Table II. Activity Coefficients, Osmotic Coefficients, and Water Activity for Aqueous NH_4Br Solutions

m_{NH_4Br}	$\gamma_B{}^a$	$\gamma_B{}^b$	$\gamma_B{}^c$	ϕ^d	a_W
0.1	0.771	0.771		0.928	0.997
0.2	0.721	0.721		0.915	0.993
0.3	0.691	0.692		0.908	0.990
0.4	0.670	0.671		0.905	0.987
0.5	0.655	0.655		0.903	0.984
0.6	0.643	0.644		0.903	0.981
0.7	0.633	0.634		0.903	0.977
0.8	0.626	0.627		0.904	0.974
0.9	0.619	0.620		0.905	0.971
1.0	0.614	0.615		0.906	0.968
1.5	0.597	0.597	0.600	0.915	0.952
2.0	0.590	0.590	0.594	0.925	0.936
2.5	0.587	0.587	0.592	0.936	0.919
3.0	0.586	0.586	0.592	0.947	0.903
3.5	0.586	0.588	0.591	0.956	0.887
4.0	0.587	0.589	0.592	0.963	0.870
4.5	0.589	0.588	0.593	0.969	0.855
5.0	0.591		0.595	0.975	0.839
5.5	0.592		0.597	0.980	0.824
6.0	0.594		0.598	0.985	0.808
6.5	0.595		0.598	0.988	0.793
7.0	0.596		0.600	0.991	0.779
7.5	0.596		0.601	0.994	0.765

[a] γ_B evaluated by Method 1, relative to NH_4Cl. Integral taken as 0.0090 m for all concentrations up to 1.5 m. [b] γ_B evaluated by Method 2, relative to KCl. [c] Results of Shul'ts and Simanova (*6*), relative to NaCl. [d] Smooth values from experiment for concentrations greater than 0.3 m. Below this concentration, values are obtained from the plot of $\phi_{NH_4Br} - \phi_{NH_4Cl}$ against m.

was solved graphically. Values of γ_B obtained from the above equation are presented in Table II. In general, they are 0.85% lower than those given by Shul'ts and Simanova (*6*) which is within the uncertainty inherent in integration of an equation of the form of Equation 1. We are unaware that this equation has been widely used, but its applicability to other salt pairs is noteworthy.

The second method consisted of evaluating Equation 2 (*5*)

$$\ln \gamma_B = \ln \gamma_K + \ln R + 2\int_0^{a_K{}^{1/2}} (R - 1)(a_K)^{-1/2} da_K{}^{1/2} \qquad (2)$$

where the subscript K refers to the standard KCl. R is the isopiestic ratio; $m_K = Rm_B$. The evaluation was performed by comparison with data for KCl (*5*) because the lowest concentrations were studied with this standard. These γ_B values thus do not incorporate the average obtained from consideration of both standard salts and do not extend to the highest concentrations reached. Smooth values of $(R - 1)$ were read from a graph, and the integral was evaluated by graphical integration. The results are compared with those of Method 1 and those of Shul'ts and Simanova in Table II. Smoothed values of the osmotic coefficients and the activity of water obtained from $-55.51 \ln a_W = -2\, m\phi$ are included; the latter values are consistent with those tabulated by Kirgintsev and Luk'yanov (*3*). The agreement between activity coefficients computed by the two methods (one or better in the last figure) suggests that most of the difference between our data and those of Shul'ts and Simanova is real and larger than the experimental error estimated at 0.2%.

As for the respective salts of Li, Na, and K, the activity coefficients of NH_4Br are seen to be higher than those of the chloride. Comparison of γ_B with values for tetraalkylammonium bromides (*4*) reveals that below 1.5 m the activity coefficients decrease in the order $NH_4{}^+ > (CH_3)_4N^+ > (C_2H_5)_4N^+ > (C_3H_7)_4N^+ > (C_4H_9)_4N^+$, but above 1.5 m the curves for the latter four salts intersect and show no rational pattern.

ACKNOWLEDGMENT

The authors thank R. A. Robinson for helpful discussion.

