THE STANDARD ELECTRODE POTENTIAL OF SODIUM

By

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SECTION I

INTRODUCTION

The reaction of the alkali metals with water disturbs
the equilibrium conditions necessary for direct measurements
of their electrode potentials. Thus for many years it was
believed impossible to determine these constants experi-
mentally. However, an indirect method which overcomes this
difficulty was devised by G. N. Lewis [16].[1] The method de-
pends on the possibility of measuring (a) the potential of a
dilute amalgam of the alkali metal with respect to an
aqueous solution of its ions and a reference electrode, and
(b) the difference in potential between the same amalgam
and the pure metal when both are immersed in a non-aqueous
conducting solution containing ions of the alkali metal.
The non-aqueous solvent must not react with the alkali metal
and must dissolve sufficient alkali salt to form a conduct-
ing solution. The success of the amalgam electrode in
aqueous solutions depends on the lowering of the activity of
the alkali metal and on the high hydrogen overvoltage of
mercury, which inhibits the reaction between the alkali metal
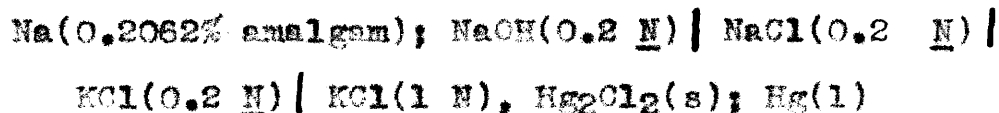and water.

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[1] Numbers in brackets refer to the reference of that
number in the bibliography.

The standard electrode potentials of all of the alkali metals have been measured by this indirect method [12, 13, 14,15]. However, these measurements have usually included one or more of the uncertainties caused by the use of liquid junctions, solutions for which the activities can only be approximated, and unreliable reference electrodes. Moreover, the determinations have only been made at one temperature.

The standard electrode potential of sodium in use today depends primarily on the value at 25° C obtained thirty years ago by Lewis and Kraus [12] for the non-aqueous cell

Na(s); NaI (in ethylamine); Na (0.2062% amalgam)

which they combined with a measurement on the aqueous cell

Na(0.2062% amalgam); NaOH(0.2 $\underline{N}$) | NaCl(0.2 $\underline{N}$) |

KCl(0.2 $\underline{N}$) | KCl(1 N), Hg_2Cl_2(s); Hg(1)

The calculation of the electrode potential from the emf of this aqueous cell involves corrections for three liquid junctions, the activity of 0.2 $\underline{N}$ sodium hydroxide, and the reference potential of the normal calomel electrode. Lewis and Randall [16] recalculated these corrections and obtained 2.7126 v for the standard electrode potential of sodium with respect to the hydrogen electrode. A more recent recalculation by MacInnes [18] in which the measurement of Lewis and Kraus on the non-aqueous cell is combined with an interpolated value for the cell

Na (0.2062% amalgam); NaCl (0.1005 m) Hg_2Cl_2; Hg(1)
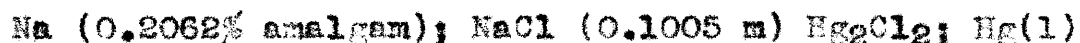
from the work of Allmand and Polack [1], gives 2.7139 v at

25° C. However, Allmand and Polack place a reproducibility of only 0.001 v on their original measurements and an interpolation of their results is possibly less precise.

Because of the importance of accurate values of the standard electrode potentials over a range of temperatures for thermodynamic and analytical calculations, it appears desirable to redetermine some of the older values. This paper gives the results of a redetermination of the standard electrode potential of sodium in which liquid junctions were eliminated and a reliable reference electrode was used. As in the pioneer work of Lewis and Kraus, a non-aqueous and an aqueous cell were used. Dimethylamine, instead of ethylamine, was used in the non-aqueous cell because Bent and Swift, Jr. [2] have shown that the former reacts with sodium much less readily than does ethylamine. The two cells may be represented by

Na(s); NaI (in dimethylamine); Na (amalgam)

and

Na(amalgam); NaCl(m), AgCl(s); Ag(s)

UNITS AND STANDARDS

According to computations to be published shortly by
C. S. Cragoe of the National Bureau of Standards [29], the
value of RT_O is 2271.16 abs. joules mole^{-1}. The value of
T_O, the temperature of the ice point, is taken as 273.16° K
[28], and the value of R is therefore 8.3144 abs. joules
deg.$^{-1}$mole^{-1}. To obtain the value of R in int. joules the
conversion factor of 1.00020 obtained from the critical
examination by Wensel [28] was used, thus giving R = 8.3127
int. joules deg.$^{-1}$mole^{-1}.

Wensel also has discussed the value of the Faraday
obtained from the silver and the iodine coulometers. The
full precision of the mean value is given by
$F = 9.650 \times 10^4$ int. coul. In chemical thermodynamics, quan-
tities of energy are frequently expressed in calories even
though these quantities are measured precisely in electrical
units. Unfortunately, the term calorie by itself is not
definite, since it may mean the heat capacity of water at some
temperature or it may signify a unit defined arbitrarily in
joules independently of the properties of water. The use of
the calorie as a unit of energy thus requires the statement of
a conversion factor which depends, for example, upon whether
the calorie recommended by the International Union of Chemistry
in 1934 [22] as 4.1833 int. joules, the International Steam
Table calorie of $\frac{3600}{860}$ abs. joules, or some other calorie is

used. The failure of many authors to state the conversion factors used in their calculations has resulted in considerable confusion and uncertainty of published values. Smith and Taylor [30] have proposed that the calorie be abandoned as a unit of energy in electrochemical investigations. In view of their proposal, the results in this paper are reported in int. joules, and the calorie is used only in calculations for comparison with measurements reported in calories by other workers.

The primary reference electrode with respect to which the values of standard electrode potentials are conventionally given is the standard hydrogen electrode, but for the actual measurements it is usually necessary to employ a secondary reference electrode. For many determinations the silver-silver chloride electrode is an excellent secondary standard. The conditions under which it is constant and reproducible have been investigated [25, 26, 27] and its value with respect to the standard hydrogen electrode has been particularly well studied over a range of temperatures (0 to 60° C) by Harned and Ehlers [6]. A recent recalculation of their results [5] yielded values which were neither seriously nor consistently different from the original figures. For the measurements of this paper, the values of Harned and Ehlers as expressed by their equation

$$E° = -0.22239 + 6.4552 \times 10^{-4}(t - 25) + 3.284 \times 10^{-6}(t - 25)^2 - 9.948 \times 10^{-9}(t - 25)^3$$

were adopted and are given in table I.

