them it is possible they would not have noticed the oxidation to the cupric state before measurement.

The initial results of the magnetic measurements of the variously treated pyridine solutions of nickel disalicylaldehyde are shown in Table II. Since the above data indicated that the nickel solutions were stable in air, the experiments were repeated without the anaerobic precautions but with chemical analysis of the solutions for nickel content after filtration. The results are shown in Table III.

The constancy of the magnetic susceptibility when calculated on the basis of the analytically determined nickelous concentrations indicates that either no univalent nickel was formed or that, if formed, it must have had the same susceptibility as the original divalent nickel and, in addition, did not react at an appreciable rate with oxygen of the air. However, it seems unlikely that the univalent state is thermodynamically stable under these conditions, as the attempted reduction with nickel metal produced no observable change even after ten days at 100°. While Fobes and Tyson[4] also concluded that the nickelous ion was not reduced to the univalent state, they apparently did not observe the unmistakable presence of nickel metal as a hydrogenation product, although their description of a green to yellow color change during the hydrogenation is consistent with our observations. One might reconcile the two studies by assuming that nickel was produced in Fobes and Vivian's reaction but that it was so finely divided that it remained unobserved in a colloidal suspension during the hydrogenation and was reoxidized by air upon exposing the products to air. In our studies the metal was formed as a nickel mirror and in such massive form that its ferromagnetic properties could readily be demonstrated through the glass walls of the container. These reactions were not more thoroughly explored since the authors of this paper were primarily interested in the cuprous solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF METALLURGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Thermodynamic Properties of the Liquid Ternary System Bismuth–Cadmium–Tin

BY SVANTE MELLGREN[1]

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The activity of cadmium in liquid Bi–Cd–Sn alloys has been determined with the aid of e.m.f. measurements. From these values the integral molar excess free energy and the partial molar excess free energies of all components have been calculated.

Elliott and Chipman[2] have recently published a thermodynamic analysis of the liquid ternary alloys Bi-Pb-Cd, Pb-Cd-Sb and Sn-Cd-Pb. In the following a similar analysis is presented for the system Bi-Cd-Sn. The partial free energy of mixing of cadmium has been determined from the e.m.f. of galvanic cells involving these alloys, pure cadmium, and a salt melt consisting of KCl, LiCl and $CdCl_2$. Therefrom, (1) the excess integral molar free energy and (2) the excess partial molar free energy of each of the three components have been calculated.

Experimental

The experimental procedure was essentially the same as that described in a previous paper by Elliott and Chipman.[3] In particular, the same type of cell with four legs, one for pure cadmium and three for alloys, was used.

To minimize changes in the alloy composition due to eventual side reactions, each leg of the cell contained as much as 8 to 10 g. of alloy or pure cadmium. The connection with the measuring circuit was made by tungsten leads sealed in Pyrex capillaries. The tips of the tungsten leads were cleaned by cathodic treatment in a NaOH solution.

The electrolyte was a mixture of 45.0 g. of KCl, 35.5 g. of LiCl and 4.3 g. of $CdCl_2$. The salts were dehydrated separately at 230 to 250° within about one day. To prevent hydrolysis during this procedure, ammonium chloride was added which decomposed to HCl and NH_3. The salt mixture was melted in an argon atmosphere and heated slowly to 600°. The melt was always clear without filtration and remained clear when kept under purified argon.

The cell was floating in a stirred bath of 10 kg. of liquid lead in an electrical furnace. The temperature of the lead-bath was kept constant within 0.2° by means of a thermocouple and a Leeds-Northrup Micromax controller. In addition, the temperature of the electrolyte in the cell was determined with the aid of a thermocouple protected by a Pyrex tube and a potentiometer. The temperature difference between the two thermocouples was always less than 0.3°, in general less than 0.1°.

The potential difference between legs containing alloys and the leg containing pure cadmium was determined consecutively at about 410, 450, 560, 530 and 475°. Within half an hour at constant temperature, no changes of the e.m.f. greater than 0.01 mv. were observed.

