

solution as the electrolyte gave cells that were rather variable and lower than 0.1128 v. Saturated cadmium iodide gave cells that started very high and decreased continuously. The bad effect of cadmium iodide is undoubtedly on the silver iodide electrode.

In connection with a study of the thermodynamics of zinc iodide in aqueous solution by means of zinc-silver iodide cells,^{2b} some cells with mercurous iodide electrodes were made from which the electromotive force of the silver-mercurous iodide cell could be calculated. The calculated values are given in Table I. The results are in

TABLE I
CALCULATED ELECTROMOTIVE FORCE OF THE CELL
Ag/AgI, ZnI₂(m)/ZnI₂(m), Hg₂I₂/Hg

ZnI ₂ , m	E ₁₅	E ₂₀	E ₂₅	E ₃₀	E ₃₅
0.01075	0.1076	0.1091	0.1106	0.1122	0.1139
.01474	.1081	.1096	.1112	.1127	.1144
.01801	.1086	.1102	.1117	.1134	.1150
.033731125	.1141	...
.06068	.1117	.1132	.1147	.1163	.1179

approximate agreement with those described above. They show that the electromotive force depends on the electrolyte concentration, which is in agreement with the theory proposed above for the variability of the mercurous iodide electrode. Table I and also some measurements of the previously described cells show that the temperature coefficient is about 0.00030 v. per degree; 0.1127 v. at 30° corresponds to 0.1112 v. at 25°.

Bates and Vosburgh⁴ found for the normal potential of the mercurous iodide electrode the value 0.0405 v. at 25°. They used rather thin layers of mercurous iodide and a molality of potassium iodide of about 0.01 and their value can be combined with 0.1112 v. to give the approximate value 0.1517 v. at 25° for the normal potential of the silver iodide electrode. Owen^{2a} found 0.1522 v. and Cann and Taylor⁶ found 0.1510 v. In view of the uncertainty of the value 0.1517 v., it cannot be considered to be in serious disagreement with either of these. Some recent measurements by Gould and Vosburgh of the silver iodide electrode against a hydrogen electrode are in as good agreement with 0.1517 v. as could be expected.

Summary

The cell Ag/AgI, I⁻/I⁻, Hg₂I₂/Hg was found to be not as reproducible or constant as experience with the two electrode systems in other cells would lead one to expect, but the most probable value based on a large number of cells leads to an approximate value for the silver iodide electrode.

The trouble with the silver-mercurous iodide cell may be summarized by saying that while each of the electrode systems is highly reproducible under favorable conditions, no single electrolyte was found that did not affect one or the other of the electrodes unfavorably.

(6) Cann and Taylor, *THIS JOURNAL*, **59**, 1484 (1937).

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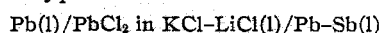
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

A Thermodynamic Study of the Lead-Antimony System

BY HARRY SELTZ AND BERNARD J. DEWITT

In the hope that the accumulation of data on the thermodynamic properties of binary liquid metal solutions may lead eventually to a better understanding of the nature of such systems, investigations along these lines are being continued in this Laboratory. In this paper the results of a study of the lead-antimony system are described. The electromotive force values of cells of the type



were measured, using the purified metals and technique described in previous publications.^{1,2}

(1) Strickler and Seltz, *THIS JOURNAL*, **58**, 2084 (1936).

(2) Seltz and DeWitt, *ibid.*, **60**, 1305 (1938).

In this work it was found possible to extend the e. m. f. readings in rather thick-walled Pyrex H-cells under vacuum up to 630° without collapse of the cells. This permitted measurements to a mole fraction of lead of 0.1 and eliminated any difficulty in the extrapolation of the activity and partial molal relative heat content curves.

Experimental Data

In Table I, the experimental results are tabulated, along with the calculated activities and relative heat contents for lead at the various mole fractions. (The subscript 1 will be used to designate values for the lead component.) At the

highest mole fraction of antimony the readings, due to separation of the solid phase, could be made over a range of only 30°; but, as in previous measurements with fused salt electrolytes, this permitted a sufficiently accurate determination of the slope of the curve to evaluate \bar{L}_1 within ± 15 cal.

TABLE I

Average number of readings per run, 20; maximum deviations, ± 0.04 mv.

