about ±50 cal. The probable errors in the heats of fusion amount to about ±40 cal. and the assumption that Kopp's law can be applied to these tellurides might introduce an error of not more than ±30 cal.

The calculations at 25° for tin telluride have been made using the γ form of the metal. Apparently this form is stable above 161° and consequently is not stable at 25°. Unfortunately no data on the heat of transition exist so that it is impossible to make calculations for the compound using the allotropic modification which is stable at 25°. The question of the existence of tellurium in two allotropic forms has been raised by S. Umino,[6] who in measuring the specific heat of tellurium up to 550° reported a transition at 348° accompanied by the absorption of 630 cal. per gram atom. However, no other investigator has mentioned this behavior and Simek and Stehlek[7] were unable to confirm his results. For this reason it has been assumed that no transition occurs. No data are available for the entropy of tellurium. Consequently the entropies of the tellurides have not been calculated.

No other measurements of the thermodynamic properties of the tellurides have been reported except those of Fabre[8] on the heats of formation. His results which were obtained by a calorimetric method are tabulated in Table VII. They are not, as will be seen, in agreement with the present values. A review of his work, however, indicates that his results may be unreliable owing to the uncertainty of some of the thermal values he used to calculate the heats of formation. Lack of data prevents recalculation of these values.

Summary

1. A potentiometric study of the tellurides of zinc, cadmium, tin and lead has been made at higher temperatures using fused salt electrolytes.
2. The method has been shown to give results which are reliable and accurate when applied to the proper substances.
3. The data thus obtained have been employed in calculating the free energies of formation, heats of formation and entropies of formation at 25°.

(6) S. Umino, *Kinzoku no Kenyku*, [10] **3**, 498 (1928).

(7) A. Simek and B. Stehlek, *Coll. Trav. Chim. Tchechosl.*, **2**, 304 (1930).

(8) Fabre, *Ann. chim. phys.*, **14**, 110 (1888).

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

A Thermodynamic Study of the Lead-Bismuth System

BY H. S. STRICKLER[1] AND HARRY SELTZ

Although the properties of the alloys of lead and bismuth have been investigated extensively, the phase diagram of the system is not well established. In the "International Critical Tables"[2] diagram, two series (α and β) of solid solutions forming a eutectic at 58 weight per cent. bismuth are shown. The limits of solubility are 18 and 99% bismuth at 0° and 37 and 97.3% bismuth at 125°, the eutectic temperature. References cited for this are Guertler[3] and Herold,[4] from whose critical reviews it is evident that the limits of solubility and the solidus curves are not too well defined. Furthermore, Solomon and Jones,[5] studying alloys of this system by means of x-rays, have found recently a new solid solution phase existing from 25 to 33% bismuth.

In the present work, thermodynamic data obtained from measurements of galvanic cells of the general form Pb/Pb^{++}/Pb (in Pb-Bi solution) have been used to calculate a considerable portion of the phase diagram, making use of the methods previously proposed by Seltz.[6]

Experimental

The cells used were of the three types:

I. Pb(l)/PbCl$_2$ in LiCl-KCl(l)/Pb(in Pb-Bi liquid solution)

IIa. Pb(s)/Pb(OAc)$_2$-NaOAc(l)/Pb(in Pb-Bi liquid solution)

IIb. Pb(s)/Pb(OAc)$_2$-NaOAc(l)/Pb(in Pb-Bi equilib. liquid and solid solutions)

III. Pb(s)/Pb(OAc)$_2$-NaOAc(l)/Pb(in Pb-Bi solid solution)

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(1) Abstracted from a thesis presented by H. S. Strickler to the Committee on Graduate Instruction of the Carnegie Institute of Technology, in partial fulfilment of the requirements for the Degree of Doctor of Science, June, 1936.

(2) "International Critical Tables," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., pp. 414-417.

(3) Guertler, "Metallographie," Vol. I, Gebrüder Borntraeger, Berlin, p. 548.

(4) Herold, *Z. anorg. allgem. Chem.*, **112**, 131 (1920).

(5) Solomon and Jones, *Phil. Mag.*, **11**, 1090 (1931).

(6) Seltz, THIS JOURNAL, **56**, 307 (1934); **57**, 391 (1935).

The liquid alloys of this system have been studied by Wagner and Engelhardt,[7] who determined the electromotive forces of cells Pb(l)/KCl–PbCl$_2$(l)/Pb(in Pb–Bi liquid solution) at two temperatures, 475 and 665°. Since no reliable values of the relative partial molal heat contents could be obtained from their data, it was necessary to study cells of Type I in the present investigation.

The metals used were purified electrolytically, the lead being plated from a Betts[8] bath and the bismuth by a method described by Swift.[9] Before use, the metals were cast under oil and then *in vacuo*. The electrolytes were prepared from commercial "chemically pure" materials without further purification.

Table I

Cells of Type Pb(l)/PbCl$_2$ in LiCl–KCl(l)/Pb(in Pb–Bi Liquid Solution)

Temp. range 380–470°; maximum deviations 0.05 millivolt

N_{Bi}	No. of obsns.	E. m. f. at 700°K., mv.	$dE/dT \times 10^6$ (volt/°C.)
0.152	7	5.32	7.4
.280	8	11.48	14.4
.400	8	19.29	20.8
.504	7	27.82	27.8
.586	8	35.94	37.6
.672	8	45.40	46.4
.770	9	59.76	64.4
.889	10	86.15	102.0

