Thermodynamic Studies of Tl-Bi Liquid Alloys

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The e.m.f. of the cell $\text{Tl(l)}/\text{TlCl}$ in $\text{KCl-LiCl}/\text{Ti-Bi(l)}$ was measured over the temperature range of 370° to 480°C . The activity curve shows a profoundly negative deviation from Raoult's law. The excess thermodynamic functions were calculated from the activity data obtained. Theoretical consideration was given for the excess functions of this system.

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I. Introduction

Previous thermodynamic studies on the Tl-Bi system have been carried out mainly by means of the electromotive force (e.m.f.) method. The e.m.f. of the $\text{Tl}/\text{Tl}^+/\text{Tl-Bi}$ cell was measured by Ölander⁽¹⁾ with solid Tl and Tl-Bi alloys (120 to 165°C , and 245 to 295°C), and that of a similar cell was also measured by Engelhardt and Wagner⁽²⁾ with liquid Tl-Bi against liquid and solid Tl (480°C and 270°C), and by Vierk⁽³⁾ with both electrodes liquid (only at 459°C). Vierk used solid glass as the solvent for the electrolyte, while Engelhardt

and Wagner KCl-MgCl_2 at 480°C and Na^+-K^+ -acetates at 270°C . Acetates were also used by Ölander for this purpose. There are no reliable recorded e.m.f. values of the liquid state for this system, except the limited data of the activities measured by Engelhardt and Wagner and by Vierk. According to Kubaschewski and Catterall's calculation⁽⁴⁾, the agreement of the calculated enthalpy of mixing based upon the above data is unsatisfactory. This may be due to the small number of experimental runs. The purpose of the present study is to measure the e.m.f. as more detailed functions of temperatures and to obtain knowledge of the activities, entropies and enthalpies of this system.

The partial molar free energy of Tl, $\Delta\bar{G}_{\text{Tl}}$, and the activity of Tl, a_{Tl} , at a temperature T are related to the

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e.m.f. as follows:

$$\Delta\bar{G}_{Tl} = -nFE = RT \ln a_{Tl}, \quad (1)$$

where F is the Faraday constant, n , the valence of Tl in the salt, E , the e.m.f., and R , the gas constant. The partial molar entropy of Tl, $\Delta\bar{S}_{Tl}$, is calculated from the temperature coefficient:

$$\Delta\bar{S}_{Tl} = nF \left(\frac{\partial E}{\partial T} \right). \quad (2)$$

And the partial molar enthalpy of Tl, $\Delta\bar{H}_{Tl}$ is obtained by combining equations (1) and (2) namely Eq. (3):

$$\Delta\bar{H}_{Tl} = \Delta\bar{G}_{Tl} + T\Delta\bar{S}_{Tl} = -nF \left\{ E - T \left(\frac{\partial E}{\partial T} \right) \right\} \quad (3)$$

The partial molar quantities of Bi are evaluated by the graphical integration of the Gibbs-Duhem equation.

II. Experimental

The use of the e.m.f. cell method for study of alloy solutions is now a standard procedure. The details of experimental methods are the same as those described elsewhere⁽⁵⁾. Electrode concentration cells of the following type were operated ($n=1$):

Tl (liquid)/TlCl in KCl—LiCl (eutectic composition)/Tl-Bi(liquid).

The cell was assembled, sealed and evacuated to a pressure of 10^{-4} mmHg to degas the metals and electrolytes. The system was held at this pressure for 2 hours, thereafter purified nitrogen gas was introduced. In the present investigation, most measurements were performed over the temperature range of 370 to 480°C. The metals used were all high-purity elements with total impurities less than 0.05 %. Temperature was measured by means of the calibrated alumel-chromel thermocouple, located at the center of the legs. The measured e.m.f. values were reproducible to better than 0.05 mV for periods of 10 to 20 minutes.

III. Results

The results of this experiment are summarized in Table 1, and the corresponding thermodynamic quantities are presented graphically in Figs. 1 to 4. Fig. 1 shows

Table 1 e.m.f. and its temperature coefficient in Tl-Bi liquid solution at 700°K.

x_{Tl}	E (mV)	$(dE/dT) \times 10^6$ (V/deg)	a_{Tl}
0.103	273.0	195.0	0.011
0.189	204.0	140.0	0.021
0.255	191.5	117.0	0.042
0.263	184.0	118.0	0.047
0.403	149.0	73.0	0.085
0.432	118.3	64.0	0.141
0.526	91.3	52.0	0.220
0.645	65.8	40.0	0.336
0.741	41.9	28.0	0.499
0.805	24.8	15.5	0.663

the activities of Tl and Bi at 700°K along with corresponding data from the earlier e.m.f. studies of Engelhardt and Wagner (751°K) and of Vierk (732°K). It will be noted that there is a reasonable agreement between the authors' results and the earlier results, and that the activity curves show profoundly negative

deviations from Raoult's law. Figs. 2 to 4 show the relative partial molar quantities of Tl and Bi, and corresponding integral values at 700°K. The excess entropies indicate slightly negative deviations from

Fig. 1 Activity curves in Tl-Bi solution.

