Activity Measurements of Liquid Bi-In Alloys by the E.M.F. Method Using Zirconia and Fused Salt as Electrolytes*

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The standard free energy of formation of In_2O_3 and the activity of the liquid Bi-In system have been determined by two types of galvanic cells as follows:

The standard free energy of formation of $\text{In}_2\text{O}_3\text{(s)}$ is represented by

$$\Delta G_{(\text{In}_2\text{O}_3)}^\circ / \text{J} \cdot \text{mol}^{-1} = -929600 + 337.0 T \pm 540 \text{ between } 875 \text{ and } 1275 \text{ K}.$$

Activities of indium and bismuth by both galvanic cells agreed very well and showed negative deviations from Raoult's law over the whole concentration range. The present result agreed well with the data measured by Niwa *et al.* and Terpilowski.

The activities of both components for the Sb-In system exhibit more negative deviations than those for the Bi-In system. It is suggested that the larger affinity of indium is exerted for antimony than that for bismuth. The minimum value of the heat of mixing measured by using zirconia-solid electrolytes is -2.08 kJ/mol at about $N_{\text{In}}=0.56$.

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I. Introduction

Indium and bismuth are known as a member of typical metals in groups IIIB and VB of the periodic table, respectively. In recent years, IIIB-VB compounds and alloys have been used for solid-state electronic devices. For example, the usefulness of the IIIB-VB compound semiconductors employed for the indium-base alloys is now generally recognized.

Therefore, the author *et al.*⁽¹⁾⁻⁽⁴⁾ and Kozuka *et al.*⁽⁵⁾⁻⁽⁷⁾ have reported new thermochemical data on liquid indium alloys based on emf measurements.

The thermodynamic properties of liquid Bi-In alloys are important not only from the stand-

point of their behavior as impurities during nonferrous smelting but also of the physical chemistry of liquid alloys. Thermodynamic properties of Bi-In alloys have been investigated by several workers⁽⁸⁾⁻⁽¹⁰⁾. Measurements by calorimetry⁽⁸⁾ and by the emf technique using fused iodide⁽⁹⁾ and bromide⁽¹⁰⁾ as electrolytes have been made to determine the partial and integral thermodynamic quantities of the alloys. Thermodynamic properties of liquid In-Bi-Pb ternary alloys have been recently determined from the measurements using Galvanic cells with zirconia-solid electrolytes⁽⁶⁾. However, the liquid Bi-In system have not been investigated by means of the same technique.

The emf method with fused iodide and bromide as electrolytes is generally restricted to a low temperature range because of the high vapour pressure of the fused iodide and bromide. Consequently, little has been known

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about the thermodynamic properties at high temperatures above 900 K.

In order to clarify the thermodynamic properties of Bi-In alloys at higher temperatures, experiments have been carried out by the emf method using zirconia-solid electrolyte. Furthermore, to criticize the results, a new method using fused-salt electrolytes has also been used simultaneously. Moreover, the activities of both components for the Bi-In system are compared and discussed in connection with the previous study on the Sb-In system⁽⁴⁾.

The Galvanic cell using zirconia as solid electrolytes are as follows:

and

The electromotive forces of these cells are given respectively by

$$E_{(\text{I})} = RT/4F \ln (p_{\text{O}_2(\text{NiO})}/p_{\text{O}_2(\text{Bi-In})}) \quad (1)$$

and

$$E_{(\text{II})} = RT/4F \ln (p_{\text{O}_2(\text{NiO})}/p_{\text{O}_2(\text{In}_2\text{O}_3)}). \quad (2)$$

Combination of eqs. (1) and (2) yields

$$(E_{(\text{II})} - E_{(\text{I})}) = RT/4F \ln (p_{\text{O}_2(\text{Bi-In})}/p_{\text{O}_2(\text{In}_2\text{O}_3)}). \quad (3)$$

Under isothermal, isobaric and reversible conditions, the partial molar free energy change of In for the dissolution is given by

$$\Delta \bar{G}_{\text{In}} = RT \ln a_{\text{In}} = -3(E_{(\text{II})} - E_{(\text{I})})F, \quad (4)$$

where E is the emf at T K after the correction of the thermo-electromotive force between the stainless steel wire and the Pt wire, $p_{\text{O}_2(\text{NiO})}^\dagger$ and $p_{\text{O}_2(\text{In}_2\text{O}_3)}$ and $p_{\text{O}_2(\text{Bi-In})}$ are the oxygen partial pressures in equilibrium with Ni-NiO, In-In₂O₃ and Bi-In alloys -In₂O₃ electrodes, respectively, R is the gas constant, a_{In} is the chemical activity of indium in the alloys, referred to a standard state of liquid indium for unit activity, T is the absolute temperature of the cell. Here the indium is saturated with ox-

ygen.

