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ULTRASONICS AND ELECTROCHEMISTRY

THE ELECTROCHEMICAL PROPERTIES OF DILUTE SODIUM AMALGAMS

by

Harry Dietrick, Ernest Yeager,
and Frank Hovorka

Technical Report No. 3
Office of Naval Research

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Project No. NR 359-277

April 1, 1953

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Technical Report No. 3
April 1, 1953

Harry Dietrick, Ernest Yeager,
and Frank Foverka

- Abstract -

The electrochemical properties of dilute sodium amalgams have been studied in terms of electrode potentials, self-discharge rates, and anodic polarization. Even at current densities as high as 1 a./cm.^{2}, the anodic polarization, as determined by the commutator method, is negligible ($<$ 1 mv.) in an agitated system. Corrosion or self-discharge rates are also very small for liquid amalgams in sodium hydroxide solutions because of the depression of the electrode potential of the sodium in the amalgam and the relatively high hydrogen overvoltage of mercury.

Activity coefficients, based on electrode potential measurements with the amalgams in sodium hydroxide solutions, are in agreement with literature values.

The relatively high electrode potential and the non-polarizability of the liquid sodium amalgams suggest their use in high drain primary cells. Only a circulation type cell in which the amalgam is constantly replenished with sodium seems feasible. The engineering difficulties, however, would be substantial.

THE ELECTROCHEMICAL PROPERTIES OF DILUTE SODIUM AMALGAMS

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Harry Dietrick, Ernest Yeager,
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INTRODUCTION:

The electrochemical behavior of sodium amalgams is of interest in terms of fundamental as well as practical applications. Examples of the former are the determination of the activity coefficients for sodium in mercury, the measurement of activity coefficients in sodium hydroxide solution and overvoltage theory. Practical applications include the production of sodium hydroxide in the Castner-Kellner cell and the development of high drain primary batteries.

As part of contract research, the anodic polarization associated with sodium amalgams in basic solution has been determined. The results are described in Part I of the report. In Part II, data for the self-corrosion of sodium amalgams in basic solution are presented. Static potential measurements have also been made and the activity coefficients for the liquid sodium amalgams calculated. The latter are included in Part III.

I. THE ANODIC POLARIZATION OF SODIUM AMALGAMS:

The oxidation potential of pure sodium metal is sufficiently high (2.7v.) that the metal reacts very vigorously even with

alkaline solutions. The reaction of sodium amalgams in the liquid range (molefraction of sodium less than 0.05) with sodium hydroxide solutions, however, is very slow because of the high hydrogen overvoltage on mercury and the depression of the oxidation potential of sodium. Thus the electrochemical properties of these amalgams can be studied without the complications normally associated with excessive self-corrosion rates.

Anodic polarization measurements have been made by the commutator or indirect method with electronic equipment described elsewhere[1]. With this apparatus, the polarizing current is periodically interrupted and the potential of the polarized electrode measured relative to a reference electrode as little as one microsecond after the interruption of the polarizing current. In this way, the i-r drop associated with the passage of the polarizing current through the solution is not incorporated in the measurements. The electronic apparatus also permits the potential of the polarized anode as well as the cathode to be determined during any one-microsecond period following either the interruption or the initiation of the polarizing current; hence, the build-up and decay curves for the polarization can be obtained.

In Figure 1 is a diagram of the electrode arrangement involved in the polarization measurements. A platinized-platinum electrode was used as a cathode as a matter of convenience. Hydrogen gas was liberated at the cathode during the polarization measurements. The surface area of the amalgam in contact with the solution was

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1. Technical Report No. 6, ONR Contract No. N7 onr 47002, Project No. NR 051 162, Western Reserve University, April, 1951.

approximately 0.5 cm^2 while the apparent surface area of the cathode was approximately 1 cm^2. The fritted glass plug was used to saturate

