Activity Measurements of Liquid Ga–Te and Ga–Sb Alloys by EMF Method with Solid Electrolyte*

By Iwao Katayama**, Jun-ichiro Nakayama***, Tetsuya Nakai**** and Zensaku Kozuka**

E. M. F. of galvanic cells with the solid electrolyte (ZrO₂+CaO) was measured to determine the activities of gallium at high temperatures in the whole composition range for liquid Ga–Te and Ga–Sb alloys, and some thermodynamic functions were derived from the results. The cells used were as follows:

(-) W, Re|Ga, Ga₂O₃|ZrO₂+CaO|Ga–Te(l), Ga₂O₃|Re, W (+),
(-) W, Re|Ga–Sb(l), Ga₂O₃|ZrO₂+CaO|Fe, Fe₂O₃|W (+)
and
(-) W, Re|Ga, Ga₂O₃|ZrO₂+CaO|Ga–Sb(l), Ga₂O₃|Re, W (+).

The activities of gallium in liquid Ga–Te alloys at 1123 K showed large negative deviations from Raoult’s law on the Te-rich side, and increased remarkably in the middle concentration range from negative to positive deviations from ideality. The activities of gallium in liquid Ga–Sb alloys at 1073 K showed moderate negative deviations from the ideality in the whole composition range.

These data are compared with published data.

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I. Introduction

Recently many studies have been carried out on alloy systems containing semiconducting compounds not only from theoretical interest but also from important industrial applications to solid state electronic devices. An accurate knowledge of the thermodynamic properties and phase diagrams of them is essential.

Ga–Te(1)–(3) is a binary alloy system typical of several liquid semiconductors, which exhibit anomalous physical and chemical properties, and contains four compounds (GaTe, Ga₂Te₃, Ga₂Te₅ and Ga₃Te₄)(1) in the solid state. On the Ga-rich side there is a liquid miscibility gap. Measurements of the physical properties(4) provide the evidence for the presence in the melt of molecular associations based on Ga₂Te₃ and GaTe.

The enthalpy of mixing(5) and the specific heat(6) of liquid Ga–Te alloys have been measured, and the heat content(7) and enthalpy of melting(7) of Ga₂Te₃ and GaTe have been reported. The activity of this system was derived by Predel et al.(8) from vapor pressure measurements at 1114 K. Other activity data are not available in the literature.

As for Ga–Sb system, direct calorimetric measurements have been performed by Yazawa et al.(9), Predel and Stein(10) and Gambino and Bros(11), and the results in the middle concentration range of the alloys show excellent agreement. But the general appearance of the enthalpy curve is different.

The activities in the liquid Ga–Sb alloys have been measured by electrochemical techniques(12)(13) and vapor pressure measurements(14)(15). Recently Anderson et al.(16) measured the activities of Ga in the high temperature galvanic cells with stabilized zirconia solid electrolytes. All of the reported results
show relatively large negative or moderate negative deviations from Raoult's law and activity values are not well defined.

The present study intends to derive the activities of Ga in the Ga–Te and Ga–Sb liquid alloys from emf measurements of the galvanic cells with the calcia stabilized zirconia as solid electrolyte in the whole concentration range.

II. Experimental

1. Materials

The alloys used in this study were prepared from high-purity materials (Ga: 99.99 mass% purity, Sb: 99.999% from Mitsubishi Metal Co., Ltd.; Te: 99.99% from Osaka Asahi Metal Mfg. Co., Ltd.). Alloy elements were weighed to give mixtures with desired compositions and melted in a sealed evacuated apparent silica ampoule at about 1150 K. Ga2O3 powder (99.99% purity from Mitsubishi Metal Co., Ltd.) was mixed with Ga and its alloys in weight ratios 1:3 and 1:12, respectively. Fe, Fe2O3 reference electrode was prepared from reduced iron powder (99.9% purity, from Toho Zinc Co. Ltd.) and Fe2O3 powder (reagent grade, Wako Pure chemical Industries Ltd.) in a similar way to that described previously(17). Zirconia solid electrolyte crucibles (0.89ZrO2+0.11CaO, OD 8 mm, ID 5 mm and length 50 mm or 300 mm) were obtained from Nippon Kagaku Togyo Co., Ltd.

