Activity Measurements of Liquid Cu-In Alloys by an EMF Method Using a Zirconia Electrolyte*

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The activity of the liquid Cu-In system has been determined by the emf measurement of the following galvanic cell:

Deviations of the activities of indium and copper from Raoult's law are positive for the indium rich region and are negative for the copper rich side of the system. The present result agreed approximately with the data measured by Azakami and Yazawa. The α functions of indium for the system show the curves against N_{In} , suggesting that the alloys are not considered as regular solution.

Heats of mixing are negative for copper rich alloys and slightly positive for indium rich alloys. The maximum and minimum values of the heats of mixing for the system are 0.40 kJ/mol at about $N_{\text{In}}=0.76$ and -2.40 kJ/mol at about $N_{\text{In}}=0.24$, respectively.

By comparing the activities and the heats of mixing of liquid Cu-In, Ag-In and Au-In alloys, it is recognized that both the activities and the heats of mixing deviate more negatively in the order of copper, silver and gold of IB metals (Cu, Ag and Au) in the periodic table. The activities and the heats of mixing of the Au-In system show considerable negative deviations and larger exothermic values, respectively, over the whole concentration range. Such a great affinity of the Au-In system compared with Cu-In and Ag-In systems may be ascribed to the differences in the electronegativities.

The thermodynamic properties of liquid alloys composed of IB metals and indium have been discussed in terms of the alloy solution theory by Engel.

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I. Introduction

In order to establish fundamentals of pyrometallurgical technology and attempt to acquire properties of liquid alloys, the author has carried out a systematic study on a thermodynamic behavior of liquid indium alloys and reported the results on several alloy systems^{(1)–(6)}. Activities in the indium alloys have also been investigated by Azakami and Yazawa⁽⁷⁾, and Zheng and Kozuka⁽⁸⁾⁽⁹⁾. The available data on the binary alloy system include alloys of the Cu-In⁽⁷⁾, Au-In⁽¹⁾, Ag-In⁽²⁾, Pb-In⁽³⁾⁽⁸⁾, Sb-In⁽⁴⁾⁽⁸⁾, Bi-In⁽⁵⁾⁽⁶⁾ and Tl-In⁽⁸⁾ systems. In this study, activity measurements of liquid Cu-In alloys have been carried out with the help of an electromotive force (emf) method utilizing a zirconia solid electrolyte. Recently, the view that IB metals might be classified into the category of transition metals owing to the characteristic behavior like transition metals has been proposed⁽¹⁰⁾⁽¹¹⁾. And the behavior of these metals is, in general, very complicated in the state of fused alloys^{(1)(2)(12)–(16)}. Therefore, the present work has been carried out as a continuation of the thermodynamic investigation of IB metals with typical normal metals showing an interaction in the liquid state.

Accordingly, the investigation made by comparing activities or heats of mixing and a phase diagram of the Cu-In system⁽¹⁷⁾ in this study with those of the Ag-In and Au-In systems in the previous report has been taken up as one of the purposes from the above-mentioned standpoint.

Only the thermodynamic investigation on liquid Cu-In alloys by Azakami and Yazawa⁽⁷⁾ is available in the literature, where the activity measurement is conducted with an emf method utilizing a liquid-salt electrolyte. The composition range of Cu-In alloys is $N_{\text{In}}=0.20-0.80$ and the temperature range is 973–1273 K. As to the heats of mixing, the measurement has been made with the whole composition range by Takeuchi and Uemura *et al.*⁽¹⁸⁾ at 1363 K and by Itagaki and Yazawa⁽¹⁹⁾ at 1373 K, respectively.

