the estimated experimental errors. The most dilute solution used in the e. m. f. measurements was 0.0005 *m*, while our measurements extend to about 0.0001 *m*; La Mer and Parks extrapolated to infinite dilution with the aid of the extended Debye–Hückel theory, while our somewhat shorter, semi-empirical extrapolation has been described above. Since the agreement is excellent at the lowest concentrations it is evident that the discrepancies at higher concentrations are not due to the different methods of extrapolation. Since La Mer and Parks have indicated the existence of certain experimental difficulties with their cells and since activity coefficients calculated from their data do not agree well with those found by Robinson and Jones[9] it seems likely that some part of the discrepancy is due to unreliability of the e. m. f. measurements. Moreover, Harned,[27] by recalculating similar data obtained by La Mer and Cowperthwaite[28] with zinc sulfate cells, has found that the method of calculation used by La Mer and Cowperthwaite introduces uncertainties aside from those inherent in the experimental work.

TABLE VI

	$\overline{L}_2$, cal./mole $CdSO_4$					
	10°C.		15°C.		20°C.	
m	Cal.	E. m. f.	Cal.	E. m. f.	Cal.	E. m. f.
0.0001	67	—	92	—	101	—
.0005	168	147	225	182	239	239
.001	254	234	316	276	337	327
.005	486	475	639	522	765	581
.01	588	568	786	650	890	740
.02	730	849	943	981	1037	1148

We have not recalculated activity coefficients for cadmium sulfate solutions at 25° by correcting freezing point data with the $\overline{L}_2$ and $\overline{C}_{p_2} - \overline{C}^{\circ}_{p_2}$ values reported here. Our measurements may be combined with the earlier, and probably less reliable, heats of solution measurements of Holsboer,[22] which extended from about 0.2 *m* to saturation at several temperatures, to compute relative heat contents and heat capacities for the entire concentration range from infinite dilution to saturation. Values for $\overline{C}^{\circ}_{p_2}$ also could be obtained by utilizing Holsboer's data. It is hoped to carry out these calculations in the near future.

We are grateful to the National Research Council for two grants in aid which made possible the construction of the apparatus used in this investigation.

Summary

Intermediate heats of dilution of aqueous cadmium sulfate solutions have been measured over the concentration range from 0.8 to 0.0001 *m* at 10, 15, and 20° and have been extrapolated to infinite dilution to obtain integral heats of dilution. No definite approach to the limiting law of Debye and Hückel is indicated at the lowest concentrations measured.

Relative partial molal heat contents and heat capacities have been calculated for the temperature and concentration ranges of the measurements and have been compared with values obtained from e. m. f. measurements by La Mer and Parks.

PITTSBURGH, PENNA. RECEIVED MARCH 2, 1938

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[27] H. S. Harned, THIS JOURNAL, **59**, 360 (1937).

[28] V. K. La Mer and I. A. Cowperthwaite, *ibid.*, **53**, 2040 (1931).

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

A Thermodynamic Study of the Cadium–Antimony System

BY HARRY SELTZ AND B. J. DEWITT

The phase equilibrium relations in the cadmium–antimony system have been studied by several investigators.[1] Thermal, microscopic, X-ray and conductivity methods have been employed. Hansen,[2] from a critical review of these data, accepts the diagram of Murakami and Shinagawa which will be used in several calculations in this paper. Two intermetallic compounds are formed, CdSb and Cd_3Sb_2. The former is stable to its melting point, 455°, while the latter is metastable at all temperatures and melts at 420°.

In pursuance of a program of investigation of the thermodynamics of metal systems, this paper describes the results of an electromotive force study of liquid cadmium–antimony solutions.

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[1] Kurnakov and Konstantinov, *Z. anorg. Chem.*, **58**, 1 (1908); Treitschke, *Z. anorg. allgem. Chem.*, **50**, 217 (1906); Murakami and Shinagawa, *Kinzoku no Kenkyu*, **5**, 283 (1928).

[2] M. Hansen, "Der Aufbau der Zweistofflegierungen," Verlag von Julius Springer, Berlin, Germany, 1936.