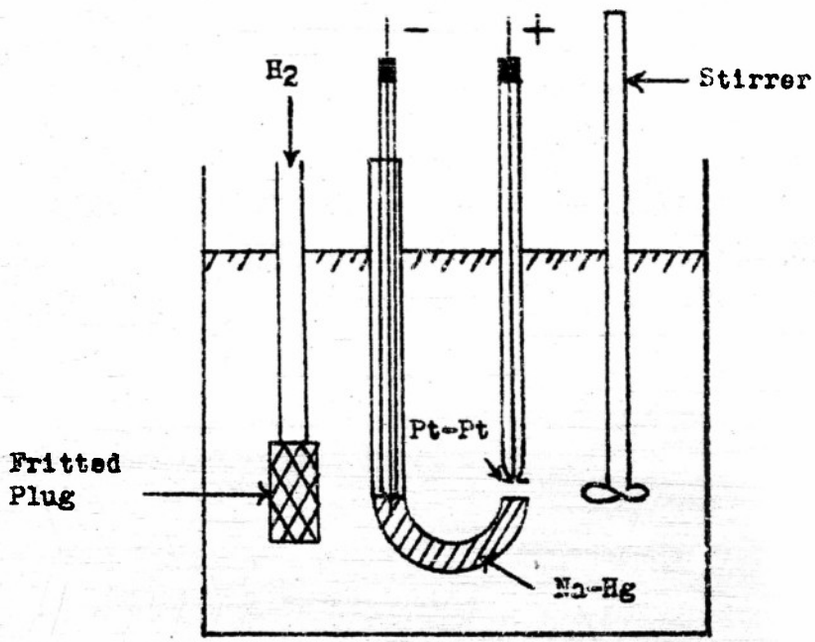

Figure 1: Cell for Polarization Measurements with Liquid Amalgams

the solution with hydrogen prior to measurements primarily in order to get reproducible values for the cathode potentials. The solution was agitated to a marked extent with a high speed stirrer during the polarization measurements. The agitation minimized concentration polarization and at the same time swept away the hydrogen gas which formed on the cathode. It should be noted that the polarizing current

was entirely controlled by the electronic equipment and independent of the cell electromotive force.

A reversible hydrogen electrode was used directly in the cell as a reference electrode for the early measurements. This electrode tended to become poisoned rather quickly because of very small quantities of mercury introduced into the solution from the anode. Hence, a saturated calomel electrode in a separate glass compartment was used as a reference electrode for most of the polarization measurements. The potential of the calomel reference electrode was checked against a reversible hydrogen electrode in the same solutions as involved in the polarization measurements. Thus the potentials of the polarized amalgam electrodes could be determined relative to the standard hydrogen electrode without the complications normally associated with liquid-junction potentials.

The graph in Figure 2 represents polarization data for an amalgam with 0.4% sodium (by weight) in 5 molar sodium hydroxide solution at 25°C. The interruption frequency for the polarizing current was 400 $sec.^{-1}$ and the interruption period (current-off) was 500 microsec. Curve I represents the terminal cell voltage and was obtained by measuring the potential between the anode and the cathode 1.5 millisec. after the initiation of the polarizing current. Voltage measurements with the electronic equipment indicated that the cell voltage had approached the steady-state value within approximately 1 mv. by this time following the initiation of the polarizing current. Curve II represents the EMF and was obtained by measuring the cell potential one microsec. following the interruption of the polarizing current. Curve III was obtained by taking the difference between the values

represented by curve I (cell voltage-current on) and curve II (cell voltage-current off). Thus, curve III represents the internal i-r drop within the cell under operating conditions. Curves IV and V represent the cathode and anode potentials, respectively, as functions of the polarizing current density. The data for curve IV were obtained by taking the difference between the cell voltage one microsec. after the interruption of the polarizing current and the potential of the anode relative to the reference calomel electrode. Both curves IV and V, however, represent the electrode potentials relative to the standard hydrogen electrode. Curve IV is typical for hydrogen overvoltage on platinized-platinum. The data for the sodium amalgam (curve V) are very interesting inasmuch as the potential measurements indicate negligible polarization for this electrode at current densities as high as 1 a./cm.^{2} when the electrolyte is agitated.

In addition to the practical significance of this extremely low polarization, this fact is of theoretical interest; it implies that the reverse process is also reversible through high current densities under similar circumstances. Such factors as hydration and ion migration through the double layer do not seem responsible for overvoltage with simple cations at current densities below 1 a./cm.^{2}.

II. THE SELF--DISCHARGE RATE OF DILUTE SODIUM AMALGAM ELECTRODES:

Quantitative information concerning the self discharge of dilute sodium amalgams is presented in Figure 3. These data were obtained by the following procedure. Approximately 250 cc. of an amalgam containing 0.61% sodium (by weight) were placed in a bottle with one