II. Experimental Principle

A cell assembly is shown below, utilizing a zirconia solid electrolyte,

The equilibrium reactions on both electrodes of the cell (I) are expressed by eqs. (1) and (2), and hence the emf value $E_{(1)}$ is given by eq. (3):

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

In eq. (3), $\Delta G_{(\text{NiO})}^\circ$ and $\Delta G_{(\text{In}_2\text{O}_3)}^\circ$ are the standard free energies of formation of NiO and In_2O_3 , respectively, and a_{In} is the activity of indium in Cu-In alloys at the temperature T . Although a_{In} can be obtained from the measured value $E_{(I)}$ at the temperature T by using $\Delta G_{(\text{NiO})}^\circ$ and $\Delta G_{(\text{In}_2\text{O}_3)}^\circ$ in the literature. To avoid the error caused by these referred values, however, the following method is used in this study. The emf value in the case of pure In being used instead of Cu-In alloys, $E_{(II)}$, is given by the following equation:

$$E_{(II)} = (\Delta G_{(\text{NiO})}^\circ - 1/3\Delta G_{(\text{In}_2\text{O}_3)}^\circ) / 2F. \quad (4)$$

Combinations of eqs. (3) and (4) yield

$$E_{(II)} - E_{(I)} = -(RT/3F) \ln a_{\text{In}}. \quad (5)$$

Thus it is not necessary for the values of the standard free energy of formation to be used when the activity of indium is to be evaluated. The oxygen solubility in the liquid indium is 0.034 mol% at 1073 K as reported by Otsuka and Kozuka⁽²⁰⁾. And if it can be assumed that dissolved oxygen in the liquid Cu-In alloys behaves similarly to that in liquid Cu-Sn alloys⁽²¹⁾⁽²²⁾, the effect of oxygen on the activity of In and Cu can be neglected.

III. Experimental Method

The experimental apparatus and method used are identical to those previously reported by the author⁽⁴⁾⁽⁶⁾. A zirconia tube is containing the weighed proportions of Cu(99.99%), In(99.999%) and In_2O_3 as a guaranteed reagent. For a reference electrode, powdered nickel of 99.8% and NiO powder were used. Both powders were thoroughly mixed in a mass ratio of 3:1. The mixture was charged upon the inner bottom of the alumina tube, into which a zirconia tube was forcibly inserted by pressure. A platinum wire upon the tip of which an iridium wire is welded was used as an electrode for a liquid alloy and In_2O_3 . Furthermore a platinum wire was used as the Ni/NiO reference electrode. In the composition range investigated, $N_{\text{In}} = 1.00-0.40$, the duration of time when an iridium wire was contacted with a liquid alloy was approximately 108 ks at the maximum. With a visual observation after the experiment is completed, no dissolved loss of the iridium into the alloy and In_2O_3 can be noticed. However since dissolution loss of the iridium wire can be observed with the experiment of a long duration of time with $N_{\text{In}} = 0.34-0.20$, the wire is immersed in the alloy electrode only during the measurement. With the naked eye, no dissolution loss of a zirconia tube can be observed throughout the whole composition range in the present experiment.

After the cell is assembled, a reaction tube is evacuated at first for approximately 3.6 ks at a room temperature and later for approximately 5.4 ks at 480 K. After that, the inside of the tube is filled with purified argon, and

then a Kanthal resistance furnace is gradually heated. 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 cell was positioned in the uniform temperature zone of 5×10^{-2} m in length within ± 1 K at the experimental temperatures. During the emf measurements, the reaction tube was filled with purified argon about 6700 Pa higher than the atmospheric pressure. The experimental temperature ranged from 937 to 1270 K. For the emf measurement, a potentiometer (No. 2722) made by Yokogawa Electric Company is used. The accuracy of this potentiometer for direct current was ± 0.1 mV. The equilibrium of the cell can be obtained at 11-18 ks after the required temperature (1050 K) is attained. After the stable emf was measured for 2-2.5 ks, the temperature was varied to the different experimental temperature. The reversibilities of emf were confirmed at various temperatures. The measured values were scattered at temperatures higher than 1273 K. Therefore the measurement has not been made beyond 1275 K.