After each run the cell was destroyed. The weight of each alloy sample was determined and compared to its original weight. The difference was in no case greater than 10 mg. Some loss was due to small amounts of alloy sticking to the glass. No indication of side reactions was found.

The observed potentials were plotted *versus* temperature. In all cases, practically straight lines were obtained. Potentials interpolated for 500° and temperature coefficients are compiled in Table I. For some alloys independent runs were reported. In general, the agreement is very satisfactory, but in some cases there are minor deviations. For the binary alloys, Bi-Cd and Cd-Sn, only a few compositions were investigated, since values obtained by previous investigators can be used for the following evaluation.

Calculations

Deviations from ideality are in general expressed in terms of activity coefficients, designated by γ_i for component i. For the present objective, it

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[1] Research Laboratory, National Lead Company, South Amboy, N. J.

[2] J. F. Elliott and J. Chipman, THIS JOURNAL, **73**, 2683 (1951).

[3] J. F. Elliott and J. Chipman, *Trans. Faraday Soc.*, **47**, 138 (1951).

TABLE I

RESULTS OF E.M.F. MEASUREMENTS ON CELLS WITH Bi–Cd–Sn ALLOYS

$y = \frac{N_{Sn}}{N_{Bi} + N_{Sn}}$	N_{Cd}	E, mv. at 500°	$10^3 \times \partial E/\partial T$ (mv./°C.)
		Cd–Bi alloys	
0.0	0.8500	4.80; 4.75	9.0; 9.8
.0	.8000	7.00; 7.00	14.0;14.0
.0	.7500	9.55; 9.55	16.8;16.8
.0	.5000	26.40;26.40	42.3;42.3
.0	.2500	50.45;50.45	78.9;78.9
		$N_{Bi}:N_{Sn}$ = 3:1	
0.25	0.8710	4.27	8.8
.25	.7795	7.67	16.5
.25	.6923	11.84	22.5
.25	.5821	18.37	31.0
.25	.4286	29.34	49.0
.25	.3333	37.32;36.85	60.0;57.5
.25	.2000	54.72	87.5
.25	.1429	65.55	103.3
.25	.0769	85.65	131.5
		$N_{Bi}:N_{Sn}$ = 1:1	
0.50	0.9048	3.14; 3.02	6.3; 6.3
.50	.8182	6.08; 6.08	12.3;12.3
.50	.7021	10.80;10.80	21.5;21.5
.50	.6000	15.92;15.92	29.5;29.5
.50	.4815	23.05;23.05	43.8;43.5
.50	.3333	34.58	61.5
.50	.2500	43.67	74.0
.50	.4290	61.45	103.0
.50	.0526	94.35	140.8
		$N_{Bi}:N_{Sn}$ = 1:3	
0.75	0.8710	4.20; 4.20	9.3;9.3
.75	.7795	7.45; 7.40	14.8;13.5
.75	.6923	10.62;10.62	23.3;23.3
.75	.5821	15.40;15.40	31.0;31.0
.75	.4286	24.00	52.3
.75	.3333	31.22	62.0
.75	.2000	46.07	89.5
.75	.0769	76.35	123.3
		Cd–Sn alloys	
1.00	0.8500	4.72	7.9
1.00	.7500	7.98; 7.85	16.0;15.8
1.00	.6500	11.46	23.5
1.00	.5000	17.50;17.00	39.8;38.9
1.00	.4000	22.80;22.90	49.0;49.0
1.00	.2500	34.15;34.90	69.8;72.3

is profitable to use the excess partial molar free energy of component i

$$\Delta F_i^x = RT \ln \gamma_i \qquad (1)$$

and the excess integral molar free energy

$$\Delta F^x = \sum_i N_i \Delta F_i^x \qquad (2)$$

in accordance with definitions suggested by Scatchard.[4]

For the binary systems Bi–Sn, Bi–Cd and Cd–Sn, the results of the following investigations are available:

