[Contribution from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology]

A CORRECTION TO THE FREEZING-POINT DIAGRAM OF LEAD-SODIUM ALLOYS

By G. Calingaert and W. J. Boesch

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The compounds capable of existing in lead-sodium alloys, as found in the literature[1] are: Na_4Pb, Na_2Pb, NaPb and Na_2Pb_5, and were identified by Mathewson as corresponding to the maxima of the freezing-point diagram of these alloys.

The thermal data obtained by one of the authors of this paper for lead-sodium alloys of approximately the composition, Na_2Pb (66.6 atomic per cent. of sodium), differed appreciably from the results reported by Mathewson. The freezing-point data were therefore determined for alloys between 50 and 75 atomic per cent. of sodium.

Experimental Procedure

The cooling curves were determined on about 100g. samples of each alloy, using a nickel crucible, an iron agitator and a well-lagged electric furnace. In order to prevent oxidation, a slow current of hydrogen was passed through the furnace during all the experiments. The temperature was read at 30- or 60-second intervals by means of a calibrated chromel-alumel thermocouple, using a Leeds and Northrup potentiometer. The thermocouple was protected from the corrosive action of the alloys by a Pyrex glass tube, which was but slightly attacked by the sodium.

The lead used was pure, as indicated both by analysis and melting-point determination. The sodium was melted and cut under paraffin oil to free it from hydroxide, and to prevent oxidation. The composition of the alloys was determined by analysis. It was found that the analytical method used by previous experimenters, namely decomposition of the alloy by water, and titration of the sodium hydroxide formed, invariably gave low results, due to incomplete decomposition of the alloy. Accurate analyses were obtained by decomposing the alloy with water, dissolving the residue in nitric acid and then converting both metals into sulfates. After separation from the lead, the sodium was determined gravimetrically as sulfate.

Results

The results are summarized in Table I and plotted in Fig. 1. Fig. 2 is a complete phase diagram of lead-sodium alloys, as given by Mathewson, but corrected according to the work of the authors for the alloys of com-

[1] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Julius Springer, Berlin, **1912**, p. 688. Mathewson, *Z. anorg. Chem.*, **50**, 172 (1906).

TABLE I

RESULTS FROM COOLING CURVES

% by wt. Na (weighed)	% by wt. Na (by analysis)	Atomic % Na (from analysis)	Temp. of first break ° C.	Eutectic crystallization Temp. ° C.	Eutectic crystallization Time sec.	Second stop in cooling curve Temp. ° C.	Second stop in cooling curve Time sec.
11.6	10.45	51.3	365[a]	...	...	...	...
12.7	11.58	54.1	358	330	40	...	...
15.00	13.95	59.4	...	324	960	178	50
16.35	15.06	61.5	366	328	660	182	120
18.75	16.60	64.2	377	325	390	182	180
18.35	16.76	64.5	382	326	360	182	230
18.75	17.68	65.9	388	326	240	182	260
19.60	18.35	66.9	396	326	150	181	280
18.75	18.53	67.0	397	327	120	183	280
22.10	19.78	69.0	395	330	30	179	170
21.85	20.25	69.6	396	323	20	182	180
22.10	21.08	70.6	400[b]	...	...	180	100
22.45	21.47	71.4	398[c]	...	...	...	...
22.70	22.45	72.3	396[d]	...	...	...	...
24.20	22.94	72.9	395[e]	...	...	...	...
25.20	23.32	73.2	391	371	120	...	...
26.10	25.50	75.7	...	372	660	...	...

Temperature at which the separation of solid solution stops: [a]350°; [b]380°; [c]387°; [d]375°; [e]370°.

position between 50 and 75 atomic per cent. of sodium. On this diagram Mathewson's data are indicated by crosses and the authors' by circles.

