Activities of Liquid Gold-Zinc and Silver-Zinc Binary Alloys by E.M.F. Measurements Using Zirconia Solid Electrolyte Cells*

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The emf of the following galvanic cells using zirconia solid electrolytes has been measured in order to obtain the standard free energy of formation of ZnO(s) in the temperature range from 818 to 986 K and the thermodynamic data of the liquid Au-Zn and Ag-Zn systems, for \( N_{Zn} = 0.25 - 0.80 \) and \( N_{Zn} = 0.27 - 0.85 \) in the temperature ranges from 918 to 1123 K and from 865 to 1152 K, respectively.

\[
\begin{align*}
\text{Pt/} & \text{Ni, NiO/ZrO}_2(\text{+CaO})/\text{Au-Zn, ZnO/Re-Pt} \\
\text{Pt/} & \text{Ni, NiO/ZrO}_2(\text{+CaO})/\text{Ag-Zn, ZnO/stainless steel}.
\end{align*}
\]

The error arising from vaporization of zinc was carefully avoided in this study. The standard free energy of formation of ZnO(s) was determined:

\[
\Delta G_{\text{ZnO}}^{\text{f}}/\text{J} \cdot \text{mol}^{-1} = -698272 + 209.07 T \text{ between 818 and 986 K.}
\]

Activity curves obtained show considerably negative deviations from Raoult’s law, especially in the Au-Zn system, suggesting a large affinity of zinc for gold and silver.

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

The activities and the heats of mixing of liquid Cu-Zn and Ag-Zn alloys are quite different from those of the liquid Au-Zn system, in which the activities show considerably negative deviations and the heats of mixing are exothermic, in the whole concentration range, owing to larger differences of electronegativity factor in the gold alloys.

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I. Introduction

The pyrometallurgical refining of crude lead, the Parkes process, in which the precious metals (Au and Ag) are extracted by the addition of zinc, has been generally used. In order to gain reliable basic data of the Parkes process, thermodynamic studies have been also carried out for these systems.

The thermodynamic properties in liquid Au-Zn\(^{(1)-(3)}\) and Ag-Zn\(^{(1)(2)(4)}\) alloys have been investigated by several workers. Measurements by vapor pressure method\(^{(1)}\), emf technique using fused salt electrolytes\(^{(2)-(4)}\) have chiefly determined the partial and integral thermodynamic quantities of the alloys.

For a long time IB precious metals, such as copper, silver and gold, have been considered to be the first normal metals after transition metal series in the periodic table. However, in recent years, the view that IB precious metals might be classified into the category of transition metals owing to the characteristic behaviors like transition metals has been proposed. Namely, Engel\(^{(5)}\) has successfully explained some properties of IB precious metal alloys based on the hypothesis that IB metals are the transition metals in which \( d \) electrons participate in the bonding.

The break points of \( \alpha_{\text{Zn}} \) function at approximately \( N_{Zn} = 0.40 \) in the liquid Au-Zn, Ag-Zn and Cu-Zn systems may be also interesting...
from the standpoint of stability theories of alloy phases. Namely, the anomalous state of the $\alpha$ function of zinc in the liquid IB metals-Zn systems seems to correspond approximately to the breakdown of the $d$ bonding at about 40 at% zinc\(^{(2)}\). The anomalies which are observed in these alloys give support to the above viewpoint. From these considerations, it can be supposed that IB metal alloys might present quite different thermodynamic features from those of the alloys composed of normal metals.

Data of the thermodynamic properties by the emf method with solid electrolytes has been hardly reported in these alloys. In order to clarify the anomalous behavior of liquid Au-Zn and Ag-Zn alloys, thermodynamic studies have been carried out by the emf method using zirconia solid electrolyte cells.