N_1	E. m. f. at 748.1°K., mv.	a_1 at 748.1°K.	$dE/dT \times 10^3$, volts/°C.	\bar{L}_1	Temp. range of meas., °C.
0.1095	79.56	0.0621	9.70	-321	600-630
.1992	58.48	.1629	7.11	-243	560-610
.3057	40.68	.2657	5.54	2	550-605
.4012	32.25	.3676	4.34	10	480-520
.4997	24.52	.4673	3.44	56	420-470
.6145	16.82	.5934	2.34	34	390-490
.7024	11.94	.6904	1.725	46	385-475
.7926	7.67	.7882	1.122	34	390-490
.8710	4.63	.8662	0.689	27	370-460

In Table II the activities and relative heat contents for both components are tabulated at round number mole fractions; the values for antimony were determined by the usual graphical methods. In the last column, the integral heat of formation, ΔH , of one mole of solution from the liquid metals is given. The activity curves at 748.1°K. are shown in Fig. 1 and the \bar{L}_1 , \bar{L}_2 and ΔH curves in Fig. 2.

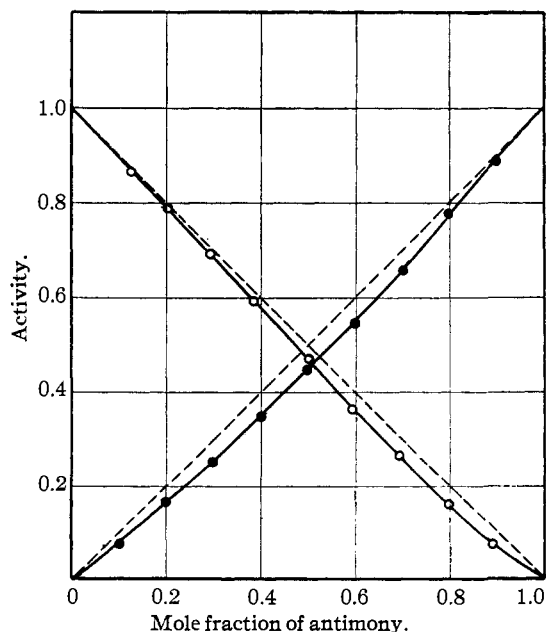


Fig. 1.—Activity curves for Pb and Sb: ○, experimental; ●, calculated.

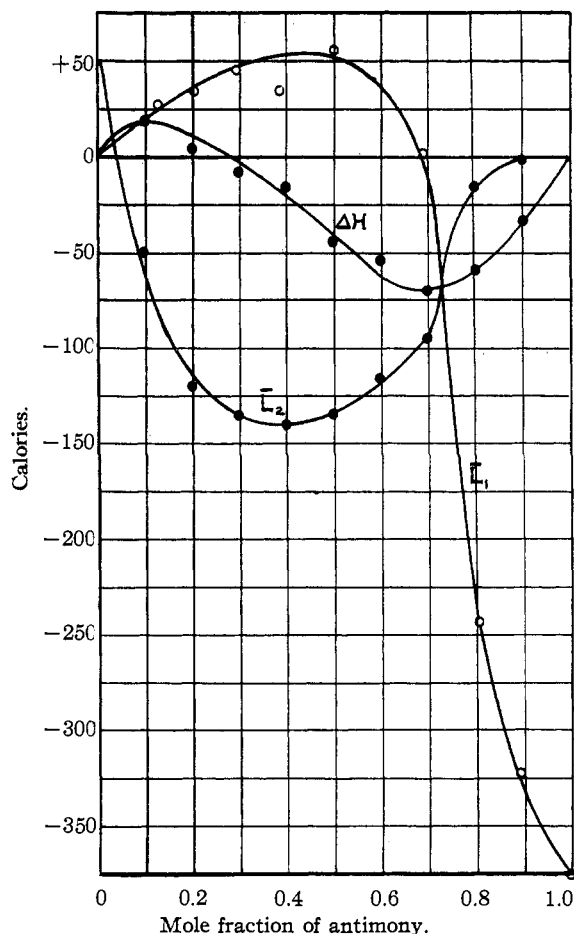


Fig. 2.—Relative heat contents and heats of formation of solutions; ○, experimental; ●, calculated.

TABLE II

N_1	at 748.1°K.				\bar{L}_1	\bar{L}_2	ΔH
	a_1	a_1/N_1	a_2	a_2/N_2			
0.0	0.000	0.748	1.000	1.000	-380	0	0
.1	.078	.780	0.894	0.993	-330	0	-33
.2	.162	.810	.777	.971	-235	-15	-59
.3	.259	.863	.660	.943	-10	-95	-70
.4	.362	.905	.549	.915	+35	-115	-55
.5	.470	.940	.450	.900	+45	-135	-45
.6	.576	.960	.348	.870	+50	-140	-16
.7	.686	.980	.251	.847	+45	-135	-9
.8	.790	.988	.162	.810	+35	-125	+4
.9	.892	.991	.078	.780	+25	-50	+18
1.0	1.000	1.000	.000	.750	0	+50	0