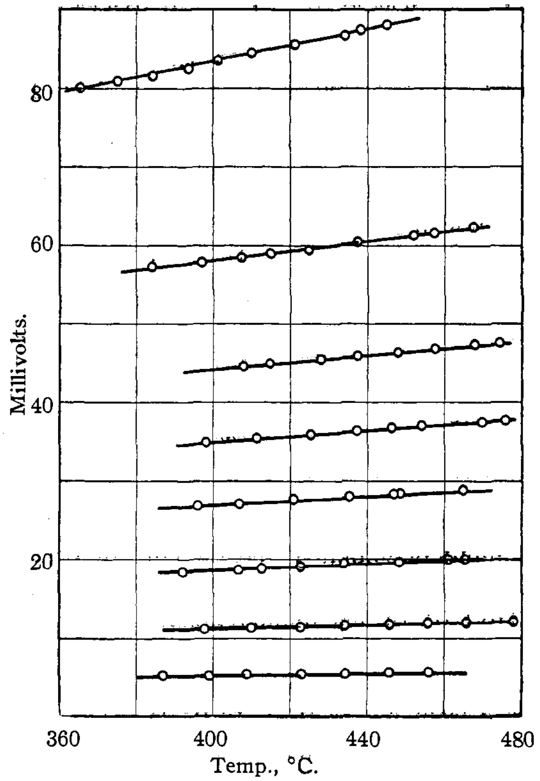

Fig. 1.—E. m. f. curves for type I cells. Starting from the bottom: N_{Bi} = 0.152; 0.280; 0.400; 0.504; 0.586; 0.672; 0.770; 0.889.

The cells of Type I were studied over the temperature range 380–470°, with variation of the composition from N_{Bi} = 0.15 to 0.89. The technique employed was, with modifications, that used by Seltz and DeHaven[10] in their study of the intermetallic compound CdSb. The pure metal was placed in one leg of a Pyrex H-cell containing the electrolyte and the weighed alloy constituents in the other. The electrolyte was the molten eutectic mixture of lithium and potassium chlorides, to which a small amount of lead chloride was added. Contact with the metals was made by tips of tungsten wire sealed into Pyrex tubing, the connections to the potentiometer being made by copper wire welded to the tungsten where it extended from the cell. The system was evacuated by means of a Cenco Hyvac pump. The cell was placed in an electrically heated furnace, manually controlled. Temperatures were determined by means of an iron–constantan thermocouple. A Leeds and Northrup type K potentiometer in conjunction with a Fritz Koehler galvanometer was used. The attainment of equilibrium was quite rapid and the cells were exceedingly steady and reproducible. The experimental results are given in Table I and are plotted in Fig. 1. The reaction occurring in these cells was the transfer of lead from the pure liquid state to a solution of a definite composition, Pb(l) = Pb(in Pb–Bi liquid solution). The free energy change of this reaction is given by the relation $\Delta F = -nFE$, and the activity (a_1) of lead in the alloy referred to the pure liquid as a standard state is then obtained from $-nFE = \Delta F = RT \ln a_1$. The change of heat content in the process is calculated from the Gibbs–Helmholtz equation $T\,dE/dT = E + (\Delta H/nF)$ and the electromotive force E of the cell at a given temperature T. ΔH is here the difference between the partial molal heat content of lead in the alloy and the molal heat content of liquid lead, and is designated as the relative partial molal heat content,[11] $\bar{L}$. The

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(7) Wagner and Engelhardt, *Z. physik. Chem.*, **A159**, 16 (1932).

(8) Betts, "Lead Refining by Electrolysis," John Wiley and Sons, Inc., New York, N. Y., 1908.

(9) Swift, This Journal, **45**, 371 (1923).

(10) Seltz and DeHaven, *Am. Inst. Mining Met. Engrs., Tech. Pub.*, 622 (1935).

(11) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

quantities calculated from the measured electromotive forces and temperatures are given in Table II.

TABLE II

N_2	N_1	a_1 (700°K.)	a_1/N_1	$\bar{L}_1$
0.152	0.848	0.838	0.989	− 6
.280	.720	.684	.950	− 65
.400	.600	.528	.880	−218
.504	.496	.398	.803	−386
.586	.414	.304	.734	−444
.672	.328	.222	.677	−604
.770	.230	.139	.604	−678
.889	.111	.058	.519	−681

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

$$\int_0^{\bar{L}_2} \mathrm{d}\bar{L}_2 = -\int_0^{N_1/N_2} N_1/N_2 \, \mathrm{d}\bar{L}_1$$

and

$$\int_0^{\log a_2/N_2} \mathrm{d} \log a_2/N_2 = \int_0^{N_1/N_2} N_1/N_2 \, \mathrm{d} \log a_1/N_1$$

The calculated terms, with those for lead at rounded mole fractions, are given in Table III.

TABLE III

N_2	N_1	a_1	a_1/N_1	a_2 (700°K.)	a_2/N_2	$\bar{L}_1$	$\bar{L}_2$
0.0	1.0	1.000	1.000	0.000	0.480	0	−925
.1	0.9	0.893	0.993	.052	.520	− 2	−907
.2	.8	.782	.978	.115	.577	− 20	−811
.3	.7	.657	.938	.195	.650	− 91	−606
.4	.6	.528	.880	.293	.732	−218	−376
.5	.5	.402	.804	.407	.814	−352	−213
.6	.4	.291	.728	.532	.886	−502	− 91
.7	.3	.197	.657	.655	.936	−628	− 20
.8	.2	.116	.580	.778	.973	−676	− 4
.9	.1	.052	.520	.896	.995	−692	0
1.0	.0	.000	.480	1.000	1.000	−700	0

Study of the Eutectic.—In order to determine the limits of solubility and the eutectic composition, cells of types IIa and IIb were studied from 200 to 120°, the maximum temperature range over which the mixture of lead and sodium acetates could be used safely. The composition was varied from N_{Bi} = 0.337 to 0.995. The experimental technique differed considerably from that previously described. The lead electrode was generally lead plated on tungsten, using a bath described by Getman,[12] though in some cases bulk electrodes, cast in the same manner as the solid alloys, were used. The alloy constituents were first melted together under mineral oil or *in vacuo*, after which the alloy button was placed under the electrolyte in the cell, which was a 25-cm. test-tube blown out at the bottom to form a depression in which the molten alloy could rest. In preparing the electrolyte, the trihydrates of lead and sodium acetates were melted together in the proportions $3Pb(OAc)_2 \cdot NaOAc$, the mixture then being dehydrated. Contact with the alloy was made by means of a tungsten lead as used for the higher temperature work. In these runs, the system was not evacuated, because of the increased deterioration of the electrolyte under such conditions. The type K potentiometer was used as before, with a sensitive type R Leeds and Northrup galvanometer. The cells were placed in an electrically heated oil-bath which, when desired, was thermostated by a mercury regulator and an Aminco supersensitive relay. Temperatures were measured by means of a copper–constantan thermocouple.