Table I.- Reference values of the standard electrode potential, E°, of the silver-silver chloride electrode and of the mean activity coefficient, f_m, of sodium chloride.

t	E°	$f_m(0.05\ m)$	$f_m(0.1\ m)$
° C	int. v		
5	-0.23391	0.8244	0.7808
10	- .23130	.8239	.7805
15	- .22851	.8233	.7800
20	- .22554	.8224	.7792
25	- .22239	.8214	.7782
30	- .21908	.8202	.7770
35	- .21562	.8189	.7756
40	- .21200	.8175	.7740

The sign of an electrode potential may be taken as
that of the hypothetical cell
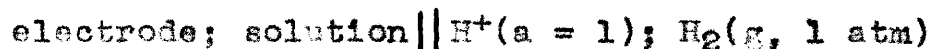
electrode; solution $\|$ $H^+(a = 1)$; $H_2(g, 1 \text{ atm})$
considered as positive when the electrode acts spontaneous-
ly as the anode and the hydrogen electrode as the cathode.
The double vertical lines indicate that liquid junctions or
their effects have been eliminated. The numerical value
depends on the scale of concentration employed [17]. It
is convenient and customary in electrochemical investigations
to follow the convention popularized by G. N. Lewis [16] --
to express concentrations on the molal basis of formula
weights of solute per 1000 g of solvent. If the subscript
m denotes this molal concentration and the subscript c
denotes concentration per 1000 cm^3 of solution, the dif-
ference between the values of a standard electrode potential
on the two scales is given by $F_m^o - E_c^o = - (RT/NF)\ln d_o$,
where d_o is the density of the pure solvent at the given
temperature and pressure. This equation may be derived in
the following way.

Activity is defined by the equation

$$F = F^o + RT \ln a$$

For a given mass, expressed on the two different scales of
concentration, F is the same while F^o and a are different. Thus

$$F = F_m^o + RT \ln a_m$$

and

$$F = F_c^o + RT \ln a_c$$

Since F_m^o and F_c^o are both constants, it follows from the
properties of the logarithm that the ratio $\dfrac{a_m}{a_c} = $ constant.

The constant may be evaluated by the following method.

Consider a solution of density d having a concentration of c moles of solute of molecular weight M per 1000 cm^3 of solution. The weight of the solvent which contains c moles of solute is

$$1000 \ d - Mc$$

One thousand grams of solute will contain

$$\frac{1000}{1000 \ d - Mc} \cdot c$$ moles of solute, but since this is the definition of the molal scale of concentration, the molality m will become

$$m = c \cdot \frac{1000}{1000 \ d - Mc}$$

and

$$\frac{c}{m} = d - \frac{Mc}{1000} \qquad (1)$$

a simple relation between these two methods of expressing the concentration of a solution. Since $a_c = f_c c$ and $a_m = f_m m$, where f_c and f_m are the corresponding activity coefficients,[2]

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[2]There are no universally established symbols for the activity coefficients on the various scales of concentration. Thus MacInnes in Principles of Electrochemistry [18] uses f for the coefficient on the volume scale and γ on the molal scale, while Dole in Experimental and Theoretical Electrochemistry (McGraw-Hill Book Company, New York, N.Y.) uses γ in the same sense as MacInnes but designates f as the

coefficient on the mole fraction scale. Clarke, in Hydrogen
Ions (Williams and Wilkins), uses γ for the coefficient on
the volume scale, while Noyes and Sherrill, in Chemical Prin-
ciples (MacMillan) use α to designate activity coefficients.
Rather than to accept any one of the existing conventions, it
seems better to use f as a general symbol for the activity
coefficient, with the subscripts m, c, or x to designate
whether the concentration is defined on the molal, volume,
or mole fraction scales, respectively.

$$\frac{f_m \cdot a_c}{f_c \cdot a_m} = d - \frac{Mc}{1000} \tag{2}$$

In aqueous solutions the infinitely dilute solution is
chosen as the standard state so that the activity coefficients
approach unity as the concentration approaches zero. Thus
eq. 2 reduces to

$$\frac{a_c}{a_m} = d_o \tag{3}$$

when m and c become zero, since the density of the solution
becomes that of the pure solvent, and this limiting case
serves for the evaluation of the constant.

The expression for the emf of an electrode as a
function of the activity on the two scales is

$$E = E_m^o - \frac{RT}{NF} \ln a_m = E_c^o - \frac{RT}{NF} \ln a_c$$

from which

$$E_m^o - E_c^o = -\frac{RT}{NF} \ln \frac{a_c}{a_m} \tag{4}$$

On substitution of the value for the activity ratio given by eq. 3, there results

$$E_m^o - E_c^o = -\frac{RT}{NF} \ln d_o \tag{5}$$

which gives the difference between the standard electrode potentials on the two scales. For aqueous solutions this difference amounts to zero at $4°$, 0.08 mv at $25°$, and 0.33 mv at $50°$ C. In some non-aqueous media, very large differences would exist.

A simple relationship between the activity coefficients on the two scales, namely

$$\frac{f_m}{f_c} = \frac{c}{d_o m} \tag{6}$$

results when the activities a_m and a_c are replaced in eq. 3 by their equivalent expressions $f_m \cdot m$ and $f_c \cdot c$, respectively.

The activity coefficients of sodium chloride at $25°$ C have been determined precisely by Brown and MacInnes [3, 19]. Their values, which are given on the volume scale, were converted to the molality scale by use of eq. 6. The coefficients so corrected for the molalities of 0.05 and 0.1 at $25°$ C were taken as standard and the values needed for the other temperatures at the same molalities were calculated with the aid of the excellent data obtained by

Robinson and Gulbransen [4, 23] on the relative partial molal heat contents of solutions of sodium chloride. From their data, the relative partial molal heat content $\overline{L}_2$ of the sodium chloride was expressed in calories as a linear function of temperature. The method of least squares was employed and the following equations were obtained:

For m = 0.05

$$\overline{L}_2 = 93.97 + 3.256(t - 25°\ C)$$

For m = 0.1

$$\overline{L}_2 = 100.09 + 4.542(t - 25°\ C)$$

The variation of the logarithm of the activity coefficient with temperature is given by the equation

$$\frac{d\ \ln\ f_m}{dT} = \frac{-\overline{L}_2}{2\ RT^2} \tag{7}$$

in which f_m is the mean activity coefficient on the molal scale and the other symbols have their usual significance. At each molality, the equation for $\overline{L}_2$ as a function of temperature was substituted in eq. 7 and, after integration, the difference between the logarithm of the activity co-efficient at a particular temperature and 25° C was computed. The mean activity coefficients thus obtained are given in columns 3 and 4 of table 1.

