THE USE OF THE GLASS ELECTRODE AS A REFERENCE ELECTRODE

BY

PAUL S. BROOKS

Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial
fulfillment of the requirements for
the degree of Doctor of Philosophy

1940

UMI Number: DP70081

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Acknowledgement

The writer takes this opportunity to express his appreciation to Dr. M. M. Haring for his suggestion of the problem and his continual aid during its completion.

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# I. INTRODUCTION

A preliminary research (1) was undertaken to determine the possibility of applying the glass electrode to the measurement of standard electrode potentials. That it could be used for such purposes seemed logical since it is known to behave like a hydrogen electrode. It has the great advantage of eliminating the necessity of calculating a junction potential since in the manner in which it was employed, the junction potential is absent from the thermodynamically derived equation for the $E^{\circ}$ value.

The results of this work were encouraging so a second research was carried out to investigate more fully the possibilities and the precision to be expected. In this work much the same technique was employed, but the measurements covered a wider range of reference electrodes and greatly improved apparatus was employed.

## II.  THEORETICAL DISCUSSION

Theory of the Glass Electrode.  (2)

The use of the glass electrode for research and routine work dates from about 1929 when MacInnes and Dole studied different types of glass for making the electrodes.

A theory of the glass electrode must account for its behavior in alkaline solutions, in very acid solutions, and in solutions of intermediate acidity.  In solutions in which the glass electrode acts as a hydrogen electrode, thermodynamics gives a clear formulation.

Imagine two hydrochloric acid solutions of different concentrations in which two connected platinum electrodes are immersed.  The circuit is completed through reference calomel electrodes.  As one Faraday of electricity flows through the cell, one equivalent of hydrogen ions is transferred from the concentrated to the dilute solution, and the free energy of transfer, measured by the E. M. F., is equal to the difference in free energy of the hydrogen ion in the two solutions.

If we consider an analogous glass electrode system in which the two platinum electrodes are replaced by a single glass membrane, and again allow one Faraday of current to pass, one equivalent of hydrogen ions is reversibly transferred from the concentrated to the dilute solution.  In this case, although the mechanism of the process is entirely different from that of the hydrogen electrode, the net result is exactly the same, the E. M. F. of the glass electrode is identical with that of the platinum electrode system, and the glass electrode behaves as a true hydrogen electrode.

It is interesting to compare the mechanism involved in the transfer of hydrogen ion in the two cases. In the case of the platinum electrode dipping into the concentrated solution, hydrogen ions are deposited on the electrode, gain one electron each, and form hydrogen gas which escapes from the solution. At the electrode dipping into the dilute solution, hydrogen gas dissolves to form hydrogen ions, giving one electron per ion to the electrode. Any other reaction which may take place on the electrode and involving electrons, oxidation-reduction for example, will interfere with the process of transferring hydrogen ions and so cause an error in the E. M. F. reading. For this reason the hydrogen electrode cannot be employed to measure pH in the presence of oxidizing or reducing substances.

The mechanism in the case of the glass electrode is entirely different. No electrons are involved, so the potential is entirely unaffected by oxidizing and reducing substances. Hydrogen ions are neither discharged as hydrogen gas on the glass nor does gaseous hydrogen form hydrogen ions; instead, the hydrogen ions pass through the glass as such without electron interchange. For solutions of high pH, where hydrogen ion concentration is very low, the flow of electricity may result in the flow of other ions. Hence, the E. M. F. no longer measures solely the free energy of transfer of hydrogen ions and the glass electrode no longer functions without error.

Another explanation of the mechanism [3], [4] holds that the conduction of electricity from one side of the glass to the other takes place almost exclusively through the sodium ions of the glass. The mechanism involves an exchange reaction between the hydrogen ions and the sodium and calcium ions of the glass. The suitability of a glass as an electrode depends upon its ability to exchange these ions.

It is known[5] that all glass electrodes show a small residual
E. M. F. across the glass membrane when identical solutions are brought
in contact with the inner and outer surfaces. The exact cause of this
so called "asymmetry potential" is not known. One hypothesis is that
the potential is due to strains in the glass since it seems to be smaller
with thin than with thick membranes. Another theory[6] holds that this
potential is due to a difference in curvature; this would suggest that a
difference in atomic arrangement in the two surfaces is responsible for
the asymmetry potential. The relationship between asymmetry potential
and membrane thickness would indicate that the atomic arrangement of the
electrode membrane is likely different both lengthwise and crosswise.

