largely attributed to the existence of compounds, cannot be quantitatively explained by the assumption that compounds exist which dissolve in mercury to give ideal solutions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Activity of Sodium and Mercury in Solid Sodium Amalgams

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The number and composition of the solid phases containing sodium and mercury have been the subject of much difference of opinion.[1] A study of the activity of sodium in the solid phase might well be expected to throw added light on this complex system.
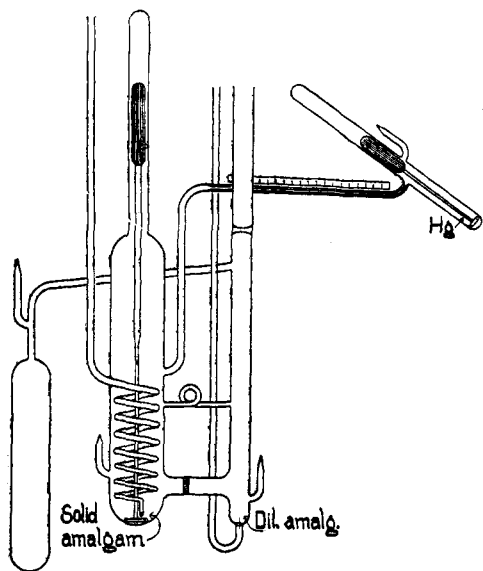

Fig. 1.

A second reason for studying the solid compounds of sodium and mercury arises in connection with the investigation of organo-metallic compounds. It is possible to determine the free energy change associated with the addition of sodium to various organic compounds by shaking the materials to be investigated with liquid sodium amalgams.[2] Many compounds, however, exhibit a stability which would necessitate the use of solid sodium amalgams in such an equilibrium determination. Recently the investigation of unsaturated hydrocarbons[3] has emphasized the need of studying such solid sodium amalgams.

(1) Paranjpe and Joshi, J. Phys. Chem., **36**, 2474 (1932).

(2) Bent et al., THIS JOURNAL, **52**, 1498 (1930); **53**, 1786 (1931); **54**, 3250 (1932); **57**, 1217, 1242, 1259, 1452, 1455 (1935); **58**, 1367 (1936).

(3) Bent and Keevil, ibid., **58**, 1367 (1936).

We have constructed cells in which one electrode is a dilute sodium amalgam and the other a solid amalgam, Fig. 1. The solid amalgams may be diluted by small additions of known quantities of mercury, thus covering the whole concentration range with one cell. The electrolyte is a solution of sodium iodide in dimethylamine. This solvent has been found to be well suited to cells of this type.[4] From the activity of the sodium the activity of the mercury can be calculated and the free energy of formation of the various solid phases.

Materials

All materials were handled in carefully evacuated and baked out glass apparatus. Stopcocks were replaced by glass tips to be broken by magnetic hammers.

Mercury was purified by washing with nitric acid and distillation.

Sodium was melted and allowed to flow through several constrictions in order to remove surface impurities. In one cell sodium was prepared by repeated distillation and this material compared with that which had only been filtered. These results justify the procedure of using material which has been subjected only to the removal of surface impurities.

Ethylamine and Dimethylamine.—Ethylamine was used in the earlier cells but is not entirely satisfactory as it reacts slowly with the amalgams. Dimethylamine has been shown by E. Swift, Jr., to be much less reactive and still to dissolve enough sodium iodide to serve as a good electrolyte. The amines were prepared in each case by treating the hydrochloride with sodium hydroxide. Much of the water vapor is removed by a reflux condenser. The amine is dried by allowing it to stand first over calcium oxide or activated alumina and then distilling it into a tube containing benzophenone and sodium–potassium alloy. The ketyl dissolves in the amine and indicates by its intense violet color the absence of all water. The amine is next shaken with fused sodium iodide in order to produce practically a saturated solution.

Sodium Iodide.—This material was first recrystallized and then fused in a covered platinum boat in a vacuum. Considerable difficulty is encountered in the process of fusion unless adequate precautions are taken. The vapor pressure of the iodide is so great at its melting point that it distils out of the platinum boat and condenses over the

(4) Bent and Swift, ibid., **58**, 2216 (1936).

surface of the quartz tube. This difficulty was avoided by covering the platinum boat with a tight fitting platinum cover. A small hole in the cover allowed a heavy platinum pin to project above the cover. When the iodide fuses the pin drops down into the boat thus indicating that the process is complete.