In the course of a run, the temperature was raised above the liquidus of the alloy, when the tungsten lead was fixed in position. Equilibrium was usually attained rapidly, after which the temperature was lowered. In only a few cases was the range of temperature above the liquidus sufficient to permit accurate measurement of the temperature coefficient for the determination of the heat content change. The first separation of solid was marked by a change in slope of the electromotive force–temperature curve, and then the temperature was decreased more slowly, at a rate of 2–4° per hour. However, the temperature was usually maintained constant for twelve hours or more at the eutectic temperature and frequently at higher temperatures. The electromotive forces then observed are designated by an asterisk. In Table IV data are given only at intervals of 5 to 10°.

In the interpretation of these data, it must be remembered that within the heterogeneous region of the system the α and β phases are in thermodynamic equilibrium, whence at a given temperature $a_{\mathrm{Pb}(\alpha)} = a_{\mathrm{Pb}(\beta)}$ and $a_{\mathrm{Bi}(\alpha)} = a_{\mathrm{Bi}(\beta)}$. Therefore, the electromotive forces of two cells $Pb(s)/Pb^{++}/Pb(\alpha)$ and $Pb(s)/Pb^{++}/Pb(\beta)$ should be identical if the α and β compositions correspond to the limits of the heterogeneous range. Thus every cell in which the alloy electrode contains the solid eutectic must show the same electromotive force (E_e) at the eutectic temperature, and E_e should also be the electromotive force of the cell $Pb(s)/Pb^{++}/Pb$(liquid eutectic) at that temperature. A summary of the electromotive forces

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[12] Getman, THIS JOURNAL, 38, 792 (1916).

observed for the various compositions at the eutectic temperature is given in Table V. From these data it is evident that the solubility of lead in bismuth is very small at this temperature, certainly $N_{Pb} < 0.005$. This value agrees well with that obtained by Herold[4] in his metallographical work, but is less than the values obtained by other investigators. On the lead side, the limit of solubility is seen to be very close to N_{Bi} = 0.360, and from the shape of the activity curve at this temperature, the limit is determined as N_{Bi} = 0.365, which is in fair agreement with the "Critical Tables" diagram.

TABLE IV

Temp., °C.	E. m. f., mv.
$N_{Bi} = 0.337$	
Alloy solid and liquid	
196.2	6.06
185.5	6.55
175.0	7.84
167.0	8.85
159.2	9.80*
148.9	10.77
138.9	11.30
Alloy solid	
130.1	11.21
$N_{Bi} = 0.360$	
Alloy liquid	
193.2	6.73
190.8	6.45
Alloy solid	
122.7	13.17*
124.5	13.02*
Solid and liquid	
183.0	6.80
179.8	7.27
135.9	12.46
128.5	12.78
$N_{Bi} = 0.378$	
Solid and liquid	
179.0	7.17
154.0	10.26
145.0	11.36
136.8	12.22*
129.6	12.92
124.8	13.36*
	(eutectic)
$N_{Bi} = 0.389$	
Alloy liquid	
194.5	7.98
184.5	7.32
Solid and liquid	
177.5	7.57
171.2	8.25
159.0	9.72
140.8	11.92*
131.4	12.87*
126.7	13.30
124.6	13.42*
	(eutectic)
$N_{Bi} = 0.42$	
Solid and liquid	
159.4	9.78
137.1	12.24
124.7	13.69
124.7	13.36*
	(eutectic)
$N_{Bi} = 0.449$	
Alloy liquid	
169.5	9.68
161.4	9.16
Solid and liquid	
159.3	9.70
150.5	10.76
139.5	12.16*
130.4	13.22
124.5	13.85
124.4	13.63
(note decrease with time)	
125.0	13.51*
	(eutectic)
$N_{Bi} = 0.542$	
Alloy liquid	
165.4	15.91
155.9	15.19
142.3	14.24
130.4	13.47
125.4	13.11
124.7	13.46
	(eutectic)
$N_{Bi} = 0.564$	
Alloy liquid	
176.1	18.27
166.2	17.60
157.3	16.87
141.2	15.77
133.3	15.20
126.0	14.63
125.0	13.49*
	(eutectic)
Melted, then cooled again	
127.0	14.75
124.7	14.60
	(supercooled)
125.5	13.62
	(just froze)
125.3	13.48*
	(eutectic)
$N_{Bi} = 0.638$	
Alloy liquid	
175.3	25.92
170.1	23.85
157.8	22.70
Solid and liquid	
151.6	20.23
145.7	18.27
129.2	14.21*
123.9	13.38
124.7	13.38
124.0	13.30
$N_{Bi}{}^{a} = 0.987$	
Solid and liquid	
172.0	26.42
167.2	25.25
154.7	21.42
143.4	18.24
137.8	16.49
130.4	14.90
126.5	14.12
$N_{Bi}{}^{a} = 0.995$	
Solid and liquid	
198.9	36.05
190.9	33.38
171.7	25.91
165.8	24.18*
158.9	22.06*
153.6	20.56
139.4	16.87*
128.6	14.25*
124.8	13.38*
	(eutectic)

[a] These alloys were vacuum-cast and annealed in the same manner as the solid alloys, which will be described later.