At any rate, each glass membrane has its own asymmetry potential
which is not constant even for the same membrane. Hence, in actual use,
the asymmetry potential must be measured frequently. The effect of the
asymmetry potential will be exhibited in the net E. M. F. of the cell.

Standard Electrode Potential

Since in this work the glass electrode is employed as an instrument for intercomparing several electrodes through their standard potentials, a discussion of the standard potential is in order.

A useful concept for the mechanism involved in a single electrode was proposed in 1880 by Nernst[7]. According to this theory there is a tendency for the atoms composing an electrode to go into solution, and a corresponding tendency for the ions of the solution to deposit on the electrode as atoms. The tendency of the atoms to go into solution as ions is expressed by the electrolytic solution pressure, P. The reverse tendency, which is determined by the ionic concentration is proportional to the osmotic pressure, p, of the solution.

If this be true, it is evident that three conditions are possible:

1) If P is greater than p, the metal will send ions into the solution until further action is stopped by the electrostatic attraction.

2) If P is less than p, ions will deposit on the electrode from the solution until the charges accumulated oppose further action.

3) If P is equal to p, neither action will occur and no potential will be developed.

After the establishment of equilibrium the electrode will be surrounded by a layer of electrical charges, known as a Helmholtz electrical double layer, which will be positive when P is greater than p, or negative when P is less than p.

In order to get the E value for a single electrode, Nernst developed a thermodynamic cycle in which ions are transferred from a solution of

osmotic pressure, p, to a solution equal in osmotic pressure to the
electrolytic solution pressure, P. Transfer may be effected either by
passage of an electric current, or by osmosis of the solvent, each process
being carried out reversibly. The work in the first case is nFE, where
E is the difference in potential between the two solutions. The work
done in the second case is

$$\int_{P}^{p} \frac{RTdp}{P} \text{ or } RT\ln \frac{p}{P} \quad (1)$$

These two expressions are equal because the work done in each case is
maximum work, and,

$$E = \frac{RT}{nF} \ln \frac{p}{P} \quad 2)$$

If the first solution has osmotic pressure, p, equal to the
electrolytic solution pressure, P, in the second solution, the above formula
gives the potential of an electrode in terms of its electrolytic solution
pressure and the osmotic pressure of the solution of its ions in which it
has been placed.

At 25° C

$$E = \frac{RT}{nF} \ln \frac{p}{P} = \frac{.059}{n} \log \frac{p}{P} \quad 3)$$

This equation provides only a qualitative interpretation of
electrode potentials since E and P cannot be evaluated except from calcu-
lations employing some arbitrarily chosen standard, the choice of which
will determine the value found.

Since the value of a single electrode potential is dependent on
the tendency of the metal to go into solution as its ions, and on the
osmotic pressure, there will be a variation with the concentration of
the ions in the solution. For this reason the definition of the standard

potential must specify a particular ionic concentration and electrode state. Keeping this in mind, the standard electrode potential has been defined[8] as "the potential of a metal in its standard state when immersed in a solution of its ions at unit activity, i.e. effective concentration of 1 gram ion per 1000 grams of solvent." Further, since no method for evaluation of the absolute potential of an electrode exists at present, a standard reference potential must be chosen. The custom is to refer all electrodes to the hydrogen electrode at one atmosphere pressure in a solution of hydrogen ions at unit activity[9]. The value of $E^{\circ} = 0$ at all temperatures is assigned to this electrode.

In order to determine the sign of the potential the following convention has been established. "The normal hydrogen electrode is placed at the left for reference and combined with the electrode in question at the right. The sign of an electrode gives the sign of the charge of the electrode against the solution when connected to a normal hydrogen electrode"[10]. This convention gives a negative sign to electrodes of metals above hydrogen and a positive sign to those below hydrogen in the usual activity series.

The standard potential or $E^{\circ}$ value for an electrode may be expressed in terms of unit activity as shown below[11].

