THE BINARY AND TERNARY ALLOYS OF CADMIUM, BISMUTH AND LEAD.

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The ternary and quaternary alloys of lead, bismuth, cadmium and tin possess special interest on account of their extended practical use as fusible alloys and as bearing metals. Of the four possible ternary series, one (the Pb, Bi, Sn series) has been thoroughly investigated—as regards both constitution and physical properties—by Charpy.[1] Two others, the Sn, Cd, Pb series, and the Sn, Cd, Bi series, have been investigated from the standpoint of constitution by Stoffel.[2] The following paper deals with the constitution of the remaining ternary series: the lead-bismuth-cadmium series. My object in undertaking this investigation was to complete the fundamental data necessary for systematic work on the constitution of the quaternary alloys of the four metals.

The thermal examination and representation of this ternary series bases itself, in the first place, on an accurate knowledge of the constitution diagrams of the three binary series of alloys: those of lead-bismuth, lead-cadmium, and cadmium-bismuth. For reasons given below I have thought it necessary or advisable to re-determine the diagrams for two of these binary series.

Practical Methods and Precautions.—The metals used by me contained the following impurities:

Lead..............	0.0002 per cent. of iron.
Cadmium..........	0.004 per cent. of iron, and a trace of arsenic.
Bismuth...........	0.002 per cent. of iron, and a trace of arsenic.

In every case the weight of alloy taken for a cooling-curve observation was 40 grams. The weighed metals were melted together in a small Battersea gold-annealing crucible under paraffin (or in a stream of carbon dioxide), and the mixture was thoroughly stirred and cast in a clean brass mold. Small pieces were then cut from every portion of the solid alloy and preserved for use as seed. In a few cases the alloy to be used as seed was pipetted out of the well-stirred molten alloy.

The apparatus used for cooling-curve work consisted of a small Battersea crucible resting in an asbestos bed inside a graphite crucible, which in turn was embedded in a mixture of sand and kieselguhr contained in a sheet-iron vessel. The thicknesses of the layers of heat-insulating materials necessary to give a convenient rate of cooling were found by a few preliminary trials. The previously prepared alloy was melted (under paraffin) in the small crucible on a separate stand, the crucible was then bedded snugly in the asbestos nest, the stirrer and thermometer

[1] "Contribution à l'Étude des alliages," 1901, p. 200, Paris.

[2] *Z. anorg. Chem.*, **53**, 137.

were warmed, and the composite crucible was then swung into position below the thermometer and stirrer, and raised until the thermometer bulb just cleared the bottom of the crucible. The outside iron vessel was then heated until the alloy was a few degrees below its first (upper) freezing point. The flame was then removed. The temperature continued to rise, until the alloy was melted and heated (usually) about 20° or 30° above its melting point. The stirrer was then started and the apparatus was allowed to cool to a convenient point for beginning the observations. With this arrangement it was not necessary to disturb anything but the small (inner) crucible, and it was found that the rate of cooling, between halting points, varied only very slightly in individual observations during the whole investigation.

Both my own earlier experiences, and deductions from the published work of other investigators, have convinced me that it is a difficult matter entirely to prevent undercooling—and, moreover, that the errors caused by this lag may, under certain conditions, be very great. I therefore took special care to provide for efficient stirring, and for the systematic and periodical addition of seed. Stirring was done by means of a glass rod bent into a circle at its lower end and embracing the stem of the thermometer. The rod was moved vertically up and down, with a force capable of regulation, by means of a clock-work arrangement, the details of which I shall be glad to give to any one interested. The stirrer was adjusted so as to stop automatically as soon as the alloy arrived at a condition of decided pastiness during cooling. This left the observer with both hands free for other work.

Beginning at a temperature 5° or 6° above the expected upper freezing point of the alloy, small portions of the cold alloy were dropped into the crucible every fifteen seconds, and this seeding was continued until it was evident that stirring had ceased to be efficient. The results satisfy me that, in cases in which the first and second freezing points fell near together, undercooling (at the second halting point) was nearly always prevented; when the alloy was too pasty to be stirred at the temperature of the second or third halting point, undercooling nearly always took place.

The temperature was read every fifteen seconds by means of a reading telescope at such a distance as to enable the observer to reach round to the crucible to drop in seed. The thermometer was hung in a wide glass tube, reaching nearly to the crucible edge, so that it was possible to see every part of the mercury thread and to avoid errors due to sudden air draughts on the exposed thermometer stem. The thermometers used were standardized at the freezing points of lead (327°) and tin (232°), and were also directly compared with a thermometer (reading to 560°) tested by the Physikalisch-Technische Reichsanstalt on August

2, 1909. The correction for the exposed column was determined on each thermometer by actual observation of the mean temperature of the exposed column, under the conditions of use obtaining in a cooling-curve observation, and the addition of the correction $n(T—t)/6300$, in which n is the length of the projecting column in degrees, T the temperature to be measured, and t the mean temperature of the exposed column. These measurements were made twice for each thermometer. Up to about 220° the agreement between the two sets of corrections was very close; from 220° to 330° the mean of the two results was used as the correction.

THE BINARY SYSTEMS.

(a) **The Lead-Cadmium Series.**—The freezing point curve of the series has been determined in part by A. Kapp,[1] in part of Heycock and Neville,[2] and in part by Stoffel.[3] Stoffel's statement of Kapp's result does not agree with the published curve. I was unable to consult Kapp's thesis, and since, also, it seemed advisable to have a complete set of determinations made by one observer with identical metals and under identical conditions throughout, I have repeated the thermal investigation with the results given in Table I and Fig. 1. The position of the eutectic point was determined according to Tammann's method of thermal analysis, by measuring the duration of the freezing of the eutectic in each of the twelve alloys studied, plotting these times vertically beneath the corresponding percentage compositions, and continuing the curves free-hand to their intersection. Using the same weight of alloy and the same conditions of cooling in each case, the measured times are proportional to the amounts of eutectic present in the various alloys.

Free-hand prolongation of the upper curves points to the eutectic composition as 82.6 per cent. by weight of Pb, 17.4 per cent. by weight of Cd. This corresponds to 72.04 atomic per cent. of Pb. The prolonged time curves intersect at about 82 per cent. by weight of Pb. (I have purposely used weight percentages in constructing the diagrams, since I consider that, in spite of certain drawbacks, this method enables one to form a mental picture of the relations more easily than the use of atomic percentages. For all important points, however, I have added the atomic figures.)

The freezing point of the eutectic I have taken as 247.3°, as given by the alloys m, j, b, c, and d. The other alloys (more widely removed from the eutectic composition) were all slightly undercooled. The result agrees well with that of Kapp —249°.

On the cadmium side the freezing-time curve points to a slight solu-

[1] Dissert., Königsberg, 1901.

[2] *J. Chem. Soc.*, 61, 888 (1892).

[3] *Z. anorg. Chem.*, 53, 137 (1907).

bility of lead in solid cadmium. On the lead side the limit of miscibility indicated is about 3 per cent. (by weight) of cadmium. Herschkowitsch

TABLE I.—THE LEAD–CADMIUM SERIES (BARLOW).

Alloy No.	Percentage composition. Weight, per cent. Pb.	Cd.	Atomic, per cent. Pb.	Cd.	Temp. of first halting point.	Temp. of eutectic crystallization.	Duration of eutectic freezing in 15-second units.
*........	100.0	0	100.0	0	327.0	...	....
a........	90.0	10.0	83.01	16.99	271.0	246.5	10.0
k........	85.0	15.0	75.45	24.55	252.0	245.6	17.0
m........	83.5	16.5	73.30	26.70	249.2	247.3	18.5
j........	82.0	18.0	71.18	28.82	248.4	247.3	21.0
b........	80.0	20.0	68.46	31.54	253.5	247.3	19.0
c........	70.0	30.0	55.87	44.13	265.0	247.1	15.0
d........	60.0	40.0	44.88	55.12	272.6	247.2	11.0
e........	50.0	50.0	35.18	64.82	275.5	245.6	10.0
f........	40.0	60.0	26.56	73.44	278.4	245.6	8.5
g........	30.0	70.0	18.87	81.13	281.6	246.2	6.0
h........	20.0	80.0	11.95	88.05	290.2	246.8	4.0
i........	10.0	90.0	5.69	94.31	301.0	245.6	1.75
*........	0.0	100.0	0.00	100.0	320.7	...	...