Furthermore, the results of the activity and the heats of mixing measurements in the liquid zinc alloys with the IB precious metals (Cu, Ag and Au)\(^{(1)-(4)(7)(8)}\) are compared with one another and discussed in connection with the alloy theories by Engel\(^{(5)(9)}\) concerning the phase stability of solid solution between IB metals and normal metals.

The cells used in the present study are:

\[
\begin{align*}
\text{Pt}/\text{Ni(s), NiO(s)}/\text{ZrO}_2(+\text{CaO})/\text{Au-Zn(1)}, & \quad \text{ZnO(s)/Re-Pt} \\
\text{Pt}/\text{Ni(s), NiO(s)}/\text{ZrO}_2(+\text{CaO})/\text{Ag-Zn(1)}, & \quad \text{ZnO(s)/stainless steel} \\
\text{Pt}/\text{Ni(s), NiO(s)}/\text{ZrO}_2(+\text{CaO})/\text{Zn(1)}, & \quad \text{ZnO(s)/Re-Pt} \\
\text{Pt}/\text{Ni(s), NiO(s)}/\text{ZrO}_2(+\text{CaO})/\text{Zn(1)}, & \quad \text{ZnO(s)/stainless steel.}
\end{align*}
\]

The emf's of these cells are given by

\[
4F(E_{(II)} - E_{(I)}) = RT \ln \left( \frac{p_{O_2}(\text{Au-Zn or Ag-Zn})}{p_{O_2}(\text{ZnO})} \right).
\]

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

\[
\Delta G_{\text{Zn}} = RT \ln a_{\text{Zn}} = -2F(E_{(II)} - E_{(I)}),
\]

where $E$ is the cell emf measured at $TK$, $E_{th}$ is the thermoelectromotive force between the stainless steel wire and the Pt wire, $p_{O_2(NiO)}$, $p_{O_2(\text{ZnO})}$ and $p_{O_2(\text{ZnO})}$ are the oxygen partial pressures in equilibrium with Ni(s)-NiO(s), Zn(1)-ZnO(s) and Au-Zn or Ag-Zn alloys(1)-ZnO(s) electrodes, respectively, $R$ is the gas constant, $a_{\text{Zn}}$ is the activity of zinc in the alloys, referred to a standard state of pure liquid zinc saturated with oxygen, and $T$ is the absolute temperature of the cell. Electrical contact with Zn(1), ZnO(s) and Au-Zn(1), ZnO(s) was allowed with a short piece of Re wire (2.45 $\times$ 10\(^{-4}\) m\(^{3}\) spot-welded to the end of the Pt wire. The thermal emf between the Re-Pt wire and the Pt wire used for measuring the emf of the cells was found to be negligible.

II. Experimental

An assembled cell employed in the present investigation was identical with that described in previous publications\(^{(6)(10)(11)}\). A zirconia tube containing weighed portions of Au (99.99\%) or Ag (99.999\%), Zn (99.999\%) and ZnO (99.999\%) was set in an alumina crucible containing a Ni-NiO powder mixture. Electrical contacts to Au-Zn or Ag-Zn alloy-ZnO electrodes and a Ni-NiO reference electrode were accomplished by the Re-Pt wire and the Pt wire, the oxidized stainless steel wire and the Pt wire, respectively. The Re-Pt wire and the stainless steel wire showed a negligibly small reaction with Au-Zn or Ag-Zn and ZnO, respectively, and stable emf's were obtained for over 126 ks. The temperature was measured by a Pt vs 13\% Rh-Pt thermocouple placed along the cell and controlled within $\pm$0.5 K by a temperature regulator. The cell was heated in a Kanthal resistance furnace having a homoge-
neous temperature zone $5 \times 10^{-2} \text{m}$ in length within $\pm 1 \text{K}$. The thermoelectromotive force between the stainless steel wire and the Pt wire had been measured in advance in the same furnace under argon atmosphere, and the results indicated

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

between $912$ and $1255 \text{K}$. (5)

