\xi_{Ga-Bi} = 0.977722$ and $\xi_{Bi-In} = 0.41742$. These coefficients and the parameters shown in Table 3 are applied to eq. (3) to derive $\Delta G_{ij}^{X}$. The derived values of $\Delta G_{ij}^{X}$ are shown in Fig. 4 as the broken lines. From this figure it is found that the experimental data are qualitatively in agreement with the derived values by use of Chou’s method in indium-poor side, but in indium-rich region the agreement between them is not good. The reason is not clear.

### Table 3 Fitting parameters in eqs. (4) and (5).

<table>
<thead>
<tr>
<th>$i-j$</th>
<th>$w$</th>
<th>$a_{ij}^{(o)}$</th>
<th>$b_{ij}^{(o)}$</th>
<th>$c_{ij}^{(o)}$</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga–In</td>
<td>0</td>
<td>494.150</td>
<td>0.7731</td>
<td>0</td>
<td>1000–1200</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>17613.68</td>
<td>−15.0736</td>
<td>0</td>
<td>1000–1200</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>20412.15</td>
<td>−17.9641</td>
<td>0</td>
<td>1000–1200</td>
</tr>
<tr>
<td>Ga–Bi</td>
<td>0</td>
<td>5976.63</td>
<td>1.9902</td>
<td>0</td>
<td>1000–1200</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3902.13</td>
<td>−0.9583</td>
<td>0</td>
<td>1000–1200</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7312.59</td>
<td>−5.5573</td>
<td>0</td>
<td>1000–1200</td>
</tr>
<tr>
<td>In–Bi</td>
<td>0</td>
<td>−6847.25</td>
<td>−1.0727</td>
<td>0</td>
<td>1000–1200</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>−1382.71</td>
<td>−0.5720</td>
<td>0</td>
<td>1000–1200</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>522.28</td>
<td>0.2691</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

*Ref. 14.*
eral model calculation proposed by Chou based on the three binary data.

REFERENCES


5) C. Bergman: Thesis in Provence University (1972), France.