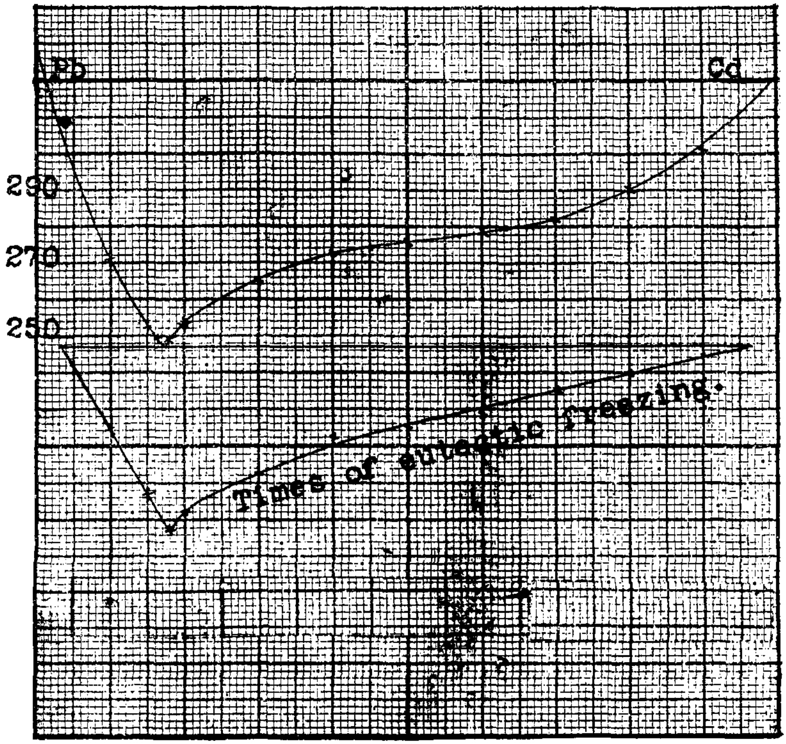


Fig. 1.—Pb–Cd series (Barlow).

(by measuring the electromotive forces of lead–cadmium alloys) found that cadmium forms mix-crystals with lead up to about 4 per cent. (atomic) of cadmium. This is 2.3 per cent. by weight. The times were measured from the cooling curves plotted on co-ordinate paper, and are given in units of fifteen seconds. The error is probably less than one time-unit in every case.

(b) **The Lead-Bismuth Series.**—The freezing-point curve has been determined by Kapp and by Charpy,[1] and is given in the upper part of Fig. 2 in weight percentages. The eutectic lies at 56.5 atomic per cent. Bi (56.6 weight per cent. Bi) and 125° C. The irregularity of the curve

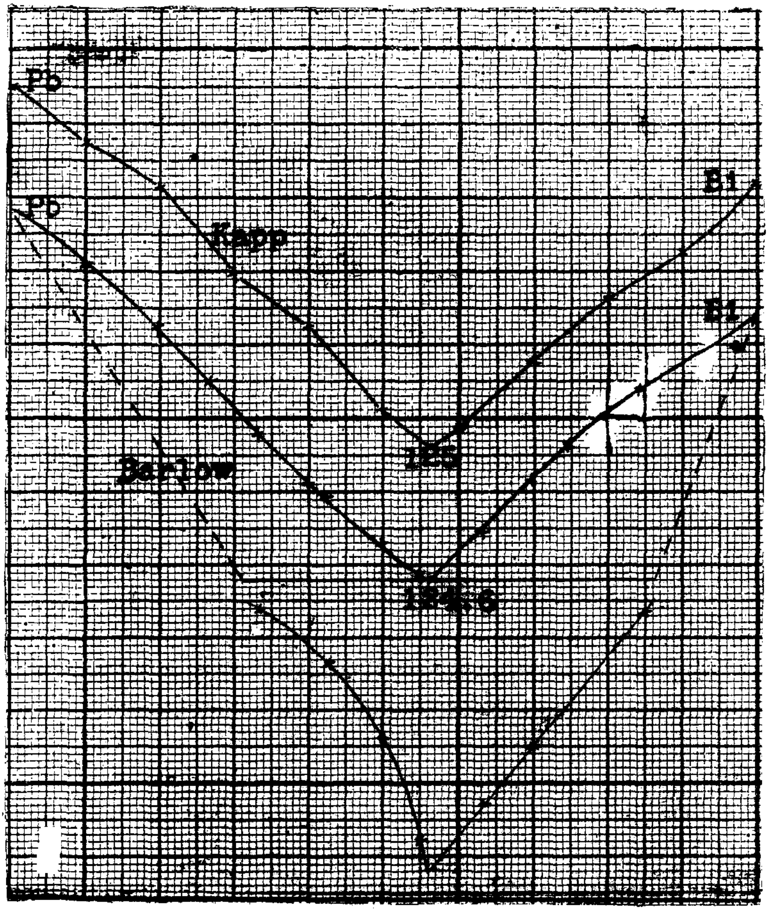


Fig. 2.—Pb–Bi series (Barlow).

[1] *Bull. soc. encour.*, 1901.

on the lead side led me to repeat the thermal analysis, with the results given in Table II and the lower part of Fig. 2.

TABLE II.—THE LEAD-BISMUTH SERIES (BARLOW).

Alloy No.	Composition. Weight, per cent. Bi.	Pb.	First halting point.	Second halting point.	Duration of eutectic freezing.
*	0.0	100.0	327.0	......	....
a	10.0	90.0	297.3	not seen	....
b	20.0	80.0	260.6	not seen	....
c	27.0	73.0	232.6	not seen	....
d	33.33	66.66	204.0	122 u. c.	less than 1
e	40.0	60.0	177.3	119 u. c.	not taken
f	42.85	57.15	170.6	117.2 u. c.	7.0
g	50.0	50.0	144.4	121.7	15.0
h	55.0	45.0	126.9	123.2	26.0
i	63.5	36.5	150.5	124.3	22.0
j	70.0	30.0	178.5	124.3	16.0
k	75.0	25.0	198.3	124.8	not taken
l	85.0	15.0	229.4	124.8	1.5
*	100.0	00.0	271.2	...	...

The eutectic, according to my results, both from the freezing-point determinations and from the times of eutectic freezing, lies at 56.5 weight per cent. Bi, and between 124.3 and 124.8°. With regard to the limits of miscibility in the solid state there is still room for doubt. Kapp and Wiedemann were both unable to observe a second freezing point in an alloy containing 30 per cent. by weight of Bi, and I have obtained almost the same limit on this side. Shepherd, on the other hand, as a result of electromotive force measurements, states that at ordinary temperatures mix-crystals are formed at each end of the series up to 10 per cent. on each side. On the bismuth side my results agree with this statement—indicating a solubility of bismuth in lead up to about 11 per cent. by weight of lead. The letters u. c. indicate "undercooled."

(c) **The Bismuth-Cadmium Series.**—The freezing-point curve has been determined both by Kapp (see above) and by Stoffel (see above). Their results (using weight percentages) are reproduced in Table III and Fig. 3. Kapp's observations on the bismuth side are too scanty to establish the course of the curve with certainty, and differ from those of Stoffel by as much as 20°. Since Stoffel has made three series of observations, with identical results, I have used his figures on the bismuth side of the eutectic, and those of Kapp on the other side, in constructing the ternary diagram. The eutectic lies at 44.5 atomic per cent. Bi (59.8 weight per cent.) and 146°. According to the investigations of Herschkowitsch and of Heycock and Neville the two metals form no solid solutions—are entirely non-miscible in the frozen state.

TABLE III.—THE BISMUTH-CADMIUM SERIES (KAPP, STOFFEL).

Composition. Weight, per cent. Cd.	Bi.	First freezing point. Kapp.	Composition. Weight, per cent. Cd.	Bi.	First freezing point. Stoffel.
90	10	297.5	40	60	146
80	20	279.0	35	65	158
70	30	254.5	30	70	176
60	40	225.5	25	75	191
50	50	193.0	20	80	206
40	60	149.0	10	90	236
20	80	185.0	..	..	...
10	90	230.0	..	..	...