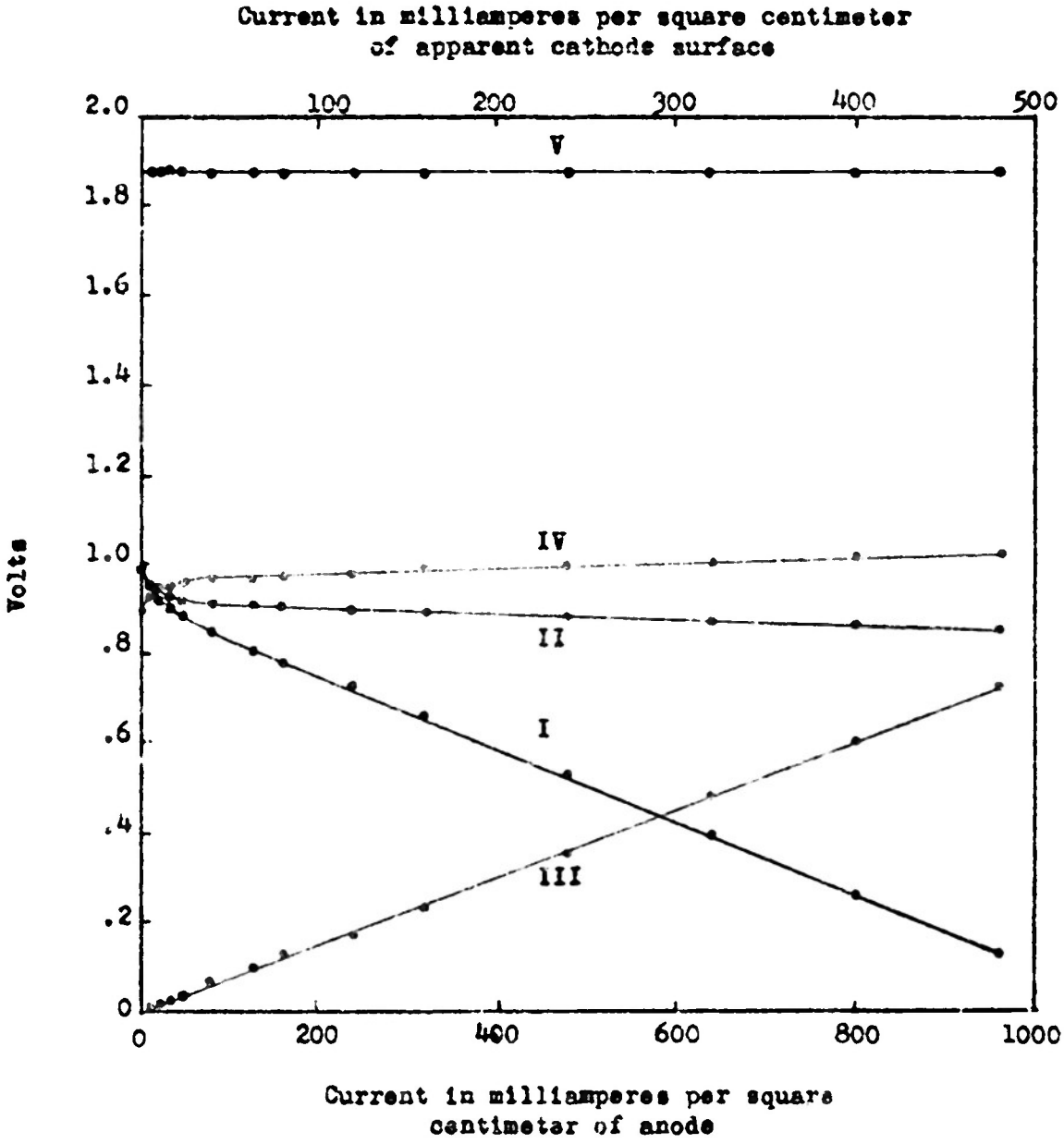

Figure 2: Cell Performance Data for a Sodium Amalgam-Hydrogen Cell (Curve I: cell voltage with current on; Curve II: cell voltage less i-r drop; Curve III: internal i-r drop; Curve IV: cathode polarization-hydrogen overvoltage on Pt-Pt; Curve V: anode polarization - Na(Hg).

liter of 5-molar sodium hydroxide. The contents of the bottle were shaken periodically. At various times, samples of the amalgam were removed from the system and weighed. The samples were then transferred into a flask containing a fixed quantity of 0.1 normal hydrochloric acid and a few particles of graphite were added. The latter produced a local couple which helped to ensure complete discharge of the amalgam. The amalgam-acid mixture was shaken, allowed to stand overnight, and then both titrated with 0.1 molar base.

From the graph in Figure 3, it is apparent that the corrosion of the amalgam in concentrated sodium hydroxide is slow. For the 0.4% sodium amalgam in 5-molar sodium hydroxide solution, the self discharge is estimated to be equivalent to less than 0.5 ma./cm^2 In the case of amalgams with concentrations of 0.1% or less (by weight), no hydrogen bubbles were evident in 5-molar base provided the surface of the amalgam were free of particles such as carbon. The relatively low corrosion rates reflect the high hydrogen overvoltage on mercury as well as the depression of the oxidation potential of the sodium through the amalgamation.

The addition of sodium chloride to the hydroxide solution to the extent of 30 g./liter does not seem to increase the self-discharge rate or to effect the electrode potential. Nitrates and other easily reduced ions produce a considerable increase in the corrosion of the amalgams as evidenced by the evolution of hydrogen gas.

At molefractions much above 0.06, sodium amalgams become solids at room temperatures, furthermore, the rate of corrosion increases very quickly and self polarization becomes excessive.