Experimental

The cells used in this investigation were of the type

Cd(l)/$CdCl_2$ in LiCl + KCl(l)/Cd(in Cd–Sb liquid solutions)

The technique of the measurements was similar to that described in previous publications.[3] C. P. cadmium, containing less than 0.005% impurities, and purified antimony were used for the electrodes. The antimony was purified by the method of Groschiff.[4] Redistilled antimony pentachloride was treated with concentrated hydrochloric acid and the precipitated chloroantimonic acid was converted to antimonic acid by ammonium hydroxide. This was dried and reduced to metal by fusion with potassium cyanide. The cadmium was melted under a fused eutectic mixture of potassium and lithium chlorides and cast in the form of thin rods to facilitate introduction into the H-cells. The e. m. f. readings for the different Cd–Sb melts were made over temperature ranges varying from 80° at the high cadmium concentrations to 20° at the high antimony concentrations where the lowest temperature was limited by the appearance of the solid phase. However, even with a 20° range the slopes of the e. m. f. curves could be determined accurately since the readings were extraordinarily steady and readily reproducible to within ±0.02 mv. The results of the measurements are summarized in Table I, along with the activities, a_1, and partial molal relative heat contents, $\bar{L}_1$, of cadmium, calculated by the usual methods using liquid cadmium as the standard state. (Throughout this paper the subscript 1 will be used to designate cadmium and subscript 2, antimony.)

TABLE I

N_1	E. m. f. at 753.1°K. mv.	a_1 753.1°K.	$dE/dT \times 10^6$ volt °C.	$\bar{L}_1$. cal.	Temp. range of measurements, °C.
0.8960	3.31	0.903	6.4	70	370–440
.8180	7.20	.801	17.5	276	370–460
.7497	11.56	.701	25.4	349	420–470
.6760	18.96	.558	48.0	793	400–450
.5880	29.69	.401	35.6	−133	450–485
.5590	33.85	.352	31.4	−471	450–480
.4340	52.00	.202	32.0	−1288	450–480
.4006	56.51	.175	38.0	−1287	460–480
.3745	59.90	.158	41.9	−1308	480–500
.3444	63.95	.140	46.7	−1328	495–515

Average no. of observations per run, 20. Maximum deviations, ±0.02 mv.

In Table II the complete thermodynamic data for both components are shown at round number mole fractions, with the values for antimony calculated by the graphical integration of the Duhem equation using liquid antimony as standard state. The extrapolation of the a_1 and $\bar{L}_1$ curves to $N_1 = 0$ presented no difficulty since the a_1 curve had become practically linear and $\bar{L}_1$ was changing very little.

TABLE II

N_1	at 753.1°K. a_1	a_1/N_1	a_2	a_2/N_2	$\bar{L}_1$	$\bar{L}_2$	ΔH per mole
1.0	1	1	0	0.20	0	420	0
0.9	0.909	1.010	0.022	.22	70	− 69	56
.8	.781	0.976	.050	.250	290	−1572	−83
.7	.600	.857	.107	.357	700	−2642	−303
.6	.416	.693	.212	.530	35	−1567	−606
.5	.274	.548	.361	.722	−960	− 319	−640
.4	.175	.438	.520	.867	−1320	− 34	−548
.3	.114	.380	.652	.931	−1340	− 7	−407
.2	.067	.335	.775	.979	−1348	0	−270
.1	.028	.280	.893	.992	−1355	0	−136
.0	.000	.250	1.000	1.000	−1360	0	0

The activity curves at 480° for the two components are shown in Fig. 1, and the $\bar{L}$ curves in Fig. 2. It is interesting to note that while the a_2 values show the expected negative deviations over the entire range of composition, the a_1 values show small but definite positive deviations at high cadmium concentrations. The $\bar{L}$ values reflect also the abnormal behavior of these solutions, due to the possible existence of compounds even in the liquid state.

Calculations

In the calculations which follow ΔH and $\Delta F°$ of fusion of cadmium and antimony at different temperatures are needed. Thermal data recommended by Kelley[5] were used to express these quantities as functions of the temperature. For antimony, at the melting point, 903.1°K., $\Delta H = 4770$ cal., and $\Delta C_p = 1.64 - 1.78 \times 10^{-3}T$. For cadmium, at the melting point, 594.1°K., $\Delta H = 1460$ cal., and $\Delta C_p = 1.67 - 2.466 \times 10^{-3}T$. We can thus write for

Sb(s) = Sb(l)

$$\Delta H = 4015 + 1.64T - 0.89 \times 10^{-3}T^2 \quad (1)$$

$$\Delta F° = 4015 - 1.64T \ln T + 0.89 \times 10^{-3}T^2 + 5.914T \quad (2)$$

and for

Cd(s) = Cd(l)

$$\Delta H = 903 + 1.67T - 1.233 \times 10^{-3}T^2 \quad (3)$$

$$\Delta F° = 903 - 1.67T \ln T + 1.233 \times 10^{-3}T^2 + 8.415T \quad (4)$$

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[3] Strickler and Seltz, THIS JOURNAL, **58**, 2084 (1936).

[4] E. Groschiff, *Z. anorg. Chem.*, **103**, 164 (1918).

[5] K. K. Kelley, "Contributions to Theoretical Metallurgy," Bulletins 383 (1935), and 393 (1936), U. S. Department of the Interior, Bureau of Mines.