IV. Experimental Results and Discussion

1. Concentration dependence of the activities of indium and copper

Figure 1 shows the emf-temperature relations at various concentrations of indium. In the experimental temperature region, the linearity can be noticed at each concentration. In Table 1, the relations between emf and temperature are shown by applying the method of least squares to the results in Fig. 1. Probable experimental er-

Fig. 1 Relation between emf and temperature of the cell, Pt/Ni(s), NiO(s)|ZrO₂(+CaO)|Cu-In(I), In₂O₃(s)/Ir/Pt.

Table 1 Temperature dependence of the electromotive forces for cell [I]: Pt/Ni(s), NiO(s)|ZrO₂(+CaO)|Cu–In(l), In₂O₃(s)/Ir/Pt.

N_{In}	$E_{(\text{I})}$ or $E_{(\text{II})}=a+bT\pm r$
1.00	$E_{(\text{II})}=394.8\times 10^{-3}-14.22\times 10^{-5}T\pm 0.20\times 10^{-3}$
0.85	$E_{(\text{I})}=395.3\times 10^{-3}-14.66\times 10^{-5}T\pm 0.14\times 10^{-3}$
0.70	$E_{(\text{I})}=397.2\times 10^{-3}-15.23\times 10^{-5}T\pm 0.15\times 10^{-3}$
0.60	$E_{(\text{I})}=400.6\times 10^{-3}-15.81\times 10^{-5}T\pm 0.19\times 10^{-3}$
0.50	$E_{(\text{I})}=407.2\times 10^{-3}-16.78\times 10^{-5}T\pm 0.12\times 10^{-3}$
0.40	$E_{(\text{I})}=411.4\times 10^{-3}-17.93\times 10^{-5}T\pm 0.43\times 10^{-3}$
0.34	$E_{(\text{I})}=407.9\times 10^{-3}-18.26\times 10^{-5}T\pm 1.21\times 10^{-3}$
0.30	$E_{(\text{I})}=402.7\times 10^{-3}-18.41\times 10^{-5}T\pm 0.45\times 10^{-3}$
0.25	$E_{(\text{I})}=389.7\times 10^{-3}-18.35\times 10^{-5}T\pm 0.44\times 10^{-3}$
0.20	$E_{(\text{I})}=374.1\times 10^{-3}-18.25\times 10^{-5}T\pm 0.47\times 10^{-3}$

$E_{(\text{I})}$ or $E_{(\text{II})}$ in V, T in K, r is the probable error.

rors are of the order of 0.12–1.21 mV. The activities of liquid indium are calculated by eq. (5) from the relations between emf and temperature, the standard state being pure liquid indium. The activity of copper can be calculated with the Gibbs-Duhem equation. In Fig. 2, the activity of this alloy system is illustrated. A solid phase region or a two phase region in the copper-rich side has been reported⁽¹⁷⁾, but the present measurements have been only carried out in the complete liquid region. Therefore, at the copper-rich side in Fig. 2, the activity curves are drawn on the assumption of supercooled liquid alloys. The activity of indium shows a negative deviation from the Raoult's law in the lower indium concentration range than around $N_{\text{In}}=0.30$ at 1050 K and $N_{\text{In}}=0.32$ at 1250 K. It deviates positively in the higher indium concentration range. The activity of copper deviates negatively in most of the whole concentration range. The activities of both components approach the Raoult's law with the increase in temperatures. As is represented from a phase diagram of the Cu–In system⁽¹⁷⁾, there exist many secondary solid solutions (electronic compounds) in a solid phase in the neighborhood of $N_{\text{In}}=0.2$ –0.3. Since the influence of such compounds might be left as clusters even in a liquid alloy, it is believed that the activities of both components of the liquid alloy negatively deviate in the copper-rich region. Also since the difference in size of atomic radius⁽²³⁾ between copper and indium in a solid phase is larger than, for example, the one between silver and indium in a solid phase as shown in Table 2, it would seem that the activity of indium for the liquid Cu–In alloys deviates more positively in the indium side compared with that for the liquid Ag–In alloys. In Fig. 3, the activity curves of both components presented by Azakami *et al.*⁽⁷⁾ and the present work are shown at 1073 K. These activity curves exhibit an almost approximated tendency. Furthermore, the α function of indium in the Cu–In system is plotted in Fig. 4. The slope of the negative curve against N_{In} becomes larger with increasing indium content, suggesting that this system cannot be considered as a regular solution.

