[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

A Thermodynamic Study of the Zinc–Indium System

BY W. J. SVIRBELY AND SIDNEY M. SELIS[1]

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Electromotive force measurements of galvanic cells consisting of liquid zinc and liquid zinc–indium alloy electrodes and solid zinc and liquid zinc–indium alloy electrodes with an intervening salt electrolyte containing zinc ion have been made over the temperature ranges of 700 to 790°K. and 635 to 690°K., respectively. Integral heats of mixing and relative partial molar free energies, heat contents and entropies for liquid alloys and activities of zinc and indium have been calculated at 700°K. The activity values at 650°K. of zinc in liquid alloys referred to pure solid zinc as the standard state were derived from measurements of cells with liquid zinc electrodes. The results are in good agreement with the experimental activities obtained from cells with solid zinc electrodes. Based on the activities in the alloys, the liquidus curve on the zinc side of the eutectic has been determined. The curve is in good agreement with results in the literature. It is shown that the liquid alloys display regular solution behavior at 700°K. over a limited concentration range. Otherwise, marked positive deviations from Raoult's law occur.

Introduction

Many bimetallic systems have been successfully studied by the use of galvanic cells. Examples of the more recent work are the studies of Seltz and his co-workers[2] and those of Kleppa.[3]

Prior to this research, no such measurements as the above had been made with alloys of zinc and indium. However, this bimetallic system has been studied by thermal and metallographic methods of analysis. The results of these studies are shown graphically in Fig. 2. As far as the liquidus curve on the zinc side of the eutectic is concerned, Wilson and Peretti[4] concluded that this portion of the curve is convex upward, while Valentiner[5] and Rhines and Grobe[6] found an inflection. The work of Valentiner is somewhat substantiated by two points determined by Grönefeld.[7]

The purpose of this research was: (1) to obtain thermodynamic data for the zinc–indium system; (2) to redetermine the liquidus curve; (3) to correlate, if possible, the results of the investigation with existing solution theories.[3,8]

Materials. Indium.—Indium (99.97% pure) was a grant from the Anaconda Mining Co., of Great Falls, Montana. Spectrographic analysis showed the presence of very small amounts of tin and copper. We hereby gratefully acknowledge the grant.

Zinc.—Zinc (99.97% pure) was obtained from A. D. MacKay Co., of New York. Spectrographic analysis indicated the presence of a very small amount of copper.

Electrolyte.—The molten electrolyte was a eutectic mixture of potassium and lithium chlorides (m.p. 354°) to which a small amount of zinc chloride had been added. The salts were of reagent grade.

Apparatus.—The cells used in this research were of the H-type described by Seltz.[2a] They were of Pyrex glass with side arms attached to each arm of the cell. Contact with an electrode was made by the tip of a tungsten wire sealed into Pyrex tubing, thus protecting it from the molten electrolyte. Connections to the Type B Rubicon potentiometer were made by copper wires welded to the tungsten wires where they extended from the cell. The cell was placed in a non-inductively wound electric furnace. Power to the furnace was manually controlled with a "Variac." Due to efficient furnace insulation, cell temperatures could be maintained constant within 0.2°. The temperature was measured with a chromel-*p*-alumel thermocouple. The thermocouple was calibrated at the freezing points of *m*-dinitrobenzene and thermometric standard samples of tin, lead, zinc and aluminum.

The Weston standard cell was calibrated against another such cell which had been recently evaluated at the National Bureau of Standards.