From the experimental solubility of oxygen in both liquid bismuth and indium in the literatures⁽¹¹⁾⁽¹²⁾, the oxygen in the molten Bi-In alloys may be neglected for its influence on the activities of both bismuth and indium.

The Galvanic cell using fused salt as electrolytes is as follows:

Under the isothermal, isobaric and reversible conditions, the partial molar free energy change for the dissolution of In is given by

$$\Delta \bar{G}_{\text{In}} = RT \ln a_{\text{In}} = -FE \quad (5)$$

where E is the electromotive force measured at T K, R is the gas constant, a_{In} is the activity of indium in the alloys, T is the absolute temperature and F is the Faraday constant. The indium chloride would contain both univalent or trivalent indium ions. However, at high temperatures used in the present study, the univalent ion is considered more stable for the indium chloride used in the fused-salt electrolytes coexisting with pure In as shown in the following equations:

II. Experimental

The structures of Galvanic cells employed in the present investigation using solid zirconia and fused salt as electrolytes are virtually identical to those described in the previous publications^{(1)-(4),(13)(14)}. In the case of the emf method using the solid electrolytes, a zirconia tube containing the weighed portions of Bi(99.9999%), In(99.999%) and In₂O₃(99.999%) was set in an alumina crucible containing a mixture of Ni-NiO powders. Electrical contacts to the electrode of Bi-In alloys-In₂O₃ and to the electrode of Ni-NiO reference were made by an oxidized stainless steel wire and a Pt wire, respectively. The stainless steel wire showed a negligibly small reaction with Bi-In alloys and In₂O₃, and the stable electromotive forces obtained

[†] $p_{\text{O}_2} = p_{\text{O}_2}(\text{Pa})/101325 \text{ Pa}$.

for over 108 ks. The thermoelectromotive force between the stainless steel wire and the Pt wire had been measured in advance in the same furnace under an argon atmosphere as follows:

$$E_{(\text{th})} = -18.10 \times 10^{-3} + 2.30 \times 10^{-5} T$$

between 912 and 1255 K (7)

where $E_{(\text{th})}$ is the thermoelectromotive force in volts.

The assembled cell was heated in vacuum from room temperature to 500 K to remove its moisture. Then, purified argon was led into the reaction tube. The experimental temperature ranged from 875 to 1275 K. In the case of Galvanic cells using fused salt as electrolyte, all the alloys were in the liquid state at the experimental temperatures ranging from 950 to 1200 K. Each cell had three electrodes, one of which was pure indium and the others were Bi-In alloys. The metal electrodes were placed in small quartz crucibles. The large crucible was made of alumina. The alloys were prepared from pure metals of Bi(99.9999%) and In(99.999%). The electrolytes were prepared by melting the chlorides of the chemical-reagent grade and holding for 7.2 ks at 480 K and then 21.6 ks at 973 K under a vacuum atmosphere. The chloride mixture was consisted of 50 mol% sodium chloride and 50 mol% potassium chloride with addition of about 5 mass% indium chloride (InCl_3). A small amount of indium metal is introduced into the alumina crucible to equilibrate with those electrolytes according to eq. (6). Electrical contacts to Bi-In alloys and the pure indium electrode were made by tungsten wires. The cell crucible, alloys, electrode leads, etc. were all assembled inside the larger quartz tube. The assembled cell was heated in vacuum from room temperature to 480 K to remove the moisture in electrolytes and in others. Then purified argon was led into the reaction tube. In all experiments, the temperature was measured by the thermocouple of pure Pt vs 13%Rh-Pt placed along the cells and controlled within ± 0.5 K by a temperature regulator. The Galvanic cells were heated in a Kanthal resistance furnace having a uniform tempera-

ture zone of 5×10^{-2} m in length within ± 1 K. During the emf measurements, the reaction tube was filled with purified argon about 6700 Pa higher than the atmospheric pressure. The electromotive force was measured by a potentiometer made by Yokogawa Electric Company with No. 2722. The accuracy of this potentiometer for direct current was ± 0.1 mV. The electromotive force was stabilized after about 2–2.5 ks for the cell with solid electrolyte and 3.6–5.4 ks for the cell with fused-salt electrolyte. The reversibilities of the electromotive force were tested at varying temperatures.