Experimental Procedure

The technique of handling cells containing solid sodium amalgams requires some comment as a great deal of difficulty was encountered. The high melting point of some of the amalgams (355°) makes it impossible to melt such an amalgam without distillation of mercury. Furthermore the amalgam adheres to the glass if clean and on cooling will crack even very rugged cells. It is almost impossible to keep amalgams in capsules and then introduce them into the cell as distillation is serious at the melting point and the labor of preparing and analyzing amalgams over the whole concentration range would be almost prohibitive.

Many types of cells were constructed and in most cases some useful data were obtained. The early cells contained ethylamine as the solvent. Later cells contained dimethylamine which is much more inert. Without going into the details of all of the types of cells investigated we will describe only the type used in constructing cells 10 and 11. Figure 1 illustrates the chief features of the cell. Contact is made with the solid amalgam by means of a long spiral which dips into the amalgam at the bottom. This was the only style of cell which was not cracked by the solidification of the amalgam. A stirrer which may be moved magnetically is also included in this cell in order to ensure homogeneity of the amalgam. A sintered Pyrex disk prevents any liquid amalgam from spattering or being dumped into the wrong electrode. A connecting tube above the level of the electrolyte equalizes the pressure on both sides and prevents undue stirring and bubbling of the electrolyte. The chief point of interest, perhaps, in this cell is the dilution device. Two types have been tried in different cells. The first type is perhaps a little more simple to construct but not quite so convenient to operate. By tipping the whole apparatus mercury in the reservoir is allowed to run into a short section of capillary which is within the reservoir. On turning the apparatus rapidly into a vertical position this slug of mercury runs down into a horizontal calibrated section of capillary tubing where it is measured by determining its length. Further tipping then pours this mercury into the cell. By this device it is possible to start with a small amount of a concentrated amalgam and carry it through practically the whole concentration range, admitting either large or small quantities of mercury as desired. A second device which accomplishes the same purpose is a little magnetic lift. In this case the apparatus need not be tipped. The reservoir is set at an angle of about 45° and within the mercury reservoir is a glass cylinder containing soft iron. To the end of this cylinder is attached a glass rod which terminates in a ring of glass which is ground to fit the inside of the tube and to be flat on its upper surface. This gives a right angle at the point of contact of ring and tube. When the cylinder is raised a drop of mercury is carried upward to the point at which it runs into the side-arm and down into the capillary

to be measured. After a little practice this was found to be a much easier method of diluting the amalgam.

Other experimental details were very similar to those previously recorded.[5] A type K potentiometer was used with a type HS galvanometer sensitive to 10^{-10} amp. The resistance of the cells was of the order of one megohm. Usually a cell could be measured to 0.01 mv. However, the e. m. f. fluctuated from day to day in the most favorable cases by several hundredths of a millivolt and, in the case of some unstable amalgams to be discussed later, by several hundredths of a volt.

In the case of low melting amalgams the electrolyte was poured into the side bulb before diluting the amalgam. The amine could then be cooled with Dry-Ice while the mercury was being added and the amalgam melted and stirred. The highest melting amalgams could only be studied by admitting nitrogen into the system as otherwise it was impossible to melt the amalgam without a great deal of distillation.

Experimental Results

The experimental results are recorded in Table I and in Fig. 2. It would be impossible to give all of the observations without taking up an inordinately great amount of space. Eleven cells

TABLE I

OBSERVED ELECTROMOTIVE FORCE

Composition of solid electrode	Mole fraction of reference electrode	Obsd. e. m. f.
Na + liq.	0.03270	0.8150
Na₈Hg + Na₈Hg₂	.03270	.7950
Na₈Hg₂ + NaHg	.03270	.7600
NaHg + Na₇Hg₈	.03270	.7400
Na₇Hg₈ + NaHg₂	.03270	.6500
NaHg₂ + NaHg₄	.03206	.1800
NaHg₄ + liq.	.03206	.0350

The error in the e. m. f. in most cases is probably not greater than 1 mv. although it may be as large as 5 mv. in the case of the fourth value in the column.

were studied, in some cases over a period of several months. In the early part of the work it seemed almost impossible to discover any meaning in the data. The e. m. f.'s were frequently very fluctuating and often an amalgam gave a higher e. m. f. after adding mercury than it did before. Gradually, however, as data were accumulated, it became evident that cells were likely to be very unstable when the composition was very near that of one of the compounds. When the composition was about half-way between that of two compounds the e. m. f. was usually very satisfactory. Frequently just after diluting an amalgam the e. m. f. would be very low and gradually rise and become steady when it came to the value at which other amalgams had become steady. A possible explanation for this phenomenon would

(5) Bent and Gilfillan, THIS JOURNAL, 55, 3989 (1933).