Experimental Procedure.—The cells were of two types

Type I Zn(l) |$ZnCl_2$ in KCl–LiCl(l) |Zn–In(l)

Type II Zn(s) |$ZnCl_2$ in KCl–LiCl(l) |Zn–In(l)

In making a run, the following procedure was used: (1) An alloy electrode was first prepared by adding weighed amounts of zinc and indium to a tube inserted in the furnace and containing molten eutectic mixture which had been thoroughly degassed after the addition of a few drops of concd. hydrochloric acid. After melting, the alloy was thoroughly mixed with the aid of a rod. Degassing again was employed at a pressure of 1 to 1.5 mm. At lower pressures, a loss of zinc occurred due to vaporization. The tube was removed from the furnace and evacuation was continued until the tube reached room temperature. The tube was broken and the solid slug of alloy was cleaned with benzene. (2) A slug of pure zinc was prepared in the same fashion. (3) A few drops of concd. hydrochloric acid was added to each leg of the cell and sufficient eutectic mixture was added so that when molten, the electrolyte would fill the cross bar. The cell was introduced into the furnace. After the electrolyte melted, small amounts of zinc chloride were added to each leg of the cell. The electrolyte was degassed and then a slug of alloy of known composition was introduced in one leg and the slug of pure zinc in the other. The leads were then introduced into the molten electrodes and the system was again degassed. The pressure was maintained overnight at 1 to 1.5 mm. with the cell temperature being about 500°. (4) The cell temperature was adjusted to 510–520° and maintained constant. The attainment of equilibrium was quite rapid. Temperature and cell voltages were measured. The temperature was lowered in about ten degree steps and after the attainment of equilibrium, the necessary voltage readings were made at each step. (5) When Type I cell readings were complete, the cell temperature was decreased until it was slightly below the melting point of zinc. On solidification of the zinc, a Type II cell resulted. Equilibrium was reached in two to three hours. Readings were taken following the same procedure as for Type I cells. (6) Analyses of some of the alloy electrode showed, within the analytical error, no change in composition. The analytical procedure, with some modifications, was that developed by Hopkins[9] for zinc–indium alloys.

Experimental Results and Discussion

Data.—The experimental electromotive forces for each alloy composition for both Type I and

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[1] (a) Abstracted from the Ph.D. thesis of Sidney M. Selis. (b) Presented in part at the New York City Meeting of the International Congress of Chemistry, September, 1951.

[2] (a) H. Seltz and H. Strickler, THIS JOURNAL, **58**, 2084 (1936); (b) B. J. DeWitt and H. Seltz, *ibid.*, **61**, 3170 (1939); (c) H. Seltz and F. J. Dunkerley, *ibid.*, **64**, 1392 (1942).

[3] (a) O. J. Kleppa, *ibid.*, **71**, 3275 (1949); (b) **72**, 3346 (1950); (c) **73**, 385 (1951).

[4] C. L. Wilson and E. A. Peretti, *Ind. Eng. Chem.*, **28**, 204 (1936).

[5] S. Valentiner, *F. Metallkunde*, **35**, 250 (1943).

[6] F. N. Rhines and A. H. Grobe, *Am. Inst. Mining Met. Engrs. Inst. Metals Div.*, **156**, Tech. Pub. 1682 (1944).

[7] Grönefeld, Diss., Clausthal, 1942.

[8] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd edition, Reinhold Publishing Corp., New York, N. Y., 1950.

[9] C. W. Hopkins, *Ind. Eng. Chem., Anal. Ed.*, **14**, 638 (1942).

Type II cells were plotted against temperature. Linear plots were obtained in all cases. The plots for each alloy involved nine to eleven experimental readings for a Type I cell and six readings for a Type II cell. The temperature ranges were from about 700 to 790°K. and 635 to 690°K. for Type I and II cells, respectively. The temperature gradient of the electromotive force for each plot was determined. Furthermore, the electromotive forces for the various alloys were determined from these plots at the arbitrarily selected temperatures of 700°K. for Type I cells and 650°K. for Type II cells.[10] These data are given in Table I.