LITERATURE CITED

(1) Chen, H., Irish, D. E., *J. Phys. Chem.*, **75,** 2681 (1971).

(2) Guggenheim, E. A., Applications of Statistical Mechanics, pp 167–9, Clarendon Press, Oxford, 1966.

(3) Kirgintsev, A. N., Luk'yanov, A. V., *Russ. J. Phys. Chem.*, **38,** 867 (1964).

(4) Lindenbaum, S., Boyd, G. E., *J. Phys. Chem.*, **68,** 911 (1964).

(5) Robinson, R. A., Stokes, R. H., Electrolyte Solutions, 2nd rev. ed., Butterworths, London, 1968.

(6) Shul'ts, M. M., Simanova, S. A., *Russ. J. Phys. Chem.*, **40,** 247 (1966).

(7) Wishaw, B. F., Stokes, R. H., *Trans. Faraday Soc.*, **49,** 27 (1953).

RECEIVED for review July 26, 1971. Accepted December 13, 1971, Work done while D.E.I. was on sabbatical leave, 1970–71.

Heats of Formation of Solid Indium–Lead Alloys

HONG-IL YOON and RALPH HULTGREN[1]

Department of Materials Science and Engineering and Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, University of California, Berkeley, Calif. 94720

Indium and lead form wide-ranging solid solutions in one another, with a single intermediate phase, β, as shown in Figure 1 (*1*). The crystal structures of all three solid phases are based on the face-centered cubic structure of Pb, but for In the c-axis is elongated about 7.6%, and for β, c is shortened by about 7%, making the two latter phases face-centered tetragonal (*6*).

The thermodynamic properties of the liquid phase are reasonably well established, but solid heats of formation have been determined only by a quantitative differential thermal analysis method (*2*) which does not have high precision. It was therefore decided to measure heats of formation by liquid tin solution calorimetry.

EXPERIMENTAL

The tin, lead, and indium used were all reported to be 99.999% pure. Nine 12-gram samples of indium–lead alloys were

---

[1] To whom correspondence should be addressed.

Heats of formation of solid indium–lead alloys at 315K were determined by liquid tin solution calorimetry. The alloys formed endothermically, except, possibly, the In phase, where $\Delta H \simeq 0$. Partial molar heats of solution of indium and lead in tin were also determined.

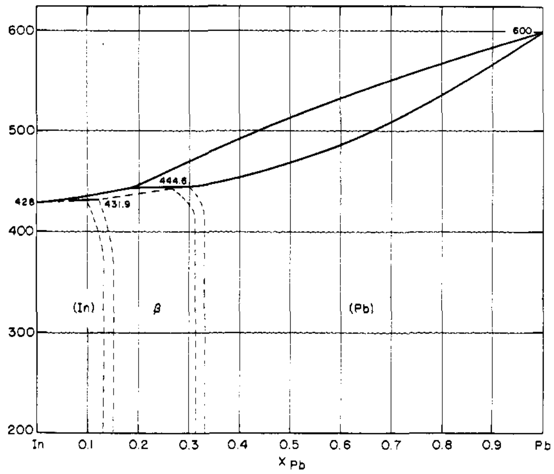

Figure 1. Phase diagram for In–Pb system

Table I. Experimental Values of Heats of Formation at 650K

$$(1 - x)\text{In}_{(s)} + x\text{Pb}_{(s)} = \text{In}_{1-x}\text{Pb}_{x(s)}$$

x_{Pb}	Phase	ΔH, experimental	ΔH, selected[a]
0.10	In	43, −18, −5, −42	−0(±36)
0.20	β	191, 199, 154, 188	190(±12)
0.30	β	279, 257, 270	270(±12)
0.40	Pb	306	300(±12)
0.50	Pb	321, 296, 303	310(±12)
0.60	Pb	275	280(±12)
0.70	Pb	251, 241	250(±12)
0.80	Pb	182, 193	190(±12)
0.90	Pb	63, 41, 107, 91	100(±12)

[a] The selected values were chosen from a plot of ΔH vs. x_{Pb}. The uncertainties are twice the standard deviation from the curve.

