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 contact with potassium chloride solutions is due to the metallic mercury which is liberated in small quantities by this reaction. Equilibrium is reached when the concentration of mercuric chloride attains a certain value; this equilibrium concentration depends partly on the concentration of potassium chloride in the electrode. The stronger the potassium chloride, the more mercuric chloride will be formed. This mercuric chloride diffuses out of the electrode through the connecting tubes and, unless an intermediate vessel is used, eventually finds its way into the hydrogen electrode chamber. Here it "poisons" the hydrogen electrode, slightly at first but more as time goes on, until no reliable measurements can be made even with freshly platinized electrodes.

A convenient test for mercuric chloride is to add a drop or two of sodium sulfide solution to the potassium chloride solution to be tested. Mercury in sufficient concentration to poison a hydrogen electrode will give a brown coloration.

A calomel half cell has been devised for use with potentiometers having a quadrant electrometer for a null instrument, which obviates the necessity of changing the intermediate solution. In this cell the potassium chloride solution is separated from the intermediate chamber by a thin (0.05 mm.) glass bulb which conducts electricity sufficiently to charge a quadrant electrometer. See Fig. 1. This half cell cannot be used with a galvanometer as the resistance of the bulb is too high, but in case an electrometer must be used for other determinations the above electrode might be convenient for work involving measurement of hydrogen-ion concentration.

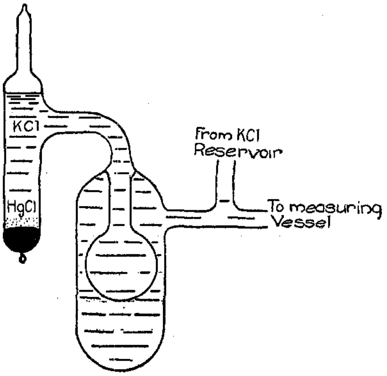

Fig. 1

It takes several days for the glass surface potentials of the bulb to become constant after the electrode is filled and, as the potential finally reached may be slightly different from that of an ordinary calomel electrode, a correction must be made for the discrepancy. This discrepancy can easily be measured by determining the potential of the mercury electrode against the hydrogen electrode in a solution of known hydrogen-ion concentration.

An electrode of this type has been used in this Laboratory for several months and has given satisfactory results.

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