TABLE I

N_{In}	Type I cells E.m.f. at 700°K., mv.	Type I cells $dE/dT \times 10^5$, volts/°K.	Type II cells E.m.f. at 650°K., mv.	Type II cells $dE/dT \times 10^5$, volts/°K.
0.099	2.10	0.293	<0	5.76
.201	3.15[b]	0.930	0.29[b]	6.42
.251	3.80	1.50	0.62	6.66
.301[a]	4.22[b]	2.00	1.10	6.92
.399	5.35	2.56	1.53	8.03
.450[a]	5.87	2.87	1.76	8.35
.500[a]	6.20[b]	3.24	1.95[b]	8.89
.601[a]	8.19	4.78	3.50	10.0
.735[a]	11.85	6.60	6.14	11.39
.812	19.47[b]	8.51	12.95[b]	13.95
.845	23.50	9.36	16.41	14.74
.899	33.37	11.09	25.22	16.80
1.00	100.0	20.7	86.45	27.0

[a] Analyses at the end of the run gave $N_{In} = 0.301, 0.452, 0.499, 0.599, 0.735$ in the order listed above. The values given in the table are weighed-in amounts. [b] Check runs on new alloys indicated a reproducibility of ±0.01 to 0.04 mv.

Measurements were made on two different cells containing pure zinc electrodes. The e.m.f. of these cells showed a maximum value of ± 0.05 mv. at 783 °K. Reproducibility of e.m.f. readings for the alloys was within this range.

Thermodynamic Calculations.—The reaction occurring in a Type I cell is

$$\mathrm{Zn(l)} \longrightarrow \mathrm{Zn\ (in\ Zn\text{–}In\ liquid\ solution)}$$

The partial molar free energy change for this reaction is given by equation 1[11]

$$\bar{F}_1(\mathrm{l}) - F_1^0(\mathrm{l}) = -n\mathfrak{F}E \qquad (1)$$

The activity $a_1(\mathrm{l/l})$ of zinc in the liquid alloy referred to pure liquid zinc as the standard state is given by equation (2)

$$\ln a_1 = (\bar{F}_1 - F_1^0)/RT \qquad (2)$$

The relative partial molar heat content of zinc in a liquid alloy referred to pure liquid zinc is given by equation (3).

$$\bar{L}_1 = n\mathfrak{F}[T(\mathrm{d}E/\mathrm{d}T) - E] \qquad (3)$$

The various thermodynamic quantities were determined at 700°K. for zinc in the liquid alloys by use of equations 1, 2 and 3 and the experimental data listed in columns 2 and 3 of Table I. In these calculations $n = 2$, $\mathfrak{F} = 23068$ cal./°K./volt and $R = 1.986$ cal./°K./mole. The results are given in Table II along with the values of the activity coefficients $\alpha_1(\mathrm{l/l})$ for zinc which are defined by equation (4)

$$\alpha_1 = a_1/N_1 \qquad (4)$$

The corresponding quantities for the second component, indium, were obtained by graphical integration of the Gibbs–Duhem equation

$$\log \alpha_2 = -\int_0^{N_1/N_2} (N_1/N_2)\ \mathrm{d}\log \alpha_1 \qquad (5)$$

$$\bar{L}_2 = -\int_0^{N_1/N_2} (N_1/N_2)\mathrm{d}\bar{L}_1 \qquad (6)$$

The results of the above calculations for indium referred to pure liquid indium are also listed in Table II. The use of equation 4 as applied to the second component led in turn to the activities $a_2(\mathrm{l/l})$ of indium in the alloys referred to liquid indium as the standard state. These activity values are also listed in Table II. The use of equation 2 as applied to the second component led next to the $\bar{F}_2 - F_2^0$ values for the indium component.

The partial molar entropies for both components were calculated by equation 7

$$\Delta\bar{F} = \bar{L} - T\Delta\bar{S} \qquad (7)$$

using the data already accumulated for each component. The results are given in the ninth and tenth columns of Table II.

The "entropy fraction" X' is defined[3] by equation (8)

$$\Delta\bar{S} = -R \ln X' \qquad (8)$$

The "entropy fractions" are given in the eleventh and twelfth columns of Table II.

The integral heat of mixing per mole of solution is defined by equation (9), namely

$$\Delta H = N_1\bar{L}_1 + N_2\bar{L}_2 \qquad (9)$$

The results are given in the last column of Table II.