MATERIALS

The mercury used in the preparation of the amalgam was virgin mercury which was purified by washing with nitric acid, distilling in a Hulett still [7], distilling in vacuum, and filtering through a fritted glass filter.

The amalgam was made electrolytically in a round bottom 1-liter flask having two sidearms for the electrodes and at the bottom an outlet tube with a stopcock and a ground joint of standard taper, as shown in figure I. Approximately 200 ml of mercury was put in the flask, A, and covered with 400 ml of a 5 percent solution of sodium hydroxide. The alkali used was of reagent grade and test showed that it conformed to the specifications of the American Chemical Society [8] for this material. One of the platinum electrodes dipped into the mercury and the other into the solution. The mercury was stirred mechanically and electrolysis was continued until a plot of current and time indicated that the desired approximate concentration had been attained. When its preparation was completed, the amalgam was transferred to the reservoir C. To relieve strain during the transfer, a flexible spiral of glass tubing, B, was inserted between the flask and the reservoir. The reservoir and spiral were evacuated before
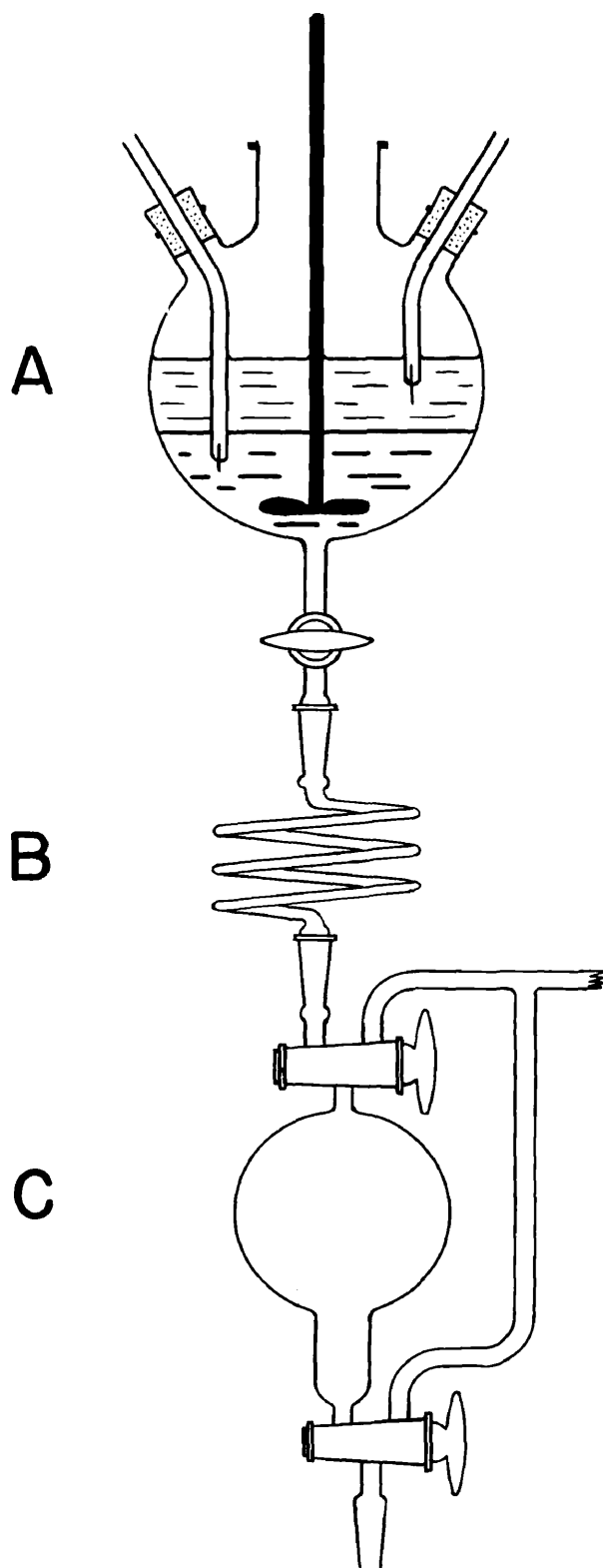
Figure I. Apparatus for preparation of amalgams

the amalgam was transferred. Dry nitrogen free from oxygen was then placed, at a pressure of about 20 cm above atmospheric, over the amalgam. The amalgam had substantially the same appearance as pure mercury and this appearance was retained throughout the investigation.

For analysis, portions of the amalgam were decomposed by water, on a steambath to hasten the rate of reaction. The resulting solutions of sodium hydroxide were separated from the mercury and an excess of standardized sulfuric acid was added from a weight burette. After boiling to remove carbon dioxide, the excess acid was titrated with standard alkali using bromthymol blue as the indicator. The analyses showed that the amalgam contained 0.06514 ± 0.00006 percent by weight of sodium. The analysis was of course more informative than fundamental for the investigation, since the concentration of the amalgam is not involved in the final calculation of the standard electrode potential.

The sodium used for one electrode of the non-aqueous cell was a commercial product which was found by test to conform to the specifications of the American Chemical Society for the reagent grade of this material [10]. A sample was converted to sodium chloride and tested for potassium [9]. Within the sensitivity of the test (0.01 percent), no potassium was found. A spectrographic examination of a sample of the metal indicated only the traces of impurities given in table II.

TABLE II

Spectrographic Analysis of Sodium

Impurity	Amount present
Silver	faint trace
Aluminum	trace
Copper	trace
Iron	trace
Potassium	weak
Magnesium	faint trace
Rubidium	faint trace
Silicon	faint trace

The dimethylamine for the solvent in the non-aqueous cell was prepared from dimethylamine hydrochloride of C.P. grade and sodium hydroxide of reagent grade. The procedure for preparing and drying the amine is described in the next section.

The sodium iodide for the electrolyte in the non-aqueous cell was of reagent grade, recrystallized, heated to incipient fusion, and stored in a desiccator until used.

The sodium chloride for the electrolyte in the aqueous cell was of reagent grade further purified by two precipitations with gaseous hydrogen chloride followed by recrystallization from redistilled water and fusion in a platinum dish. A sample was shown by test [9] to contain less than 0.01 percent of potassium.

The aqueous solutions were prepared to have the desired concentrations on the molal scale (formula weights of salt per 1000 g of water) by weighing the dry salt and the added redistilled water. Calibrated weights were used and all weighings were corrected for air buoyancy.

The nitrogen used for an inert atmosphere was freed from oxygen, and other undesirable gases, by passage over hot reduced copper and through columns containing dilute alkali and dilute acid. That which was used in contact with the amalgam and in the preliminary sweeping out of the cell was dried with anhydrous magnesium perchlorate (anhydrone) and that used to eliminate oxygen from solution was bubbled through a solution of the same concentration.