(1) Bi–Sn Alloys.—Seltz and Dunkerley[5] have calculated the values of the activity coefficient γ_{Sn} from e.m.f. measurements on cells of type Sn | SnCl$_2$ | Bi–Sn alloy. Values of γ_{Bi} have been deduced with the aid of the Gibbs–Duhem equation. From the values for 365°, values for 500° have been obtained with the aid of the Gibbs–Helmholtz equation. Values of ΔF_{Bi}^x, ΔF_{Sn}^x and ΔF^x are compiled in Table II. Values of ΔF_{Sn}^x for small concentrations of Sn are somewhat uncertain because of extrapolation. The values of ΔF_{Bi}^x at small concentrations of Bi are possibly too high. Slightly different values for ΔF_{Sn}^x between N_{Sn} = 0.7 and 0.9 (corresponding to deviations of 0.1 mv. in the e.m.f. values) would yield ΔF_{Bi}^x = 335 cal. rather than 445 cal. for N_{Bi} = 0.

(2) Bi–Cd Alloys.—Potential measurements on cells involving Bi–Cd alloys have been made by Taylor[6] and by Elliott and Chipman.[3] Results reported in Table I are substantially in accordance with those of previous investigators. Values of ΔF_{Cd}^x have been calculated directly (see Fig. 1, curve A), and values of ΔF_{Bi}^x have been deduced with the aid of the Gibbs–Duhem equation (see Fig. 3, curve A). Values of $\Delta F_{Cd}^x/(1 - N_{Cd})^2$ are not nearly constant as in other systems but rise sharply at $N_{Cd} \sim 1$ as is shown in Fig. 2 of Elliott and Chipman's paper. Thus, $\Delta F^x{}_{Bi}$ can be calculated from the Gibbs–Duhem equation with a reasonable degree of accuracy only up to about N_{Cd} = 0.75; values for higher cadmium concentrations are highly uncertain.

TABLE II

DATA FOR THE BINARY SYSTEM Bi–SN AT 500° ACCORDING TO E.M.F. MEASUREMENTS BY SELTZ AND DUNKERLEY

N_{Bi}	N_{Sn}	ΔF_{Bi}^x, cal.,	ΔF_{Sn}^x, cal.	ΔF^x, cal.
1.0	0.0	0	(216)	0
0.9	.1	3	(178)	(21)
.8	.2	4	198	43
.7	.3	14	153	56
.6	.4	35	117	68
.5	.5	58	90	74
.4	.6	94	68	78
.3	.7	143	41	72
.2	.8	207	23	60
.1	.9	(319)	9	(40)
.0	1.0	(445)	0	0

(3) Cd–Sn Alloys.—Potential measurements on cells with Cd–Sn alloys have also been made by Taylor[6] and Elliott and Chipman.[3] The values recorded in Table I agree satisfactorily with those of previous studies but favor a slightly higher curve in the $\Delta F_{Cd}^x/(1 - N_{Cd})^2$ *versus* N_{Cd} plot used for the calculation of ΔF_{Sn}^x with the aid of the Gibbs–Duhem equation. Curves for ΔF_{Cd}^x and ΔF_{Sn}^x as functions of the alloy composition are shown as curves E in Figs. 1 and 4, respectively.

The excess integral molar free energy ΔF^x for the ternary system was calculated according to Darken.[7] Values of $\Delta F_{Cd}^x/(1 - N_{Cd})^2$ for constant values of y were calculated and integrated

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(4) G. Scatchard, *Chem. Revs.*, **44**, 7 (1949).

(5) H. Seltz and F. J. Dunkerley, THIS JOURNAL, **64**, 1392 (1942).

(6) N. W. Taylor, *ibid.*, **45**, 2865 (1923).

(7) L. S. Darken, *ibid.*, **72**, 2909 (1950).