Plots of activities and "entropy fractions" at 700°K. are given in Fig. 1.

The reaction occurring in Type II cells is

$$\mathrm{Zn(s)} \longrightarrow \mathrm{Zn(in\ Zn\text{–}In\ liquid\ solution)}$$

Applying equations 1, 2 and 4 and the experimental data listed in the fourth and fifth columns of Table I, one obtains the thermodynamic quantities at the arbitrarily chosen temperature of 650°K. listed in the second and third columns of Table III referred to pure solid zinc as the standard state.

Comparison of Data from Type I and Type II Cells.—If the activity of zinc in a liquid alloy relative to liquid zinc as the standard state, *i.e.*, $a_1(\mathrm{l/l})$, is known at a certain temperature, its activity at the same temperature relative to solid zinc as the standard state, *i.e.*, $a_1(\mathrm{l/s})$, can be calculated by means of equation (10).

$$a_1(\mathrm{l/s}) = a_1(\mathrm{l/l}) \times a_1^\circ(\mathrm{l/s}) \qquad (10)$$

where $a_1^\circ(\mathrm{l/s})$ is the activity of pure liquid zinc based on pure solid zinc. It is thus possible to

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[10] The alloy $N_{In} = 0.099$ in a Type II cell was measured over a temperature range of 665 to 690°K. Extrapolation to 650°K. gave a negative e.m.f. value. It will be seen later from the phase diagram that the liquidus temperature for the alloy is above 650°K.

[11] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923. See this reference for notations and definitions used in this paper.

TABLE II

SUMMARY OF THERMODYNAMIC DATA CALCULATED AT 700°K. FOR TYPE I CELLS

N_1	N_2	$a_1(1/1)$	$\alpha_1(1/1)$	$a_2(1/1)$	$\alpha_2(1/1)$	$\bar{L}_1$, cal./mole	$\bar{L}_2$, cal./mole	$\Delta\bar{S}_1$, cal./°K./mole	$\Delta\bar{S}_2$, cal./°K./mole	X_1'	X_2'	ΔH, cal./mole
1.000	0.000	1.000	1.000	0.000	...	....	....	..	..	1.00	0	0
0.901	.099	0.933	1.036	.468	4.729	−2.3	2926	0.14	5.6	0.931	.057	290
.799	.201	.901	1.128	.559	2.783	155	2014	.43	4.03	.806	.131	529
.749	.251	.882	1.177	.601	2.395	309	1491	.69	3.14	.706	.206	606
.699	.301	.869	1.243	.626	2.081	451	1120	.92	2.53	.630	.280	653
.601	.399	.837	1.393	.673	1.686	580	869	1.18	2.03	.552	.359	695
.550	.450	.823	1.502	.689	1.524	656	768	1.32	1.84	.514	.396	707
.500	.500	.814	1.628	.698	1.395	761	652	1.50	1.65	.469	.436	706
.399	.601	.762	1.910	.736	1.225	1166	325	2.21	1.07	.320	.584	661
.265	.735	.675	2.547	.797	1.085	1585	112	3.04	0.61	.216	.736	503
.188	.812	.524	2.787	.846	1.042	1851	35.5	3.93	.38	.138	.826	377
.155	.845	.459	2.961	.868	1.027	1939	17.6	4.32	.31	.114	.855	316
.101	.899	.331	3.277	.907	1.009	2043	2.2	5.11	.20	.076	.903	208
.000	1.000	.000	...	1.000	1.000	2072	0	..	0	0	1.00	0

compare the experimental values of $a_1(1/s)$ at 650° K. obtained from Type II cells with calculated values of $a_1(1/s)$ derived from data obtained from Type I cells.