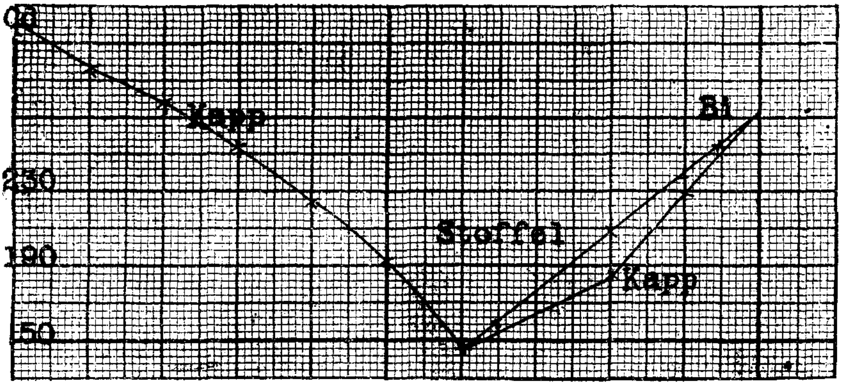


Fig. 3.—Cd–Bi series.

THE TERNARY SYSTEM: LEAD-BISMUTH-CADMIUM.

(1) **Representation of Results.**—The percentage composition of a mixture of three components may be expressed by a system of triangular co-ordinates (cutting, most simply, at 60°) in one plane. If we wish to obtain a complete representation of the equilibrium relations between the various phases of a ternary system, *temperature* must also be expressed, and must necessarily be measured along an axis lying outside of the plane of the paper, and, most simply, vertical to that plane. Within the resulting prism the seven or more surfaces of equilibrium involved may be constructed.

To represent such an equilibrium-solid clearly by a drawing is a difficult matter. If, however, we content ourselves with the representation of the upper surfaces alone (on which lie the *first* freezing points of all the possible mixtures) the projection of these surfaces on the co-ordinate triangle by means of contour lines results in a clear and intelligible diagram.

The upper surfaces of such a solid will have the general appearance of Fig. 4*a*—three more or less curved and inclined surfaces meeting in three channels or grooves (DX, EX, FX), which, in turn, dip towards their intersection at the point X. The curve ADC is the upper freezing-point curve of the binary series AC, while D represents the position of the eutectic of this series. The projection of the surfaces AEXD, etc., on the triangular plane HGK (the base of the model) would have the general appearance of Fig. 4*b*, the dotted lines representing isotherms.

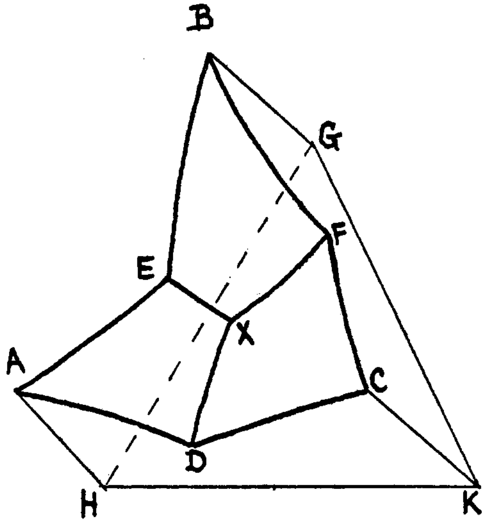


Fig. 4*a*.

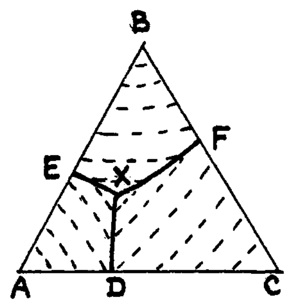


Fig. 4*b*.

Within this triangular space any point represents a mixture of the three components, A, B, C. The sum of the three lines drawn from such a point to the sides of the triangle, parallel to the sides taken in regular order, is always equal to the length of the side of the triangle. This length may be divided into 100 equal parts, when the sum of the co-ordinates drawn in this way becomes 100 per cent. of the mixture. For example, the composition marked by the point 41 in Fig. 8 is 30 per cent. Bi, 10 per cent. Pb, 60 per cent. Cd, if the measurements are made as indicated by the arrows in the margin. For a point falling on one of the sides of the triangle one co-ordinate disappears; thus the point 1 represents an alloy of composition 25 per cent. Bi, 75 per cent. Cd (the distance 1K being equal to the distance 1Bi). At the points A, B, and C, two co-ordinates vanish. A co-ordinate surface ruled according to this plan permits one to make measurements more easily than when the co-ordinates are drawn vertically to the sides of the triangle—the *altitude* of the triangle being taken as 100 per cent.

(2) **Plan of Exploration.**—The exploration of the upper equilibrium surfaces is best made by means of a number of *systematic* surveys, carried out and utilized as explained below. Consider, first, the freezing of the

binary alloy marked 1 in Fig. 5, and assume that the two metals A and C form no solid solutions and no chemical compounds. The alloy contains more than the eutectic proportion of A. On cooling a molten mixture of this composition, freezing begins at a certain temperature. The substance which freezes out is pure A. The composition of the still molten

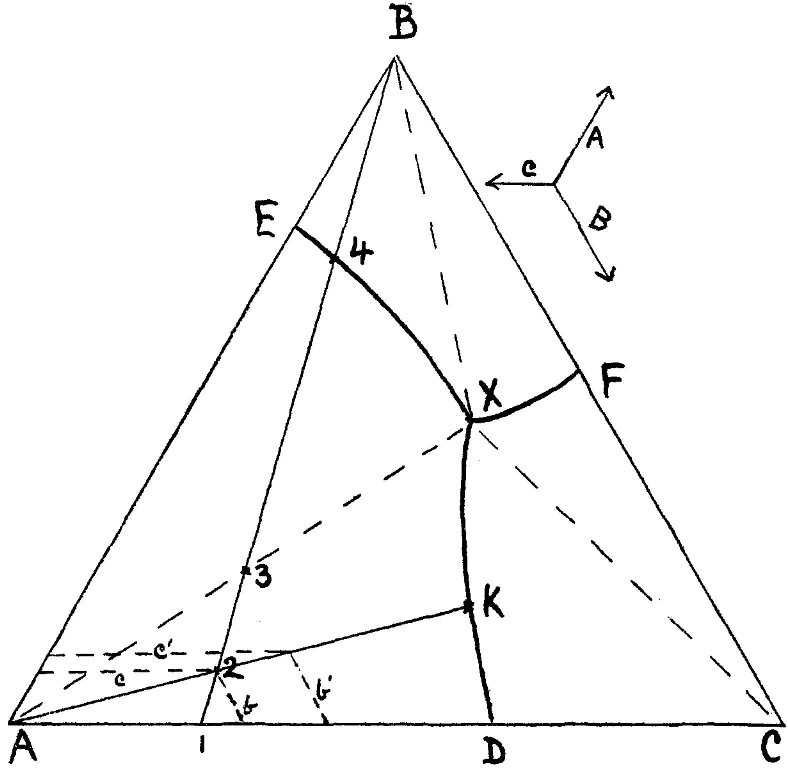


Fig. 5.

mass therefore moves along the line AC towards C, the freezing point of the molten part gradually falling as the composition changes. When the alloy has reached the freezing point of the eutectic D the composition of the mother metal has also reached the composition of the eutectic, and the remaining melt therefore freezes completely at this temperature, before cooling farther. The solid alloy consists simply of the first-frozen crystals of pure A surrounded by the later-freezing eutectic mixture D. The cooling curve will therefore show two (and only two) sudden changes of direction (down to the point at which D has begun freezing): an upper one, at the temperature at which "excess" A begins to freeze out, and a lower one, at the temperature at which the eutectic begins (and continues) to freeze out.

Consider, now, the freezing of the ternary alloy marked 2. At a certain temperature pure A begins to separate out. The molten part therefore becomes richer in both B and C, and both B and C are enriched in the same proportion. In order, however, that the proportion between the pairs of co-ordinates, *cb*, *c'b'*, etc., should remain fixed, the composition of the still-molten part must move along the line AK, formed by continuing the line joining A and 2. When this composition has reached the point K, all the A in excess of the binary eutectic proportion has been frozen out at a gradually falling temperature and the binary eutectic (D) begins to crystallize. The molten part therefore becomes progressively richer in B, since both A and C are being continuously removed. Solidification continues, at temperatures gradually falling, and on KX, until the temperature and composition corresponding to X are reached, when the remaining melt freezes as the ternary eutectic at a constant temperature. The cooling curve will accordingly show three sudden changes of direction down to the point at which X has begun freezing: the first at the excess A freezing point, the second at the temperature at which the binary eutectic begins to freeze, and the third at the ternary eutectic freezing point.