The silver-silver chloride electrodes were of the thermal-electrolytic type and were equilibrated [25, 26, 27] in the cell for at least two days before use. The method of preparation of these electrodes was the same as that given in a previous paper [27]. Two of these electrodes were used in the aqueous cell and their differences in emf were always less than 0.01 mv.

APPARATUS AND PROCEDURE

The non-aqueous cell, H, and the apparatus for filling
it are represented in figure II. The auxiliary apparatus
consisted of a still, A, a drying tube, B, filled with
drierite (anhydrous calcium sulfate), a drying tube, C,
filled with hydralo (anhydrous aluminum oxide), and an
amine reservoir, D. At E was placed a magnetic hammer by
means of which the capillary inner seal, I, could be broken
when desired. The bottom of one limb of the cell was fitted
with a standard taper ground joint to accommodate the amal-
gam reservoir and the other limb with a capillary tube sealed
to a bulb from which the sodium for one electrode was later
filtered into the cell through the capillary. The horizontal
connecting arm of the two limbs was provided with a pocket
and a tube through which the electrolyte, sodium iodide,
was placed in the cell. A tube for introducing the solvent
was also provided. Platinum wires for contact with the
electrodes were sealed in soft glass tubes which in turn
were joined to the cell by means of graded soft glass
to Pyrex seals.

One hundred grams of dimethylamine hydrochloride was
placed in the still pot and a solution containing sodium
hydroxide in excess of the amount necessary to liberate the
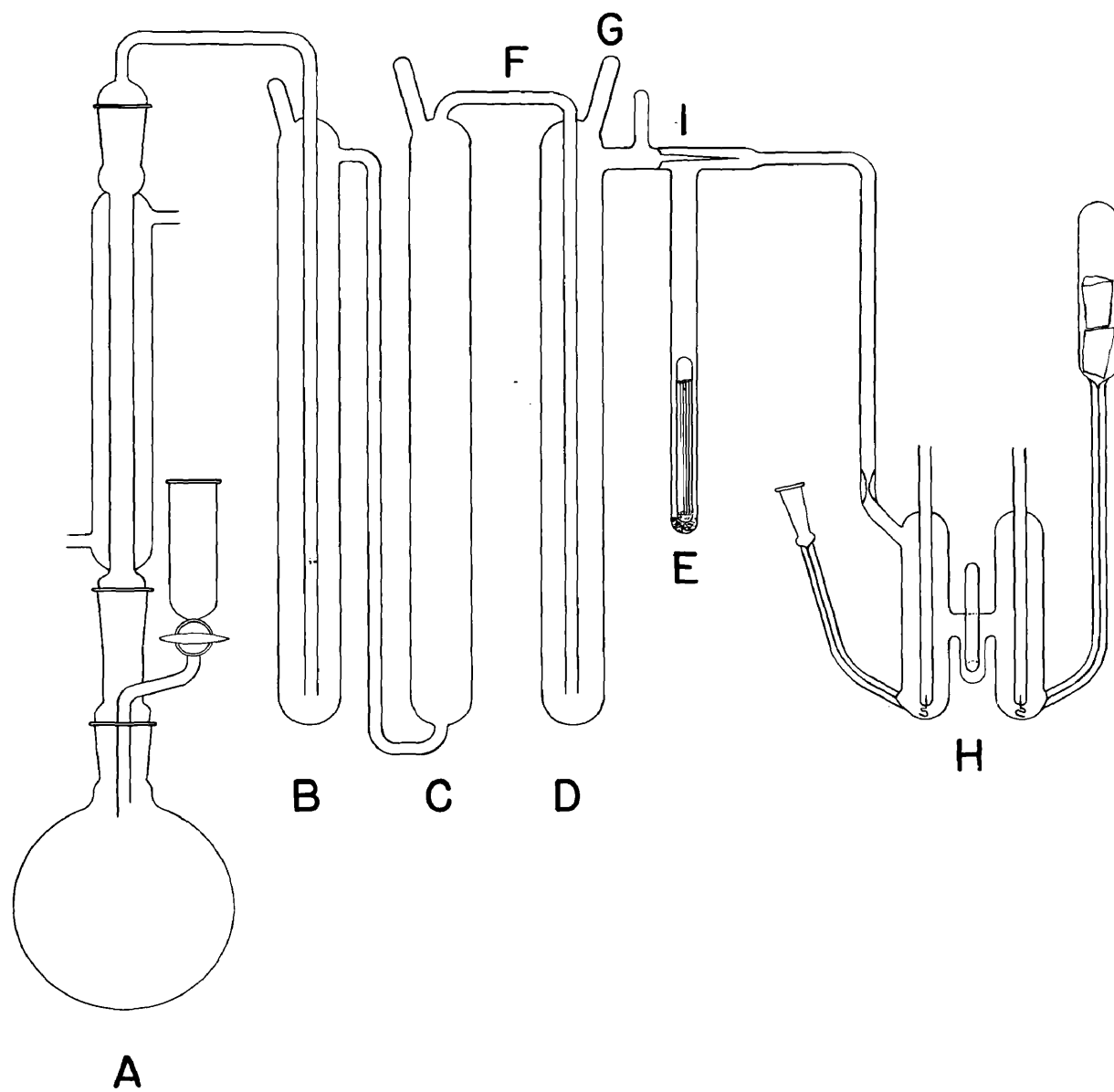free amine was added through the funnel inlet. With cold

Figure IX. Non-aqueous cell and auxiliary apparatus

water circulating through the condenser, the still pot was gently heated. Tube G was open to the atmosphere at this time. Dimethylamine distilled into the receiver, D, which had been filled partially with shavings of sodium and immersed in a cooling bath containing solid carbon dioxide in a mixture of chloroform and carbon tetrachloride. When distillation was completed, the receiver was sealed off at F. The tube G was then connected to a vacuum system and the source of pure dry nitrogen. Residual air in the receiver was removed by alternate evacuation and admission of nitrogen after which the receiver was sealed at G under the vapor pressure of the dimethylamine at the temperature of the cooling bath. The cooling bath was removed and the receiver was allowed to attain the temperature of the room. The liquid amine was thus stored over sodium until needed.

The amalgam reservoir was next connected to the cell by means of the standard taper joint, sodium was placed in the bulb provided for it, and the sodium iodide was added. The apparatus was evacuated, a sufficient quantity of amalgam was introduced, and the side arm leading to the amalgam reservoir was sealed off close to its limb of the cell. The bulb containing the sodium was heated and the liquid metal flowed through the capillary to the other cell limb and, at the same time, was filtered from oxide crust. This side arm was then sealed off. After this, the cell was surrounded by the cooling bath, the capillary inner seal was broken, and the amine was distilled into the cell.