Fig. 2 Free energy of mixing and partial molar quantities at 700°K.

Fig. 3 Entropy of mixing.

those of the ideal solution. The excess heats and excess entropies of the Tl-Bi liquid alloys are tabulated in Table 2.

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IV. Discussion

Kubaschewski and Catterall⁽⁴⁾ tabulated values of entropy and enthalpy of this system by using Engelhardt and Wagner's results⁽²⁾. But the latter measured the

Fig. 4 Enthalpy of mixing.

Table 2 Thermodynamic values of Tl-Bi liquid alloys.

x_{Tl}	ΔS_m	$-S_m^e$	$-H_m^e$ (present)	$-\Delta H_m$ (Wittig & Müller)
0.1	0.59	0.15	354	267
0.2	0.84	0.15	656	494
0.3	1.07	0.13	885	703
0.4	1.22	0.12	1050	888
0.5	1.27	0.11	1136	1026
0.6	1.25	0.09	1146	1083
0.7	1.12	0.08	1068	1025
0.8	0.93	0.06	872	827
0.9	0.59	0.05	555	480

ΔS_m and S_m^e : cal·deg⁻¹·mole⁻¹; $\Delta H_m = H_m^e$: cal·mole⁻¹

e.m.f. at only two temperatures, 270°C and 480°C. Thus the values of the former may be somewhat unreliable in view of the difficulty of interpolating over such a wide range on the basis of the results only at those two temperatures.

Heat contents at various temperatures between 20°C and 500°C were determined by Kubaschewski⁽⁶⁾ for two compositions: $x_{\text{Tl}} = 0.333$ and 0.400. These may be used⁽⁴⁾, together with the heat contents of Tl and Bi⁽⁷⁾ and the enthalpies of mixing of Ölander⁽¹⁾ in the solid state, to calculate the enthalpies of mixing of the corresponding liquid alloys from the liquid metals. Recently Wittig and Müller⁽⁸⁾ have measured the enthalpies of mixing in this system at 350°C by a calorimetric method. These may be compared with the heats obtained from the e.m.f. data. Those values are tabulated in Table 3. In comparison with earlier e.m.f. data, the present e.m.f. results are very near to the heat data. The calorimetric method is more reliable for the

enthalpy of mixing and the calculation for entropy of mixing is made by combining those enthalpies with the energy of mixing obtained by the e.m.f. method.

It is interesting to compare the present result with the theoretical equations for the energies of alloys. The atomic radii of Goldschmidt is 1.71 Å for Tl and 1.82 Å for Bi, but the metallic radii are respectively 1.71 Å

Table 3 Enthalpy of mixing of Tl-Bi liquid alloys (cal·mole⁻¹)

x_{Tl}	0.333	0.375	0.400
by Wagner	-450		-540
by Vierk	-115	-135	-155
by ΔC_P	-690		-925
by the authors	-910	-1000	-1050
by Wittig & Müller			-1090

and 1.70 Å⁽⁹⁾. In the liquid state the cohesion of Bi atoms may be more metallic than in the solid state. Consequently, the spheres of both metals may be regarded as having the same radii in the liquid alloys. Then the size effect may be negligible in the Tl-Bi liquid solution. The most prominent contribution to the excess enthalpy is due to the difference of electronegativities of the two metals (Tl: 1.5, Bi: 1.8) or an electron transfer.

The asymmetric behavior of the excess heats can be explained in terms of the electron transfer theory⁽¹⁰⁾⁽¹¹⁾, if the number of valence electrons is $Z_{\text{Tl}} = 3$ for Tl and $Z_{\text{Bi}} = 5$ for Bi in accordance with the positions in the periodic table. When the size effect can be neglected the electron transfer theory of metallic solution gives

$$\left(\frac{\alpha_{\text{Bi}}}{\alpha_{\text{Tl}}}\right) \cong \left(\frac{Z_{\text{Tl}}}{Z_{\text{Bi}}}\right)^{1/3}$$

Here, α_{Bi} and α_{Tl} are given by

$$\lim_{x_{\text{Tl}} \rightarrow 0} \Delta H_m / x_{\text{Tl}} = \alpha_{\text{Bi}} \quad (\text{in Bi side}),$$

and

$$\lim_{x_{\text{Bi}} \rightarrow 0} \Delta H_m / x_{\text{Bi}} = \alpha_{\text{Tl}} \quad (\text{in Tl side}).$$

The predicted relation then becomes

$$\left(\frac{\alpha_{\text{Bi}}}{\alpha_{\text{Tl}}}\right)_{\text{theor.}} \cong \left(\frac{3}{5}\right)^{1/3} = 0.84.$$

The observed ratio is

$$\left(\frac{\alpha_{\text{Bi}}}{\alpha_{\text{Tl}}}\right)_{\text{obs.}} \cong 0.6.$$

Hence, the form of energetic asymmetry may qualitatively be explained by the electron transfer theory.

Finally, it is interesting to note that the excess entropy has a slightly negative value in the liquid alloys in spite of its positive values in the solid alloys. Probably this may be due to the reason that the covalent bonding of Bi atoms in the solid state disappears in the liquid state.

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