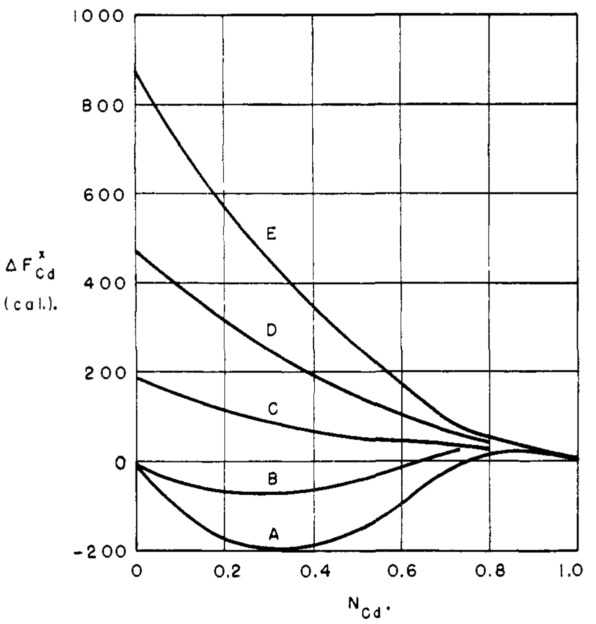

Fig. 1.—Excess partial molar free energy $\Delta F_{Cd}{}^x$ *versus* mole fraction of cadmium N_{Cd} for 500° and various ratios of $y = N_{Sn}/(N_{Bi} + N_{Sn})$: (A) $y = 0.0$, (B) $y = 0.25$, (C) $y = 0.50$, (D) $y = 0.75$, (E) $y = 1.0$.

with respect to N_{Cd}. To obtain the most reliable data for ΔF^x, Darken's equation (2) was integrated with $N_{Cd} = 0$ as the lower limit in accordance with Equation (12) of Elliott and Chipman's paper.[2] Values of ΔF^x at the lower limit were derived from measurements on the binary system Bi–Sn. Figure 2 shows iso-ΔF^x curves in the Gibbs triangle for the ternary system Bi–Cd–Sn.

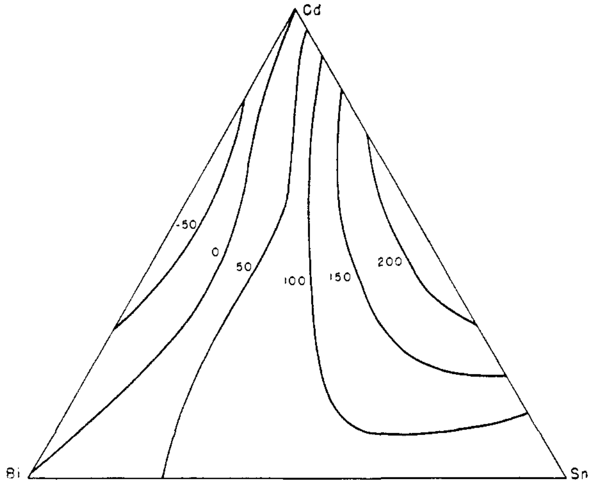

Fig. 2.—Iso-ΔF^x curves in 50-calorie steps for the system Bi-Cd-Sn at 500°.

Values of the excess partial molar free energies of Bi and Sn have been deduced with the aid of the relations

$$\Delta F^x_{Bi} = \Delta F^x + (1 - N_{Bi})(\partial \Delta F^x/\partial N_{Bi})_{N_{Cd}/N_{Sn}} \quad (3)$$

$$\Delta F^x_{Sn} = \Delta F^x + (1 - N_{Sn})(\partial \Delta F^x/\partial N_{Sn})_{N_{Cd}/N_{Bi}} \quad (4)$$

The right-hand side expressions in equations (3) and (4) may be obtained as the right-hand ordinate intercepts of tangent lines on curves ΔF^x *versus* N_{Bi} and curves ΔF^x *versus* N_{Cd} for constant ratios of N_{Cd}/N_{Sn} and N_{Cd}/N_{Bi}, respectively. The attainable accuracy of this procedure obviously decreases with increasing distance from the right-hand ordinate. Since each curve is constructed by using only five points (including the point $\Delta F^x = 0$ at the right-hand side), the accuracy is very moderate for $N_{Bi} = 0$ and $N_{Cd} = 0$, respectively, especially in the case of high amounts of the slopes and large curvatures. Values of ΔF^x_{Bi} and ΔF^x_{Sn} obtained in this way are listed in Table III.