When sufficient amine had been introduced to come above the horizontal limb, the cell was sealed off from the filling apparatus. Thorough mixing of the solution in the cell was accomplished by alternate cooling of the vapor space of each cell limb causing a movement of the electrolyte from one limb to the other.

The main requirements upon which the design of the aqueous cell was based are: (1) an easily renewable amalgam electrode to present a reproducible and unpolarized surface for each measurement; (2) a means for removal of used amalgam to prevent continuous reaction with the solution; (3) a means for renewal of the electrolyte to eliminate solution which has reacted with amalgam; and (4) the exclusion of oxygen.

The design adopted for the aqueous cell is shown in figure III. The cell proper, G, consisted of a longer limb for the capillary amalgam electrode and a shorter one for the silver-silver chloride electrodes. The electrode tubes were sealed to ground joints of standard taper. The apparatus was made of Pyrex glass except for graded soft glass to Pyrex seals on the two silver-silver chloride electrode tubes, which facilitated sealing in the platinum wires to hold these electrodes. It should be noted that one of the intermediate glasses present in these graded seals was found to be attacked by solutions of sodium chloride. The amount of decomposition was great enough to cause mechanical failure

SAT'D. NITROGEN
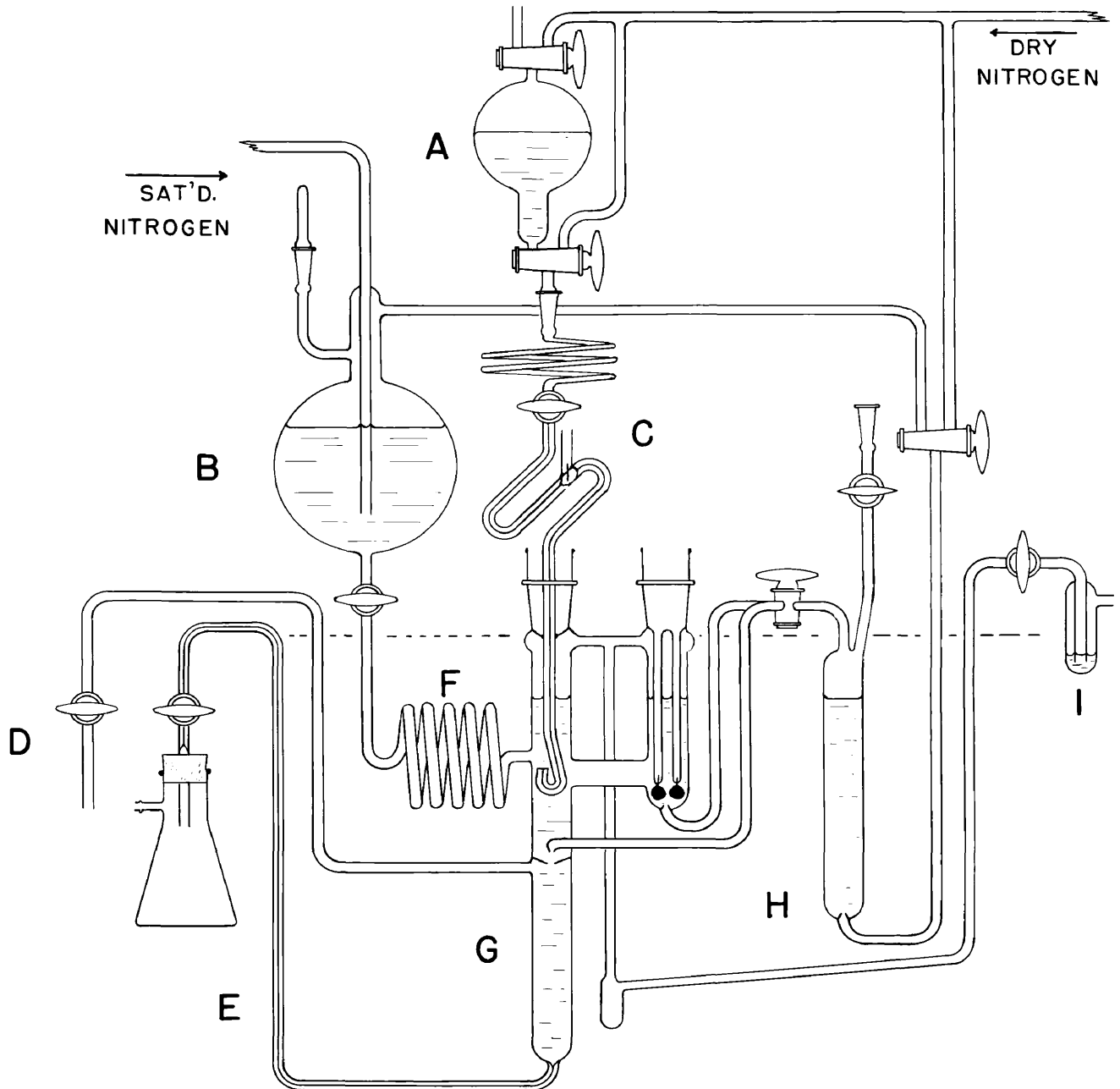
DRY NITROGEN

A

B

C

D

E

F

G

H

I

Figure III.   Aqueous cell and auxiliary apparatus

in a relatively short time and, for this reason, the
graded seals were so placed as to be above the level of the
solution in the cell at all times. Each limb contained a
gas-bubbling tube so that nitrogen could be passed through
either at will. The gas outlet, I, common to both limbs,
was provided with a sump to prevent condensed water vapor
from returning to the cell when measurements were made at
temperatures above that of the laboratory. The longer limb
had a funnel-shaped partition just below the bubble tube.
A small orifice in this partition permitted drops of used
amalgam to fall to the bottom and hindred back diffusion
of amalgam decomposition products. An outlet tube, D,
just below this partition, for removing solution, and a
capillary tube, E, for withdrawing used amalgam from the
bottom, were sealed to the amalgam limb.

The capillary amalgam electrode was given an S-turn,
C, because with a straight capillary tube a break and
consequent gap in the column of amalgam sometimes occurred
at the contact wire. The upward flow of amalgam past the
contact wire eliminated this annoyance. To insure further
against a break in the column of amalgam and to avoid pre-
liminary contact and reaction of the amalgam with the so-
lution, the capillary was first filled, by suction, with
pure mercury up to and through the stopcock bore, before
it was placed in the cell. To facilitate alignment with
the amalgam reservoir, A, and to take up changes

in strain, a flexible glass spiral was sealed between the stopcock and ground joint of the amalgam electrode.