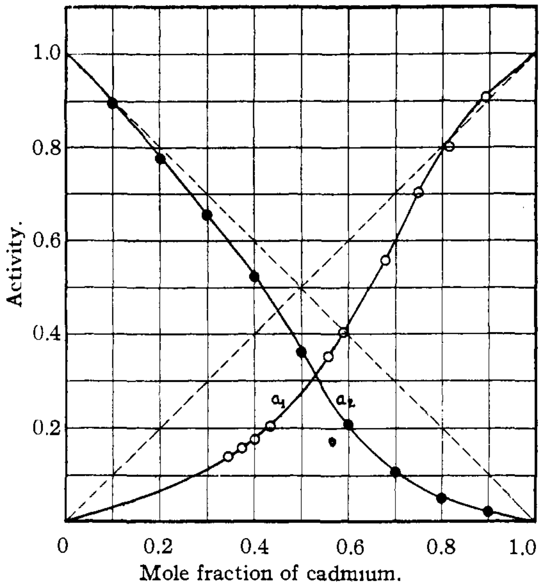

Fig. 1.—Activity curves for Cd and Sb: ○, experimental; ●, calculated.

In addition, thermal data for the formation of CdSb have been determined by Seltz and DeHaven.[6] From their results we can calculate, assuming ΔC_p constant

$$\text{Cd(l)} + \text{Sb(l)} = \text{CdSb(s)};\ \Delta H = -9550;\quad \Delta F^\circ = -9550 + 8.52T \quad (5)$$

Heats of Formation of Cd–Sb Solutions and Heat of Fusion of CdSb.—The heat of formation of one mole of a solution of cadmium and antimony can be calculated from the relation: $\Delta H = \Delta L = N_1\bar{L}_1 + N_2\bar{L}_2$. These values are shown in column 8 of Table II and are plotted in Fig. 2. A minimum occurs at a composition corresponding to CdSb amounting to −640 cal. or to −1280 cal. per mole of the compound. Combining this with equation (4) we obtain for the heat of fusion of the compound

$$\text{CdSb(s)} = \text{CdSb(l)};\ \Delta H = 8270 \text{ cal.}$$

Comparison of Activity Data with the Phase Diagram.—The solid phase which appears from the antimony-rich melts has been shown to be practically pure antimony (less than 0.1% Cd), and the solubility curve has been established accurately by the different investigators. From this curve the activity of antimony in the equilibrium liquid can be calculated and compared with that determined in this investigation. The activity of solid antimony relative to liquid antimony at any temperature is derived from equation (2). The ΔF° from this equation at any temperature is for the change Sb(s) = Sb(l) and hence the negative of this value must equal $RT \ln a_s$, a_s, in turn, must equal a_2 in the equilibrium liquid at this temperature. The values so obtained can then be compared with those determined from the e. m. f. measurements. The agreement is good as shown in Table III, and indicates that the extrapolation of the activity data is satisfactory.

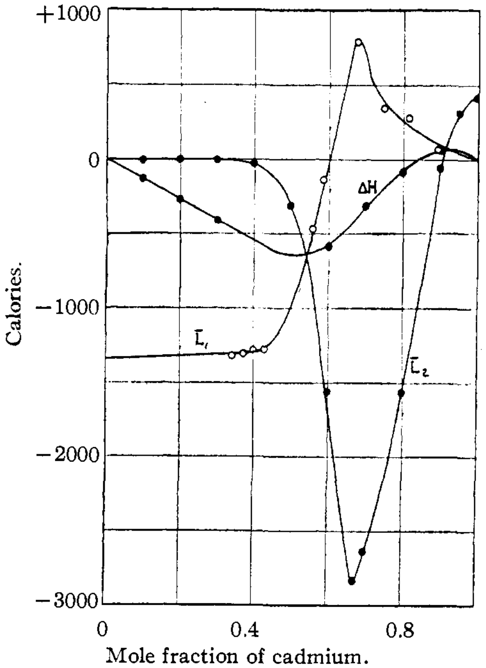

Fig. 2.—Relative heat contents and heat of formation of solutions: ○, experimental; ●, calculated.

TABLE III

Temp., °K.	Solubility N_2	a_2 (Phase diagram)	a_2, E. m. f.
869.1	0.9	0.901	0.893
825.1	.8	.778	.775
777.1	.7	.651	.652
753.1	.65	.583	.585

ΔF° and ΔH of Formation of CdSb(s) and Cd_3Sb_2(s).—From the established solubility curves of CdSb and Cd_3Sb_2 and the activities of Cd and Sb in the solutions the free energies and heats of formation of these compounds can be calculated. At a temperature where in the equilibrium liquid the activity of cadmium is a_1 and of antimony is a_2 we can write

$$\text{Cd}(a_1) + \text{Sb}(a_2) = \text{CdSb(s)};\ \Delta F_T = 0$$

and hence at this temperature for

$$\text{Cd(l)} + \text{Sb(l)} = \text{CdSb(s)};\ \Delta F^\circ_T = -RT \ln \frac{1}{a_1 \times a_2}$$

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[6] Seltz and DeHaven, *Am. Inst. Min. and Met. Eng. Tech. Pub.*, 622, 1935.