The assembled cell was heated in vacuum from room temperature to $500 \text{K}$ to remove the moisture in Ni-NiO, Au-Zn or Ag-Zn alloys-ZnO electrodes and others, and then purified argon was led into the reaction tube. During the emf measurements in the temperature range from $918$ to $1123 \text{K}$ in the Au-Zn alloys, from $865$ to $1152 \text{K}$ in the Ag-Zn alloys, respectively, the reaction tube was filled with purified argon, whose pressure was kept at $6700 \text{Pa}$ higher than the atmospheric pressure. The emf was measured by a Yokogawa Electric 2722 DC potentiometer that allowed the emf values to be read within the accuracy of $\pm 0.1 \text{mV}$. The time necessary for the emf to attain a steady value at a constant temperature was quite short, and reproducibilities and reversibilities of emf were checked by temperature cycling. In preparing specimens of the Au-Zn and Ag-Zn alloys, the error arising from volatilization of zinc was carefully avoided. During the measurements of emf, effective composition changes from free vaporization of zinc in the alloys could be avoided because of the larger affinity of zinc for gold and silver.

III. Results and Discussion

1. Standard free energy of formation of ZnO(s)

The results for cell(II) are shown in Figs. 1 and 2 as illustrated "Pure Zn" line. By using the least squares method, the lines in Figs. 1 and 2 were represented as

$$E/V = 598.31 \times 10^{-3} - 10.18 \times 10^{-5}T \pm 0.358$$

$$\times 10^{-3} \text{ between } 818 \text{ and } 986 \text{K}, \quad (6)$$

where the thermoelectromotive force between the stainless steel wire and the Pt wire in Fig. 2 had been corrected and probable errors were calculated numerically from the Pure Zn lines in Figs. 1 and 2. The standard free energy of formation of ZnO(s) was calculated based on eq. (6) and the standard free energy of formation of NiO(s) by Charette and Flengas. The
calculated value was shown by a solid line in Fig. 3, and the dotted line and so forth show other reliable data\(^{(13)-(15)}\). These lines were found to be agreement each other.

### 2. Activities

The temperature variation of emf are shown in Figs. 1 and 2. The extent of errors, i.e., probable errors, of emf's was calculated numerically to be from 1.27 to 2.35 mV in the Au–Zn system and from 0.04 to 0.19 mV in the Ag–Zn system, respectively.

The activities of both components at 1023 K and 1073 K are illustrated in Figs. 4 and 5. Both of the systems show considerably negative deviations from Raoult's law, especially in the Au–Zn system, suggesting a large affinity between zinc and gold. The activities of both components approach the ideality with increasing temperature. The activity data presented by Yazawa et al.\(^{(2)}\) and Hultgren et al.\(^{(16)}\) are also shown in Figs. 6 and 7, indicating the trend similar to the author's results.

The phase diagram of the Au–Zn system shows intermetallic compounds such as \(\alpha_1, \beta', r, r_1\), and \(e\). The Ag–Zn equilibrium diagram

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**Fig. 3** Standard free energy of formation of ZnO(s).

**Fig. 4** Activity curves in the liquid Au–Zn system.

**Fig. 5** Activity curves in the liquid Ag–Zn system.

**Fig. 6** Activity curves in the liquid Au–Zn system (1023 K).
also shows secondary solid solutions or electron compounds such as $\beta$, $\zeta$, $\gamma$ and $\epsilon^{(19)}$. These compounds in the solid state seem to have some effect on the activities of both components for the alloys in the molten state. Then the observation is in agreement with the phase diagrams of these systems.