TABLE V

N_{Bi}	Temp., °C.	E_e, mv.
0.337	124.5	<11.21
.360	124.5	13.02*
.378	124.8	13.36*
.389	124.6	13.42*
.420	124.7	13.36*
.449	125.0	13.51*
.542	124.7	13.46
.564	125.0	13.49*
.564	125.3	13.48*
.638	124.0	13.30
.995	124.8	13.38*

From the chosen value for E_e, 13.40 mv., the activity of lead in the eutectic is calculated to be 0.457, referred to solid lead as the standard state. In order to find the activity referred to pure liquid lead, it is necessary to calculate the activity at this temperature of liquid lead relative to the solid. At 600°K. (327°C.), the melting point of lead, the activity is unity, for there the fugacities are identical. Therefore, the equation

$$R \ln a = \bar{L}/T + \text{const.}$$

becomes at that temperature

$$0 = L/600 + \text{const.}$$

it being assumed that the heat of fusion of lead does not change with temperature, accurate thermal data for any other treatment being lacking. Using the value 1161 cal. for the heat of fusion from the "International Critical Tables," and calculating at the eutectic temperature, one obtains the value 1.641 for the activity of liquid lead relative to the solid. On dividing 0.457 by this figure, one obtains 0.279 for the activity of lead in the eutectic (a_e) with reference to liquid lead.

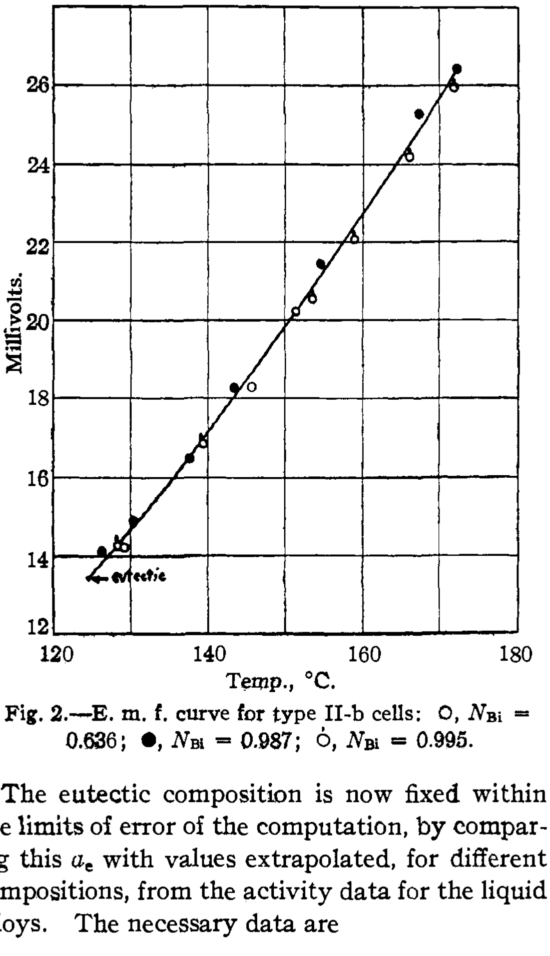

Fig. 2.—E. m. f. curve for type II-b cells: ○, N_{Bi} = 0.636; ●, N_{Bi} = 0.987; ȯ, N_{Bi} = 0.995.

The eutectic composition is now fixed within the limits of error of the computation, by comparing this a_e with values extrapolated, for different compositions, from the activity data for the liquid alloys. The necessary data are

$$N_2 = 0.510,\ a_1 = 0.320$$
$$N_2 = 0.540,\ a_1 = 0.283$$
$$N_2 = 0.563,\ a_1 = 0.257$$

Plotting activity *versus* mole fraction, one finds graphically the composition corresponding to a_e to be N_2 = 0.544. The accuracy of this calculation was checked experimentally by determining the behavior of alloys whose compositions were close to the above value. The data for these confirmatory runs are given in Table VI.

The eutectic composition is thus determined at N_{Bi} = 0.547 (54.9 wt.%), in excellent agreement with the calculated value, considering the lengthy extrapolation of the liquid data. From the intersection of the electromotive force–temperature curves for the eutectic composition in the liquid and solid states, the eutectic temperature is found to be 125°, confirming the previously accepted value. The values of the eutectic composition as determined by other investigators vary, but in general are somewhat higher, the "Critical Tables" diagram giving the value 58%, while Guertler[8] lists 55.8% (Kapp[13]) and 56.5% is the value accepted by Herold[4] from Barlow's[14] data.

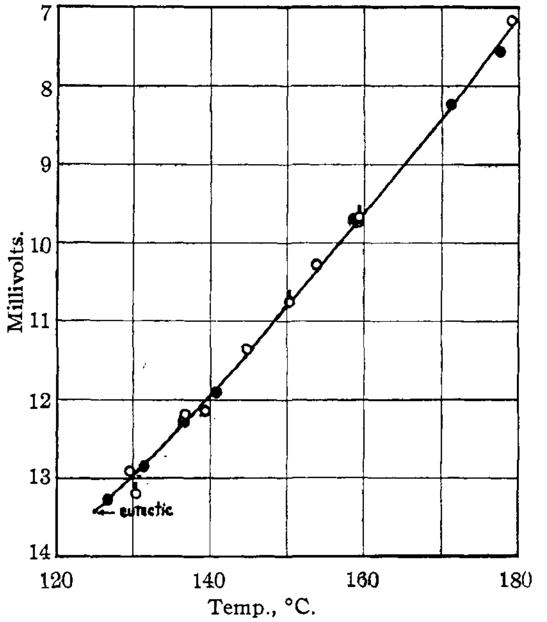

Fig. 3.—E. m. f. curve for type II-b cells: ○, N_{Bi} = 0.378; ●, N_{Bi} = 0.389; ◒, N_{Bi} = 0.420; ȯ, N_{Bi} = 0.449.

