[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Activity of Sodium in Dilute Sodium Amalgams

BY H. E. BENT AND E. SWIFT, JR.

The thermodynamic properties of sodium amalgams have been investigated previously by a number of workers.[1] The potentiometric method of Richards and Conant used, as an electrolyte, an aqueous solution of sodium hydroxide. Lewis and Kraus,[2] in determining the standard electrode potential of sodium used a solution of sodium iodide in ethylamine. By combining these two sets of data one can calculate the activity of sodium in dilute sodium amalgams referred to the pure metal as the standard state. Recently, however, it has been shown that the potential of a concentration cell may be affected by the nature of the electrolyte.[3] The explanation for this behavior is not known but presumably the electrolyte either alters the number of equivalents of alkali metal transferred per faraday due to the formation of a complex ion or gives rise to some side reaction. It therefore seemed desirable to check data previously reported by the use of other solvents and with varying concentrations of electrolyte.

A further reason for again studying these amalgams arose in the effort to interpret the shape of the curve obtained by plotting the values of the logarithm of the activity coefficient against the concentration of the sodium. The variation in the values determined for the most dilute solutions on account of reaction with the aqueous electrolyte made it impossible to distinguish between a physical and a chemical explanation for the deviations from Raoult's law in this region.

Finally, it seemed worth while to develop the technique of these measurements to a considerably higher point before studying further amalgams of the other alkali metals. We are interested in having data on the thermodynamic properties of alkali metal amalgams in connection with a program of studying the free energy of formation of various organo metallic compounds with the aid of amalgams.

The most accurate element in this investigation seemed to be the determination of the potential between amalgams of various concentrations. We therefore attempted to bring the various other errors down to the order of 0.01%. We first investigated a number of solvents in order to find one which would dissolve sufficient sodium iodide to give a good conductivity and still not react with the sodium amalgam or metallic sodium. Great care was exercised in filling the cells and in controlling the temperature during measurement. Finally, considerable time was spent in improving the accuracy of the analysis and discovering the sources of error in this determination.

Solvent.—The solvents heretofore used in the study of amalgam concentration cells have been water, ethylamine and ether. Water obviously is far from ideal on account of its rapid reaction with amalgams. Ethylamine, used by Lewis and Kraus, is very much better but even this solvent reacts slowly with metallic sodium. Ether is better from the standpoint of reaction with the metal. However, as shown by Gilfillan, the electromotive forces obtained by dissolving organo metallic compounds in ether are not reproducible and do not agree with those obtained with other solvents.

Dimethylethylamine was prepared by treating dimethylamine with diethyl sulfate at 80° for twenty-four hours. The yield was very poor—about 1%. The product was purified by distillation and dried before using. Dimethylamine, diethylamine and ethylamine were purchased from Eastman Kodak Co. and purified and dried before use. The amine was first dried by distillation onto calcium oxide or activated alumina and then onto sodium benzophenone. It was sealed in glass capsules which were later broken into an evacuated system. The sodium iodide was fused in vacuum in a platinum boat according to the method of Forziati.[4] As will be seen from Table I only ethylamine and dimethylamine dissolve sufficient sodium iodide to be suitable solvents.

TABLE I

SPECIFIC CONDUCTANCE

	Mhos
Dimethylethylamine + NaI (satd.)	$<10^{-10}$
Diethylamine	3×10^{-12}
Diethylamine + NaI (satd.)	3×10^{-9}
Dimethylamine	1×10^{-10}
Dimethylamine + NaI (satd.)	2×10^{-4}
Ethylamine	1×10^{-9}
Ethylamine + NaI (satd.)	$>1 \times 10^{-4}$

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[1] (a) Richards and Conant, THIS JOURNAL, **44**, 601 (1922); (b) Bent and Hildebrand, *ibid.*, **49**, 3011 (1927); (c) Gilfillan and Bent, *ibid.*, **56**, 1505 (1934).

[2] Lewis and Kraus, *ibid.*, **32**, 1459 (1910).

[3] Bent and Gilfillan, *ibid.*, **55**, 247 (1933).

[4] Forziati, *ibid.*, **58**, 2220 (1936).

These two amines were then compared to determine the relative speed of the reaction with alkali metal. For this purpose sodium-potassium alloy was introduced into a small tube connected to a second tube carrying a pair of platinum electrodes. The amine could be distilled into the tube containing the electrodes to measure its conductivity or the solution could be poured in and the course of the reaction followed by the change in conductivity. It was found that ethylamine reacted about one hundred times faster than dimethylamine and gave solutions which were of the order of one hundred times more conducting as a result of reaction with the alloy. This treatment is probably much more severe than necessary but gives a rapid method of comparing the inertness of the two liquids. The ethylamine very quickly became colored and at times bubbles could be observed rising from the surface of the alloy in contact with this liquid, while the dimethylamine remained perfectly clear. The results of these experiments are recorded in Table II and indicate clearly that dimethylamine is much to be preferred.