Figure 8 shows activity curves of both components in the liquid Cu–Zn$^{(7)}$, Ag–Zn and Au–Zn systems at 1073 K. The activities of both components in these systems exhibit considerably negative deviations, especially in the Au–Zn system. Those of both components in the Cu–Zn and Ag–Zn systems agree very well over the whole concentration range. Such a great affinity of the Au–Zn system compared with the Cu–Zn and Ag–Zn systems may be ascribed to the differences in the electronegativities, because the electron concentration must be the same for IB metals–Zn systems. Great significance of the electronegativity factor has been discussed by Hume-Rothery$^{(18)}$ for the stability of intermediate phases between IB and normal metals. The necessary data are tabulated in Table 1. Such discussion made for solid alloy phases are also quite interesting for the comprehension of the thermodynamic behavior of liquid alloys.

The above result is also quite interesting as viewed in the light of the theory of Engel for copper alloys$^{(5)}$. IB noble metals have long been considered to be the first normal metals after transition metals series in the periodic table. However, of late years, the view that IB noble metals might be classified into the category of transition metal owing to the characteristic behaviors like transition metals has been introduced. Engel$^{(5)}$ has successfully explained some properties of solid IB metal alloys based on the hypothesis that the distribution of electrons in IB metals is not that of a closed $d$ shell and one outer electron, but that of 8.5$d$ electrons and 2.5 outer electrons on the average and these unfilled $d$ electrons participate in atomic bonding. From these in-

Table 1 Differences in electronegativity, $x$ and atomic radius, $R$.

| Alloy    | $\Delta x$ | $\Delta R$ (pm) |
|----------|------------|-----------------|
|          | Darken et al.$^{(19)}$ | Pauling$^{(20)}$ | Pauling$^{(20)}$ |
| Cu–Zn    | 1.0        | 0.3             | 10 |
| Ag–Zn    | 0.7        | 0.3             | 6  |
| Au–Zn    | 1.9        | 0.8             | 6  |
vestigations, it can be imagined that liquid IB metal alloys might present quite different thermodynamic features from those of the alloys composed of 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(11). The anomalies which are observed in Figs. 8 and 9 give support to the above viewpoint. Adding a normal metal such as zinc in the IB metals for alloying results in the breakdown of the d bonding. For instance, at the solubility limit of a solid solution, namely at 38% Zn in the Cu-Zn system, most of the copper atoms supply only one outer bonding electron per atom and very few copper atoms have unfilled d shells. In Fig. 9, the anomalous state of the α function of zinc in the liquid IB metals-Zn systems seems to correspond approximately to the breakdown of the d bonding at about 40at% zinc(2)(9). In conclusion, in the alloys of IB noble metals with zinc, the α solid solution range may be assumed to be transition metal behavior, and alloys having more than 0.4 mole fraction of zinc are expected to show normal metal behavior.

3. Free energy, heats of mixing

The partial and integral molar quantities were derived from the experimental data. The integral molar free energy of the Au-Zn and Ag-Zn systems showed considerably larger negative values than those of the ideal molar free energy. The observed peak reaches $-27.61 \text{ kJ/mol}$ for about $N_{\text{Zn}} = 0.49$ at 1073 K in the Au-Zn system and $-11.05 \text{ kJ/mol}$ for about $N_{\text{Zn}} = 0.48$ in the Ag-Zn system. The heats of mixing are considerably exothermic, especially in the Au-Zn system. The peak reaches $-16.99 \text{ kJ/mol}$ at about $N_{\text{Zn}} = 0.48$ in the Au-Zn system and $-5.27 \text{ kJ/mol}$ at about $N_{\text{Zn}} = 0.46$ in the Ag-Zn system. Similar results have been reported in the previous work(2). The results are in good agreement with the present work.

The heats of mixing in the liquid Cu-Zn(8), Ag-Zn and Au-Zn systems are illustrated in Fig. 10. The general tendency has much the same analogy with the case of activities reported in Fig. 8. Namely, the heats of mixing of the liquid Cu-Zn and Ag-Zn alloys agree
well on the whole and are quite different from those of the liquid Au-Zn system. They are considerably exothermic in the Au-Zn alloys, owing to the larger electronegativity factor in the gold alloys over the whole concentration range.

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