The electromotive force data obtained in the slow-cooling of the alloys inside the heterogeneous

TABLE VI

N_{Bi} = 0.541		N_{Bi} = 0.543		N_{Bi} = 0.547	
Temp., °C.	E. m. f., mv.	Temp., °C.	E. m. f., mv.	Temp., °C.	E. m. f., mv.
Alloy liquid		Alloy liquid			
173.2	16.30	177.7	16.80	165.4	16.27
163.0	15.61	170.5	16.30	155.6	15.64
150.2	14.66	164.2	15.83	150.1	15.12
143.0	14.18	155.0	15.25	142.3	14.59
132.3	13.42	147.7	14.66	131.4	13.84
127.4	13.11	129.5	13.47	125.8	13.46*
125.4	12.94			124.1	13.30
E at 124.5° (extrapolated) = 12.87 mv.		E at 124.5° (extrapolated) = 13.10 mv.		123.2	13.20
				122.6	13.12
				121.8	13.02
a_1 (referred to liquid) = 0.287		a_1 (referred to liquid lead) = 0.284		120.7	12.94
				119.0	12.77

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(13) Kapp, *Ann. Physik*, [4] **6**, 771 (1901).

(14) Barlow, This Journal, **32**, 1390 (1910).

region were evidently for cells of Type IIb. If the two solutions, solid and liquid, composing the alloys under these conditions were in equilibrium, then the same electromotive force should be observed in different runs (on the same side of the eutectic) at the same temperature. As the data and Figs. 2 and 3 show, this has been realized approximately. If the liquidus data obtained by thermal analysis are correct, the activity at a given temperature can be calculated from the data of the study of the liquid alloys, and some further idea as to the attainment of equilibrium in the cooling process can be obtained. A few of these calculations are tabulated in Table VII. The liquidus data of Barlow were employed, and the usual extrapolations and conversions to the same reference state (here solid) were made. The agreement is fair with the exception of the value at 63.5%. However, it is probable that Barlow's determination of the liquidus was here at fault, as will be indicated later.

TABLE VII

Composition, wt. % (Barlow)	Temp., °C.	E. m. f., mv.	a_1, obsd.	a_1, calcd.
40.0	177.3	7.50	0.679	0.670
50.0	144.4	11.47	.528	.524
63.5	150.5	20.00	.334	.300
75.0	198.9	36.05	.170	.163

Study of the Solid Phases.—In the investigation of the cells of Type III, the chief difficulty encountered was in obtaining homogeneous electrodes. Further, the probable existence of solid phases other than α complicated the interpretation of some of the data. The range of composition covered was from $N_{\mathrm{Bi}} = 0.05$ to 0.33. The experimental arrangement was that used in the investigation of the eutectic. The electrolyte was also the same. The cells were merely Pyrex test-tubes of various sizes, depending on the number and dimensions of the electrodes placed at one time in the cell. The preparation of the alloys was, however, entirely different. It was found most convenient to cast and anneal the alloys *in vacuo* in Pyrex glass containers. These containers or electrode forms were of two types, constructed as follows. For the simpler variety, a 30-cm. piece of 5-mm. Pyrex tubing was partially constricted in the oxy-gas flame about 7 cm. from one end. Into this was slipped a length of tungsten wire, one end of which was wound into a spiral. The spiral was placed about 3 mm. from the constriction and the wire was then sealed into the glass. The short end of the tube was then bent at right angles. The other type of form was of more complex construction. A piece of Pyrex capillary was sealed at both ends to sections of 5 mm. tubing, one being about 7 cm. long and the other 20 cm. The tungsten wire was sealed into the capillary close to one end. Then the short piece of tubing was bent at right angles, and the capillary through 180°. The simpler variety was designed for use where the alloy was to be cast and annealed below the solidus, while the other was used when the alloy was to be slow-cooled. In casting the electrodes, the weighed materials were placed directly in the glass container. The open end of the electrode form was then attached to the Cenco Hyvac pump, and the metals were melted, degassed and finally sealed *in vacuo*. When the electrode was to be used, the glass was broken away cleanly from the alloy about 2 mm. below its tip. The electrode was placed immediately in the cell.

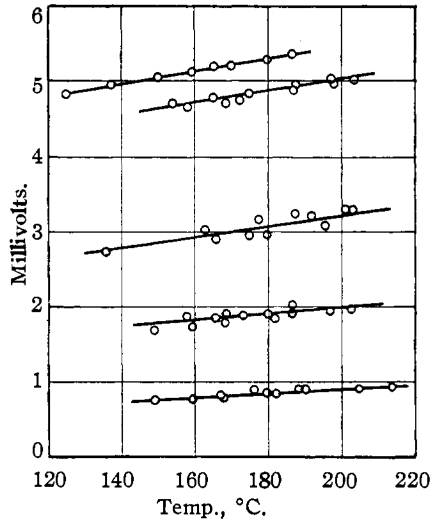

Fig. 4.—E. m. f. curves for type III cells: Starting from the bottom: $N_{\mathrm{Bi}} = 0.050$; 0.096; 0.147; 0.200; 0.225.

For annealing, a small oil-bath and an electric furnace were used. When an alloy was to be slow-cooled, the electric furnace was connected in series with a variable electrolytic resistance, alternating current being used. The construction of the electrolytic resistance is briefly described. Two copper or brass rod electrodes were placed in a large bottle, containing a predetermined amount of calcium chloride solution. The solution was cooled by circulating water through glass tubing placed in the jar. Water was dropped in at a steady rate from a capillary connected with a constant-head device, thus lowering the conductivity of the solution and slowly decreasing the current passing through the furnace.