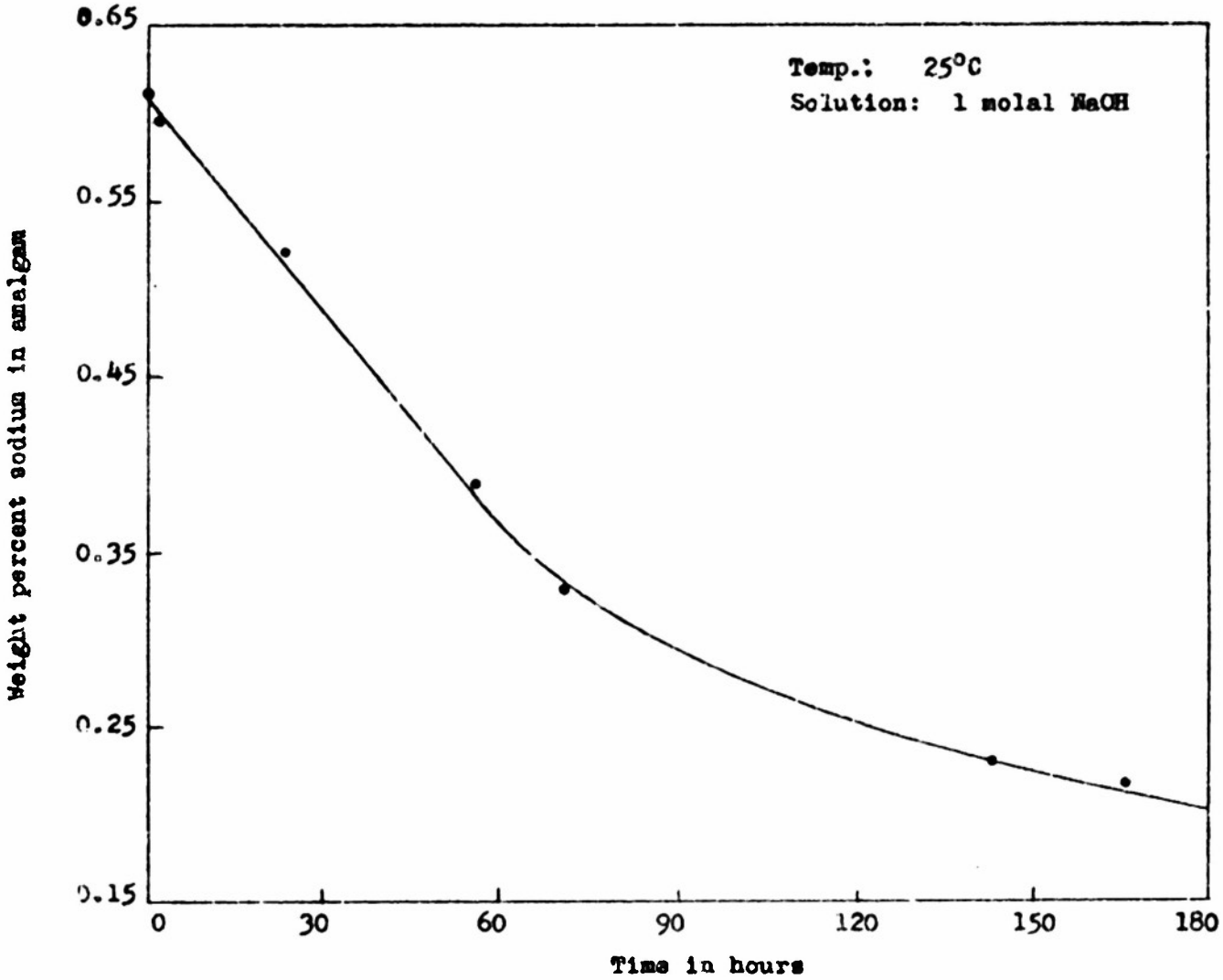

Figure 3: The Corrosion of Liquid Sodium Amalgams in Sodium Hydroxide Solution as a Function of Time

III. THE ELECTRODE POTENTIAL AND ACTIVITIES OF DILUTE SODIUM AMALGAMS:

The reversible potentials and activity coefficients of liquid sodium amalgams have been studied by many investigators. Historical accounts of the early work on amalgams through 1906 may be found in a paper by Richards and Forbes[2], and through 1919 in a publication by Richards and Conant[3].

In the latter paper, the electromotive forces of many sodium - amalgam concentration cells were measured in aqueous sodium hydroxide solutions. Bent and Hildebrand[4] used Richards' and Conant's data to calculate the activities of sodium in the amalgams, referred to pure sodium as the reference state:

$$\lim_{X_{Na} \to 1} \left[\frac{a_{Na}}{X_{Na}} \right] \longrightarrow 1$$

The deviations from perfect solution found in sodium amalgams are in part associated with compound formation. Both vapor pressure and electrode potential data for dilute sodium amalgams may be explained in terms of the formation of the compound $Na\,Hg_{16}$.