TABLE II

SPECIFIC CONDUCTANCE OF AMINES IN CONTACT WITH NaK ALLOY

Time, hrs.	Dimethylamine	Ethylamine
0	10^{-10}	10^{-9}
1	10^{-9}	5×10^{-8}
24	2×10^{-9}	4×10^{-7}
48	3×10^{-9}	6×10^{-7}

Analysis.—Since the analysis of the amalgams is the part of the problem which introduces the greatest part of the experimental error, a great deal of time was spent in improving this procedure. A great many precautions were taken in standardizing the acid used in the titration and in extracting the sodium from the amalgam. Only a few of these will be mentioned here. The carefully purified sodium carbonate was fused in a stream of dry carbon dioxide. All titrations were carried out in quartz flasks with air, free from carbon dioxide, passing through the flask at the end-point. Weight burets were used, one containing sulfuric acid approximately 0.5 *N* and the other acid approximately 0.01 *N*. Standard base was not used in the titration, the initial alkaline solution being decanted from the amalgam in order that an excess of acid could be added to remove the last of the sodium. The initial alkaline solution was then added and the titration carried just to the end-point with brom thymol blue. All amalgams were prepared by distilling mercury onto sodium which had been filtered through several constrictions. The amalgam was then transferred to storage flasks and capsules which had been baked and evacuated at 450°. Samples were removed for analysis or for the preparation of a cell by means of tips broken by magnetic hammers. The general style of cell was the same as that used by Gilfillan.[5] No stopcocks were used at any point in the line, however. With the aid of the above precautions the precision of the analysis appeared to be 0.02% as judged by the agreement of successive runs.

Thermostat.—The temperature of the thermostat was controlled by means of a 24-junction copper–constantan thermocouple. The potential from this thermocouple was balanced by a small potentiometer which was kept, with dry cells used for its operation, in another thermostat at 25°. When off balance the current generated deflected a spot of light thrown by a spot light onto a galvanometer and reflected to a photocell. The remainder of the control is illustrated in Fig. 1. This use of the thyratron in a phase-shift circuit results in an adjustment of the current sixty times a second. This arrangement was worked out with the details as shown in the figure by Professor W. B. Nottingham of Massachusetts Institute of Technology and proved very satisfactory. There was no tendency of the temperature to oscillate and the temperature could be kept constant at any desired point to 0.01°. Greater precision could have been obtained by using a larger thermostat and a thermocouple with a greater number of junctions or a more sensitive galvanometer. All that was necessary to operate the cell at lower temperature was to adjust the temperature roughly by an increase in the flow of cooling water and then to set the potentiometer for the desired temperature. Switch "G" was added in order to allow the temperature to be raised rapidly.

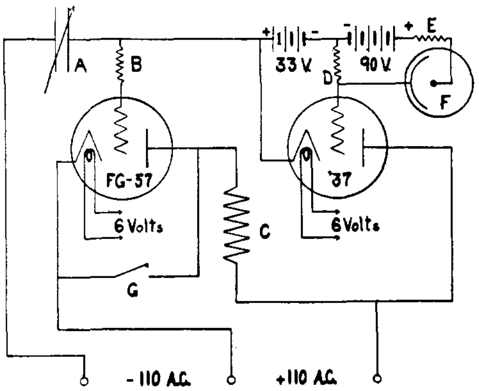

Fig. 1.—Control circuit used for thermostat: A, 0.0001 mfd. variable condenser; B, 50,000-ohm variable resistance; C, 125-watt "lagless" heater (in bath); D, 10-megohm resistance; E, 2-megohm resistance; F, photoelectric cell, type 71-A; G, switch used for rapid heating.

Experimental Results

Seven cells were constructed including eight amalgams of varying concentrations, one of which was two phase. One cell was designed to permit successive dilution of the electrolyte. Over a range of one thousandfold in the concentration of sodium iodide there was no change in the e. m. f. which was greater than the experimental error. However, in the case of the most dilute solutions the resistance was so high that it was difficult to obtain measurements which were reproducible to better than about 1%. This experiment proves that there is no variation in e. m. f. with this electrolyte comparable to the 50% variation found by Gilfillan with ether solutions of organo metallic

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

TABLE III

MOLE FRACTION OF AMALGAMS AND OBSERVED E. M. F.