Suppose, now, that we observe the cooling curves of a *series* of alloys lying on the line 1B. The first freezing points will lie on a curve sloping from both sides towards the point 4, at which the eutectic line EX is cut. The second freezing points of all alloys between 1 and 3 will fall at temperatures gradually lower and lower along the curve DX. The alloy 3 will show only two freezing points—that of excess A and that of the ternary eutectic. (An alloy whose composition falls on such a line as DX will also show only two freezing points—those of the binary and ternary eutectics.) From 3 to 4 the second freezing points will lie at points along X4, at gradually rising temperatures moving towards 4. Beyond point 4 the excess metal is no longer A, but B. Alloys between 4 and B begin separating pure B at certain temperatures, the composition of the molten part moving towards the line EX, and cutting it in every case at the point 4, and then following the curve 4X. In other words, the second freezing point of all alloys between 4 and B is fixed at the temperature indicated by 4.

If we consider the alloy 1 as a single component, and pure B as the second component, we can plot the first and second freezing points of the series just as in the case of a system of two elementary components, and we shall obtain a diagram of the general appearance of Fig. 6. The temperature X is indicated (although only approximately—because of the difficulty of observing all the second freezing points with great accuracy) by the intersection of the sloping branches of the second freezing-point curves: the temperature 4 is at the intersection of the upper freezing-point curves and also at the intersection of the horizontal branch and one of the sloping branches of the second freezing-point curve.

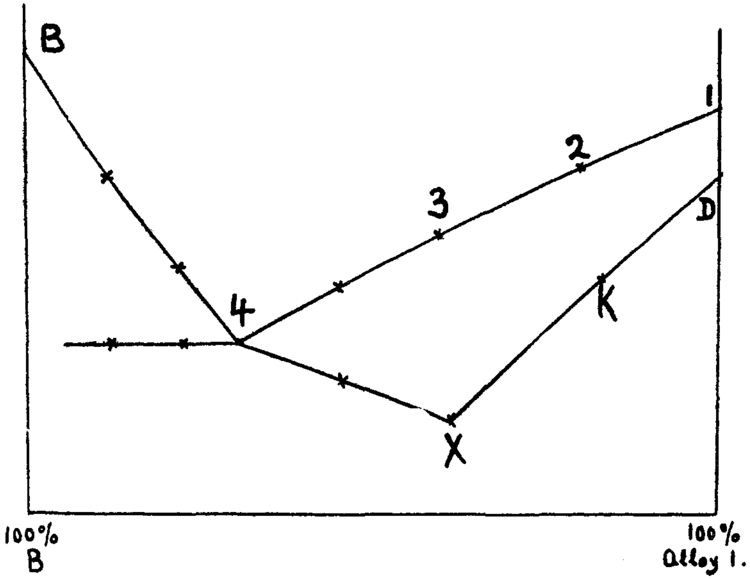


Fig. 6.

Such a survey series as 1B will furnish not only a series of first freezing points, but also an intersection on a binary eutectic line, and at least an approximation to the position of such a critical line as AX. (The line AX divides the region occupied by the alloys consisting of excess A, plus AC eutectic, plus ternary eutectic, in the solid state, from the region occupied by the alloys consisting of excess A, plus AB eutectic, plus ternary eutectic. The lines BX and CX perform analogous functions. The types included by each of the six spaces ADX, AXE, etc., will be apparent from the diagram (Fig. 5)). By taking several such surveys from each angle of the triangle we can obtain a sufficient number of binary intersections to establish the courses of the lines EX, FX and DX. The position of the ternary eutectic is established by the intersection of the binary curves prolonged, together with the approximations to the positions of AX, BX and CX, and other aids to be mentioned later.

Special Case (Survey III).—With one exception, the surveys made in this investigation are of the above type—cutting only one binary eutectic line. Survey III cuts two binary lines. The course of the two freezing-point curves may be understood by reference to Fig. 7 and the following indications:

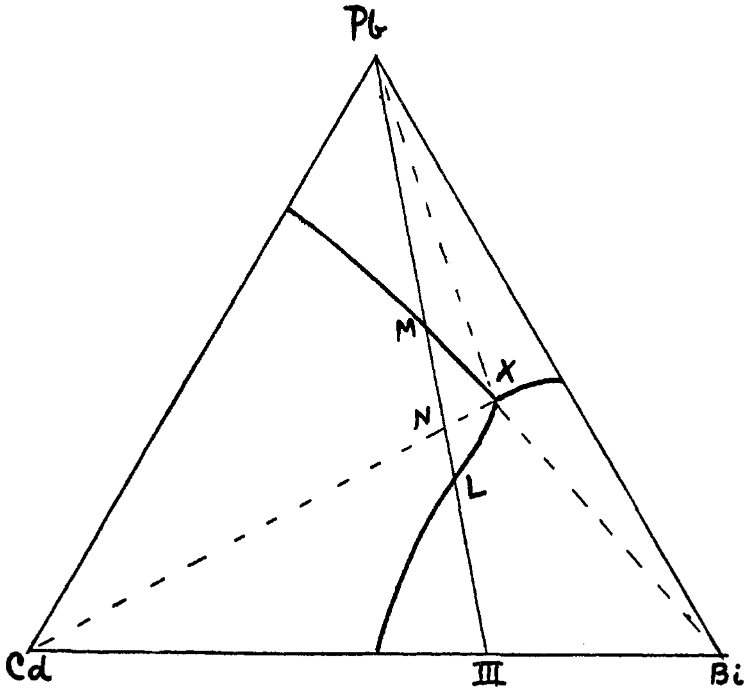


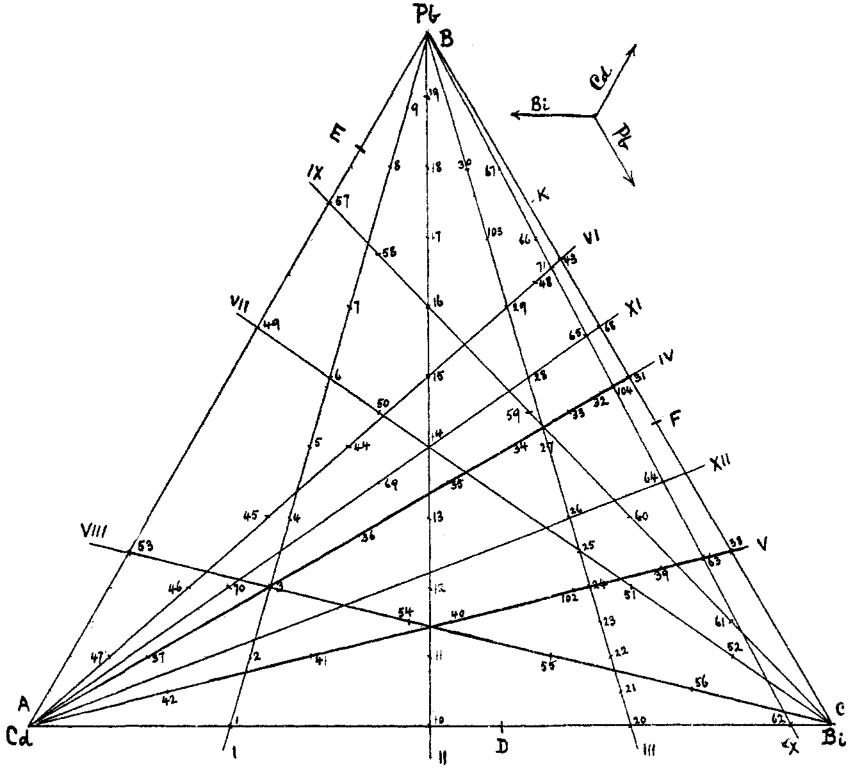
Fig. 7.

	Excess metal.	Eutectic.	1st f. p.	2nd f. p.
From III to L........	Bi	Cd, Bi	falls	falls along DL
From L to N.........	Cd	Cd, Bi	rises	falls along LX
From N to M.........	Cd	Cd, Pb	rises	rises along XM
From M to Pb........	Pb	Cd, Pb	rises	fixed at M

The actual courses of these lines are shown in Survey III, Fig. 10*a*.