2. Other thermodynamic quantities

Thermodynamic quantities at 1250 K have been in-

Fig. 2 Activity curves in the liquid Cu–In alloys from the electromotive force of galvanic cells with the solid electrolyte.

roduced from the measured emf values. The free energy of mixing has slightly larger negative values compared with ΔG^{id} , and the peak value of ΔG shows -8.50 kJ/mol in the neighborhood of $N_{\text{In}}=0.40$. In Fig. 5, heat of mixing of the alloy system is illustrated. The heat of mixing shows positive values, although they are very slight ones, that is to say, it is endothermic, in the high composition side rather in the neighborhood of $N_{\text{In}}=0.60$. In the meanwhile, the heat of mixing shows negative values at the higher composition side of copper rather than in the neighborhood of $N_{\text{In}}=0.60$. In other words, it is exothermic. Despite this fact, its exothermic degree is not so high. The peak values show $\Delta H_{\text{max}}=0.40$ kJ/mol in the neighborhood of $N_{\text{In}}=0.76$ and $\Delta H_{\text{min}}=-2.40$ kJ/mol in the neighborhood of $N_{\text{In}}=0.24$. In Fig. 6, the values of the heats of mixing obtained by Takeuchi *et al.*⁽¹⁸⁾, Itagaki *et al.*⁽¹⁹⁾, Azakami *et al.*⁽⁷⁾ and the present study are illustrated. Although there is a difference between the measured values in this study and the ones by the emf method utilizing a liquid-salt electrolyte, the present result shows the values approximated to the ones directly measured with the calorimetry by Takeuchi *et al.*⁽¹⁸⁾ and Itagaki *et al.*⁽¹⁹⁾ According to Azakami *et al.*⁽⁷⁾, a long time is required to stabilize the emf for the measurement at $N_{\text{In}}=0.201$ in the high copper concentration range. Therefore the measurement is restrictedly made at just two points of 1073 K and 1273 K. In such a case, a problem is believed to reside with the measurement accuracy of the temperature dependency of

Table 2 Differences in electronegativity, χ and atomic radius, R .

Alloy	$\Delta\chi$		ΔR (pm)
	Darken <i>et al.</i>	Pauling	
Cu–In	0.8	0.2	–40
Ag–In	0.5	0.2	–24
Au–In	1.7	0.7	–24

Fig. 3 Activity curves in the liquid Cu-In alloys (1073 K).
 ---△--- T. Azakami and A. Yazawa (emf, fused-salt electrolytes).
 —○— This study (emf, solid electrolytes).

Fig. 4 Alpha function (α_{In}) of indium for the liquid Cu-In alloys from the electromotive force of galvanic cells with the solid electrolyte.

the emf which is one of the fundamental data for calculation of the heat of mixing. Since the accuracy of the data on the heat of mixing at the copper side in particular is not high, the differences from other three data are imagined to have appeared. In general, from the results of the emf measurements as in this experiment, the activity and the free energy of mixing can be obtained accurately. However, as regards the heat of mixing, some degree of errors cannot be avoided. The results in this study are almost approximated to the directly measured values by calorimetry which is supposedly, as a measuring method of the heat of mixing, more accurate than by an indirect measuring method. Thus it can be said that good results have been brought about from the successful measurement made within experimental error as the measured values of the heat of mixing due to the emf method of the indirect measurement. Figure 7 shows a ξ function ob-

Fig. 5 Heats of mixing in the liquid Cu-In alloys (1250 K).