The values of the excess partial molar free energies of Bi and Sn may also be obtained without calculating ΔF^x. According to Wagner[8]

$$\Delta F^x_{Bi}(y, N_{Cd}) = \Delta F^x_{Bi}(y, N_{Cd} = 0) + \left\{\int_0^{N_{Cd}} \left[\frac{\Delta F^x_{Cd}}{(1 - N_{Cd})^2} - y \frac{\partial}{\partial y} \frac{\Delta F^x_{Cd}}{(1 - N_{Cd})^2}\right] \mathrm{d}N_{Cd})\right\}_y - \frac{N_{Cd}}{1 - N_{Cd}} \Delta F^x_{Cd}(y, N_{Cd}) \quad (5)$$

$$\Delta F^x_{Sn}(y, N_{Cd}) = \Delta F^x_{Sn}(y, N_{Cd} = 0) + \left\{\int_0^{N_{Cd}} \left[\frac{\Delta F^x_{Cd}}{(1 - N_{Cd})^2} + (1 - y) \frac{\partial}{\partial y} \frac{F\Delta^x_{Cd}}{(1 - N_{Cd})^2}\right] \mathrm{d}N_{Cd}\right\}_y - \frac{N_{Cd}}{1 - N_{Cd}} \Delta F^x_{Cd}(y, N_{Cd}) \quad (6)$$

where $y = N_{Sn}/(N_{Bi} + N_{Sn})$ and the integrands in brackets are the left-hand and the right-hand ordinate intercepts of the tangent lines on curves ΔF^x_{Cd} *versus* y. Values of ΔF^x_{Bi} and ΔF^x_{Sn} obtained in this way are presented in Figs. 3 and 4. No values for ΔF^x_{Bi} ($y = 1$, N_{Cd}) are shown in view of the uncertainty of the value of ΔF^x_{Bi} ($y = 1$, $N_{Cd} = 0$) in Table II.

TABLE III

COMPARISON OF VALUES OF ΔF^x_{Bi} AND ΔF^x_{Sn} CALCULATED BY MEANS OF DIFFERENT METHODS

N_{Cd}/N_{Sn}	y	ΔF^x_{Bi}(cal.) from eq. (3)	ΔF^x_{Bi}(cal.) from eq. (5)
1:3	0.25	− 3	+ 2
1:3	.50	− 13	− 16
1:3	.75	− 30	− 20
1:1	.25	− 24	− 20
1:1	.50	−110	−116
1:1	.75	−204	−216
3:1	.25	− 90	−102
3:1	.50	−260	−292
3:1	.75	−360	−372

N_{Cd}/N_B	y	ΔF^x_{Sn}(cal.) from Eq. (4)	ΔF^x_{Sn}(cal.) from eq. (6)
1:3	0.0	360	330
1:3	.25	264	290
1:3	.50	168	175
1:3	.75	60	65
1:1	.0	750	650
1:1	.25	504	480
1:1	.50	310	310
1:1	.75	120	120
3:1	.0	820	880
3:1	.25	700	710
3:1	.50	520	520
3:1	.75	250	270

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(8) C. Wagner, "Thermodynamics of Alloys," Translated by S. Mellgren and J. H. Westbrook, Addison-Wesley Press, Inc., Cambridge, Mass., 1952, p. 21, Eqs. (1-80) and (1-81).