The solution reservoir, E, consisted of a round-bottom flask having a capacity of 1 liter, to which were sealed inlet and outlet tubes for nitrogen, a tube for filling with solution, and a spiral, F, connecting it to the cell. The reservoir was supported above the cell at the temperature of the laboratory. The function of the spiral was to bring the solution to the temperature of the thermostat before it entered the cell. Nitrogen, saturated with water vapor at room temperature, was passed through the reservoir to displace oxygen from the solution and on through the saturator, H, which was immersed in the thermostat and filled with some of the same solution, and then through the cell to outlet I. Before filling the cell and saturator, dry nitrogen was passed through them overnight and during this time a ground-glass plug took the place of the silver-silver chloride electrode tube. After the cell and saturator were filled with the oxygen-free solution, the silver-silver chloride electrodes were inserted and nitrogen was bubbled through for at least two days, to insure complete equilibrium of these electrodes with the solution [25, 26, 27] before measurements were made. The next step was to connect the amalgam reservoir with the capillary electrode, evacuate the flexible spiral, and fill it with amalgam.

When a sufficient amount of amalgam had been passed through the capillary to displace pure mercury, reproducible potential differences were obtained. During the measurements, fresh solution was passed through the amalgam limb of the cell at a rate of about 2 ml per minute. With this rate of flow, no detectable drift of the emf, which would result if any appreciable change in composition of the solution were caused by reaction with the amalgam, was observed. To make sure of this, the amalgam limb was occasionally drained and refilled with fresh solution without causing any appreciable change in emf.

To bring the measured emf within the range of the potentiometer, an unsaturated Weston standard cell was connected in opposition to the aqueous cell and the difference in emf was observed. This unsaturated standard cell was kept in an insulated box, and its emf was determined before and after each series of measurements.

Stationary and flowing amalgams were tried and the former proved to be more satisfactory. A fresh drop of amalgam was produced on the electrode tip and emf readings were made. The readings quickly reached a maximum, which was within less than 0.1 mv of the initial value, and then varied only a few hundredths of a millivolt from this value for a longer period of about one minute, after which a slow but definite decrease in emf occurred. Each fresh droplet behaved in the same manner, and the maximum reading of each was recorded. The emf reported at each temperature is the average of at least

ten such readings, with an average deviation of about
±0.02 mv. After each series of measurements was completed,
the solution level was lowered so that the capillary tip
was out of the electrolyte but the silver-silver chloride
electrodes were still immersed in the solution. This was done
to minimize reaction with the amalgam during the periods be-
tween observations. The old electrolyte was drained and fresh
was run in before each new series of measurements.

Both the aqueous and non-aqueous cells were immersed in
an oil thermostat which was equipped with a cooling unit for
maintaining temperatures below that of the room to a con-
stancy of ±0.03° C. For temperatures above that of the room,
the constancy was better than ±0.01° C. The temperatures
were read with a Beckman thermometer, the setting of which
was checked at each temperature with a platinum resistance
thermometer.

The measurements of electromotive force were made with
a calibrated Rubicon Type B potentiometer and a pair of
saturated Weston standard cells which were kindly made, cali-
brated, and supplied by G. W. Vinal and L. H. Brickwedde of
the Electrical Division of the National Bureau of Standards.
These cells were housed in a temperature control box es-
pecially designed for saturated standard cells [21]. The
galvanometer employed was a Leeds and Northrup Type R instru-
ment which had a resistance of 495 ohms and a current sensi-
tivity of 0.000092 microamp/mm/m.

On any one day, measurements were made at only one temperature. The first measurements were made at 25° C and, as soon as these were completed, the temperature of the bath was lowered to approximately 20° C. On the following day the temperature was adjusted closely to 20° C. Thus the temperature was within a few tenths of a degree of the desired value for at least 18 hours and within a few hundredths for at least 2 hours before observations were started. This procedure was continued for successive 5-degree intervals down to 5° C. Following the measurements at 5°, the temperature was brought back to 25° C in one step for a test of reproducibility and hysteresis. The reproducibility was within a few hundredths of a millivolt and no hysteresis effects were observed. The temperature was then raised in 5-degree steps up to 40° and brought back in one step from 40 to 25°. This procedure was applied to both the non-aqueous and aqueous cell. Two concentrations of the solution of sodium chloride, 0.05 and 0.1 m, and one concentration of the amalgam, 0.06514 percent by weight of sodium, were used.

1. Non-aqueous Cell

The measured values of the emf of the non-aqueous cell

Na(s); NaI(in dimethylamine; Na(0.06514% amalgam)

at the different temperatures are given in column 2 of

table III. The method of least squares was employed and the

equation obtained

$$E = 0.88578 + 0.00008390(t - 25) + 0.000000762(t - 25)^2$$

expresses the data with average and greatest deviations of

0.02 and 0.06 mv, respectively. The chemical reaction which

takes place in the operation of the cell is

Na(s) = Na(0.06514% amalgam)

The values of the change in partial molal free energy, $\Delta \bar{F}$,

accompanying the cell reaction were computed from the relation-

ship $\Delta \bar{F} = -FE$, where F is the Faraday and the E is taken from

the equation. They are listed in column 3 of table III. The

values of $\Delta \bar{S}$, the change in partial molal entropy, given in

the fourth column were obtained from the relationship

$\Delta \bar{S} = F \, dE/dT$ in which $dE/dT = 0.0008390 + 0.000001524(t - 25)$.

The values of $\Delta \bar{H}$, the change in partial molal heat content,

listed in the fifth column, were calculated from the equation

$\Delta \bar{H} = \Delta \bar{F} + T\Delta \bar{S}$.

Dent and Swift, Jr. [2] have measured similar cells and

have given equations for the calculation of the activity, $\Delta \bar{F}$,

TABLE III

Values for the nonaqueous cell: Na(s); NaI in $(CH_3)_2NH$;

Na(0.06514% amalgam)

Reaction: Na(s) = Na(0.06514% amalgam)

t	E	$\Delta \overline{F}$	$\Delta \overline{S}$	$\Delta \overline{H}$
° C	int. v.	int. joules / mole	int. joules / mole deg.	int. joules / mole
5	0.88442	-85343	5.16	-83909
10	.88467	-85372	5.89	-83703
15	.88500	-85403	6.63	-83494
20	.88537	-85438	7.36	-83280
25	.88577	-85477	8.10	-83063
30	.88626	-85517	8.83	-82840
35	.88667	-85566	9.57	-82617
40	.88720	-85615	10.30	-82389

and $\Delta \bar{H}$ for different mole fractions of sodium in sodium amalgam at temperatures between 5° and 25° C. The values of $\Delta \bar{F}$ computed from their equations agree with ours to 0.06 percent in the comparable range of 5° to 25° C. The values of $\Delta \bar{S}$, which depend on the temperature coefficient of emf, differ by 5 to 6 percent and the values of $\Delta \bar{H}$ differ by about 0.2 percent. Considering the small magnitude of $\Delta \bar{S}$ and that the comparison is made with interpolated data, the agreement appears adequate.