No.	N_2	5°	15°	25°	Reference electrode
1	Two phase	0.01600 ± 20	0.02348 ± 1	0.03157 ± 5	4
2	0.0489708	....	.05582	.05732	5
3	.0394227	.03920	.04020	.04131	5
4	.0336062	.02980	.03066	.03151	5
5	.0177086	.00000	.00000	.00000	5
6	.0120373	− .01418	− .01460	− .01501	5
7	.0042270	− .04631	− .04777	− .04921	5
8	.00042375	− .10497	− .10844	− .11193	5
3	.0394227	− .81600	− .81445	− .81338	Sodium
3	.0394227			− .81336	
7	.0042270			− .89418	Sodium

compounds. The cross checks obtained by comparing various pairs of amalgams in a single cell were usually good to 0.01 mv. The values for pairs of amalgams occurring in different cells were good to 0.03 mv. From all of these cells data were obtained over many weeks and at 5, 15 and 25°. Two cells contained metallic sodium. The results are given in condensed form in Table III. From these data three equations were obtained by the method of least squares to represent log a_2/N_2 as a function of N_2. The form of expression found satisfactory is of the familiar type, $\log a_2/N_2 = a + bN_2 + cN_2^2$, the last term contributing relatively little to the expression. The average deviation of the experimental points from the curve was 0.0015, which corresponds to about 0.06 mv. error in the e. m. f. or about 0.1% in the analysis of the more concentrated amalgams. It was found possible to combine these three equations, obtained by least squares

$$\log a_2/N_{2\,25^\circ} = -12.81441 + 15.6130N_2 + 7.530N_2^2$$
$$\log a_2/N_{2\,15^\circ} = -13.32030 + 15.87260N_2 + 7.110N_2^2$$
$$\log a_2/N_{25^\circ} = -13.86807 + 16.1820N_2 + 5.970N_2^2$$

into a single simple equation involving the temperature without seriously sacrificing the accuracy of the data. This equation is

$$\log a_2/N_2 = \frac{-8387.6}{T^{1.138}} + \frac{338.2}{T^{0.54}}N_2 + 7.0N_2^2$$

Values of log a_2/N_2 calculated by means of this equation usually differed from those calculated by the three separate equations given above by less than 0.001. From this more general equation the following equations have been derived for the partial molal free energy, entropy and heat content of sodium and mercury, following the methods used by Bent and Gilfillan.

$$\overline{F}_2 = 4.57393\,T\log N_2 - \frac{38364.30}{T^{0.138}} + 1546.9N_2T^{0.46} + 32.0N_2^2T$$

$$\overline{S}_2 = -4.57393\log N_2 - \frac{5294.27}{T^{1.138}} - \frac{711.574}{T^{0.54}}N_2 - 32.0N_2^2$$

$$\overline{H}_2 = \frac{-43658.57}{T^{0.138}} + 835.3N_2T^{0.46}$$

$$\overline{F}_1 = 4.57393\,[T\log N_1 - 169.1N_2^2\,T^{0.46} - (338.2T^{0.46} + 14T)\,x\,(N_2^3/3 + N_2^4/4\ldots)]$$

$$\overline{S}_1 = -4.57393\,[\log N_1 - \frac{77.786}{T^{0.54}}N_2^2 - \left(\frac{155.57}{T^{0.54}} + 14\right)(N_2^3/3 + N_2^4/4\ldots)]$$

$$\overline{H}_1 = 4.57393\,[-91.3\,N_2^2T^{0.46} - 182.6T^{0.46}\,(N_2^3/3 + N_2^4/4\ldots)]$$

Introducing the values for the e. m. f.'s of sodium to the saturated amalgams into the equation obtained by the method of least squares for each temperature and solving for the concentration, three values were obtained for the solubility of sodium in mercury.

TABLE IV

SOLUBILITY OF SODIUM IN MERCURY

Temp., °C.	Mole fraction of Na
5	0.043955
15	.04870
25	.05380

Our results may be compared first with those of Lewis and Kraus. They report an e. m. f. between an amalgam whose concentration is 0.2062 wt. % sodium and pure sodium of 0.8456 which is equal to 0.8453 international volt.(6) We find from our equation a value for this e. m. f. of 0.8448 using the equation derived from the experimental data at 25° and a value of 0.8449 v. using our more general equation which includes the temperature. The disagreement between our value and that of Lewis and Kraus is considerably more than the experimental error which they attribute to their result. A check on our result has been obtained by A. F. Forziati using entirely different apparatus in work soon to be reported. His measure-

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(6) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 415.

ments agree with our results for the e. m. f. between sodium and an amalgam of a given concentration to 0.1 mv. Our agreement with Lewis and Kraus in the temperature coefficient of this cell is not entirely satisfactory. They report a value of −0.0000408 v. per degree for the range 10–35°. As will be seen from Table V the temperature coefficient is changing rather rapidly with the temperature. The average value which we obtained by calculating the activity at 10 and 35° does not agree well with that of Lewis and Kraus and the value at 25° is still further from their value.