III. Results and Discussion

1. Standard free energy of formation of solid indium oxide (In_2O_3)

The electromotive forces of cell (II) are shown in Fig. 1 as illustrated as "Pure In" line. By using the least-squares method, this line in Fig. 1 was represented as

$$E_{(\text{II})}/V = 376.71 \times 10^{-3} - 11.92 \times 10^{-5} T \pm 0.204 \times 10^{-3}$$

between 875 and 1275 K, (8)

where probable errors were calculated

Fig. 1 Relation between electromotive force and temperature for the cell, Pt/Ni(s), $\text{NiO(s)}/\text{ZrO}_2(+\text{CaO})/\text{Bi-In (l)}$, $\text{In}_2\text{O}_3(\text{s})/\text{stainless steel}$.

numerically from the line for pure indium in Fig. 1. Equations (9) and (10) are given for the equilibrium reactions in both electrodes for cell (II),

and

Therefore, the electromotive force, $E_{\text{(II)}}$, for cell (II) can be given by

$$E_{\text{(II)}} - E_{\text{(I)}} = (\Delta G_{\text{(NiO)}}^\circ - 1/3\Delta G_{\text{(In}_2\text{O}_3)}^\circ)/2F. \quad (11)$$

When eqs. (7) and (8) are substituted in eq. (11), one can obtain

$$\Delta G_{\text{(In}_2\text{O}_3)}^\circ/\text{J} \cdot \text{mol}^{-1} = -929600 + 337.0 T \pm 540$$

between 875 and 1275 K. (12)

Here the following standard free energy of formation of NiO(s) by Charette and Flengas⁽¹⁵⁾ was employed for the calculation of eq. (11):

$$\Delta G_{\text{(NiO)}}^\circ/\text{J} \cdot \text{mol}^{-1} = -233650 + 84.9 T \pm 140$$

between 911 and 1376 K, (13)

where probable errors are also shown in eq. (13). The standard free energies of formation of $\text{In}_2\text{O}_3\text{(s)}$ have been reported by various workers^{(3)(16)–(20)} as shown in Fig. 2 and also by others^{(21)–(23)}. They are in good agreement with the present work.

Fig. 2 Standard free energy of formation of $\text{In}_2\text{O}_3\text{(s)}$.

2. Activities of components in alloys

Figure 1 shows the relation between the electromotive force and temperature for various alloy compositions in the case of using the solid electrolyte. The extent of probable errors of electromotive forces was calculated numerically to be from 0.03 to 0.34 mV.

For the case of the fused-salt electrolyte, the emf between the two pure indium electrodes should be reduced to zero. In practice, however, it was 0.22 and 0.32 mV as the extent of probable errors at 1000 and 1200 K, respectively. The electromotive forces at ten different alloy compositions are plotted against temperature in Fig. 3. The probable errors were calculated numerically from the lines to be from 0.04 to 0.13 mV.

The activity curves of both components in the standard state of pure liquid metal at 900 and 1200 K are illustrated in Fig. 4 for the case of the solid electrolyte. Figure 5 is the results by Galvanic cells with the fused-salt electrolyte at 1000 and 1200 K. The activities of indium and bismuth show both negative but moderate

Fig. 3 Relation between electromotive force and temperature for the cell, $\text{W/In(l)/InCl(KCl, NaCl)/Bi-In(l)/W}$.

Fig. 4 Activity curves in the liquid Bi-In system from the electromotive force of galvanic cells with the solid electrolyte.