The data for the solid alloys are given in Table VIII and plotted in Fig. 4. The length of annealing or conditions of slow-cooling are always specified. Reproducibility of electromotive forces with different alloys of the same composition was the sole criterion of sufficient heat treatment. The data for compositions $N_{\mathrm{Bi}} = 0.050$ to 0.200 may be considered satisfactory, but those for the region $N_{\mathrm{Bi}} = 0.225 - 0.330$ are not accurate. The discrepancies may be attributed to nonattainment of homogeneity in the alloys or to the presence of phase changes. The difficulties in the first case might arise from the decreased velocity of diffusion in the solid state at these lower temperatures, and to the greater spread between liquidus and solidus curves. However, evidence for the existence of another solid phase has been offered by Solomon and Jones,[5] and behavior pointing to some abnormality in this region of the system has been definitely noted here. The first

TABLE VIII

CELLS OF TYPE $\mathrm{Pb(s)/Pb(OAc)_2\text{-}NaOAc(l)/Pb(in\ Pb\text{-}Bi\ Solid\ Solution)}$

Run no.	N_{Bi}	Heat treatment and annealing times Hours	°C.	No. of obs.	Temp. range of measurement, °C.	E. m. f., mv.	$\mathrm{d}E/\mathrm{d}T \times 10^6$ volts/°C.	Deviation from mean curve, mv.
1	0.050	140	200	3	149–213	0.83 at 160°	2.0	±0.05
2	.050	320	200	4				
3	.050	500	200	4				
4	.097	274	200	4	149–202	1.82 at 160°	4.8	± .08
5	.096	461	200	6				
6	.096	309	200	3				
7	.147	298	200	4	135–200	2.73 at 124.5°	6.7	± .1
8	.147	Slow-cooled 2°/hr., then annealed 140 hrs. at 190°		5				
9	.147	460	200	2				
10	.200	309	200	6	157–200	4.69 at 160°	8.33	± .05
11	.201	88	200	5				
12	.225	Slow-cooled 2°/hr., then annealed 40 hrs. at 155°		8	....124.5–185	4.83 at 124.5°	9.0	± .05

The behavior of alloys from $N_{\mathrm{Bi}} = 0.25$ to $N_{\mathrm{Bi}} = 0.33$ is shown by the following data.

$N_{\mathrm{Bi}} = 0.250$

Run 13

Quick-cooled, then annealed. No significant change of electromotive force after 71 hours at 175°. For temperature coefficient:

Temp., °C.	E. m. f., mv.
156.0	5.97
167.2	6.18
175.0	6.32
183.6	6.49

$\mathrm{d}E/\mathrm{d}T = 19.0 \times 10^{-6}$ v./°C.

$N_{\mathrm{Bi}} = 0.330$

Run 18

Slow cooled as above

Temperature 131.2°

Time, hrs.	E. m. f., mv.
0.0	12.02
20.6	10.44
68.9	9.91
91.7	9.82
123.5	9.67

$E_\infty = 9.32$ millivolts (extrapolated)

$\mathrm{d}E/\mathrm{d}T = 20.8 \times 10^{-6}$ v./°C.

$N_{\mathrm{Bi}} = 0.248$

Run 14

Slow-cooled, then annealed 50 hours at 155°. Steady decrease of electromotive force at various temperatures with time observed.

Time, hrs.	
	at 174°
0	7.31
12	7.02
	at 163°
0	6.95
17	6.66

When decrease with time appeared to stop, the data below were obtained for the temperature coefficient.

Temp., °C.	E. m. f., mv.
139.4	6.26
152.9	6.45
155.9	6.47
160.4	6.52
171.3	6.67

$\mathrm{d}E/\mathrm{d}T = 13.3 \times 10^{-6}$ v./°C.

$N_{\mathrm{Bi}} = 0.298\text{–}0.299$

Run 15

Annealed 290 hours

Temp., °C.	E. m. f., mv.
144.0	5.54
150.0	5.64
156.0	5.77
161.5	5.88

Run 16

Temp., °C.	E. m. f., mv.
149.8	5.91
156.0	6.05
160.6	6.09
163.8	6.18
168.6	6.22
172.0	6.29

$\mathrm{d}E/\mathrm{d}T = 18.3 \times 10^{-6}$ v./°C.

$N_{\mathrm{Bi}} = 0.298$

Run 17

Slow-cooled, then placed in cell and decrease of electromotive force with time noted.

Temperature 147.7°

Time, hrs.	E. m. f., mv.
0.0	9.30
47.0	7.95
115.0	7.43
163.0	7.27

$E_\infty = 6.82$ mv., extrapolated

From a temperature coefficient determination.

$\mathrm{d}E/\mathrm{d}T = 17.6 \times 10^{-6}$ v./°C.

effect is a marked increase in electromotive force–temperature slope observed with alloys of composition $N_{\mathrm{Bi}} = 0.225$ in passing through the narrow temperature range 185–190°. The fact that the activities for $N_{\mathrm{Bi}} = 0.250$ and 0.300 are considerably above the values read from a smooth curve drawn from the limit of solubility to $N_{\mathrm{Bi}} = 0.200$ constitutes the second definite indication. Other less marked irregularities also have been observed.

In Table IX, the activity and $\bar{L}_1$ data for the compositions $N_{\mathrm{Bi}} = 0.050$ to 0.200 at 124.5° are given, together with data representative of the region $N_{\mathrm{Bi}} = 0.225 - 0.330$. The activities are plotted *versus* mole fraction of bismuth in Fig. 5, where the dotted line indicates the possible appearance if the unusual results noted are due to the presence of two solid phases. It should be noted that in the first range practically perfect solution behavior prevails.

