PHYSICAL CHEMISTRY

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Abstract

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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF LIQUID ALLOYS OF INDIUM WITH BISMUTH

The thermodynamic functions of the In–Bi system were studied in the temperature interval 240–300°C by the emf method. The following concentration cell was investigated:
$In_{liq} \mid In^{+}$ (in a melt of $KCl, LiCl, ZnCl_2$) $\mid (N_1In + N_2Bi)_{liq}$. The electrolyte used was a salt mixture containing: KCl 11 wt.%, LiCl 10 wt.% and $ZnCl_2$ 79 wt.%, with a melting point of ~ 220°C.

The electrolyte was prepared as follows. Commercially pure anhydrous $ZnCl_2$ was heated in a furnace until melting. The melt, at red-heat temperature, was blown through with a stream of hydrogen chloride until

Table 1

Values of the activities of indium and bismuth in alloys

	573°K	573°K	553°K	553°K	533°K	533°K	513°K	513°K
N_{In}	a_{In}	a_{Bi}	a_{In}	a_{Bi}	a_{In}	a_{Bi}	a_{In}	a_{Bi}
0,0	0,000	1,000	0,000	1,000	0,000	1,000	0,000	1,000
0,1	0,177	0,987	0,175	0,985	0,172	0,983	0,169	0,980
0,2	0,331	0,956	0,385	0,954	0,318	0,951	0,315	0,948
0,3	0,455	0,850	0,447	0,844	0,439	0,838	0,430	0,833
0,4	0,564	0,753	0,554	0,747	0,548	0,742	0,535	0,738
0,5	0,655	0,636	0,647	0,632	0,636	0,628	0,625	0,624
0,6	0,726	0,508	0,720	0,505	0,715	0,502	0,708	0,498
0,7	0,775	0,369	0,779	0,368	0,783	0,366	0,787	0,366
0,8	0,813	0,225	0,816	0,225	0,819	0,226	0,825	0,226
0,9	0,867	0,102	0,871	0,102	0,875	0,103	0,880	0,103
1,0	1,000	0,000	1,000	0,000	1,000	0,000	1,000	0,000

no vapors were released and a completely transparent liquid was obtained. Anhydrous zinc chloride was used for preparing the electrolyte. For this purpose, thoroughly dried KCl and LiCl were added to the required amount of molten $ZnCl_2$. Hydrogen chloride was passed through the molten salt mixture until the

Fig. 1. Integral heats of mixing in the In–Bi system. a–experimental data; b–data (2); v–data (1)

Figure 1: Fig. 1. Integral heats of mixing in the In–Bi system. a–experimental data; b–data (2); v–data (1)

Fig. 2. Activities of indium in the In–Bi system; designations are the same as in Fig. 1

Figure 2: Fig. 2. Activities of indium in the In–Bi system; designations are the same as in Fig. 1

turbidity disappeared. After this, a certain amount of the ion-forming salt InCl was added to the melt.

For preparing the alloys, indium of 99.999% purity and chemically pure bismuth were used. The emf values of the alloys were measured at temperatures of 240, 260, 280, and 300°. The dependence E—$f(T)$, within the experimental error, may in all cases be regarded as linear. From the obtained emf values, the activity values were calculated according to the formula:

$$\lg a_{\mathrm{In}} = -\frac{zFE}{4{,}576 \cdot T}.$$

The valence of indium was taken to be unity.

The activity of bismuth in the alloy was calculated by graphical integration of the Gibbs–Duhem equation. The smoothed activity values were used for calculating the corresponding partial and

integral thermodynamic quantities. The values of the activities and thermodynamic functions are collected in Tables 1 and 2.

The accuracy of the quantities obtained can be estimated from the error in determining E. An error of $\sim 1.5\%$ in the determination of E leads to errors in the values of a of $\sim 1.5\%$, and in the values of $\Delta\overline{H}$ and $\Delta\overline{S}$, respectively, of $\sim 22\%$ and $\sim 35\%$.

Fig. 1. Integral heats of mixing in the In–Bi system. a–experimental data; b –data (^{2}); v–data (^{1}).

Fig. 2. Activities of indium in the In–Bi system; designations are the same as in Fig. 1.

The thermodynamic functions of liquid alloys of the indium–bismuth system were determined by Terpilovskii (^{1}), who measured the emf of the cell

$$\mathrm{In}_\ell \mid \mathrm{In}^+ \text{ (in molten LiBr, KBr, InBr)} \mid (N_1\mathrm{In} + N_2\mathrm{Bi})_\ell$$

in the range 400–500°C, and also by Wittig and Miller ([2]), who determined the heats of mixing directly in a calorimeter at 350°C. Using the formulas of the theory of regular solutions, the latter two authors calculated, from data on the heats of mixing, the partial heats of mixing for indium and bismuth. In Fig. 1 the values of ΔH obtained by us are compared with the data of the previous authors. The following characteristic circumstance may be noted: the value of the integral heat of mixing decreases rather regularly with decreasing temperature; at 450° it is 597 cal/g-at, at 350° 440 cal/g-at, and at 270° 340 cal/g-at. In addition, according to our data ΔH has both a region of negative values and a region of positive values. A similar transition can be traced quite clearly if one compares the values of $\Delta\overline{H}_{\text{In}}$ obtained for different temperatures.

An interesting feature of the indium–bismuth system is the change in the sign of the deviations from ideality with change in temperature (see Fig. 2). The negative deviations, quite considerable at 450°C, decrease sharply as the temperature is lowered to 100°C, and with a further lowering of the temperature (270°C) become positive. A similar process can be traced for a number of liquid alloys that in the solid state form a series of compounds (K–Hg; Cu–Cd, etc.). The immediate cau-

The reason for this is the change in the value of ΔS^{ex} from relatively small and positive at high temperatures to very considerable and negative at low temperatures.

Table 2

Thermodynamic functions of indium–bismuth alloys at 543°K

N_{In}	$\Delta\bar{H}_{\text{In}}$, cal/g-at	$\Delta\bar{H}_{\text{Bi}}$, cal/g-at	ΔH, cal/g-at	$\Delta\bar{S}_{\text{In}}$, cal/deg·g-at	$\Delta\bar{S}_{\text{Bi}}$, cal/deg·g-at	ΔS, cal/deg·g-at	ΔS^{ex}, cal/deg·g-at
0.0	(−415)	0.00	0.00	(3.95)	0.00	0.00	0.00
0.1	−457	−37	−96	1.40	0.22	0.34	−0.40
0.2	−495	−76	−167	0.62	0.33	0.36	−0.62
0.3	−525	−113	−237	0.25	0.38	0.34	−0.86
0.4	−530	−153	−298	0.10	0.47	0.32	−1.00
0.5	−452	−230	−336	0.22	0.49	0.37	−0.99
0.6	−245	−457	−334	0.62	0.47	0.52	−0.80
0.7	+132	−516	−212	0.72	0.73	0.72	−0.48
0.8	+190	−437	+65	0.68	2.35	0.91	−0.13
0.9	+147	−173	+115	0.27	4.25	0.66	−0.07
1.0	0.00	(+93)	0.00	0.00	(4.45)	0.00	0.00

Note. Values in parentheses were obtained by extrapolation.

Apparently, in the present case the character of the nearest environment changes with changes in concentration and temperature.

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Cited Literature

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2. F. Wittig, E. Miller, *Zs. phys. Chem.*, **21**, 71 (1959).

Note: Figure translations are in progress. See original paper for figures.