From thermodynamics,

$$\Delta F = - nFE \qquad 4)$$

and in a chemical reaction as

$$aA + bB = gG + hH \qquad 5)$$
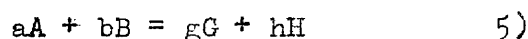
$$- \Delta F = RT\ln K - RT\ln \frac{a_G^g \cdot a_H^h}{a_A^a \cdot a_B^b} \qquad 6)$$

If the reacting materials are all at unit activity (i.e. the effective concentration is one mol per 1000 grams of solvent) $\Delta F$ is written

as $\Delta F^\circ$, and the last term of equation 6) becomes zero. Thus,

$$\Delta F^\circ = - RT \ln K \qquad (7)$$

Substituting equation 4) in equation 6),

$$E = \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln \frac{a_G^g \cdot a_H^h}{a_A^a \cdot a_B^b} \qquad 8)$$

Here again in the special case that reactants and products are all at unit activity equation 8) becomes

$$E^\circ = \frac{RT}{nF} \ln K \qquad 9)$$

Substituting 9) in 8)

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_G^g \cdot a_H^h}{a_A^a \cdot a_B^b} \qquad 10)$$

The standard electrode potential has already been defined as the potential of a metal in its standard state immersed in a solution of its ions at unit activity. Therefore, equation 10) can be employed to express the relation between the standard electrode potential, $E^\circ$, and the electrode potential, $E$, for any activity of the ions.

For an electrode of a metal, M, in a solution of its ions, $M^+$, of activity, $a_{M^+}$, and connected to the reference hydrogen electrode, the cell is:

$$H_2 \ (p = 1 \ atm.), \ H^+(a = 1) \ M^+, \ M \qquad 11)$$
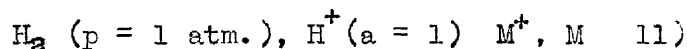
The reaction for this cell is written:

$$1/2 \ H_2 + M^+ = H^+ + M \qquad 12)$$
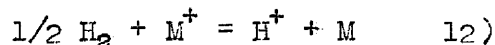
Applying equation 10)

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{H^+} \cdot a_M}{\sqrt{a_{H_2}} \ a_{M^+}} \qquad 13)$$

But in equation 13) $a_{H^+}, a_{H_2}$, and $a_M$ are fixed at unity. So

the equation becomes

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{1}{a_{M^+}} \quad . \quad 14)$$

or its equivalent,

$$E = E^{\circ} + \frac{RT}{nF} \ln a_{M^+}$$

Therefore, knowing the value of E and the value of $a_{M^+}$, the $E^{\circ}$ value can be calculated.

Similar considerations will be applied to the use of the glass electrode in the following section.

## Application of the Glass Electrode

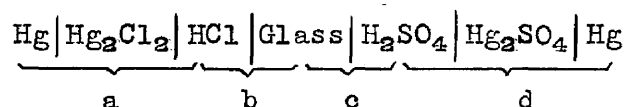The foregoing considerations may be applied to the measurement of standard potentials with the glass electrode in the following manner.

For the electrode, $SO_4^= | Hg_2SO_4 | Hg$, a cell using a calomel reference electrode was assembled as shown:

$$\underbrace{Hg | Hg_2Cl_2 | HCl}_{a} \; \underbrace{| Glass |}_{b} \; \underbrace{H_2SO_4}_{c} \; \underbrace{| Hg_2SO_4 | Hg}_{d}$$

For such a cell, the overall E. M. F. should be the sum of the various junction potentials, or,

$$E_{cell} = E_a + E_b + E_c + E_d \qquad 16)$$

Evaluating these junction potentials and substituting in equation 16) results in the following equation for $E_{cell}$ at $25°$ C.

$$E_{cell} = \left[ E_a^o - .05915 \log \frac{1}{\alpha_{Cl^-}} \right] + \left[ E_b^o - .05915 \log \frac{1}{\alpha_{H_b^+}} \right]$$
$$+ \left[ E_c^o - .05915 \log \alpha_{H_c^+} \right] + \left[ E_d^o - \frac{.05915}{2} \log \alpha_{SO_4^{--}} \right] \qquad 17)$$

But, since the glass electrode is sensitive only to $H^+$,

$$E_b^o = - E_c^o \qquad 18)$$

and these two terms cancel from equation 17). By this cancellation and combination where possible in equation 17), equation 19) results:

$$E_{cell} = E_a^o - .05915 \log \frac{1}{\alpha_{HCl}} + E_d^o - .02958 \log 4(\gamma m_{H_2SO_4})^3 \qquad 19)$$

From which

$$E_{cell} = E_a^o - .1183 \log \frac{1}{\gamma m_{HCl}} + E_d^o - .02958 \log 4(\gamma m_{H_2SO_4})^3 \qquad 20)$$

Solving equation 20) for $E_d^o$, the standard potential,

$$E_d^o = E_{cell} - E_a^o + .1183 \log \frac{1}{\gamma m_{HCl}} + .02958 \log 4(\gamma m_{H_2SO_4})^3 \qquad 21)$$

The equation in this form was employed for the calculation of the $E^o$ value for the electrode $SO_4^{--} | Hg_2SO_4 | Hg$.