Fig. 6 Heats of mixing in the liquid Cu-In alloys.
 — S. Takeuchi *et al.* (calorimetry: 1363 K).
 - - - K. Itagaki and A. Yazawa (calorimetry: 1373 K).
 - · - T. Azakami and A. Yazawa (emf, fused-salt electrolytes: 1273 K).
 — This study (emf, solid electrolytes: 1250 K).

tained from the heat of mixing which is regarded as adequate measured values acquired by the present work, Takeuchi *et al.*⁽¹⁸⁾ and Itagaki *et al.*⁽¹⁹⁾ Such an extent of difference between the ξ function obtained from the present study and the values from heats of mixing by calorimetry is within experimental error. All the three values indicate curves whose tendencies closely resemble

Fig. 7 ξ function in the liquid Cu-In alloys.
 ---x--- S. Takeuchi *et al.* (calorimetry: 1363 K).
 ---△--- K. Itagaki and A. Yazawa (calorimetry: 1373 K).
 —○— This study (emf, solid electrolytes: 1250 K).

Fig. 8 Excess integral molar properties for the liquid Cu-In alloys (1250 K).

each other. Namely, the curves of negative slopes for the ξ function against N_{In} become larger with increasing indium content. The curves show a remarkable change in the high composition side of copper, and from these results it can hardly be said that the alloy system in question reveals subregular-solution⁽²⁴⁾ behavior. In Fig. 8, excess quantities of the alloy system, i.e. excess free energy, heat of mixing, and excess entropy are illustrated. There exist peak values with respective quantities in the

neighborhood of $N_{\text{In}}=0.25$, and it is distinctive for the individual values to take inverse symbols of $-$ and $+$ at the high composition side of indium.

3. Concentration dependence of activities and heats of mixing of liquid IB metals (Cu, Ag and Au)-indium alloys

Figure 9 shows the activities of indium for the Cu-In, Ag-In⁽²⁾ and Au-In⁽¹⁾ systems measured with the emf method in the present and previous studies by the author *et al.* In this figure, the activities of copper, silver and gold obtained from the three systems by the Gibbs-Duhem equation are illustrated as well. By comparing these systems, it is explained that the activities of both the components deviate more negatively in the order of copper, silver and gold of IB metals in the periodic table, except for the activity of indium in the indium-rich side more than $N_{\text{In}}=0.3$ in the Cu-In system. This might be due to the differences in size of atomic radii⁽²³⁾ as shown in Table 2, because the electronegativity factor is nearly the same for the Cu-In and Ag-In systems. Activities of both components of the liquid Au-In system show a considerable negative deviation over the whole concentration range. Such a great affinity of the Au-In system compared with Cu-In and Ag-In systems may be ascribed to the differences in the electronegativities⁽²⁵⁾⁽²⁶⁾, because the electron concentration must be the same for the IB metals-In systems.

In Fig. 10, heats of mixing in the Cu-In, Ag-In and Au-In systems are illustrated. Tendencies of heats of mixing for these systems show almost the same as in the case of the activities. In other words, the Cu-In system is exothermic in the copper-rich side, whereas it is a slightly endothermic in the indium-rich side. The Ag-In and Au-In systems are exothermic over the whole composition region. And the exothermic value of the Au-In system is remarkably greater than that for the Ag-In system. The

Fig. 9 Activity curves in the liquid Cu-In, Ag-In and Au-In alloys (1073 K).

—○— This study (Cu-In system: emf, solid electrolytes).
 ---△--- K. Kameda *et al.* (Ag-In system: emf, solid electrolytes).
 ---x--- K. Kameda *et al.* (Au-In system: emf, fused-salt electrolytes).