Fig. 5 Activity curves in the liquid Bi-In system from the electromotive force of galvanic cells with the fused-salt electrolyte.

deviations from the Raoult's law, suggesting a moderate affinity between indium and bismuth. The activities of both components approach to the ideality at higher temperature. By comparing Fig. 4 and Fig. 5, it is to be noted that the activity curves of both components using solid zirconia and fused salt as

Fig. 6 Activity curves in the molten Bi-In alloys.
 ---■---: J. Terpilowski (emf, fused-bromide electrolytes: 673 K),
 ---□---: K. Niwa *et al.* (emf, fused-iodide electrolytes: 900 K),
 —○—: This study (emf, solid electrolytes: 900 K),
 ---●---: This study (emf, fused-salt electrolytes: 1000 K).

the electrolyte agree very well over the whole concentration ranges.

In Fig. 6, the activity curves of the alloy components in the literature⁽⁹⁾⁽¹⁰⁾ and the present work are shown for various temperatures. The result of the present work agrees well with those measured by Niwa *et al.*⁽⁹⁾ and Terpilowski⁽¹⁰⁾, if the activities are compared at the same temperature.

The phase diagram of the Bi-In system⁽²⁴⁾ shows intermetallic compounds such as InBi for $N_{\text{In}}=0.5$, In_2Bi for $N_{\text{In}}=0.67$, which are formed at the temperatures below 383 and 362 K, respectively. These compounds in the solid state would give negative deviations of the activities of both components for the alloys in the molten state. The present observation is in agreement with the above anticipation.

Furthermore, the α function of indium obtained by the solid electrolyte is plotted in Fig. 7. It is a negative convex curve against N_{In} , suggesting that this system cannot be considered as a regular solution.

Fig. 7 Alpha function (α_{In}) of indium for the liquid Bi-In alloys from the electromotive force of galvanic cells with the solid electrolyte.

Fig. 8 Activity curves in the liquid Bi-In and Sb-In systems (1200 K).

- : Bi-In system (emf, solid electrolytes),
- : Bi-In system (emf, fused-salt electrolytes),
- : Sb-In system (emf, solid electrolytes),
- : Sb-In system (emf, fused-salt electrolytes).

3. A comparison of activity curves between the liquid Bi-In and Sb-In alloys

Figure 8 shows the activity curves of the com-

ponents in the liquid Bi-In and Sb-In systems at 1200 K measured by using both solid and fused-salt electrolytes. As pointed out above, the Bi-In constitution diagram⁽²⁴⁾ shows that the intermediate phases such as InBi, In₂Bi only in the temperatures below 383 and 362 K, respectively. On the other hand, the Sb-In equilibrium diagram⁽²⁴⁾ shows the intermetallic compound such as InSb for $N_{\text{In}}=0.5$, which has a relatively higher melting temperature at 803 K. The activities of the components in these liquid systems would be influenced by the stability of intermediate phases in the solid state. Namely, the activities of the components for the Sb-In system would exhibit greater negative deviations than those for the Bi-In system. The effect by the former intermetallic phase would be considered to be remained greater in the molten state than that by the latter intermediate compounds.

4. Free energies, heats and entropies of mixing

The partial and integral molar quantities of the Bi-In system have been calculated from the experimental data at 1200 K. The integral molar free energy obtained by the emf technique with solid electrolyte showed greater negative values than that of the ideal molar free energy. The observed minimum value was -8.93 kJ/mol for about $N_{\text{In}}=0.51$. The heats

Fig. 9 Heats of mixing in the molten Bi-In system.

- : F. E. Wittig *et al.* (calorimetry: 973 K),
- : J. Terpilowski (emf, fused-bromide electrolytes: 673 K),
- : K. Niwa *et al.* (emf, fused-iodide electrolytes: 900 K),
- : This study (emf, solid electrolytes: 1200 K),
- : This study (emf, fused-salt electrolytes: 1200 K).

of mixing from the solid-electrolyte cells are exothermic. The minimum value was -2.08 kJ/mol at about $N_{\text{In}}=0.56$. In Fig. 9, heats of mixing of the molten alloys are plotted as a function of composition. Similar results have been reported previously⁽⁸⁾⁻⁽¹⁰⁾. In general, the heats of mixing by means of calorimetry would be more accurate than those by the emf technique, in good agreement with the values by Wittig *et al.*⁽⁸⁾ obtained by calorimetry. The entropies of mixing measured by using the solid-electrolyte cells are roughly approximated by that of ideal molar entropy. The observed minimum value was -5.31 J/mol·K for about $N_{\text{In}}=0.52$.

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