For calculation of $E^o$ for the electrode $Cl^-|AgCl|Ag$ using a quinhydrone reference half cell, the cell employed was

$$Pt\,|\,\underbrace{(H_2Q,Q)\,|\,HCl}_{a}\,|\,\underbrace{Glass}_{b}\,|\,\underbrace{HCl}_{c}\,|\,\underbrace{AgCl\,|\,Ag}_{d}$$
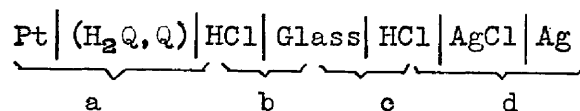
The equation for the $E^o$ value of the half cell, $Cl^-|AgCl|Ag$, then results from a similar derivation:

$$E_{cell} = E_a + E_b + E_c + E_d \qquad 22)$$

Evaluating the various potentials as before,

$$E_{cell} = \left[E_a^o - .05915 \log \alpha_{H_b^+}\right] + \left[E_b^o - .05915 \log \frac{1}{\alpha_{H_b^+}}\right]$$
$$+ \left[E_c^o - .05915 \log \alpha_{H_c^+}\right] + \left[E_d^o - .05915 \log \alpha_{Cl^-}\right] \qquad 23)$$

Combining and cancelling where possible gives

$$E_{cell} = E_a^o + E_d^o - .05915 \log \alpha_{HCl} \qquad 24)$$

or the equivalent expression,

$$E_{cell} = E_a^o + E_d^o - .1183 \log \gamma\, m_{HCl_c} \qquad 25)$$

from which

$$E_d^o = E_{cell} - E_a^o + .1183 \log \gamma m_{HCl_c} \qquad 26)$$

For purposes of intercomparison, each cell studied was measured against the others as references. The derivation for each cell will not be given, but instead the cells studied will be listed and with each the final form of the equation used for calculation of the $E^o$ value. In each case the half-cell used as reference is placed on the left hand side while the half-cell on the right is the one whose $E^o$ value is to be found. The following list is complete, including the two for which the $E^o$ value has been derived above.
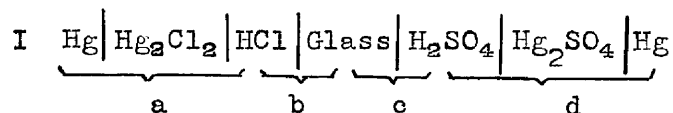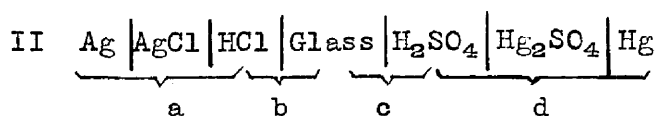
I $\quad \underbrace{Hg\,|\,Hg_2Cl_2\,|\,HCl}_{a}\,|\,\underbrace{Glass}_{b}\,|\,\underbrace{H_2SO_4}_{c}\,|\,\underbrace{Hg_2SO_4\,|\,Hg}_{d}$

$$E_d^o = E_{cell} - E_a^o + .1183 \log \frac{1}{\gamma m_{HCl}} + .02958 \log 4(\gamma m_{H_2SO_4})^3 \qquad 27)$$

II   $\underbrace{Ag \,|\, AgCl \,|\, HCl}_{a} \,\underbrace{|\, Glass \,|}_{b}\, \underbrace{H_2SO_4 \,|}_{c}\, \underbrace{Hg_2SO_4 \,|\, Hg}_{d}$

$$E_d^o = E_{cell} - E_a^o + .1183 \log \frac{1}{\gamma m_{HCl}} + .02958 \log 4 \,(\gamma m_{H_2SO_4})^3 \qquad 28)$$