(3) **Results.**—In Fig. 8 I have indicated the directions of the surveys used for exploration, and the compositions of the alloys actually submitted to cooling-curve observation. The alloys are numbered to aid in identifying them in the following tables and diagrams.

In Table IV, I have given the compositions, the first, second, and third freezing points of the alloys, arranged in their respective survey series. The letters n. t. signify that the halting point in question was not looked for—the observation of the cooling curve being stopped at some higher temperature. The letters u. c. indicate that the temperature was observed, but was manifestly incorrect as a result of undercooling. Pronounced undercooling was recognized at a second point only three or four times: the plotted cooling curves show that although undercooling took place in other cases, it was only very slight—not enough to interfere with the accurate determination of the freezing point, and usually extending through only a few tenths of a degree. In many cases the


Pb
B
Bi
Cd
Pb
A
Cd
C
Bi
D
E
F
K
I
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III
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V
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VII
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IX
X
XI
XII

Fig. 8.

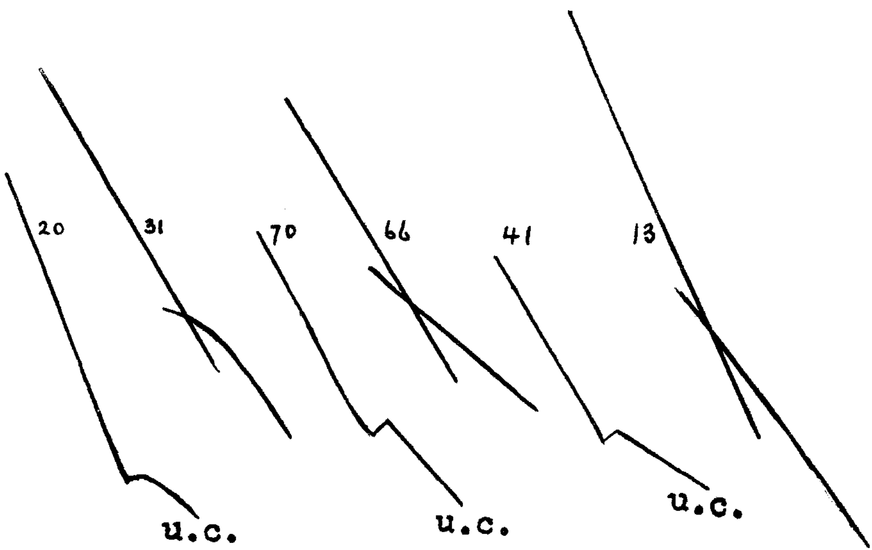
20
31
70
66
41
13
u.c.
u.c.
u.c.

Fig. 9.

two branches cut sharply. (Typical examples of observed cooling curves showing undercooling and a sharp intersection, respectively, are reproduced in Fig. 9.) Undercooling at the ternary point was naturally of more frequent occurrence, but of no importance. The ternary point was purposely not looked for in many of the alloys widely removed in composition from the ternary eutectic, since it could be determined with less likelihood of undercooling in alloys nearer the eutectic composition.

TABLE IV.—COMPOSITIONS AND FREEZING POINTS OF THE TERNARY ALLOYS OF LEAD-BISMUTH-CADMIUM.

Survey. No.	Alloy. No.	Composition. Weight, per cent. Pb.	Bi.	Cd.	Temp. of freezing points. 1st.	2nd.	3rd.
I..	1	0.00	25.0	75.0	267.0	146.0	....
	2	10.0	22.5	67.5	263.5	115.0	91
	3	20.0	20.0	60.0	260.0	106.0	u. c.
	4	30.0	17.5	52.5	259.0	152.0	u. c.
	5	40.0	15.0	45.0	257.0	182.0	n. t.
	6	50.0	12.5	37.5	255.0	203.2	n. t.
	7	60.0	10.0	30.0	252.0	215.2	n. t.
	8	80.0	5.0	15.0	236.5	234.3	n. t.
	9	88.0	3.0	9.0	268.0	234.3	n. t.
II..	10	0.0	50.0	50.0	191.0	143.9	none
	11	10.0	45.0	45.0	203.0	121.9	n. t.
	12	20.0	40.0	40.0	211.0	n. t.	n. t.
	13	30.0	35.0	35.0	218.6	95.0	n. t.
	14	40.0	30.0	30.0	223.0	127.8	n. t.
	15	50.0	25.0	25.0	225.5	165.4	n. t.
	16	60.0	20.0	20.0	224.5	192.0	n. t.
	17	70.0	15.0	15.0	216.0	213.0	n. t.
	18	80.0	10.0	10.0	241.8	216.2	n. t.
	19	90.0	5.0	5.0	290.0	n. t.	n. t.
III..	20	0.0	75.0	25.0	190.0	146.0, 145.0	none
	21	5.0	71.25	23.75	170.4, 169.7	135.8, 135.5	91.4
	22	10.0	67.5	22.5	156.7, 155.0	130.6, 130.0	92, 91
	23	15.0	63.75	21.25	134.6, 133.0	124.6, 124.6	92, 92
	24	20.0	60.0	20.0	119.9, 119.6	119.5, 119.2	92, 91
	25	25.0	56.25	18.75	127.6, 126.0	110.6, 110.3	91.2
	26	30.0	52.5	17.5	132.0, 132.0	not seen	92.0
	27	40.0	45.0	15.0	147.0, 146.0	98.7, 98.4	88 u. c.
	28	50.0	37.5	12.5	159.0, 159.0	128.0, 128.0	n. t.
	29	60.0	30.0	10.0	165.4, 163.5	165.4	n. t.
	103	70.0	22.5	7.5	210.0	n. t.	n. t.
	30	80.0	15.0	5.0	249.5	n. t.	n. t.
IV..	31	50.0	50.0	0.0	144.4	124.8	none
	32	47.5	47.5	5.0	118.6	100.0	u. c.
	33	45.0	45.0	10.0	125.0	108.0	n. t.
	34	40.0	40.0	20.0	180.2	107.0	n. t.
	35	35.0	35.0	30.0	212.0	107.0	n. t.
	36	27.5	27.5	45.0	243.8	107.0	u. c.
	3	20.0	20.0	60.0	260.0	106.0	n. t.
	37	10.0	10.0	80.0	284.0	n. t.	n. t.

TABLE IV (*Continued*).

Survey. No.	Alloy. No.	Composition. Weight, per cent. Pb.	Bi.	Cd.	Temp. of freezing points. 1st.	2nd.	3rd.
V..	38	25.0	75.0	0.0	198.3	124.8	none
	63	24.1	72.3	3.8	180.0	97.0	n. t.
	39	22.5	67.5	10.0	154.0, 156.0	108.5, 108.0	91.6
	24	20.0	60.0	20.0	119.5	119.5	91.6
	102	19.5	58.5	22.0	125.1, 124.8	118.7, 118.6	n. t.
	40	15.0	45.0	40.0	200.0	114 u. c.	92.0
	41	10.0	30.0	60.0	246.6, 248.0	u. c.	91.4
	42	5.0	15.0	80.0	282.0	u. c.	n. t.
VI..	43	66.66	33.33	0.0	204.0	124.8	none
	48	63.33	31.66	5.0	181.9	n. t.	n. t.
	29	60.0	30.0	10.0	165.4	165.4	n. t.
	15	50.0	25.0	25.0	225.5	165.4	n. t.
	44	40.0	20.0	40.0	247.5	n. t.	n. t.
	45	30.0	15.0	55.0	264.0	165.3	n. t.
	46	20.0	10.0	70.0	274.2	165.3	n. t.
	47	10.0	5.0	85.0	292.0	165.4	n. t.
VII..	49	57.14	0.0	42.86	272.0	247.3	none
	6	50.0	12.5	37.5	255.0	203.2	n. t.
	50	44.6	22.0	33.4	239.8	167.0	n. t.
	14	40.0	30.0	30.0	223.0	127.8	n. t.
	25	25.0	56.25	18.75	127.6	110.6	91.2
	51	20.0	65.0	15.0	138.0, 138.8	117.7, 117.6	92.0
	52	10.0	82.5	7.5	210.0, 212.0	118.2, 118.0	n. t.
VIII..	53	25.0	0.0	75.0	286.0	247.3	none
	3	20.0	20.0	60.0	260.0	106.0	u. c.
	54	15.0	40.0	45.0	218.4	116.0	n. t.
	55	10.0	60.0	30.0	138.0	133.6	91.5
	56	5.0	80.0	15.0	199.0	133.6	n. t.
IX..	57	75.0	0.0	25.0	260.0	247.3	none
	58	67.5	10.0	22.5	241.8	219.6	n. t.
	16	60.0	20.0	20.0	224.5	192.0	n. t.
	59	45.0	40.0	15.0	166.0	118.5	91.5
	60	30.0	60.0	10.0	122.0	102.0	91.0
	61	15.0	80.0	5.0	208.6	102.4	92.0
X..	62	0.0	95.0	5.0	253.0	146.0	....
	63	24.1	72.3	3.8	180.0	97.0	91.0
	64	35.0	61.75	3.25	139.0	103.0	91.0
	104	48.7	48.7	2.6	130.0	108.7	91.0
	65	56.0	41.8	2.2	156.0	109.0	u. c.
	71	65.5	32.7	1.8	194.0	109.0	n. t.
	66	70.0	28.5	1.5	218.0	n. t.	n. t.
	67	80.0	19.0	1.0	254.0	n. t.	n. t.
XI..	68	57.15	42.85	0.0	170.6	124.8	none
	65	56.0	41.8	2.2	156.0	109.0	n. t.
	28	50.0	37.5	12.5	159.0	128.0	n. t.
	14	40.0	30.0	30.0	223.0	127.8	n. t.
	69	35.0	26.25	38.75	240.0	132.0	n. t.
	70	20.0	15.0	65.0	269.6	131.0	n. t.