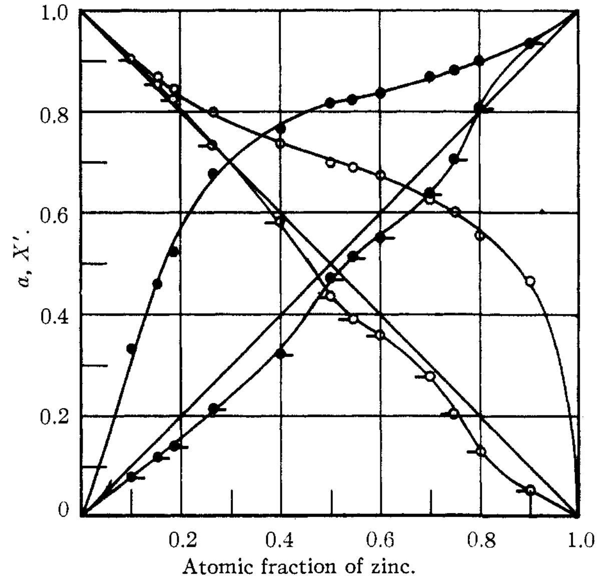

Fig. 1.—Activities and "entropy fractions" in the system Zn(l)–In(l) at 700°K.: ●, a_{Zn} (700°K., exp.); ●- X'_{Zn} (700°K., exp.); ○, a_{In} (700°K., calcd.) ; -○, X'_{In} (700°K., calcd.).

The procedure is as follows: By means of equation (11) and the $a_1(1/1)$ and $\bar{L}_1$ data in Table II

$$R \ln a_1 = (\bar{L}_1/T) + C \qquad (11)$$

one evaluates a constant C for each alloy. Assuming constancy of $\bar{L}_1$ and C for each alloy over the temperature range from 700 to 650°K., a reapplication of equation (11) with T = 650°K., will give the value of $a_1(1/1)$ for each alloy at 650°K. referred to the supercooled liquid zinc; at the melting point of pure zinc, the activity is unity for both liquid and solid zinc, hence equation (11) becomes equation (12)

$$0 = \frac{\Delta H_1}{T_m} + C_1 \qquad (12)$$

TABLE III

ACTIVITIES AT 650°K. FOR TYPE II CELLS

N_1	a_1 (1/s), exp.	α_1 (1/s) exp.	a_1 (1/s) calcd.
0.799	0.990	1.237	0.994
.749	.978	1.305	.980
.699	.961	1.375	.974
.601	.947	1.575	.944
.550	.939	1.712	.933
.500	.933	1.866	.928
.399	.882	2.217	.883
.265	.803	3.03	.806
.188	.630	3.335	.634
.155	.556	3.587	.559
.101	.406	4.02	.406

Using the value of 1860 cal. for the fusion heat[12] and 419.95° for the melting point[13] of zinc, the constant C_1 was evaluated. Assuming constancy for C_1 and for the heat of fusion from the m.p. to 650°K., a reapplication of equation (11) with T equal to 650°K. yielded a value of 1.095 for $a_1°(1/s)$; one can now apply equation (10) and calculate $a_1(1/s)$ for each alloy at 650°K. The final results are given in the last column of Table III.

The deviation between the experimental and calculated values of $a_1(1/s)$ is ±0.6% or less in all cases except at the value of N_1 = 0.699, in which case it is 1.3%. The agreement between the two sets of results is quite satisfactory and can be considered as a measure of the reliability of the experimental data.

The Liquidus Curve.—According to Rhines and Grobe,[6] the maximum solid solubility of indium in zinc is 0.2% or a N_{Zn} value of 0.999. It is thus possible to check the liquidus curve on the zinc side of the eutectic since the solid phase there is practically pure zinc. The method[2a] of calculation was as follows: (1) The activities of zinc in the liquid alloys referred to pure liquid zinc, *i.e.*, $a_1(1/1)$ values, were determined for different temperatures in the range 460–680°K. by the procedure already described. (2) Activities of pure liquid zinc relative to pure solid zinc, *i.e.*, $a_1°(1/s)$ values, were derived at the same temperatures by the

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[12] A. Olander, *Z. physik. Chem.*, **A164**, 428 (1933).