TABLE IX

N_{Bi}	a_1 (124.5°)	a_1/N_1	$\bar{L}_1$
0.050	0.956	1.00	0
.096	.908	1.00	0
.147	.853	1.00	0
.200	.774	0.97	−50

		Mode of treatment
0.225	0.754	Slow-cooled
.250	.730	Quick-cooled and annealed
.248	.700	Slow-cooled
.298	.733	Quick-cooled and annealed
.298	.688	Slow-cooled
.330	.590	Slow-cooled

Determination of the Phase Diagram of the System.—In the previous section, the limits of solubility have been found to be $N_{\mathrm{Bi}} = 0.365$ and $N_{\mathrm{Bi}} = 0.995$, and the eutectic composition has been determined as $N_{\mathrm{Bi}} = 0.547$. It is possible to check the liquidus curve on the bismuth side of the eutectic since, from the above, the solid phase there is practically pure bismuth. On the lead side, accepting the liquidus data of Barlow,[14] the solidus may be calculated up to about 20% bismuth. The methods of calculation are briefly as follows. The activity of solid relative to liquid bismuth is calculated at several temperatures between the eutectic and the melting point. In the equation for the dependence of this activity on temperature, the heat of fusion is assumed independent of the temperature, since no reliable heat capacity data for bismuth are available. The value of the heat of fusion used here is 2518 calories, the mean of the results of several investigators listed by Awbery and Griffiths.[15] The activity curves of bismuth in the liquid alloys are now extrapolated to these temperatures. The intersection of one of these curves with a calculated activity of solid bismuth fixes the liquidus composition for that particular temperature. The results, tabulated in Table X, are in fair agreement with Barlow's data, but those of Kapp are found to be far too low. In a similar manner, the solidus on the lead side of the eutectic is calculated. From the smoothed curve through Barlow's liquidus data, the temperatures corresponding to various concentrations are read. The activities of lead in the liquid alloys are now extrapolated to those temperatures by the usual procedure. The standard state is changed by multiplying these values by the activity of liquid lead relative to solid lead, whence the activities are referred to solid lead. Since at a given temperature the activity in the equilibrium solidus and liquidus must be the same, the activity curves for the solid solutions may be extrapolated to the chosen temperatures, where by interpolation the solidus composition is fixed. These results also are listed in Table X. A survey of the literature on the sys-

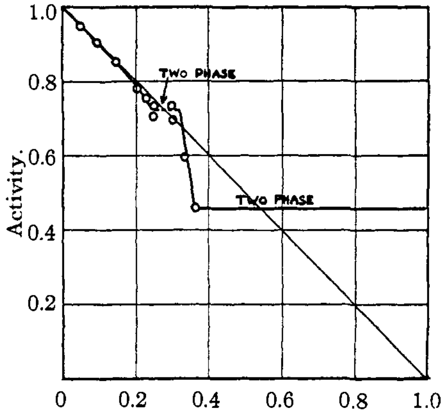

Fig. 5.—Activity of lead in solid lead-bismuth alloys at 124.5°.

TABLE X

Liquidus temp., °C.	N_{Bi}, calcd.	N_{Bi} (from curve through Barlow's data)	Solidus temp., °C.	N_{Bi}, calcd.
140	0.581	0.598	312	0.026
180	.685	.698	295	.056
213	.789	.793	279	.087
250	.915	.920	250	.141
			220	.197

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(15) Awbery and Griffiths, *Proc. Phys. Soc.* (London), **38**, 378 (1926).

tem has failed to reveal any other accurate solidus data.

The results of the above determinations and calculations are summarized graphically in Fig. 6

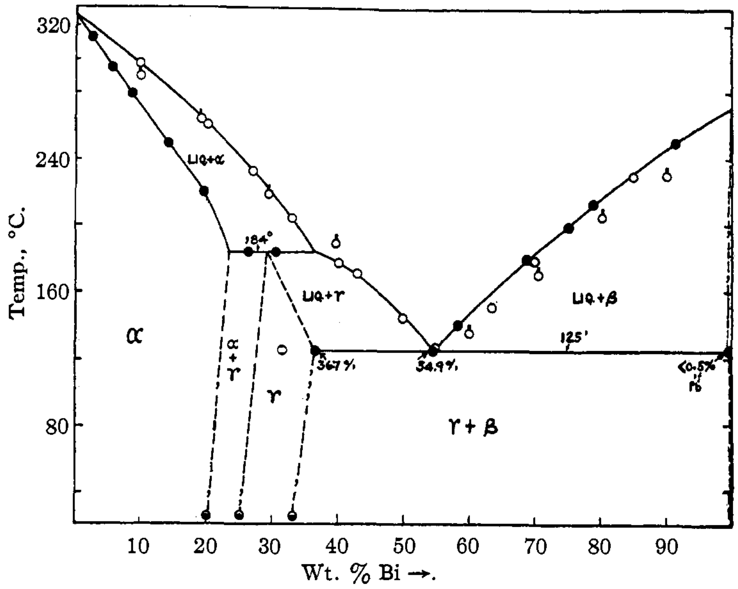

Fig. 6.—Phase diagram for the Pb–Bi system: ●, this study; ○, Barlow; ⦶, Kapp; ⊖, Solomon and Jones.

where data from other studies of the system are plotted also. The possible change of the solubility of bismuth in lead with temperature is indicated by the dotted line drawn from Solomon and Jones' limit of 33% at room temperature to our value at 125°. In drawing a smooth curve through all of Barlow's liquidus data on the lead side, the shape of the curve indicates the possibility of a peritectic. This, with the behavior of the solid alloys previously mentioned, and the report of Solomon and Jones, led us to postulate such a transition at about 180°. This was subsequently verified by thermal analysis, the temperature being fixed at 184°. In the thermal work, large amounts of the metals, 150 to 300 g., were taken and a differential copper–constantan thermocouple was used. The effect was observed with a 26 and a 30% alloy, but not with a 37% alloy, whose liquidus was about two degrees under the peritectic temperature. It should be noted that Hansen[16] has postulated the existence of the peritectic change for this system in his recent treatise, based entirely on the x-ray study of Solomon and Jones and on superconductivity measurements of Meisner.[17]

Regular Solution Behavior of the Liquid Alloys

Hildebrand,[18] in the study of deviations from perfect solution behavior, introduced the term "regular solutions" to apply to those in which, due to the absence of particular orientations, the partial molal entropies of the constituents may be assumed the same as in an ideal solution of the same composition. Where the atomic volumes are the same, which is true for lead and bismuth, his most recent treatment yields the result

$$\overline{U}_1 - U_1^0 = [(\Delta U_1^0)^{1/2} - (\Delta U_2^0)^{1/2}]^2 N_2^2$$

where $\overline{U}_1$ and U_1^0 are the partial molal and molal total energies, respectively, of the first constituent and where the ΔU terms represent the energies of vaporization. As may easily be shown, the equation may be converted by a simple assumption into the form

$$RT \ln a_1/N_1 = bN_2^2$$

where a_1/N_1 is the activity coefficient of the first component and "b" represents the square of the quantity in brackets above. In this case, because of the extreme variation of reported values for the heat