In Figs. 10*a*, 10*b*, 10*c*, I have represented the sections revealed by the survey lines, and also the second freezing-point curves. It should be

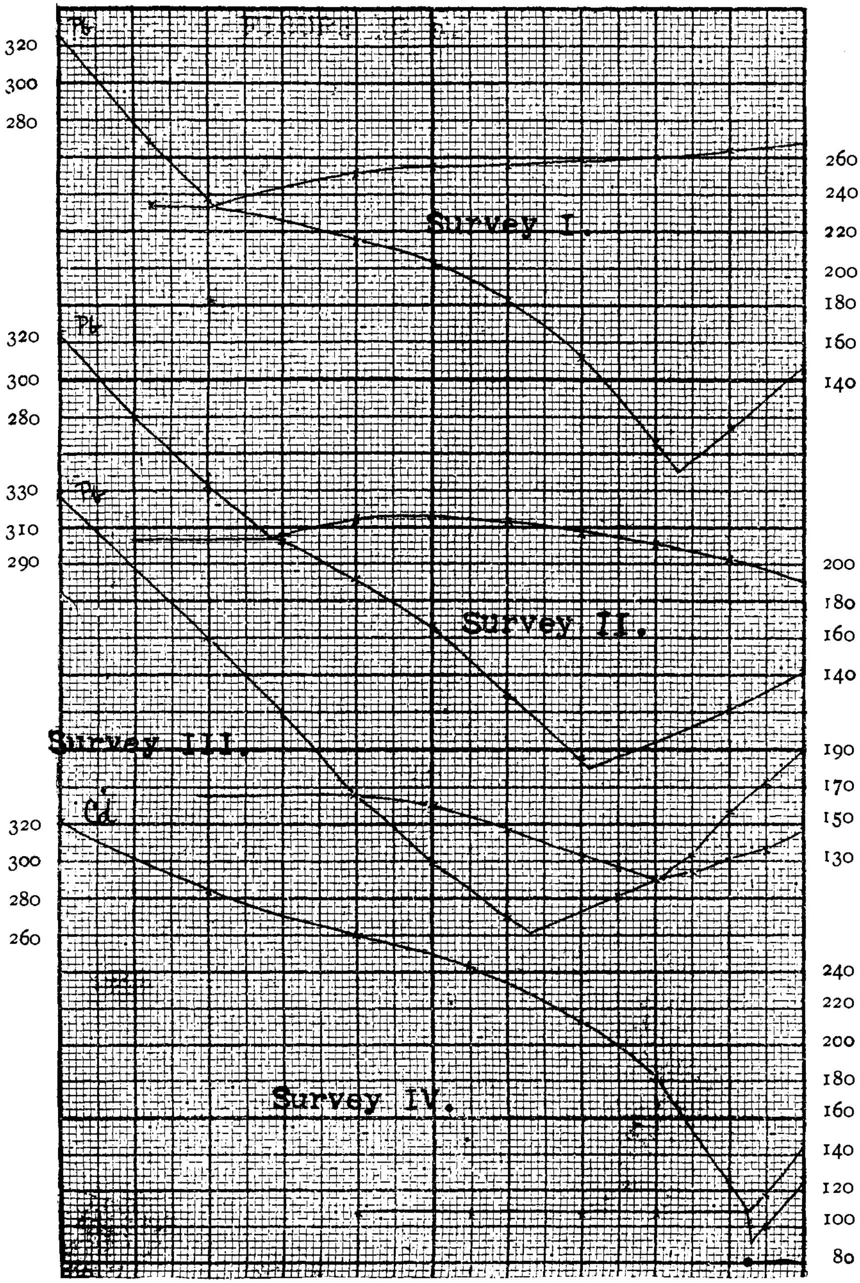

Fig. 10*a*.

understood that the *compositions* corresponding to the observed *second* points (with one exception) are not known at the time of making the survey. They lie, of course, somewhere on the respective binary eutectic lines, but the exact courses of these lines are not known at this stage

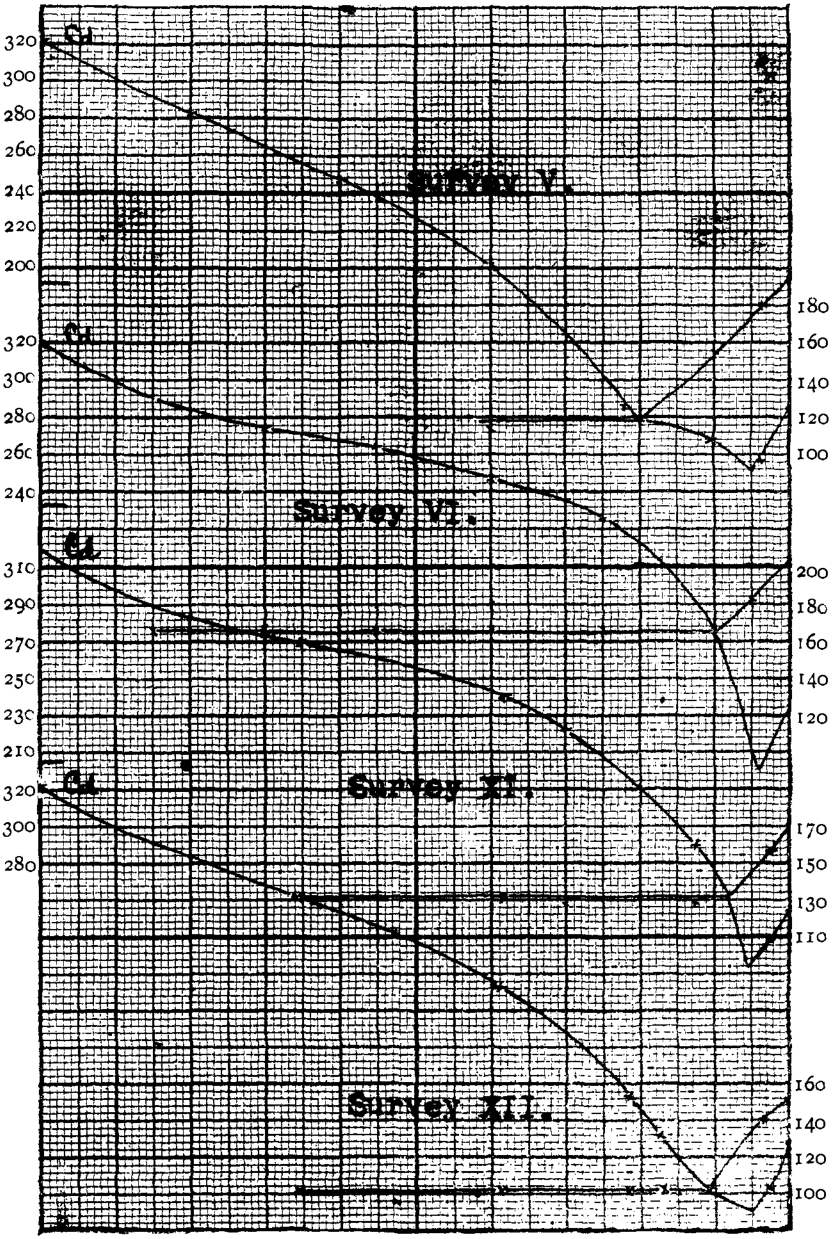

Fig 10*b*.