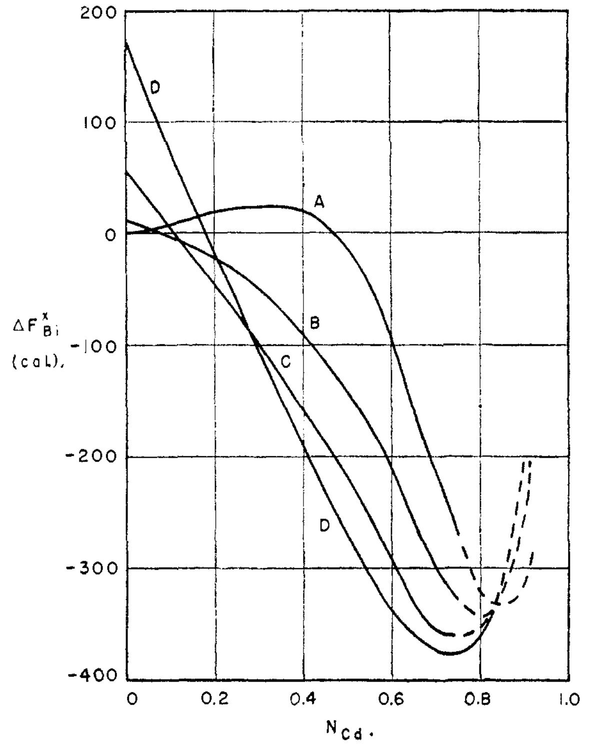

Fig 3.—Excess partial molar free energy ΔF_{Bi}^x *versus* mole fraction of cadmium for 500° and various ratios of $y = N_{Sn}/(N_{Bi} + N_{Sn})$: (A) $y = 0.0$, (B) $y = 0.25$, (C) $y = 0.50$, (D) $y = 0.75$.

Table III shows a comparison of the values of ΔF^x_{Bi} and ΔF^x_{Sn} calculated with the aid of equations (3) and (5), and (4) and (6), respectively. Mathematically, these equations are equivalent. Thus, the deviations in the numerical values of ΔF^x_{Bi} and ΔF^x_{Sn} are a measure of the error introduced by using the ordinate intercepts of tangent lines on curves constructed from only five points. In addition, there are errors due to those in the experimental values of ΔF^x_{Cd}.

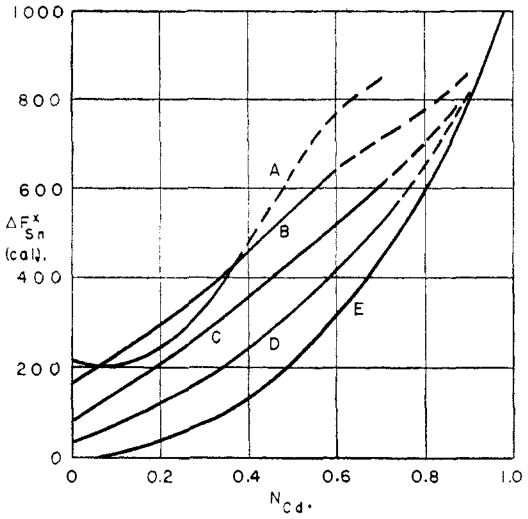

Fig. 4.—Excess partial molar free energy ΔF_{Sn}^x *versus* mole fraction of cadmium for 500° and various ratios of $y = N_{Sn}/(N_{Bi} + N_{Sn})$: (A) $y = 0.0$, (B) $y = 0.25$, (C) $y = 0.50$, (D) $y = 0.75$, (E) $y = 1.0$.

A possible error in the potential of the galvanic cells of 0.1 mv. corresponds to an uncertainty of 5 cal. in $\Delta F^x_{Cd}/(1 - N_{Cd})^2$ for $N_{Cd} = 0$, but to an uncertainty of 80 cal. for $N_{Cd} = 0.75$, and to an uncertainty of 500 cal. for $N_{Cd} = 0.9$. No calculations are possible for alloys containing more than 75 atomic per cent. of Cd, since in the present case it is impossible to extrapolate values of $\Delta F^x{}_{Cd}/(1 - N_{Cd})^2$ from reliable data for lower cadmium concentrations because values of $\Delta F^x_{Cd}/(1 - N_{Cd})^2$ increase sharply beyond $N_{Cd} \cong 0.75$.

Enthalpy and entropy values have not been calculated since the possible errors are still larger and deviations from ideality are small.

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