Thus, at the melting point of the compound, 728.1°K., for a mole fraction 0.5, $a_1 = 0.268$ and $a_2 = 0.356$ as calculated from the values at 753.1°K. by the usual methods. This gives −3390 cal. for $\Delta F^\circ_{728.1}$ of formation of the compound in close agreement with the value of −3350 cal. from the data of Seltz and DeHaven, equation (5). By similar calculations from the solubility curve at 718.1, 708.1, 698.1 and 688.1°K. corresponding ΔF° values have been obtained. From the equation $\left(\frac{\delta \Delta F^\circ/T}{\delta 1/T}\right)_p = \Delta H$, a plot of $\Delta F^\circ/T$ *vs.* $1/T$ permits of a graphical evaluation of the heat of formation of the compound from the liquid elements. This calculation neglects the ΔC_p terms for the reaction, since no heat capacity data are available for CdSb(s). The ΔH determined by this method is −9680 cal., also in fair agreement with the value of equation (5) −9550 cal. Again, from the metastable solubility curve for Cd_3Sb_2 a like treatment leads to a determination of the thermodynamic quantities for this compound. These calculations may involve considerable error, however, since there is some disagreement in the metastable phase diagrams of the different investigators. The data for both compounds are given in Table IV and the plots of $\Delta F^\circ/T$ against $1/T$ are shown in Fig. 3. The linear form of these plots seems quite satisfactory.

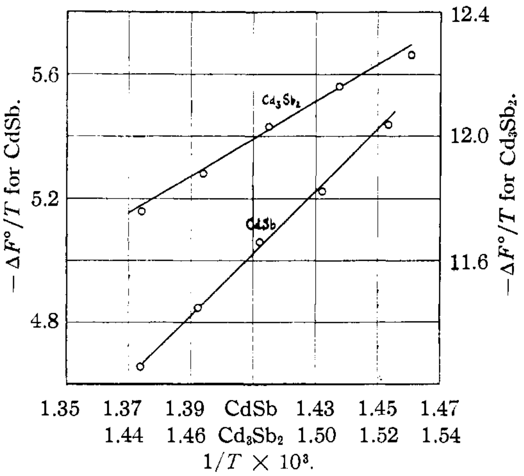

Fig. 3.—Solubility data for CdSb and Cd_3Sb_2.

TABLE IV

Temp., °K.	Soly. N_1	a_1	a_2	ΔF°_T
		ΔF° for CdSb(s)		
728.1	0.500	0.268	0.357	−3390
718.1	.585	.388	.225	−3480
708.1	.625	.466	.169	−3580
698.1	.650	.521	.140	−3640
688.1	.675	.578	.113	−3740
		ΔF° for Cd_3Sb_2(s)		
693.1	0.600	0.416	0.194	−8155
683.1	.642	.506	.140	−8105
673.1	.670	.575	.112	−8095
663.1	.695	.631	.094	−8060
653.1	.720	.705	.078	−8000

From the calculations at 693.1°K. for Cd_3Sb_2 we obtain for the reaction

$$3Cd(l) + 2Sb(l) = Cd_3Sb_2(s);\quad \Delta H_{693.1} = -6020 \text{ cal.};\quad \Delta F^\circ_{693.1} = -8155 \text{ cal.}$$

and for the reaction

$$3Cd(s) + 2Sb(s) = Cd_3Sb_2(s);\quad \Delta H_{298.1} = 7832;\quad \Delta F^\circ_{298.1} = 1587;\quad \Delta S^\circ_{298.1} = 20.98 \text{ e. u.}$$

which gives for Cd_3Sb_2(s); $S_{298.1} = 78.9$ e. u.

Summary

1. The activities and relative partial molal heat contents of cadmium and antimony in their liquid alloys have been determined. The abnormal values of these quantities indicate the existence of compounds in the liquid phase.

2. The heat of fusion and the heat and free energy of formation of CdSb have been calculated, and the latter two values shown to be in agreement with those previously determined at lower temperatures with solid electrodes.

3. The heat and free energy of formation of the unstable Cd_3Sb_2 have been calculated. From these data the entropy of this compound at 298.1°K. is found to be 78.9 e. u.

PITTSBURGH, PENNA. RECEIVED MARCH 28, 1938