of the investigation. The one point in each survey which can be directly utilized is that at which the survey line cuts the binary eutectic line; both the temperature and composition represented by this point can be determined with considerable accuracy. I have shown below how the other observed second points in a survey series may be made use of to

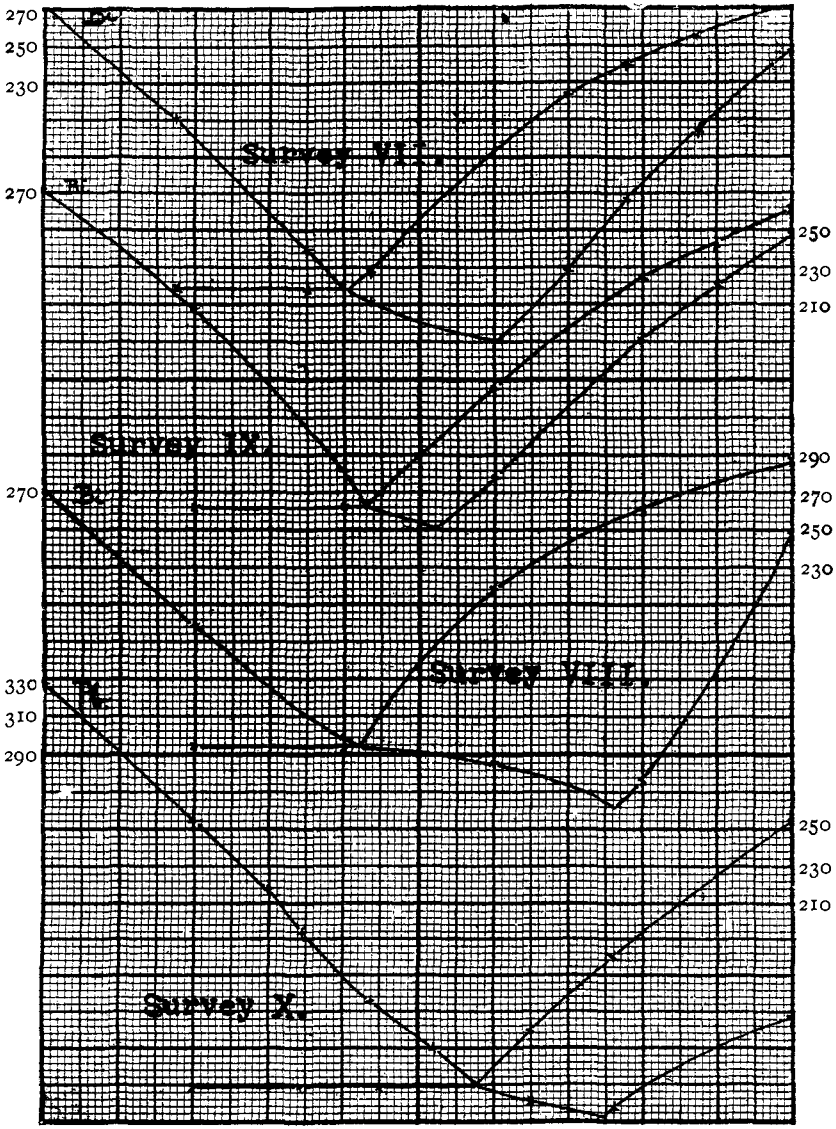

Fig. 10c.

check the courses of the eutectic lines after these lines have been determined from the survey-eutectic line intersections.

Many of the cooling-curve observations were repeated. In some cases both results are given in Table IV, in order to show the sort of agreement obtained. In other cases the average of the two (or three) results, or the single result, is used.

(4) **Construction of the Ternary Diagram.**—The first step was to mark on the triangular co-ordinate surface the positions of the survey lines, and the first freezing points observed at the respective compositions. The next step was to mark on the sides of the triangle points showing the positions of the three binary eutectics, and also a series of first freezing points (on each side of the triangle) ten degrees apart—taking these points from the binary diagrams shown in Figs. 1, 2, and 3.

The next step was to establish the direction of each one of the binary eutectic curves. For this purpose the intersections of these curves by the eleven survey lines were used. These intersections are given in the subjoined table (Table V):

TABLE V. SURVEY-BINARY CURVE INTERSECTIONS.

Survey No.	Composition at cut. Weight, per cent. Pb.	Bi.	Cd.	1st and 2nd freezing points.
I	78.5	5.375	16.125	234.3
II	71.2	14.40	14.40	214.0
IIIa	20.0	60.0	20.0	119.5
IIIb	60.0	30.0	10.0	165.4
IV	46.0	46.0	8.0	108.0
V	20.0	60.0	20.0	119.5
VI	60.0	30.0	10.0	165.4
VII	23.09	59.6	17.31	118.0
VIII	10.5	58.0	31.5	133.6
IX	32.25	57.0	10.75	102.0
X	42.7	54.435	2.865	109.0
XI	52.57	39.43	8.0	131.0

The cut on Survey V is actually at 20.5 per cent. Cd, and about 119°, while the cut on III is at 20 per cent. Cd. These points lie so near together that they are taken as coincident in the ternary diagram at alloy 24—the temperature assigned being 119.5°. Through the intersections found above, the curves DX, EX, and FX were drawn, as far as the points on IX, IV, and X, respectively. As an aid to the free-hand prolongation of these curves, and as a means of checking the accuracy of the work done, four additional check (or secondary) surveys were made: Survey XII, from Cd to Pb, 36.5 per cent.; Bi, 36.5 per cent. Survey XIII, from Cd to Pb, 40 per cent.; Bi, 60 per cent. Survey XIV, from Cd to Pb, 46.5 per cent.; Bi, 33.5 per cent. Survey XV, from Bi to Cd, 9.7 per cent.; Pb, 90.3 per cent. Survey XII, included in Fig. 10*b*, may serve as an example of the results obtained by these secondary surveys. The following observations were used in constructing the curve:

	Pb.	Bi.	Cd.	1st point.	2nd point.
Cut on I..............	12.5	21.87	65.63	262.0	103.0
Cut on VIII...........	17.5	30.0	52.5	241.0	96.0
Cut on II.............	22.0	39.0	39.0	213.0	102.0
Cut on VII............	28.57	50.0	21.43	153.0	102.0
Cut on III............	30.0	52.5	17.5	132.0	102.0
Cut on IX.............	32.62	56.5	10.87	101.8	101.8
Cut on X..............	35.0	61.75	3.25	139.0	103.0
Cut on Pb–Bi..........	36.5	63.5	0.0	150.0	124.8

The temperatures assigned are taken from the previously completed curves for Surveys I, VIII, etc.

The other secondary surveys (XIII to XV) give curves almost as smooth as XII. To avoid crowding the diagram, and because no *new* experimental results are involved, Surveys XIII to XV are not inserted in the main diagram. Their cuts on the curves DX, etc., were, however, used provisionally as guides in prolonging these curves.

The next step in the construction of the ternary diagram was to establish temperatures differing by 10° on the eutectic curves. For this purpose I fitted the edge of a strip of co-ordinate paper to the curve as drawn, and marked on the paper the intersections of the survey lines with the binary lines. I then removed the paper strip, erected perpendiculars at the points marked, proportional to the temperatures indicated, completed the curve free-hand, made marks at the edge of the strip vertically beneath temperatures differing by 10°, and finally replaced the strip and transferred the marks to the binary eutectic curves.