III  $\underbrace{Pt \,|\, (H_2Q,Q) \,|\, HCl}_{a} \,\underbrace{|\, Glass \,|}_{b}\, \underbrace{H_2SO_4 \,|}_{c}\, \underbrace{Hg_2SO_4 \,|\, Hg}_{d}$

$$E_d^o = E_{cell} - E_a^o + .02958 \log 4(\gamma m_{H_2SO_4})^3 \qquad 29)$$

IV  $\underbrace{Hg \,|\, Hg_2Cl_2 \,|\, HCl}_{a} \,\underbrace{|\, Glass \,|}_{b}\, \underbrace{HCl \,|}_{c}\, \underbrace{AgCl \,|\, Ag}_{d}$
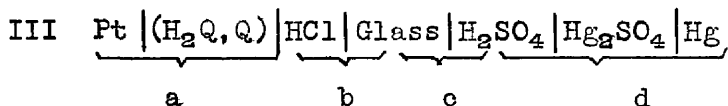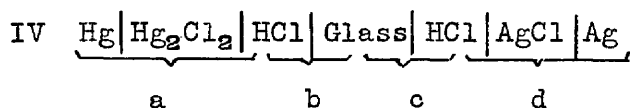
$$E_d^o = E_{cell} - E_a^o + .1183 \log \frac{1}{\gamma m_{HCl_a}} + .1183 \log \gamma m_{HCl_c} \qquad 30)$$
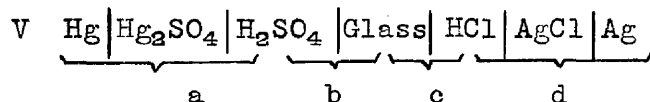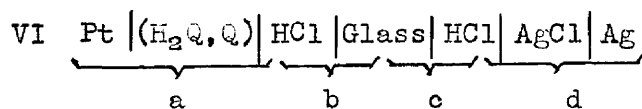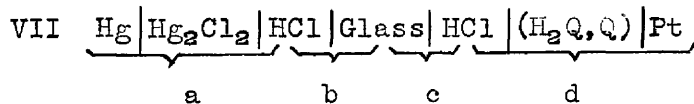
V  $\underbrace{Hg \,|\, Hg_2SO_4 \,|\, H_2SO_4}_{a} \,\underbrace{|\, Glass \,|}_{b}\, \underbrace{HCl \,|}_{c}\, \underbrace{AgCl \,|\, Ag}_{d}$

$$E_a^o = E_{cell} - E_a^o + .02958 \log \frac{1}{4(\gamma m_{H_2SO_4})^3} + .1183 \log \gamma m_{HCl} \qquad 31)$$

VI  $\underbrace{Pt \,|\, (H_2Q,Q) \,|\, HCl}_{a} \,\underbrace{|\, Glass \,|}_{b}\, \underbrace{HCl \,|}_{c}\, \underbrace{AgCl \,|\, Ag}_{d}$

$$E_d^o = E_{cell} - E_a^o + .1183 \log \gamma m_{HCl} \qquad 32)$$

VII  $\underbrace{Hg \,|\, Hg_2Cl_2 \,|\, HCl}_{a} \,\underbrace{|\, Glass \,|}_{b}\, \underbrace{HCl \,|}_{c}\, \underbrace{(H_2Q,Q) \,|\, Pt}_{d}$

$$E_d^o + E_{cell} - E_a^o + .1183 \log \frac{1}{\gamma m_{HCl}} \qquad 33)$$

VIII  $\underbrace{Hg \,|\, Hg_2SO_4 \,|\, H_2SO_4}_{a} \,\underbrace{|\, Glass \,|}_{b}\, \underbrace{HCl \,|}_{c}\, \underbrace{(H_2Q,Q) \,|\, Pt}_{d}$

$$E_d^o = E_{cell} - E_a^o - .02958 \log 4(\gamma m_{H_2SO_4})^3 \qquad 34)$$

IX  $\underbrace{Ag \,|\, AgCl \,|\, HCl}_{a} \,\underbrace{|\, Glass \,|}_{b}\, \underbrace{HCl \,|}_{c}\, \underbrace{(H_2Q,Q) \,|\, Pt}_{d}$

$$E_d^o + E_{cell} - E_a^o + .1183 \log \frac{1}{\gamma m_{HCl}} \qquad 35)$$

X $\quad$ Ag| AgCl | HCl | Glass | HCl | Hg$_2$Cl$_2$ | Hg

$\qquad$ a $\qquad$ b $\qquad$ c $\qquad$ d
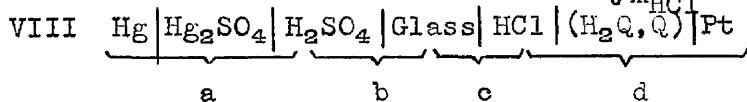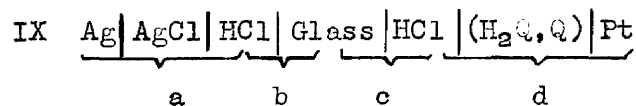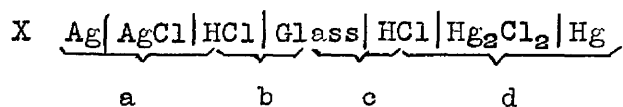
$$E_d^O = E_{cell} - E_a^O + .1183 \log \frac{1}{\gamma m_{HCl_b}} + .1183 \log \gamma m_{HCl_c} \qquad 36)$$