2. Experimental apparatus and procedures

Experimental details have been outlined previously(18). Re wires (0.254 mmφ, 10 mm) were spot-welded to W wires for both the reference and alloy electrodes. As there existed some volatile component in the electrode in this study, the cell was designed to minimize composition changes resulting from volatilization. The space above the electrode in the electrolyte crucible was filled with a tight-fitting alumina tube in which a lead wire was fixed with high temperature zirconia cement.

After the cell was assembled, the reaction tube was evacuated and flushed with purified argon. This operation was two or three times repeated. After that the temperature was raised to a desired value. The emf of the cell was measured with a digital voltmeter with a printer (Multi-Logging Meter AD-5311, A and D Co. Ltd.). Equilibrium was considered to have been attained, when the measured emf varied only by ±0.1 mV during the period over 3600 s.

III. Results and Discussion

1. Ga–Te system

The emfs of cell I were measured. Initial equilibration times were (1.08–1.44)×104 s. On changing the temperature, equilibration at a new temperature took a very short period of time.

The cell was investigated in the temperature range 931–1075 K for XGa=0.10–0.30, 1090–1180 K for XGa=0.45–0.60 and 1058–1173 K for XGa=0.70–0.92, where XGa represented mole fraction of Ga in the alloy. When the cell containing high concentration of Te in the alloy electrode was held above 1073 K for a long time, emf of the cell continuously decreased, and there was evidence of volatilization of Te in the cooler part of the cell holder. So the measurements were performed in the lower temperature range. For the alloys of XGa=0.40 to 0.45, stable emf could not be obtained. Experimental results are listed in Table 1.

The relations between emf (E/mV) and temperature (T/K) are obtained by least squares regression analysis, and are represented in Table 2. Data for XGa=0.8, 0.9 and 0.92 are summarized in an equation. Activities of Ga (aGa) in the alloys at 1123 K were calculated by use of eq. (1) and the data are shown in Table 2.

where F: the Faraday constant (9.6485×104 Cmol⁻¹), R: the gas constant (8.3144 K⁻¹ mol⁻¹) and ΔG°Ga/Jmol⁻¹: partial molar free energy of mixing of Ga. Error limits in the activity values were derived only from the uncertainty in emf values.
Table 3 shows the activities and free energies of mixing at 1123 K derived from the data in this study with the help of interpolation and extrapolation. In the calculation the following general relations are used:

\[ \alpha_{Ga} = \frac{(\ln \gamma_{Ga})}{(1 - X_{Ga})^2} \]  

(3)

and

\[ \Delta G = X_{Ga} \Delta \bar{G}_{Ga} + X_{Te} \Delta \bar{G}_{Te}, \]  

(4)

where \( \gamma_{Ga} \) is the activity coefficient of Ga and \( \Delta G/\text{Jmol}^{-1} \) is the integral molar free energy of mixing.

In Fig. 1 activity data of liquid Ga–Te alloys are shown with the results by Predel et al.\(^{(8)}\) from vapour pressure measurements. Activity values of Te by Predel et al. and our values are in good agreement in high concentration range of Te. Our results confirm the existence of the miscibility gap on the Ga-rich side, and the gap on the lower Ga side is obtained from the activity curve: \( (T/K, X_{Ga}) = (1050, 0.73), (1100, 0.74) \) and \((1150, 0.75)\).

The activity coefficient of Ga at infinitely dilute solution of Te was calculated from the activity values by extrapolation to \( X_{Ga} = 0 \): log \( \gamma_{Ga} \) in Te = −2.32 at 1123 K.

We can calculate a quantity \( S_{cc} \), the long wave length limit of the concentration-concentration correlation function, according to the treatment of McAlister and Crozier\(^{(19)}\) with the activity data in the present study:

\[ S_{cc} = X_{Te} (\partial \ln \alpha_{Ga})/\partial X_{Ga}^{-1}. \]  

(5)

The calculated results are shown in Fig. 2. The minimum close to \( X_{Ga} = 0.4 \) suggests the formation of molecules of \( \text{Ga}_2 \text{Te}_3 \) in the liquid alloys. Both \( \Delta G \) and \( \Delta H^{(5)} \) have minimum values close to \( X_{Ga} = 0.4 \) in the liquid state.
2. Ga–Sb system