Fig. 10 Heats of mixing in the liquid Cu-In, Ag-In and Au-In alloys.
 — This study (Cu-In system: emf, solid electrolytes: 1250 K).
 - - - K. Kameda *et al.* (Ag-In system: emf, solid electrolytes: 1250 K).
 - · - K. Kameda *et al.* (Au-In system: emf, fused-salt electrolytes: 1127 K).

fact suggests that differences in electronegativity⁽²⁵⁾⁽²⁶⁾ among copper, silver, and indium in a solid phase respectively reveal the same values as shown in Table 2. On the other hand, the differences in atomic radius⁽²³⁾ are larger with the Cu-In system compared with the Ag-In system. Thus it may be imagined that the heat of mixing in the Cu-In system is exothermic in a smaller quantity than the one of the Ag-In system. Also it may be presumed that it contributes to the behavior revealing a very slight endothermic phenomenon in the high concentration range of indium. In the meantime, in the Au-In system, there exist stoichiometric compounds such as AuIn, AuIn₂ besides the electronic compounds in the gold side. Since the melting points of the above mentioned compounds are considerably high, it is surmised that these compounds are very stable ones. It is also assumed that influence of such compounds is related to extreme greatness of the electronegativity of gold as shown in Table 2. Accordingly it is believed that influence of intermetallic compounds still remains as clusters possibly caused by electronegativity factors in the low concentration region of gold besides the properties like the ones of transition metals in the high composition side of gold the same as Cu-In and Ag-In systems even after a liquid alloy is formed. Thus it is supposed that the behavior of the activities of both the components and the heats of mixing of the Au-In system is revealed as noticed in Figs. 9 and 10.

The above result is also quite interesting as viewed in the light of the theory of Engel for copper alloys⁽¹⁰⁾⁽¹¹⁾. For a long time IB metals, such as copper, silver and gold

have been considered as one electron metals with a completely filled d shell, thus being the first typical normal metal after the transition metals. However, he assumed that IB metals are the transition metals in which d electrons participate in the bonding. Thus, the IB metals have around 2.5 outer electrons and 8.5 d electrons whereby 2.5 outer electrons and 1.5 electrons participate in the bonding. An addition of typical normal metals with closed inner shells prevents the formation of d bonds between the IB metal atoms and the added atoms. Prevention of the d bond formation will eliminate the source of energy used to excite d electrons and the concentration of unfilled d shells must decrease. The limit of the α phase constitutes the critical range of the catastrophic breakdown of d bonding. From these investigation, it can be imagined that liquid IB metal alloys might present quite different thermodynamic features from those of typical normal metals. Hence, for example, thermodynamic quantities in liquid IB metals-In alloys have been contrasted with those in the Pb-In alloys which are composed of both typical normal metals⁽³⁾. The anomalies which are observed in Figs. 9 and 10 give support to the above viewpoint. Namely, the activities and the heats of mixing in the liquid IB metals-In alloys seem to be well explained by assuming that the filling of d shell in copper, silver and gold is incomplete and the electron transfer from indium atoms to IB metal atoms occurs in these systems, unlike the Pb-In system composed of both typical normal metals.

V. Conclusion

The activity of the liquid Cu-In system has been determined by the emf measurement of the galvanic cell with solid electrolytes for $N_{\text{In}}=0.20-0.85$ at 937–1270 K. Deviations of the activities of indium and copper from Raoult's law at 1050 K and 1250 K are positive for the indium rich side and are negative for the copper rich region of the system. Heats of mixing at 1250 K are negative for copper rich alloys and slightly positive for indium-rich alloys. In comparison with the activities and the heats of mixing of liquid Cu-In, Ag-In and Au-In alloys, it is observed that those deviate more negatively in the order of copper, silver and gold of IB metals in the periodic table. The activities and the heats of mixing for the Au-In system would exhibit greater negative deviations and larger exothermic values, respectively, than those for the Cu-In and Ag-In systems. Such a great affinity of the Au-In system compared with the Cu-In and Ag-In systems may be ascribed to the differences in electronegativity.

The thermodynamic properties of liquid alloys composed of IB metals (Cu, Ag and Au) and indium have been discussed in terms of the alloy solution theory by Engel⁽¹⁰⁾⁽¹¹⁾. Namely, the activities and the heats of mixing for the liquid alloys seem to be consistently explained on the assumption that the filling of d shell is incomplete for IB metals as well as the transition metals, whereas it is complete for indium, that is, typical normal metal.

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