Since the normal boiling point of dimethylamine is about +7° C, the pressure in the aqueous cell varies from approximately 1 atm. at the lowest temperature to approximately 3.3 atm. at 40° C. Data on the vapor pressure of dimethylamine are given by Simon and Huter [24]. The change in emf with pressure is given by the equation $dE/dP = -\Delta \bar{V}/F$, in which $\Delta \bar{V}$ is the difference between the partial molal volume of sodium in the amalgam and of pure sodium. The partial molal volume of sodium in an amalgam containing 0.06514 percent of the alkali metal was estimated from the specific volume data of Maey [20] to be 15.79 cc and that of pure sodium is 23.71 cc, so that $\Delta \bar{V} = 7.92$ cc. From this data dE/dP is calculated to be 0.008 mv per atmosphere. The calculated corrections ranged from less than 0.01 mv to a maximum of only 0.02 mv and were not applied to the data.

2. Aqueous Cells

The results with the aqueous cells are given in table IV.

TABLE IV

Values for the aqueous cells: Na(0.06514% amalgam); NaCl(0.05 or 0.1 m), AgCl(s); Ag(s)

Reaction: Na(0.06514% amalgam) + AgCl(s) = NaCl(0.05 or 0.1 m) + Ag(s)

t	E m = 0.05	$\frac{2RT}{F}\ln(0.05 f_m)$	E° m = 0.05	E m = 0.1	$\frac{2RT}{F}\ln(0.1\ f_m)$	E° m = 0.1	Av. E°
° C	int. v	int. v	int. v	int. v	int. v	int. v	int. v
5	2.20084	-0.15282	2.04802	2.17009	-0.12220	2.04789	2.04796
10	2.20440	- .15560	2.04880	2.17304	- .12442	2.04862	2.04871
15	2.20775	- .15838	2.04937	2.17586	- .12665	2.04921	2.04929
20	2.21086	- .16118	2.04968	2.17850	- .12890	2.04960	2.04964
25	2.21382	- .16399	2.04983	2.18105	- .13116	2.04989	2.04986
30	2.21669	- .16682	2.04987	2.18337	- .13344	2.04993	2.04990
35	2.21943	- .16965	2.04978	2.18548	- .13574	2.04974	2.04976
40	2.22196	- .17250	2.04946	2.18757	- .13805	2.04952	2.04949

In columns 2 and 5 are listed the observed emfs with the two
concentrations of electrolyte employed. The E° values were
obtained by adding to the E values the terms
$(2 RT/F) \ln(f_m \cdot m)$, in which f_m is the activity coefficient on
the molal scale, given in table I. The last column lists the
average value for E° obtained from the two concentrations of
electrolyte. As a test of the reliability of the observations,
the ratios of the activity coefficients were calculated by
the equation $F \Delta E = 2 RT \ln(2f_{0.1}/f_{0.05})$, in which ΔE is the
difference between the emf of the two aqueous cells, at a
given temperature, and corresponds to the transfer
$NaCl(0.1 m) = NaCl(0.05 m)$. The ratios so computed were com-
pared with the ratios of the values given in table I, which
were used in the computations of E°. The results are given
in table V. Over the entire temperature range, the greatest
difference found between the two sets of ratios is four parts
and the average difference is two parts in 1000. This agree-
ment is satisfactory since the differences in emf were ob-
tained indirectly as the differences between quantities near-
ly 100 times larger. However, these differences in emf are
not of sufficient accuracy to justify their use for calcu-
lations of the changes in entropy and heat content accompany-
ing the transfer of sodium chloride between the two concen-
trations.

Table V

Ratios of Activity Coefficients

t	ΔE	$f_{0.05}/f_{0.1}$ from E	$f_{0.05}/f_{0.1}$ from table I
5	0.03075	1.0528	1.0558
10	.03136	1.0516	1.0556
15	.03189	1.0521	1.0555
20	.03236	1.0538	1.0554
25	.03277	1.0568	1.0555
30	.03332	1.0568	1.0556
35	.03395	1.0551	1.0558
40	.03439	1.0573	1.0562

3. Combinations of Cells

By adding to each E of the aqueous cells given in table IV, the E of the non-aqueous cell at the same temperature as given in table III, the emfs of the cells

$$Na(s); NaCl(0.05 \text{ or } 0.1 \text{ m}), AgCl(s); Ag(s)$$

are obtained for each temperature. Again employing the method of least squares, the results are expressed by the following equations:

For m = 0.05,

$$E = 3.09964 + 0.0006699(t - 25) - 0.00000240(t - 25)^2$$

with average and greatest deviations of 0.02 and 0.05 mv.

For m = 0.1,

$$E = 3.06679 + 0.0005671(t - 25) - 0.00000241(t - 25)^2$$

with average and greatest deviations of 0.03 and 0.07 mv.

A rather severe test of the data may be made by taking the second derivatives of these equations to calculate the difference between the molal heat capacities of the products and reactants of the cell reaction

$$Na(s) + AgCl(s) = NaCl(0.05 \text{ or } 0.1 \text{ m}) + Ag(s)$$

by means of the relationship $\Delta \bar{C}_p = TF d^2E/dT^2$. The value thus found may be compared with the algebraic sum of the molal heat capacities directly observed, since

$$\Delta \bar{C}_p = \bar{C}_p(Ag) + \bar{C}_p(NaCl, 0.05 \text{ or } 0.10 \text{ m}) - \bar{C}_p(Na) - \bar{C}_p(AgCl)$$

At 25° C and m = 0.05, for example, $\Delta \bar{C}_p$ is calculated from the second derivative to be -138 int. joules as compared with -133 for the sum of the separately measured quantities. A more interesting comparison is that of the value calculated

for $\bar{C}_p$(NaCl, 0.05 or 0.1 m) with its value obtained from measurements of heats of dilution. Thus, from the values of $\bar{C}_p$ for silver (25.3), sodium (28.4), and silver chloride (52.6) listed in the International Critical Tables [11], and result from this work of -138 int. joules for $\Delta \bar{C}_p$, the partial molal heat capacity of 0.05 m sodium chloride solution is calculated to be -82.3 int. joules or -19.7 calories. Gulbransen and Robinson [4, 23], from calorimetric measurements of the heats of dilution of solutions of sodium chloride, expressed its partial molal heat capacity in calories by the equation $\bar{C}_p = -21.9 + 15.8\ m^{1/2}$, which yields -18.4 calories for 0.05 m with a probable error which they estimate to be not more than 15 percent. The agreement at 0.1 m is not quite as close, the present measurements giving -19.8 calories as compared with the calorimetric value of -16.9 calories; a difference of 2.9 calories. However, it is quite satisfactory for a comparison which involves a second derivative and data on specific heats from various sources.