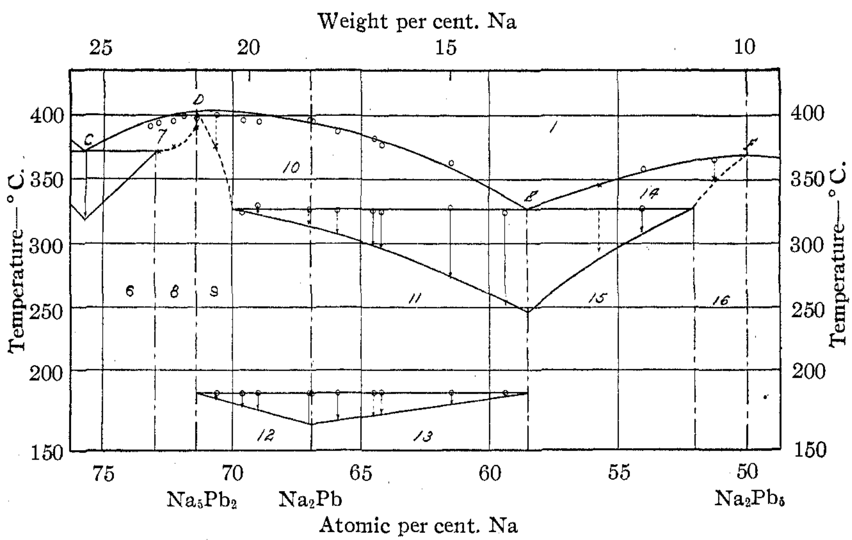

Fig. 1

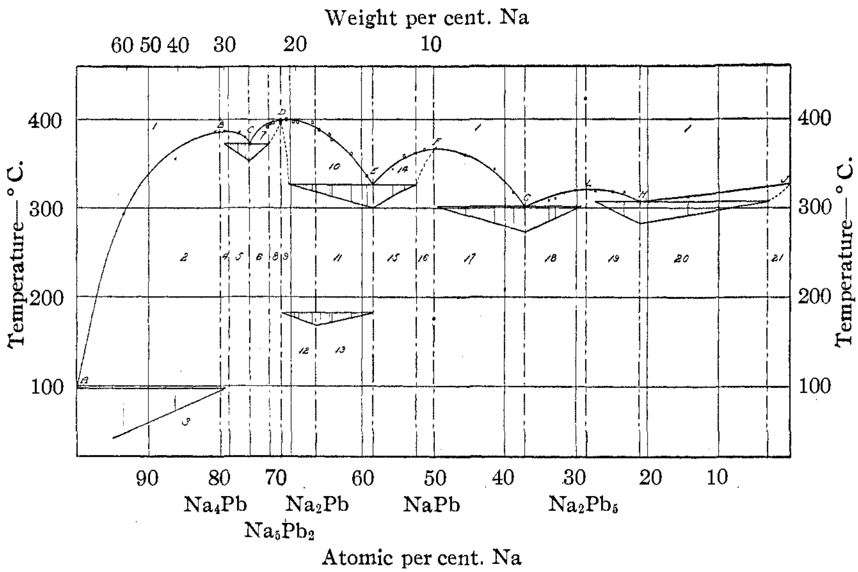

Fig. 2

1. Melt
2. Melt + Na_4Pb
3. Na_4Pb + A
4. Solid solution (Na_4Pb – Na_5Pb_2)
5. Na_4Pb + Na_5Pb_2 + C
6. Na_5Pb_2 + Na_4Pb + C
7. Melt + solid solution
8. Solid solution (Na_5Pb_2 – NaPb)
9. Solid solution (NaPb – Na_5Pb_2)
10. Melt + solid solution
11. Na_5Pb_2 + E
12. Na_2Pb + Na_4Pb
13. Na_2Pb + NaPb
14. Melt + solid solution
15. NaPb + E
16. Solid solution (NaPb – Na_5Pb_2)
17. NaPb + G
18. Na_2Pb_5 + G
19. Na_2Pb_5 + H
20. [Pb, Na_2Pb_5] + H
21. Solid solution (Pb, Na_2Pb_5)

The interpretation of the above data is given in the following tables.

Table II

Pure Compounds

Formula	Atomic % of Na	M. p.
NaPb................	50.0	366
Na_5Pb_2..............	71.4	400
Na_2Pb..............	66.6	Dec. 182

Table III

Eutectics

Compounds in eutectics	Atomic % of Na	Temperature of eutectic crystallization
NaPb + Na_5Pb_2...	58.8	327
Na_5Pb_2 + Na_4Pb..	76.6	372

Table IV

Solid Solutions

Compounds in solution	NaPb + Na_5Pb_2	NaPb + Na_5Pb_2	Na_5Pb_2 + Na_4Pb
Atomic % of Na.......	50.0–52.0	70.0–71.4	71.4–72.4

Discussion

These results indicate that the following corrections should be made to the diagram as reported by Mathewson.

1. The pure compound separating from alloys of composition between 58.8 and 76.6 atomic per cent. of sodium is Na_5Pb_2 and not Na_2Pb.

2. This compound forms solid solutions with both NaPb and Na_4Pb and not only with the latter.

3. Alloys of composition between 58.8 and 71.4 atomic per cent. of sodium rearrange at 182° on cooling; the compound Na_5Pb_2 disappears, and a new compound, Na_2Pb, is formed.

It is concluded therefrom that the freezing-point diagram of lead-sodium alloys, as given in the literature should be replaced by the Fig. 2 given above.

The failure of earlier work to show the exact reaction taking place in alloys can be attributed to two reasons: (1) the insufficient number of points investigated; (2) the too rapid rate of cooling which does not enable the slight changes such as that corresponding to the formation of Na_2Pb to be detected.

Summary

It is shown that the pure compound separating from alloys of lead and sodium, whose composition is between 58.8 and 76.6 atomic per cent. of sodium, is Na_5Pb_2, this compound forming solid solutions with both NaPb and Na_4Pb.

Alloys containing 58.8 to 71.4 atomic per cent. sodium rearrange at 182° on cooling, the compound Na_5Pb_2 disappears and a new compound Na_2Pb is formed.

The complete diagram of lead sodium alloys is given corrected for the above results.

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NOTE

A Source of Trouble in Electrometric Measurements of Hydrogen-Ion Concentration.—If a mercury-calomel-saturated potassium chloride half cell is used for electrometric measurements of hydrogen-ion concentration, it is advisable to introduce an intermediate vessel of potassium chloride solution, which may be renewed from time to time, between the end of the tube leading from the calomel electrode and the "salt bridge" or connecting tube leading to the measuring vessel.

A reason commonly given in the literature for this precaution is that it avoids danger of the potassium chloride in the mercury electrode chamber becoming contaminated by substances that might diffuse back from the measuring vessel.

In the opinion of the authors, the real danger is this: mercuric chloride is formed in the mercury calomel cell according to the well-known reaction, $Hg_2Cl_2 \rightleftarrows HgCl_2 + Hg$. The gray color of calomel which has been in