Discussion of Results

The forms of the activity and \bar{L} curves for this system are surprising when compared with those of the previously studied lead-bismuth solutions. Here, the negative deviations of the activities are comparatively slight, with the extrapolated Henry's law value for the activity coefficient, a_1/N_1 , reaching a value of only 0.740, while for

the lead-bismuth system this value is 0.480. Furthermore, the lead-bismuth solution followed "regular" solution behavior closely, with a "b" value of -1200 . A plot of $\log a_1/N_1$ vs. N_2^2 for this system, Fig. 3, indicates clearly the deviations from such behavior, and this is demonstrated further by the forms of the \bar{L} and ΔH curves, which are not compatible with the regular solution concepts. In fact, it would seem that two

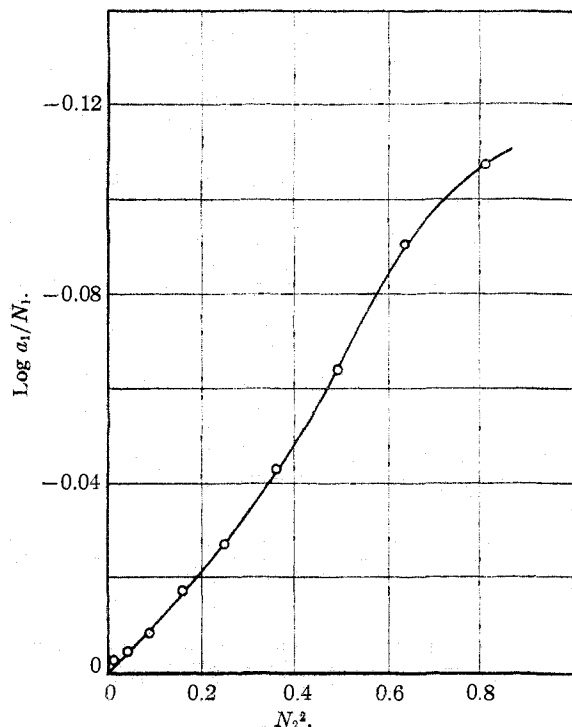


Fig. 3.—Deviations from "regular" behavior.

opposing factors contribute to the deviations from Raoult's law, one tending to produce positive and the other negative deviations. This is not apparent in the activity curves which show negative deviations over the entire range at this temperature. However, with positive values of \bar{L}_1 at higher mole fractions, the activity coefficients would tend to become greater than one at lower temperatures. At lower concentrations of lead, on the other hand, the negative \bar{L}_1 values would decrease the activity coefficients to yet smaller values. For the cadmium-antimony system,² in which intermetallic compounds separate in the solid state, these opposing influences are more pronounced; the activity curve for cadmium shows both positive and negative deviations at 753.1°K . Similar results, not yet published, have been obtained for the zinc-antimony system.

Calculation of Solid-Liquid Equilibria

Solid-liquid equilibria in the lead-antimony system have been studied by several investigators and the data have been reviewed critically by Hansen.³ It has been established that the system shows a simple eutectic with α - and β -solid solutions of antimony in lead and lead in antimony respectively as the solid phases. The eutectic temperatures and compositions reported range between 245 – 252° and 12.1 – 13% antimony. From the activity data for the two components in the liquid state, it should be possible to calculate these conditions more accurately and also to establish the solid solubility limits of the α - and β -phases at the eutectic. For these calculations the free energies of fusion of the two components are needed, and the heats of fusion and the heat capacity data recommended by Kelley⁴ lead to the equations:

$$\text{Sb(s)} = \text{Sb(l)}; \Delta F^\circ = 4015 - 1.64T \ln T + 0.89 \times 10^{-3}T^2 + 5.914 T \quad (1)$$

$$\text{Pb(s)} = \text{Pb(l)}; \Delta F^\circ = 969 - 1.03 T \ln T + 1.01 \times 10^{-3}T^2 + 4.371 T \quad (2)$$

Hansen³ has accepted 247° for the eutectic temperature and 13% antimony, corresponding to a mole fraction $N_2 = 0.2027$, for the composition of the eutectic liquid. From the experimental activity and \bar{L} values, we calculate at this temperature and composition $a_2 = 0.1556$. From equation (1) the activity of pure solid antimony, $a_2(\text{s})$, relative to pure liquid as the standard state, is calculated to be 0.1451 . At this temperature, it is obvious that a liquid containing 13% antimony cannot exist in equilibrium with even pure solid antimony. Taking the lower limit of the reported values of 12.1% ($N_2 = 0.1898$), we calculate $a_2 = 0.1457$, which likewise is greater than $a_2(\text{s})$ at this temperature. Since the β -solid solution has been shown to contain at least 4% of lead, it would seem that 247° is too low for the eutectic temperature. To confirm this conclusion, cooling curves were taken on 12 and 13% melts using the calibrated chromel-alumel couples employed in the e. m. f. studies. In both runs, complete solidification took place when the temperature reached 250° . At this temperature $a_2(\text{s})$ is calculated to be 0.1487 and a_2 for a 13% solution is 0.1557 , which indicates that even at this temperature the eutectic must be richer in

(3) M. Hansen, "Der Aufbau der Zweistofflegierungen," Verlag von Julius Springer, Berlin, Germany, 1936, p. 984.