The emfs of cells II and III were measured.

\[
\begin{align*}
\text{(-)} \ W, \text{Re} | \text{Ga–Sb(I)}, \ Ga_2O_3 | \text{ZrO}_2 \\
+ \text{CaO} | \text{Fe, Fe}_2\text{O} | \text{W (+).} \quad \text{(II)}
\end{align*}
\]

\[
\begin{align*}
\text{(-)} \ W, \text{Re} | \text{Ga, Ga}_2\text{O}_3 | \text{ZrO}_2 \\
+ \text{CaO} | \text{Ga–Sb(I), Ga}_2\text{O}_3 | \text{Re, W (+).} \quad \text{(III)}
\end{align*}
\]

The results are summarized in Tables 4 and 5. In order to derive the activity of Ga from the emf values of cell II, eq. (5) for cell IV was used.

\[
E/\text{mV} = 519.6 - 0.2322 \ T/\text{K} \pm 1.4^{(20)}.
\]

The relations between \(E\) and \(T\) are represented in Table 6 with derived activity values of Ga at 1073 K. Indirect measurements (cell II) caused a little large errors in the activity because of the uncertainty in emfs in

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Table 4 Experimental EMF Data of cell (II).

| \(X_{\text{Ga}}\) | \(T/\text{K}:E/\text{mV}\) |
|----------------|-----------------|
| 0.10 | 1022:188.3 1037:183.9 1072:174.5 1063:176.8 1107:164.1 1100:160.0 |
| 0.20 | 1129:158.5 1068:174.7 |
| 0.40 | 1121:187.7 |
| 0.60 | 1102:213.9 1105:221.7 1123:217.5 |
| 0.70 | 1036:238.4 1026:241.1 1058:233.1 1079:227.9 1088:225.3 1078:228.3 |
| 0.80 | 1059:247.4 1061:241.8 1052:243.5 1072:239.5 1088:235.3 1080:237.5 |
| 0.90 | 1100:232.8 1124:227.3 |
| 1.00 | 1024:259.1 1039:255.3 1068:248.4 1058:240.7 1082:245.2 1100:240.9 |
| 1.10 | 1092:242.9 1113:238.0 1121:236.3 |
| 1.20 | 1028:265.5 1047:261.8 1041:262.7 1079:254.3 1071:255.3 1100:248.7 |
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In a similar way to Ga–Te alloys, thermodynamic quantities are calculated and are represented in Table 7. The activity of Ga is shown in Fig. 3 with the results by other investigators. Our results are in good agreement with the values by Anderson et al.\(^\text{16}\) in the middle concentration range of the alloys, but their values scattered somewhat largely in both high and low concentration ranges of Ga. Although the activity coefficients did not fall adequately on a smooth curve for the composition, the activity coefficients at infinitely dilute solutions at 1073 K were estimated from the values in Table 7 as follows: \(\log \gamma_{\text{Ga}}^\circ\) in Sb = 0.292 and \(\log \gamma_{\text{Sb}}^\circ\) in Ga = -0.514.

In both cases of Ga–Te and Ga–Sb alloys, the temperature ranges investigated are too narrow to derive accurate values of enthalpy and entropy of mixing from the temperature dependence of emfs.

**Table 5** Experimental EMF data of cell (III).

| \(x_{\text{Ga}}\) | \(T/K:E/\text{mV}\) |
|------------------|------------------|
| 0.10             | 1091:92.9        |
|                  | 1078:91.7        |
|                  | 1136:96.5        |
|                  | 1088:92.7        |
| 0.30             | 1088:51.9        |
|                  | 1125:53.6        |
|                  | 1098:52.1        |
|                  | 1066:50.5        |
|                  | 1116:52.8        |
|                  | 1144:53.9        |
|                  | 1096:51.7        |
|                  | 1091:51.3        |
| 0.50             | 1010:49.5        |
|                  | 1153:54.7        |
|                  | 1087:52.2        |
| 0.75             | 1092:30.1        |
|                  | 1058:29.0        |
|                  | 1123:31.5        |
|                  | 1039:29.2        |
|                  | 1073:30.4        |
|                  | 1109:31.4        |
|                  | 1084:30.6        |
|                  | 1034:28.6        |
| 0.80             | 1140:32.2        |
| 0.90             | 1169:12.0        |
| 1                 | 1169:12.0        |