Lewis and Kraus[5] determined the standard electrode potential of sodium by measuring the EMF between a sodium amalgam and a normal calomel electrode in 0.2 molar sodium hydroxide solution and the EMF between the amalgam and sodium metal in a solution of sodium iodide in

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2. T. Richards and G . Forbes, Carnegie Inst. Pub., 56, 1 (1906).
3. T. Richards and J. Conant, J. Am. Chem. Soc., 44, 601 (1922).
4. H. Bent and J. Hildebrand, ibid., 49, 3011 (1927).
5. G. N. Lewis and C. Kraus, ibid., 32, 1459 (1910).

ethylamine[6,7]. Their data may be combined with that of Richards and Conant in order to calculate the activity of sodium in dilute amalgams.

The activity of sodium in concentrated liquid amalgams[8] and in solid amalgams[9] has been investigated. The activity of sodium in concentrated liquid sodium amalgams containing a molefraction of about 0.85 of sodium was found to be approximately the same as that of sodium metal.

The electrochemical properties of dilute sodium amalgams also have been studied[10] in concentration cells containing a solution of sodium iodide in dimethylamine. The results obtained in the non-aqueous cells were compared[10] with those of Richards and Conant. The agreement between these two sets of data is good.

The low corrosion rates and the reversible characteristics of sodium amalgams (demonstrated in Parts I and II) lead to confidence in the validity of activity data based on measurements with sodium amalgams in aqueous solutions.

In Figure 4 is a graph of the potentials of liquid sodium amalgams in a 0.9902-molal sodium hydroxide solution at 25°C. Potential measurements were made with a mercury-mercuric oxide reference electrode containing sodium hydroxide of the same concentration as in contact with the amalgam. This reference electrode was subsequently

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6. The nature of the electrolyte has been shown[7] to affect the potential of an amalgam-concentration cell in some cases. Bent and Gilfillan found erratic potentials for a cell involving a potassium amalgam-pure potassium couple in a solution of potassium triphenylmethyl in diethyl ether.

7. H. Bent and E. Gilfillan, ibid., 55, 247 (1933).
8. E. Gilfillan and H. Bent, ibid., 56, 1505 (1934).
9. H. Bent and Forziati, ibid., 58, 2220 (1936).
10. H. Bent and E. Swift, ibid., 58, 2216 (1936).

checked against a reversible hydrogen electrode in 0.9902-molal sodium hydroxide solution. All potential measurements were obtained with a Leeds and Northrup potentiometer, type K-2. The general agreement between duplicate determinations was of the order of a few tenths of a millivolt. The concentration of the sodium in each amalgam was determined by the back-titration procedure described in Part I.

The values on the left ordinate in Figure 4 represent the potentials of the amalgams relative to a reversible hydrogen electrode in a 0.9902-molal sodium hydroxide solution. The values on the right ordinate represent the potentials of the amalgams relative to a standard hydrogen electrode (without liquid junction potential) and are based on the assumption that the activity of the hydroxide ion is the same as the mean activity of the electrolyte.

The electrode potentials represented in Figure 4 should obey the Nernst equation:

$$\mathcal{E} = \mathcal{E}^{\circ}_{Na(Hg)} - \frac{RT}{\mathcal{F}} \ln \frac{(a_{\pm})^2 (p_{H_2})^{1/2}}{K_w \; a_{Na}} \qquad (1)$$

where $\mathcal{E}$ is the cell reaction potential (EMF) of the cell

Na (Hg) | NaOH | H_2 (Pt-Pt);

$\mathcal{E}^{\circ}_{Na(Hg)}$ is the standard oxidation potential for the amalgamated sodium, $a_{\pm}$ is the mean activity of the sodium hydroxide, K_w is the ionization constant for water, and $a_{Na(Hg)}$ is the activity of the dissolved sodium in the amalgam in terms of the reference state:

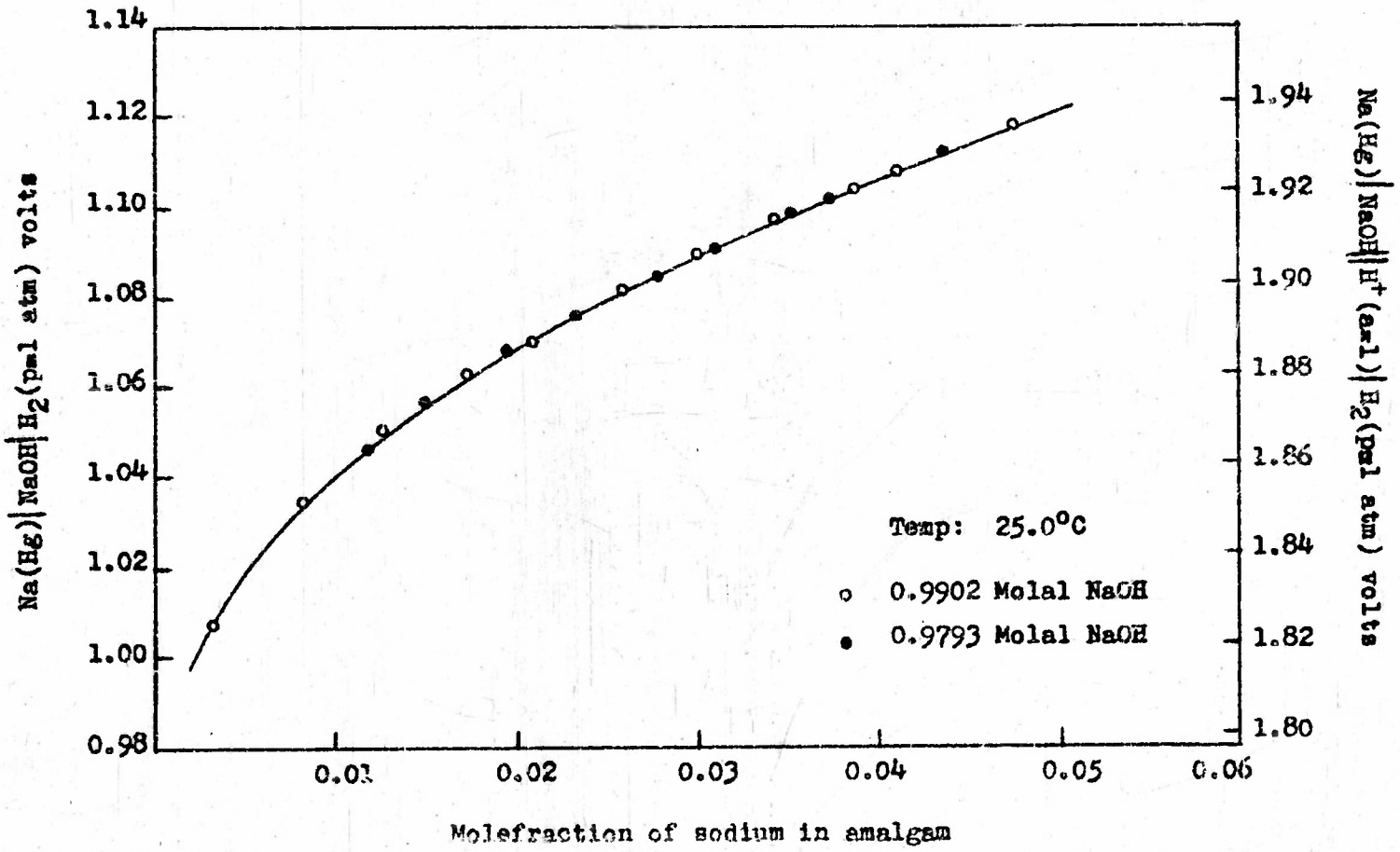

Figure 4: The Electrode Potentials of Dilute Sodium Amalgams

$$\lim_{X_{Hg}\to 1}\left[\frac{a_{Na}}{X_{Na}}\right] \longrightarrow 1 \qquad (2)$$

where X_{Na} and X_{Hg} are the molefractions of the sodium and mercury, respectively. According to the data[11] of Harned and Hecker, the interpolated value for the mean activity coefficient of the sodium hydroxide at 25°C is 0.679. Eq. (1) may then be expressed in the form:

$$\mathcal{E} - 0.05915 \log X_{Na} = \mathcal{E}^{\circ}_{Na(Hg)} - 0.05915 \log 4.375\cdot 10^{13} + 0.05915 \log \frac{a_{Na}}{X_{Na}} \qquad (3)$$

From equations (2) and (3), it is apparent that

$$\lim_{X_{Hg}\to 1}\left[\mathcal{E} - 0.05915 \log X_{Na}\right] \longrightarrow \mathcal{E}^{\circ}_{Na(Hg)} - 0.05915 \log 4.375\cdot 10^{13} \qquad (4)$$

Thus, by extrapolation of the term $[\mathcal{E} - 0.05915 \log X_{Na}]$ to zero molefraction of sodium, the standard electrode potential for the amalgamated sodium can be evaluated in terms of the reference state given above. By this procedure, the value for $\mathcal{E}^{\circ}_{Na(Hg)}$ is found to be + 1.9566 volts in contrast to the usual value of + 2.7 volts for pure solid sodium. The 0.7- volt difference is not surprising in view of the large amount of heat liberated upon formation of the liquid sodium amalgams.

Figures 5 and 6 represent graphs of the activities and activity coefficients for the sodium in the liquid amalgams as obtained in two

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11. H. Harned and J. Hecker, J. Am. Chem. Soc., 55, 4838 (1933), as quoted by H. Harned and B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd. Ed., New York, Reinhold Publishing Co., 1950, p. 560.

separate series of measurements. The activity data have been calculated from the potential measurements in Figure 4 by means of equation (1). The electrode potential data of Richards and Conant[3] and Bent and Swift[10] have also been used to calculate values for the activities and activity coefficients in terms of equation (1) and the reference state indicated by equation (2). These values are also shown in Figures 5 and 6. The agreement is quite satisfactory, particularly when one considers that Bent and Swift worked in non-aqueous media.