(4) K. K. Kelley, Bureau of Mines Bulletin 383 (1935) and 393 (1936).

lead for equilibrium. Taking the lower limit of 12.1%, we calculate that $a_2 = 0.1458$, which is now less than the value $a_2(s) = 0.1487$. Assuming Raoult's law to be obeyed in the dilute β -solid solutions, as has been shown to be true for lead-bismuth solid solutions,¹ we calculate for the solid solubility of lead in antimony at the eutectic temperature, $N_\beta = 0.1458/0.1487 = 0.973$, which corresponds to a solubility of 4.51% of lead. In a similar manner, the composition of the α -solid solution at the eutectic can be determined. The activity of solid lead, relative to liquid, from equation (2) is 0.8694, and a_1 for the 12.1% solution is 0.8132, which gives for the solid solubility

$N_\alpha = 0.936$, corresponding to a solubility of 3.86% of antimony.

Summary

1. The activities and relative heat contents of lead and antimony in their liquid alloys have been determined.

2. The eutectic temperature for the system has been shown to be 250° and the eutectic composition 12.1% antimony. The eutectic solids have been calculated to have the compositions 3.86% antimony for the α -phase and 4.51% lead for the β -phase.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Proof of the Steric Nature of the Ortho Effect in the Hydrogen Exchange Reactions of Aromatic Tertiary Amines

BY WELDON G. BROWN, ALEX H. WIDIGER AND NICHOLAS J. LETANG

It has been postulated previously¹ that the acid catalyzed hydrogen exchange reactions of dimethylaniline and its derivatives take place through a direct addition of deuterons at the ortho or para positions, giving rise to tautomeric forms of the amine salt with a quinoid type of structure. In view of the requirement in classical structural theory that the dialkylamino group should be coplanar with the quinonoid ring in these forms, it was possible to interpret the inhibiting effect of an ortho nitro group, which had been observed in a study of the exchange reactions of the nitrodimeylanilines in deuterioalcohol, as a steric effect having to do with the obstruction offered by the nitro group to the attainment of a coplanar configuration. Several further examples of inhibition of the hydrogen exchange reaction by ortho substituents have since been discovered and it is now obvious that the ortho effect is as characteristic for this reaction as it is for numerous other reactions of aromatic tertiary amines.²

In an effort to test experimentally the validity of this theory of the ortho effect in hydrogen ex-

change reactions, two independent lines of approach were explored. One obvious method of attack was to vary the size of the ortho substituent in the expectation that as the size of the group becomes small the inhibiting effect should diminish or eventually vanish. The series selected for this purpose was that of the bromo, chloro and fluoro derivatives of dimethylaniline (cf. Fig. 1). The second line of attack was based

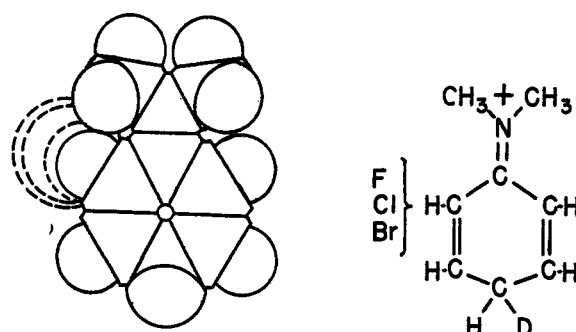


Fig. 1.—On the left, representation based on scale atomic models of the structures indicated on the right. The dotted lines show approximately the relative dimensions of F, Cl and Br.

on the argument that if the amino nitrogen were to be linked to the ortho carbon atom in such a way as to form a five-membered ring, as in N-methylindoline (I), which would necessarily be coplanar with the benzene ring, there should be no ortho effect. A similar result was predicted for

(1) Brown, Kharasch and Sprowls, *J. Org. Chem.*, in press.

(2) The literature on the subject of ortho effects in the reactions of aromatic tertiary amines, particularly with regard to the reactions with methyl iodide, nitrous acid, diazo compounds, and formaldehyde, is too extensive to be cited here in detail, but the very extensive work of the late Julius von Braun in this field deserves special mention. For a review on the subject of ortho effects in general, see Ludwig Anschütz, *Z. angew. Chem.*, **41**, 691 (1928).