be that on cooling a liquid amalgam a solid solution is first formed which gradually goes over into the two stable crystalline compounds. Another curious phenomenon was that frequently an e. m. f. was observed corresponding to a pair of compounds which could not possibly represent the over-all composition of the electrode. In fact further dilution would in these cases sometimes raise the e. m. f. to that to be expected from the total composition of the electrode, as is shown by the points in Fig. 2. This phenomenon can
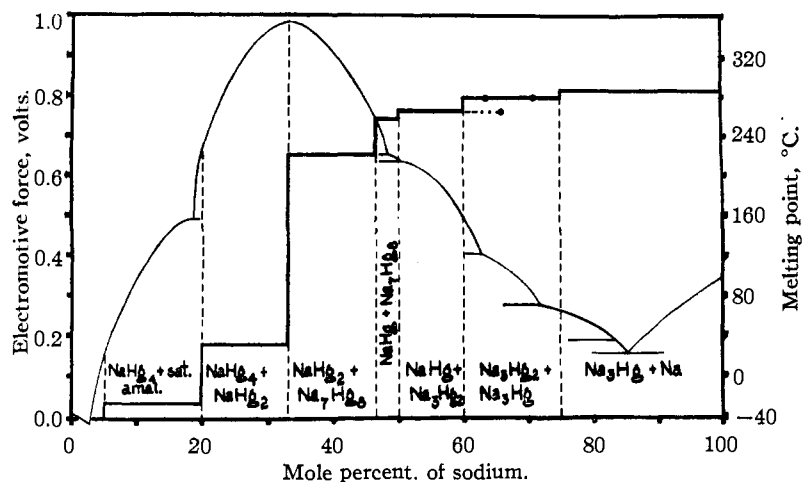

Fig. 2.

only mean that, on cooling, the liquid becomes supersaturated with respect to several compounds simultaneously and that it is more or less a matter of chance which compounds are formed. The curious part of this behavior, however, is that these metastable compounds are able to dominate the situation and determine the value of the e. m. f. of the cell.

The experimental results given in Fig. 2 and in Table I give the e. m. f. produced by the difference in the activity of sodium in a dilute amalgam and a solid amalgam. A typical half cell reaction at the solid amalgam electrode is $2NaHg_2 = NaHg_4 + Na^+ + (-)$ and at the dilute amalgam electrode is $Na^+ + (-) = Na_{dil. amalg.}$. Since it has been shown[6] that the activity of sodium in a saturated amalgam in which the mole fraction of sodium is 0.857 is the same as that of solid sodium, our measurements may all be referred to pure metal by taking our first electrode as our point of reference. This then gives the activity of sodium in the various two-phase solid amalgams as shown in the first five entries in Table II. These data

(6) Gilfillan and Bent, THIS JOURNAL, **56**, 1505 (1934).

we hope to use in interpreting reactions involving solid sodium amalgams.

Knowing the activity of sodium over the whole range of concentration one would expect to be able to calculate the activity of mercury by a process similar to that employed in using the partial molal equation[7]

$$\log \frac{a_1}{N_1} = - \int_0^{N_2} \frac{N_2}{N_1} d \log \frac{a_2}{N_2}$$

In this case the process is one of summation due to the formation of definite compounds. Table II gives the data for the activity of mercury over the whole range of concentration and also the free energy of formation of the various solid compounds. The first five equations represent the reactions involved in our cells, giving rise to the observed e. m. f.'s. The values of ΔF are calculated from the experimental measurements. The value for reaction 6 has been taken from the data of Bent and Swift.[4] Reactions 7–11 are of interest in indicating the relative stability of the various compounds and are also useful in calculating the activity of mercury in these solid amalgams. Reactions 12–16 describe the changes involved in starting with sodium and adding mercury. If a cell were possible which would be reversible to mercury rather than to sodium the e. m. f. would be determined by these equations. The next-to-the-last column in the table gives the method of computing the various values of ΔF. The numbers in parentheses refer to equations given in the same table. The equations when combined as indicated give the desired reaction and the corresponding value for ΔF.

The last column of the table gives the activity of sodium (a_2) and the activity of mercury (a_1) in solid amalgams of various concentrations. The liquid phase, occurring at 85 atom % sodium is not discussed here as it has been reported previously.[6] The activity of sodium in this liquid amalgam is practically the same as that of the pure metal.

The equations written in Table II are deduced

(7) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 269.