The linear dependence of the logarithm of the activity coefficients on molefraction of sodium in the liquid amalgams is interesting and can be partially rationalized in terms of compound formation between the sodium and mercury.

IV. THE SIGNIFICANCE OF DILUTE SODIUM AMALGAMS IN BATTERY DEVELOPMENT:

The relatively high electrode potential and the virtual non-polarizability of the dilute sodium amalgam anode suggest its use in high drain primary batteries. If the sodium amalgam anode is used with an oxygen electrode, an EMF of approximately 1.8 volts is obtained with 5-molar sodium hydroxide as the electrolyte. Sodium hydroxide would also be the product of the cell reaction; hence, the cell would generate its own electrolyte.

There are obvious disadvantages associated with the use of sodium amalgams in primary cells. Not the least of these are the weight of the mercury and the relatively low sodium content of the liquid amalgams. Solid sodium amalgams corrode at an excessive rate and polarize very readily. In a large installation the liquid sodium amalgam could be

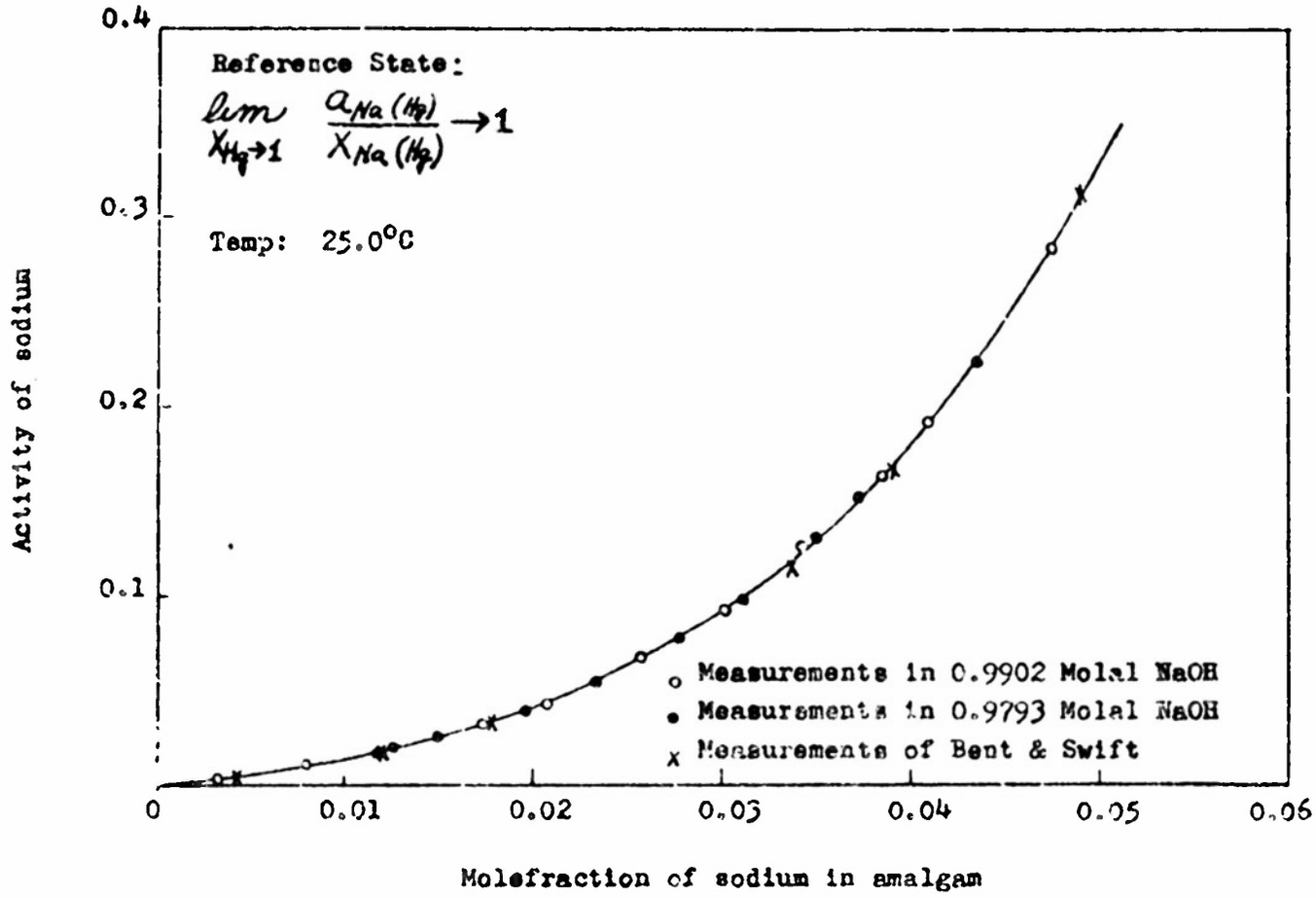

Figure 5: Activities of Sodium in Dilute Sodium Amalgams

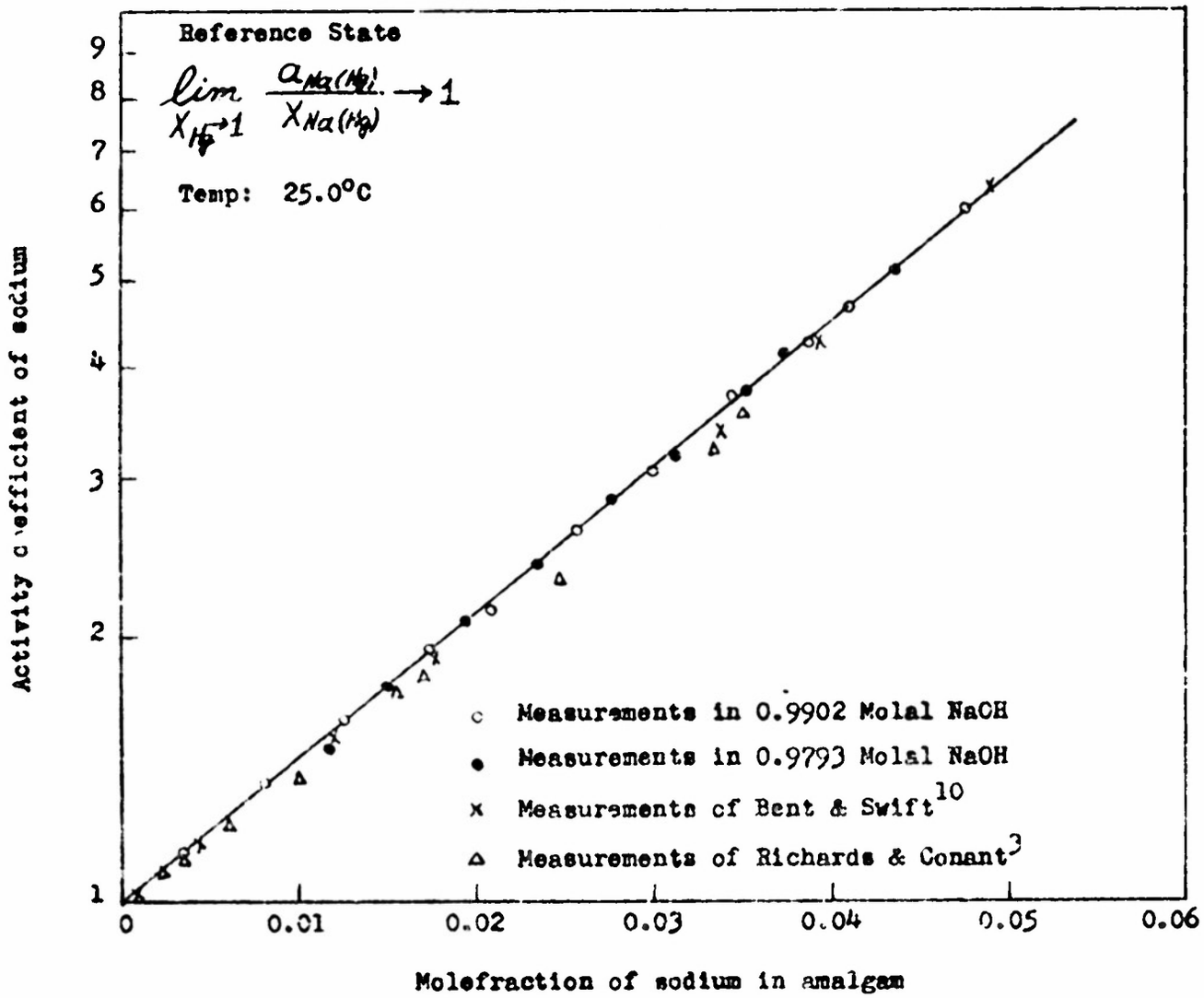

Figure 6: Activity Coefficients of Sodium in Dilute Sodium Amalgams

circulated with a special reactor outside the cells in which the sodium is continuously dissolved in the mercury. Isolation pumps would permit the anodes of cells in series to be constantly replenished with fresh amalgam. A horizontal-type construction would probably be most practical with porous separators of some type to isolate the amalgam from the cathode in the event that the cells were tilted. The engineering problems would be substantial, however.

The idea of using mixtures of metals for anodes in primary cells is promising. In good part the depression of the electrode potential of sodium in mercury is associated with the formation of a compound of the type $NaHg_{16}$.