For the cell

Na(s); NaCl(f_m.m = 1), AgCl(s); Ag(s)
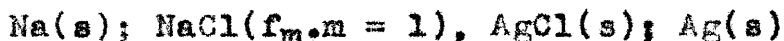
the value of E° at each temperature was obtained by adding to each average E° for the aqueous cell, given in the last column of table IV, the corresponding E for the non-aqueous cell, given in table III. The results which are given in table VI may be expressed by the equation

$E° = 2.93564 + 0.0001096(t - 25) - 0.00000268(t - 25)^2$

obtained by the method of least squares. The equation expresses

TABLE VI

Combination of the aqueous and non-aqueous cells: Na(s);

NaCl(mf_m = 1), AgCl(s); Ag(s)

Reaction: Na(s) + AgCl(s) = NaCl(mf_m = 1) + Ag(s)

t	E°	Δ F°	Δ S°	Δ H°
° C	int. v	int. joules / mole	int. joules / moles deg.	int. joules / mole
5	2.93238	-282975	20.9	-277156
10	2.93338	-283072	18.3	-277879
15	2.93429	-283158	15.8	-278619
20	2.93501	-283229	13.2	-279369
25	2.93563	-283289	10.6	-280134
30	2.93616	-283336	8.0	-280914
35	2.93643	-283369	5.4	-281702
40	2.93669	-283390	2.8	-282507

the tabulated results with an average deviation of 0.02 and a greatest deviation of 0.04 mv. Table VI also includes the changes in partial molal free energy, entropy, and heat content accompanying the cell reaction, calculated with the aid of the equation and its first derivative.

4. The Standard Electrode Potential of Sodium

The emf of the hypothetical cell

$$Na(s); Na^+(f_m \cdot m = 1) \parallel H^+(f_m \cdot m = 1); H_2(g, 1 \text{ atm})$$
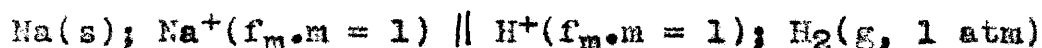
may be found by adding the standard electrode potential of the silver-silver chloride electrode, given in table I, to the electrode potential of the cell

$$Na(s); NaCl(f_m \cdot m = 1), AgCl(s); Ag(s)$$

given in table VI, at each temperature. The E° value thus obtained at each temperature is the standard electrode potential of sodium. These final results are given in table VII together with the value of E°, ΔF°, ΔS°, and ΔH° calculated from the equation

$$E^\circ = 2.71324 + 0.0007532(t - 25) + 0.000000668(t - 25)^2$$

This least square equation expresses the observations in the temperature range of 5° to 40° C, with an average deviation of 0.02 and a greatest deviation of 0.05 mv. The smoothed values of E° calculated from the equation and given in column 3 of table VII are recommended as "best" values for the standard electrode potential of sodium.

The accuracy of the final results depends on a number of factors. Leaving out of consideration, for the moment, the

TABLE VII

The Standard Electrode Potential of Sodium

t	E° from measurements	E° from equation	$\Delta F°$	$\Delta S°$	$\Delta H°$
° C	int. v	int. v	$\dfrac{\text{int.joules}}{\text{mole}}$	$\dfrac{\text{int.joules}}{\text{mole deg.}}$	$\dfrac{\text{int.joules}}{\text{mole}}$
5	2.69847	2.69846	-260401	70.0	-240921
10	2.70208	2.70206	-260749	70.7	-240732
15	2.70578	2.70578	-261108	71.4	-240545
20	2.70947	2.70949	-261466	72.0	-240353
25	2.71324	2.71324	-261828	72.7	-240155
30	2.71708	2.71703	-262193	73.4	-239956
35	2.72082	2.72084	-262561	74.0	-239754
40	2.72469	2.72466	-262930	74.7	-239543

reference silver-silver chloride electrode, the most critical of these factors and the calculated influence of their estimated uncertainties are:

1. The activity coefficients of sodium chloride, including their corrections to the different temperatures (0.03 mv).

2. Accuracy and constancy of temperatures (0.01 mv).

3. Polarization of the amalgam electrode in the aqueous solution (0.02 mv).

4. Calibration of potentiometric and standard cells (0.02 mv).

5. The concentrations of the aqueous solutions (0.005 mv).

6. Accidental errors (0.01 mv).

7. Neglect of pressure corrections (0.00 to 0.02 mv).

The square root of the sum of the squares of these errors gives 0.04 to 0.05 mv for an estimate of the overall accuracy of the measurements. The reference values of the silver-silver chloride electrode are probably good to about the same amount, so that the values obtained for the standard electrode potential of sodium are considered to be correct to within 0.1 mv.

SECTION VI

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THE STANDARD ELECTRODE POTENTIAL OF SODIUM

By John Keenan Taylor

Abstract

The reaction of the alkali metals with water disturbs
the equilibrium conditions necessary for direct measurements of
their electrode potentials. An indirect method which over-
comes this difficulty depends on the possibility of measur-
ing (a) the potential of a dilute amalgam of the alkali metal
with respect to an aqueous solution of its ions and a
reference electrode and (b) the difference in potential be-
tween the same amalgam and the pure metal when both are im-
mersed in a nonaqueous conducting solution containing ions of
the alkali metal. The standard electrode potentials of all
of the alkali metals have been measured by this method but
the results are somewhat uncertain, due to the inclusion in
the measurements of liquid junctions, solutions for which the
activities can only be approximated, and unreliable reference
electrodes.

This paper gives the results of a redetermination of the
standard electrode potential of sodium, in which these sources
of error were eliminated. The two cells may be represented by

Na(s); NaI (in dimethylamine); Na (amalgam)

and

Na (amalgam); NaCl(m), AgCl(s); Ag(s).

2

All-glass cells were designed and constructed. The cell for use with the aqueous solution was so arranged as to renew conveniently the amalgam electrode and the solution and to exclude oxygen. Measurements were made at 5° temperature intervals over the temperature range of 5° to 40° C and the standard electrode potential, E°, for Na(s); Na$^+$ was obtained. The final results may be expressed by the equation

$E^\circ = 2.71324 + 0.0007532(t - 25) + 0.000000688(t - 25)^2,$

in which E° is in int. volts and t is in ° C. The various thermodynamic quantities derivable from the data were computed.