[13] H. M. Cyr, *Trans. Am. Electrochem. Soc.*, **52**, 349 (1927).

method already described. The reciprocals of these values yielded $a_1°(s/l)$ figures, *i.e.*, activities of pure solid zinc referred to pure liquid zinc. (3) The $a_1°(s/l)$ data were plotted against temperature; for each temperature $a_1(l/l)$ values were plotted against the corresponding N_1 values. Then, for a given temperature, that value of N_1 was determined for which the corresponding $a_1(l/l)$ value was equal to the $a_1°(s/l)$ value.

The results of the calculations are listed in Table IV and are plotted in Fig. 2 in comparison with the results of other workers. The liquidus curve obtained in this research is in good agreement with the results of Valentiner[5] over most of the concentration range.

Discussion.—Reference to Fig. 1 shows that large positive deviations from Raoult's law exist for both components over most of the concentration range. The "entropy fraction" curve for indium shows within experimental error an ideal entropy of mixing ("regular solutions") over the concentration range of 0.65 N_{In} to 1.00 N_{In} and positive entropy deviations over the remainder of the range when compared with the ideal solution. The "entropy fraction" curve for zinc shows positive entropy deviations from $N_{Zn} = 0$ to $N_{Zn} = 0.8$ and negative entropy deviations over the rest of the concentration range. The system shows a positive heat of mixing, *i.e.*, heat absorption, over the whole concentration range with the maximum in the curve at a N_{Zn} value of 0.53, *i.e.*, the maximum is displaced toward the side of the smaller atom. This last observation is in agreement with the conclusions of Kleppa.[3c]

Referring again to the "entropy fraction" curve for indium where regular solution behavior with a positive deviation of Raoult's law was exhibited, theory shows[14] that the solutions formed in that concentration range have a positive heat of mixing. This is in accord with our results. Referring next to the "entropy fraction" curve for zinc in the region where negative entropy deviations occurred, one may argue[3c] that the tendency toward positive deviations from Raoult's law as indicated by the positive heat of mixing in that concentration range was enhanced by the negative entropy deviation giving the system a marked positive deviation from ideality on the zinc rich side of the system compared to the situation which exists on the indium rich side. We do not believe that arguments similar to the above can safely be presented for the remainder of the concentration range for the system.

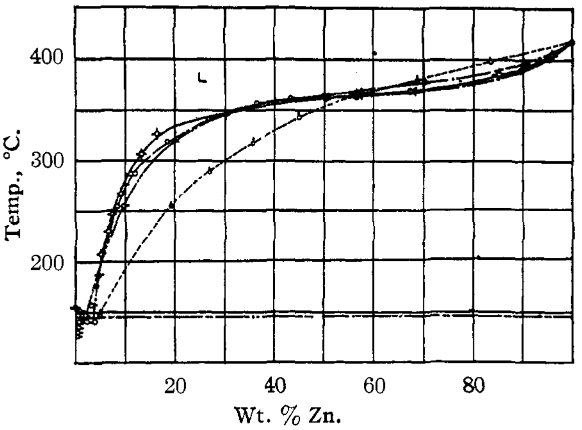

Fig. 2.—Zinc–indium phase diagram: O-, Rhines and Grobe; O, Valentiner; O:, Gronefeld; Ȯ, Wilson and Peretti; -ϕ-, this study.

TABLE IV

LIQUIDUS TEMPERATURES FOR ZINC–INDIUM ALLOYS

t, °C.	N_{Zn}	Wt. % Zn
186.8	0.085	5.02
206.8	.092	5.46
226.8	.111	6.64
246.8	.127	7.65
266.8	.152	9.26
286.8	.183	11.31
306.8	.208	13.01
326.8	.256	16.39
346.8	.431	30.14
366.8	.694–0.704	56.37–57.54
386.8	.909	85.04
406.8	.975	95.69

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[14] Reference 8, page 47.