**Table 6** Temperature dependence of the emf of cells (II) and (III), and activities of Ga in Ga–Sb liquid alloys at 1073 K.

| \(x_{\text{Ga}}\) | \(E/\text{mV}\) | \(a_{\text{Ga}}\) |
|------------------|----------------|-----------------|
| 0.10             | 1049.0 ± 0.2972 | 7.2 ± 0.005     |
| 0.20             | 1046.7 ± 0.2497 | 7.0 ± 0.007     |
| 0.40             | 1049.0 ± 0.2431 | 7.2 ± 0.014     |
| 0.50             | 1048.9 ± 0.2332 | 7.2 ± 0.021     |
| 0.60             | 1049.1 ± 0.2347 | 7.2 ± 0.025     |
| 0.70             | 1050.9 ± 0.2289 | 7.2 ± 0.037     |
| 0.10             | 4.0 ± 0.0814    | 7.0 ± 0.001     |
| 0.30             | 11.4 ± 0.0372   | 7.0 ± 0.003     |
| 0.50             | -4.9 ± 0.0325   | 7.0 ± 0.005     |
| 0.75             | 4.6 ± 0.0064   | 7.0 ± 0.005     |
| 0.80             | 2.0 ± 0.0059   | 7.0 ± 0.003     |
| 0.90             | -14.6 ± 0.0166 | 7.0 ± 0.006     |

**Table 7** Activities of Ga and Sb, and free energies of mixing of Ga–Sb liquid alloys at 1073 K.

| \(x_{\text{Ga}}\) | \(a_{\text{Ga}}\) | \(a_{\text{Sb}}\) | \(-\Delta G/\text{J} \cdot \text{mol}^{-1}\) |
|------------------|----------------|----------------|--------------------------|
| 0.1              | 0.052          | 0.900          | 3480                     |
| 0.2              | 0.108          | 0.794          | 5620                     |
| 0.3              | 0.189          | 0.660          | 7050                     |
| 0.4              | 0.277          | 0.538          | 7900                     |
| 0.5              | 0.378          | 0.417          | 8240                     |
| 0.6              | 0.486          | 0.306          | 8090                     |
| 0.7              | 0.619          | 0.195          | 7370                     |
| 0.8              | 0.764          | 0.103          | 5980                     |
| 0.9              | 0.901          | 0.040          | 3710                     |

cells IV and II especially on the Ga rich side of the alloys, so direct measurements with cell III were performed.

In a similar way to Ga–Te alloys, thermodynamic quantities are calculated and are represented in Table 7.

The activity of Ga is shown in Fig. 3 with the results by other investigators. Our results are in good agreement with the values by Anderson et al.\(^\text{16}\) in the middle concentration range of the alloys, but their values scattered somewhat largely in both high and low concentration ranges of Ga. Although the activity coefficients did not fall adequately on a smooth curve for the composition, the activity coefficients at infinitely dilute solutions at 1073 K were estimated from the values in Table 7 as follows: \(\log \gamma_{\text{Ga}}^\circ\) in Sb = 0.292 and \(\log \gamma_{\text{Sb}}^\circ\) in Ga = -0.514.

In both cases of Ga–Te and Ga–Sb alloys, the temperature ranges investigated are too narrow to derive accurate values of enthalpy and entropy of mixing from the temperature dependence of emfs.

Fig. 3 Activities of Ga in the liquid Ga–Sb alloys.
IV. Conclusion

E. M. F. of the galvanic cells with the solid electrolyte (ZrO$_2$+CaO) was measured to derive the activity of Ga for liquid Ga–Te and Ga–Sb alloys. The following results were obtained:

1. The activities of Ga in liquid Ga–Te alloys at 1123 K showed large negative deviations from Raoult’s law on the Te–rich side, and increased remarkably in the middle concentration range from negative to positive deviations from the ideality.

2. The activities of Ga in liquid Ga–Sb alloys at 1073 K showed moderate negative deviations from the ideality in the whole concentration range.

These data are compared with published data.

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