Before using the points so found as starting points from which to begin drawing the isotherms, I checked their positions as follows: The second freezing point of alloy No. 2 was observed at 115°. A straight-edge placed so as to join Cd with alloy No. 2 cut the curve DX at, or

Alloy.	Observed. 2nd point.	Binary cut. (See above.)	Alloy.	Observed. 2nd point.	Binary cut. (See above.)
2	115.0	about 116.0	17	213.0	213.0
3	106.0	about 108.0	21	135.8	about 137.0
4	152.0	about 153.0	22	130.6	about 130.6
5	182.0	about 184.0	23	124.6	about 125.0
6	203.2	about 205.0	24	120.0	about 120.0
7	215.2	about 217.0	25	110.7	about 112.0
11	121.9	about 130.0	27	98.7	about 97.0
13	95.0	in the gap	28	128.0	about 130.0
14	127.8	about 130.0	39	108.0	about 108.0
15	165.4	about 165.4	50	167.0	about 170.0
16	192.0	about 192.0	54	116.0	about 117.0
			58	219.6	about 222.0
			59	118.5	about 117.0
			63	97.0	in the gap

about, 116°. This agreement confirms the positions of the points assigned to 110° and 120° on curve DX. Proceeding in this way I obtained the following checks. Except for alloy No. 50 (and possibly alloy No. 58) the results justified me in using the points marked on the binary curves.

The isotherms were then drawn in, and Fig. 11 was produced. For the sake of attaining clearness in reproducing the diagram on a small scale I have marked only the positions of the isotherms, the binary eutectic curves, and the ternary eutectic. The investigated alloys are shown in Fig. 8. The data for these alloys can easily be found by reference to Table IV.

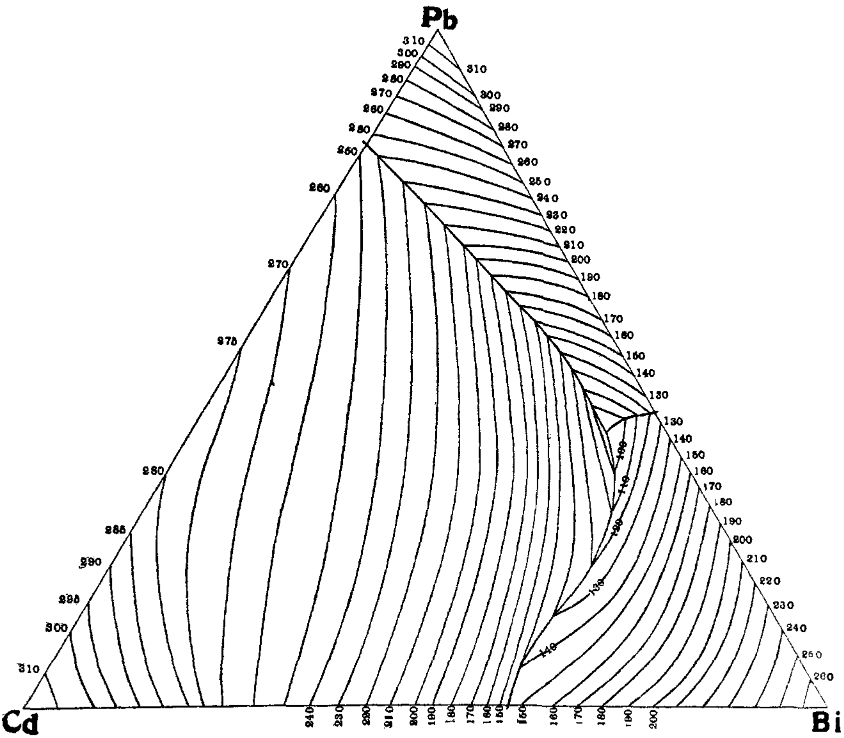

Fig. 11.—Isotherms of first freezing-points of cadmium–bismuth–lead alloys (Barlow).

REMARKS ON THE TERNARY DIAGRAM.

The three-curved surfaces all present convex sides towards the angles of the triangle. In other words, the depression of the freezing point of bismuth (for example) caused by the addition of a small amount of either lead or cadmium alone is less than that produced by the addition of an equal weight of a *mixture* of lead and cadmium; so, too, for the depression of the freezing point of lead and of cadmium.

The gradual and peculiar alteration (near the cadmium angle) of the course of the isotherms running from EX to the Cd–Bi line is what might have been expected from the shape of the freezing-point curve of the lead–cadmium series—and to some extent also from that of the lead–bismuth series. (In order to follow this gradual change of course I have inserted three isotherms between the ten-degree steps near the Cd angle.) Thus the Cd–Pb freezing-point curve shows an *inversion* from concave (from above) to convex at about 50 per cent. Cd, or about where the 275° isotherm emerges on the Pb–Cd side of the ternary diagram. In accordance with this the ternary isotherms are concave between Cd and, say, the 280° isotherm, almost straight from this point to the end of Survey VII, and gradually become convex from VII on to the eutectic E. On the Cd–Bi side the ternary isotherms retain their concavity up to the 250° isotherm—which is almost a straight line for the greater part of its course. In both cases the inversion in the freezing-point curve of the binary series evidences itself in the ternary diagram. From 250° on, towards the ternary eutectic, the isotherms are very nearly parallel.

The Ternary Eutectic.—The curves DX, EX, FX, continued free-hand from their cuts on IX (and XII), IV, and X (and XV), respectively, intersect at about 8 per cent. Cd, 40 per cent. Pb and 52 per cent. Bi.

An alloy of 5 per cent. Cd, 40 per cent. Pb, 55 per cent. Bi, was allowed to cool to 91.5°, with constant stirring and seeding, and a part of the still molten substance was then drawn by means of a suction pump into a glass tube provided with an asbestos filtering plug at its lower end. This, on analysis, gave Pb 4.11 per cent., Bi 50.5 per cent., Cd (by difference) 8.4 per cent. I am not convinced, however, of the possibility of so regulating the tightness of the asbestos plug and the force of the suction as to prevent minute crystals of a frozen excess metal, or a frozen binary eutectic, from being mechanically washed up into the tube with the molten ternary eutectic.

Cooling curves were taken of a number of alloys near the composition just given. Two of these alloys showed a very slight pause at 92°, and a sharply defined ternary freezing point at 91.4 to 91.5°. The composition of the ternary lies very near this point and may be taken, for the present, as Pb 40.2 per cent., Bi 51.65 per cent., Cd 8.15 per cent. The freezing point, as a mean of twenty determinations, lies at 91.5°, and this number, in fact, was found in the four or five cases in which special care was taken to observe the point accurately. It is interesting to note that, of the four possible *ternary* eutectics of the four metals (Sn, Cd, Pb and Bi), this one has the lowest freezing point. The ascertained temperatures are:

Sn–Cd–Pb,	Stoffel,	145°
Sn–Cd–Bi,	Stoffel,	103°
Sn–Pb–Bi,	Charpy,	96°
Pb–Bi–Cd,	Barlow,	91.5°

NOTE.—In sixteen of the alloys investigated a transformation point was noted (in addition to the three freezing points) at a fixed temperature, approximately 124°. In every instance observed the transformation took place below the temperature at which binary eutectic had begun freezing. The phenomenon was not noticed early in the investigation, and the data at hand are not sufficient to enable me to fix the limits of composition within which the change takes place. If the halt is caused by the formation in the partly-solid alloy of a binary or ternary compound, the extent to which this compound may form mix-crystals with the three pure metals will decide whether it is necessary to introduce another surface—roughly triangular in outline—at the point now assigned to the ternary eutectic. I intend to resume the investigation of the transformation at an early date, and ask for a reasonable time reservation for this purpose.

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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

STUDIES IN VAPOR PRESSURE: III. A STATIC METHOD FOR DETERMINING THE VAPOR PRESSURES OF SOLIDS AND LIQUIDS.[1]

BY ALEXANDER SMITH AND ALAN W. C. MENZIES.

Received August 20, 1910.

This paper consists of five sections dealing, respectively, with:

(1) The sources of error of a more general character involved in vapor pressure measurement.

(2) A critical résumé of the characteristics of the older methods, with particular reference to the individual sources of error in each.

(3) A description of the present apparatus.

(4) A criticism of this apparatus, in relation to the various sources of error.

(5) A set of measurements of the vapor pressures of water, made with a view to testing the efficiency of the apparatus.

The apparatus was applied in a redetermination of the vapor pressure of mercury, and in a quantitative study of the chemical constitution of calomel vapor, which will be described in separate papers.

Section 1. General Sources of Error Involved in Vapor Pressure Measurement.

A critical study of the very voluminous literature of vapor pressures reveals the fact that, where two or more independent series of values for the same substance are in existence, inconsistency is the rule and substantial quantitative agreement throughout two comparable series the exception. The differences range from a few tenths of a millimeter

[1] This paper, and the two following, were read at the Boston meeting of the Society, on Dec. 30, 1909.