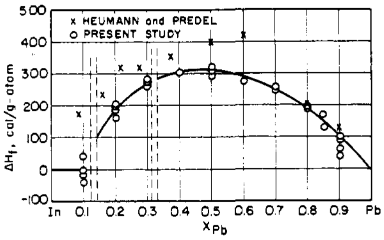

Figure 2. Heats of formation of In–Pb alloys at 315K

prepared. Weighed quantities of metal were mixed and sealed in borosilicate glass tubes containing an atmosphere of helium plus 4% hydrogen. Melting was done approximately 20° higher than the liquidus temperature. After melting, the alloys were shaken vigorously and quenched in ice water. No loss in weight during melting was found. After cold working, the alloys were again sealed in borosilicate glass tubes and homogenized for seven days at 10–15°C below the solidus. Filings were taken from both ends of each ingot, mixed together, and strain-annealed at 100°C for 15 min. X-ray diffraction showed the phases to be homogeneous and to have lattice constants corresponding to their compositions.

The liquid tin solution calorimeter has been described previously (*5*), so a very brief description of the method will suffice. About 500 mg of alloy are dropped into the calorimeter containing about 200 grams of Sn at about 650K. From the measured heat effect is subtracted the heat effects of corresponding amounts of the pure components. The result is the heat of formation of the alloy at the temperature from which it is dropped; in this case 315K.

Three to five runs per day are made in the calorimeter. After four days, the calorimeter is dismantled and a fresh tin bath added. This is allowed to come to a steady state in temperature over the weekend and a second series is begun. Each day one of the samples was pure tin to calibrate the heat capacity of the calorimeter. A small increase of heat capacity as the amount of liquid metal increases proves the calorimeter is functioning properly. Near the beginning of a series, samples of pure Pb and pure In are dropped; also near the end, when the amount of dissolved material is about 1.25 at. %. The heat effects, within experimental error, were independent of concentration.

Subtracting the known heat contents of the pure liquid metals from their heat effects when dissolving in tin, one obtains the partial molar heats of solution at 650K:

$$\Delta \bar{H}_{Pb} = 1402, 1410, 1419, 1420, 1406, 1393, 1436, 1391$$

$$\Delta \bar{H}_{In} = -188, -176, -149, -160, -171, -172, -163, -161$$

From which we obtain:

$$\Delta \bar{H}_{Pb,\ 650K,\ x_{Sn} = 1} = 1410\ (\pm 11)\ \text{cal/g-atom}$$

$$\Delta \bar{H}_{In,\ 650K,\ x_{Sn} = 1} = -168\ (\pm 8)\ \text{cal/g-atom}$$

The uncertainties are twice the standard deviation of the mean. These values compare with 1360 (*3*) and −203 (*4*) cal/g-atom, respectively, found in the literature at nearly the same temperature.

The experimental values of the heats of formation are given in Table I and are plotted in Figure 2, along with the values of Heumann and Predel (*2*) calculated from liquid heats of formation and the heats of fusion of the alloys measured by differential thermal analysis. The agreement is relatively good. The present values are to be preferred, since liquid tin solution calorimetry is known to be a more accurate method.

ACKNOWLEDGMENT

Stanley Ross gave valuable assistance in the measurements.

LITERATURE CITED

(1) Hansen, M., *Constitution of Binary Alloys*, 2nd ed., p 855, McGraw-Hill, New York, N.Y., 1958.
(2) Heumann, T., Predel, B., *Z. Metallk.*, **57**, 50 (1966).
(3) Kleppa, O. J., *J. Phys. Chem.*, **59**, 175 (1955).
(4) Orr, R. L., *Trans. Met. Soc. AIME*, **236**, 1445 (1966).
(5) Orr, R. L., Goldberg, A., Hultgren, R., *Rev. Sci. Inst.*, **28**, 767 (1957).
(6) Pearson, W. B., "A Handbook of Lattice Spacings and Structures of Metals and Alloys," pp. 84, 290, Pergamon Press, London, 1967.

RECEIVED for review July 29, 1971. Accepted December 16, 1971. This work was conducted under the auspices of the U. S. Atomic Energy Commission.