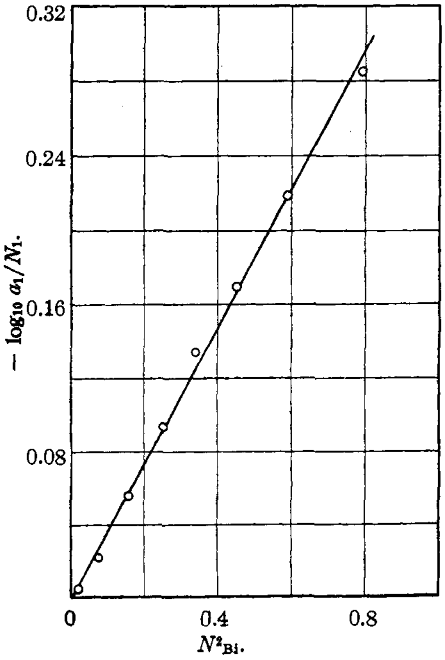

Fig. 7.—Regular solution behavior of liquid alloys.

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[16] M. Hansen, "Der Aufbau der Zweistofflegierungen," Julius Springer, Berlin, 1936.

[17] Meisner, *et al.*, *Ann. Phys.*, **13**, 979 (1932).

[18] Hildebrand, "Solubility," A. C. S. Monograph, No. 17, 2nd edition, 1936.

of vaporization of bismuth, it was impossible to evaluate the term $[(\Delta U_1^0)^{1/2} - (\Delta U_2^0)^{1/2}]^2$. However, as a test for regular solution behavior, the quantity "b" was calculated from the experimental data and its approximate constancy with variation of composition demonstrated. The results of these calculations are given in Table XI and plotted in Fig. 7. Also, it may be shown that from the above $dE_1/dT = -R/nF \ln N_1$ for regular solutions; that is, the slope of the electromotive force–temperature curve should be a function of composition only. This is true for the lead–bismuth liquid alloys, as shown by the values in Table XII.

TABLE XI

N_2	N_2^2	a_1/N_1	$\log_{10} a_1/N_1$	"b"
0.152	0.023	0.989	−0.0048	− 666
.280	.079	.950	− .0223	− 911
.400	.160	.880	− .0555	−1112
.504	.254	.803	− .0953	−1202
.586	.343	.734	− .1345	−1255
.672	.452	.677	− .1694	−1202
.770	.594	.604	− .2190	−1182
.889	.792	.519	− .2848	−1153

TABLE XII

N_2	$\log_{10} N_1$	dE/dT, calcd. volts/°C. × 10^6	dE/dT, obsd. volts/°C. × 10^6
0.152	−0.0716	7.2	7.4
.280	− .1427	14.2	14.4
.400	− .2218	22.0	20.8
.504	− .3045	30.2	27.8
.586	− .3830	38.0	37.6
.672	− .4841	48.0	46.4
.770	− .6383	63.3	64.4
.889	− .9547	94.7	102.0

Summary

1. Methods of calculation have been presented whereby thermodynamic data can be used to establish accurately the conditions of phase equilibria in binary systems.

2. The activities and relative partial molal heat contents of lead and bismuth in their liquid alloys have been determined, and it is shown that the alloys may be classified as regular solutions.

3. The activities and relative partial molal heat contents of lead in solid solutions of lead and bismuth have been determined accurately up to 20% bismuth, and the approximate activities have been established from 22.5 to 33% bismuth.

4. The eutectic composition and temperature are fixed at 54.7 atomic per cent. bismuth and 125°. The compositions of the two solid phases comprising the eutectic solid have been found to be 36.5 atomic per cent. bismuth and practically pure bismuth.

5. The liquidus curve on the bismuth side of the eutectic and the solidus on the lead side up to 20% bismuth have been calculated.

6. The indicated existence of a peritectic at 184° on the lead side of the system has been verified by thermal analysis.

7. A revised phase diagram of the system is presented.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Zinc and Zinc Amalgam Electrodes

BY WILLIAM J. CLAYTON AND WARREN C. VOSBURGH

The difference of potential between zinc and saturated zinc amalgam electrodes in a solution containing zinc ion was considered by Cohen in 1900 to be practically zero.[1] This conclusion was based partly on the results of earlier workers and partly on some measurements of his own. The results of the latter measurements, given in a footnote in the same article[1] (pp. 618–619), are 0.570 mv. at 25° and 0.488 mv. at 0° for the cell

$$Zn(s)/Zn^{++}/Zn \text{ (satd. amalgam)} \qquad (1)$$

On the basis of these results Scatchard and Tefft[2] and Shrawder, Cowperthwaite and La Mer[3] used the value 0.6 mv. at 25° in the calculation of the normal electrode potential of zinc. Puschin[4] found a value of about −2 mv. for cell 1. Garner, Green and Yost[5] have assumed that the electromotive force of cell 1 is zero.

In this investigation the electromotive force of cell 1 has been found to be zero. A similar cell in which a superficially amalgamated zinc electrode was substituted for the pure zinc electrode was found to have zero electromotive force also. The

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[1] Cohen, *Z. physik. Chem.*, **34**, 612 (1900).

[2] Scatchard and Tefft, THIS JOURNAL, **52**, 2280 (1930).

[3] Shrawder, Cowperthwaite and La Mer, *ibid.*, **56**, 2348 (1934).

[4] Puschin, *Z. anorg. Chem.*, **63**, 230 (1903).

[5] Garner, Green and Yost, THIS JOURNAL, **57**, 2056 (1935).