TABLE V

CALCULATED VALUES OF dE/dT

Temp., °C.	$-dE/dT$
5	0.000059
15	.000043
25	.000029
10–35	.000032

We have also compared our data with those of Richards and Conant. Their experimental data are shown by crosses on our plot in Fig. 2. They did not determine the potential of any amalgam against sodium. Their points have been placed on our plot by arbitrarily adding a constant to the values of log a_2/N_2 which would give the best agreement with their data. The agreement of their data with those reported in this investigation seems remarkably good considering the difficulties which they encountered in working with water solutions. Their data have been calculated in a similar manner by Bent and Hildebrand but these results do not entirely agree with our present calculations, apparently due to some error in the earlier calculations.

We have also compared our temperature coefficients with those observed by Richards and Conant. The agreement here is remarkably good, probably within our experimental error.

TABLE VI

COMPARISON OF dE/dT WITH DATA OF RICHARDS AND CONANT

Amalgams of R. and C.	dE/dT R. and C.	dE/dT B. and S.
18–20	0.093	0.091
18–19	.156	.151
20–21	.164	.158
21–22	.059	.062

Finally, from our equations we have calculated the free energy of formation of $NaHg_4$ and values for the solubility of sodium in mercury. These data were obtained from measurements on the two-phase amalgam. The potential between the two-phase amalgam and sodium is shown in Fig. 2 and gives, with the aid of the equation for the curve, the concentration of the liquid phase. From the activity of sodium and mercury in this amalgam we then calculate the value −18,296 kcal. for ΔF.

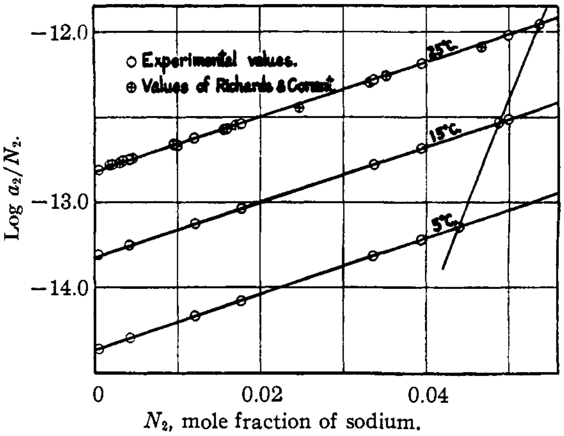

Fig. 2.—○, Experimental values; ⊕, values of Richards and Conant.

The choice of explaining the deviation from ideal solution by either compound formation or a more general physical picture seems to be pretty clearly answered by our data. Whatever compounds may be present at higher concentrations the behavior of the dilute amalgams cannot be explained by such assumptions alone. The plot of log a_2/N_2 is perfectly straight down to our most dilute amalgam. It has been shown by Bent and Hildebrand that even a compound containing as much mercury as $NaHg_{16}$, which is about as much as one can reasonably postulate, still gives a slight upward curvature in the very dilute range of concentration.

Summary

1. The thermodynamic properties of dilute sodium amalgams have been determined by means of concentration cells containing sodium iodide in dimethylamine as the electrolyte.

2. The solubility of sodium in mercury has been determined at 5, 15 and 25°.

3. The experimental results are compared with those of Richards and Conant on concentration cells and Lewis and Kraus on the sodium electrode.

4. The data on very dilute amalgams indicate that deviations from Raoult's law, which can be

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.

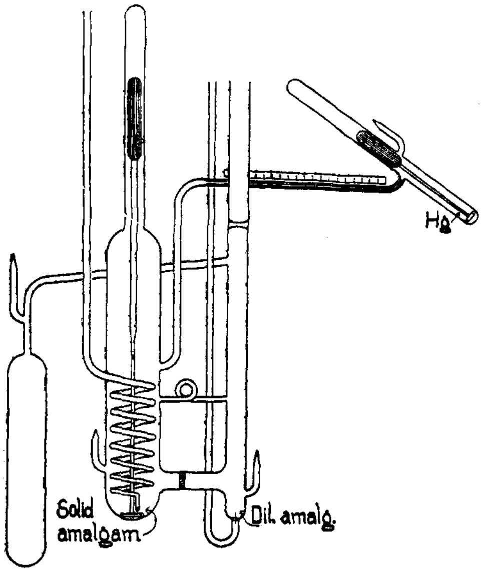

Fig. 1.

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.

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

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(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).

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