<div align="center">TABLE II</div>

		$-\Delta F$, kcal.	Equations used	a_2
1	$Na_3Hg_2 + 3Na = 2Na_3Hg$	1.384		0.459
2	$2NaHg + Na = Na_3Hg_2$	1.269		.117
3	$Na_7Hg_8 + Na = 8NaHg$	1.730		.0539
4	$4NaHg_2 + 3Na = Na_7Hg_8$	11.417		.00162
5	$NaHg_4 + Na = 2NaHg_2$	14.672		1.75×10^{-11}
6	$4Hg + Na = NaHg_4$	18.296		
7	$2Hg + Na = NaHg_2$	16.484	$^{1}/_{2}((5) + (6))$	
8	$8Hg + 7Na = Na_7Hg_8$	77.353	$(4) + 4(7)$	
9	$Hg + Na = NaHg$	9.885	$^{1}/_{8}((3) + (8))$	
10	$2Hg + 3Na = Na_3Hg_2$	21.039	$(2) + 2(9)$	a_1
11	$Hg + 3Na = Na_3Hg$	11.212	$^{1}/_{2}((1) + (10))$	6.0×10^{-9}
12	$NaHg_2 + 2Hg = NaHg_4$	1.812	$(6) - (7)$	0.217
13	$Na_7Hg_8 + 6Hg = 7NaHg_2$	38.035	$7(7) - (8)$	2.25×10^{-5}
14	$7NaHg + Hg = Na_7Hg_8$	8.158	$(8) - 7(9)$	1.05×10^{-6}
15	$Na_3Hg_2 + Hg = 3NaHg$	8.616	$3(9) - (10)$	4.8×10^{-7}
16	$Na_3Hg + Hg = Na_3Hg_2$	9.827	$(10) - (11)$	6.2×10^{-8}

partly from the work of Vanstone,[8] Schuller[9] and Kurnakow[10] and partly from the results of this investigation. Vanstone and Schuller agree very well in the formulas to be assigned to the various compounds. Both agree in writing $NaHg_4$, $NaHg_2$, $NaHg$, Na_3Hg_2 and Na_3Hg. The compound Na_7Hg_8 is perhaps not quite so certain. Schuller writes $Na_{12}Hg_{13}$. Kurnakow agrees with the above list although he does not report either of these last two compounds or Na_3Hg_2.

The results of our investigation agree perfectly with the list of Vanstone. We are not able to contribute anything very definite to the discussion of the compound Na_7Hg_8 although we did have a few points which could most readily be interpreted as due to some such compound. The evidence is very good, however, in the case of the compound $NaHg_4$. The change in e. m. f. was abrupt and large at 20 atom % sodium and the e. m. f. beyond this point is that observed between a saturated amalgam and one in which the concentration of sodium is 3.27 atom %.[4] This clearly indicates that no compound was present such as $NaHg_5$ or $NaHg_6$ as has been previously suggested.

The activities listed in the last column give information which will be useful in studying chemical reactions involving solid amalgams. The activity of mercury gives a measure of the efficiency of sodium in replacing liquid air or Dry-Ice as a mercury trap in a vacuum line.[11] At 25° the vapor pressure of mercury above liquid

85 atom per cent. amalgam is 1.2×10^{-11} mm. while the vapor pressure of mercury at the temperature of Dry-Ice is 10^{-9} mm. Hence this liquid amalgam should be one hundred times as good as Dry-Ice in removing mercury vapor in a vacuum line. We may also conclude from the data in the last column that on heating a solid amalgam the metal which will distil will probably be mercury. This follows from the fact that at room temperature the ratio of the vapor pressure of mercury to that of sodium is about 10^{11}. Consequently, even in amalgams rich in sodium the mercury will have the higher vapor pressure. At elevated temperatures it is not as easy to make predictions. Undoubtedly the mercury will have the higher pressure from all amalgams except possibly those richest in sodium. The higher heat of vaporization of sodium would tend to increase its vapor pressure faster than that of mercury but this would be complicated by the change in the stability of the various compounds which would probably tend to increase the vapor pressure of mercury.

Conclusions

1. A potentiometric method is described for studying intermetallic compounds at room temperature.

2. Values are given for the free energy of formation of $NaHg_4$, $NaHg_2$, $NaHg$, Na_3Hg_2 and Na_3Hg. The value for Na_7Hg_8 is not so reliable.

3. The activity of mercury and sodium in solid amalgams of all concentrations is computed.

(8) Vanstone, Trans. Faraday Soc., 7, 42 (1911).
(9) Schuller, Z. anorg. Chem., 40, 385 (1904).
(10) Kurnakow, ibid., 23, 434 (1900).
(11) Poindexter, Phys. Rev., 28, 208 (1926).

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