XI $\quad$ Hg | Hg$_2$SO$_4$ | H$_2$SO$_4$ | Glass | HCl | Hg$_2$Cl$_2$ | Hg

$\qquad$ a $\qquad$ b $\qquad$ c $\qquad$ d
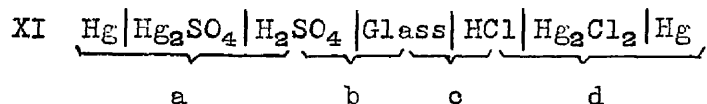
$$E_d^O = E_{cell} - E_a^O + .02958 \log \frac{1}{4(\gamma m_{H_2SO_4})^3} + .1183 \log \gamma m_{HCl} \qquad 37)$$

In all of these equations the symbols used have the following significance.

$E_d^O$ $\quad$ The standard potential of the electrode measured as unknown.

$E_a^O$ $\quad$ The standard potential of the reference electrode.

$E_{cell}$ $\quad$ The measured E. M. F. of the unknown cell corrected for

$\qquad$ asymmetry potential.

$\gamma$ $\quad$ Activity coefficient of acid used.

m $\quad$ Molality of acid.

By measuring these cell combinations at various concentrations it was possible to determine the $E^O$ values for the half-cells and to intercompare the various references through the values obtained. $E^O$ for the reference was, in every case, taken as the best literature value.

## III.  EXPERIMENTAL

Apparatus

Glass Electrode

The electrode used was a commercial type designed by Ellis and Kiehl and marketed by the Hellige Company.  The electrode is shown schematically in figure I in which the lettered parts are as follows:

A.  Detachable electrode

B.  Permanent electrode

C.  Small cup for holding the electrolyte

D.  Stopcock

E.  Rubber bulb for filling the electrode

F.  Cylindrical glass electrode membrane

G.  Capillary tube

H.  Metal contact

I.  Extension on glass membrane

The technique employed will be discussed in a later section.

Galvanometer

The galvanometer used was the Leeds and Northrup dual type galvanometer, 2480-C.  It has the following characteristics:

Sensitivity, 0.0005 $\mu$a /mm.

Period, 3 seconds

Damping resistance, 15,000 ohms

Coil resistance, 1000 ohms.

Thermionic Amplifier

In any high resistance system, such as the glass electrode system, special equipment is necessary because of the very small currents to be measured.  Further, since the currents are so small the effect of electro-
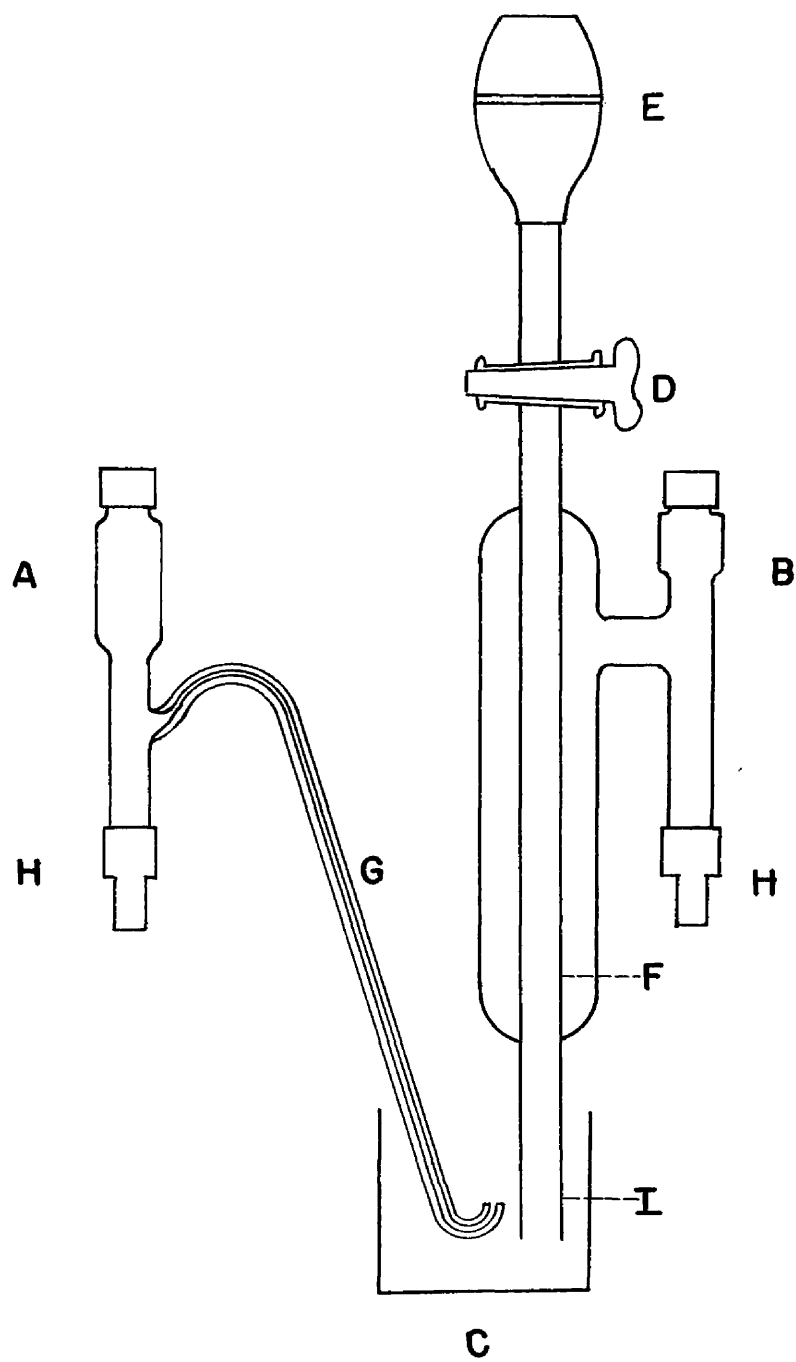
FIGURE I

GLASS ELECTRODE

static disturbances and stray currents of various kinds become so pronounced that the system must be thoroughly shielded in order to make the use of sensitive instruments possible.  For measurements of this kind apparatus employing electron tubes have been found most applicable because of their sensitivity and the small amount of current drawn.

In the present research the instrument used was a Leeds and Northrup Thermionic amplifier, No. 7673.  The wiring diagram[12] for this amplifier is shown in figure II.  The electron tube in this amplifier is one manufactured by the Westinghouse Company and listed as electrometer tube RH-507.  This tube is known as an "inverted triode" tube, and has the normal functions of grid and plate reversed.

The anode current was supplied by a small C battery.  The current was 6 V. rather than 4.5 V. as shown in the diagram.  The current was allowed to flow continuously to keep it constant.  The filament current was, in the early part of the work, supplied by a lead storage battery, and later by a group of Eveready air cells.  The latter were found to be more satisfactory.  While the amplifier was not in use, the current was allowed to flow through a resistance equal to that of the amplifier in order to keep it constant.

In operating the amplifier, f and j are used to adjust the electrical zero of the galvanometer.  The unknown E. M. F. is measured by connecting a potentiometer to terminals marked POT and the unknown cell to terminals marked E. M. F.  By releasing switch X to the upper position the control electrode is charged to a negative potential equal to the potential of the housing plus the unknown E. M. F., if the potentiometer is zero.  By adjusting the potentiometer until the galvanometer returns to its original position, the unknown E. M. F. can be determined and is equal to the potentiometer reading at balance.
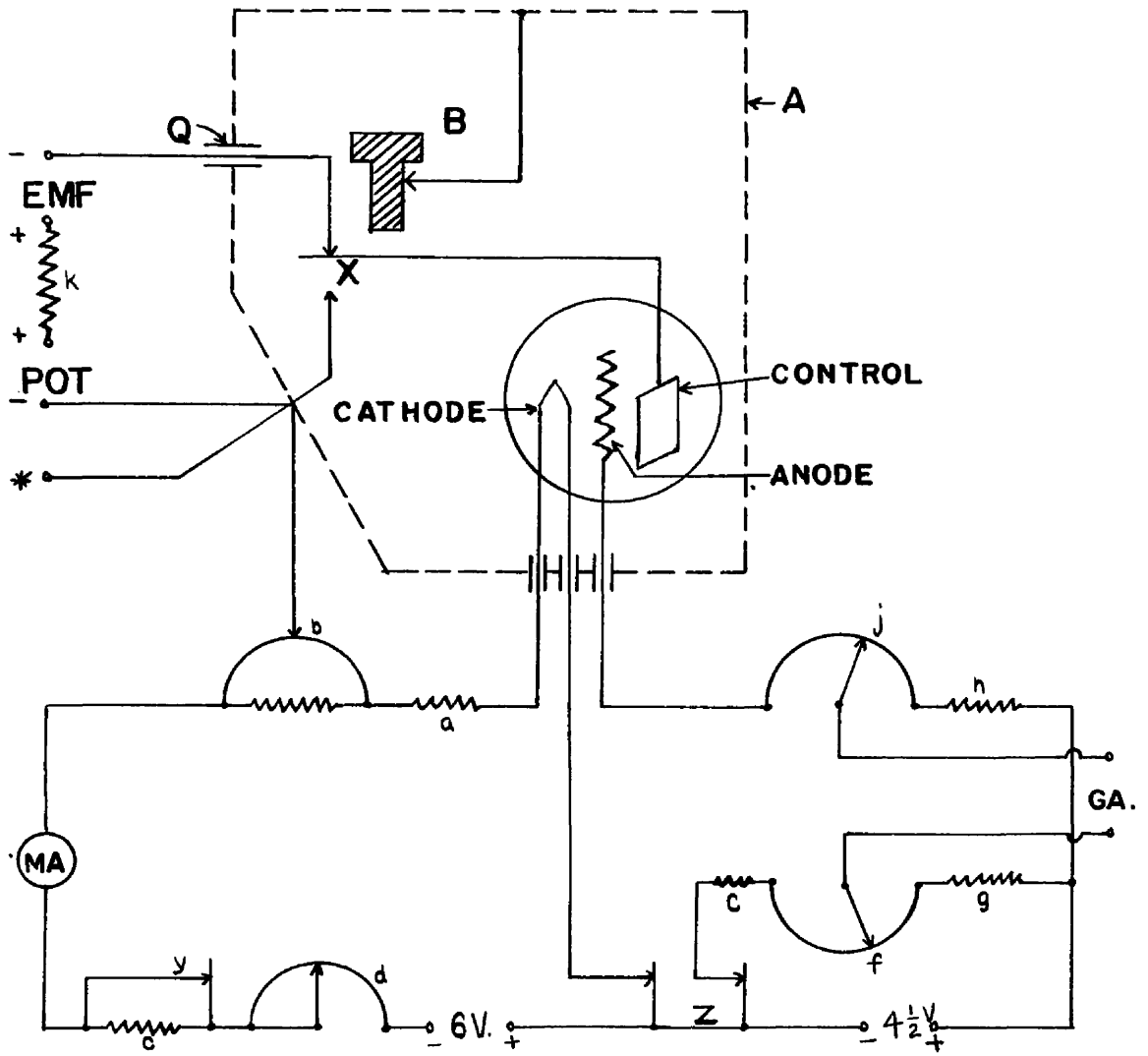
FIGURE II

AMPLIFIER CIRCUIT

The circuit employed for E. M. F. measurement is shown diagrammatically in Figure III. The E. M. F. leads passing into the metal box of the air bath were insulated by 2 1/2 inch quartz tubes set in large rubber stoppers. These leads between the amplifier and the air bath were shielded by a U shaped aluminum sheet.

Potentiometer

All E. M. F. measurements were made with a Leeds and Northrup Type K potentiometer.

Constant Temperature Air Bath

Constant temperature for cell measurements was maintained in an air bath regulated by a mercury thermoregulator and supersensitive relay which kept the temperature constant at $25° \pm 0.1°$ C. Heating was accomplished by means of a small 12 watt carbon filament light bulb mounted in the top of the box. Cooling was effected by a copper coil through which cold water was circulated. Stirring was effected by a relatively large aluminum propellor driven externally.

The steel box, 8" x 12" x 16" in size, was covered with prestwood which acted as insulation to prevent excessive heat losses through the metal walls. The metal walls served as a shield for the unknown cell and prevented errors due to stray currents.

Weights

The weights used were calibrated against a 10 gram weight calibrated by the Bureau of Standards.
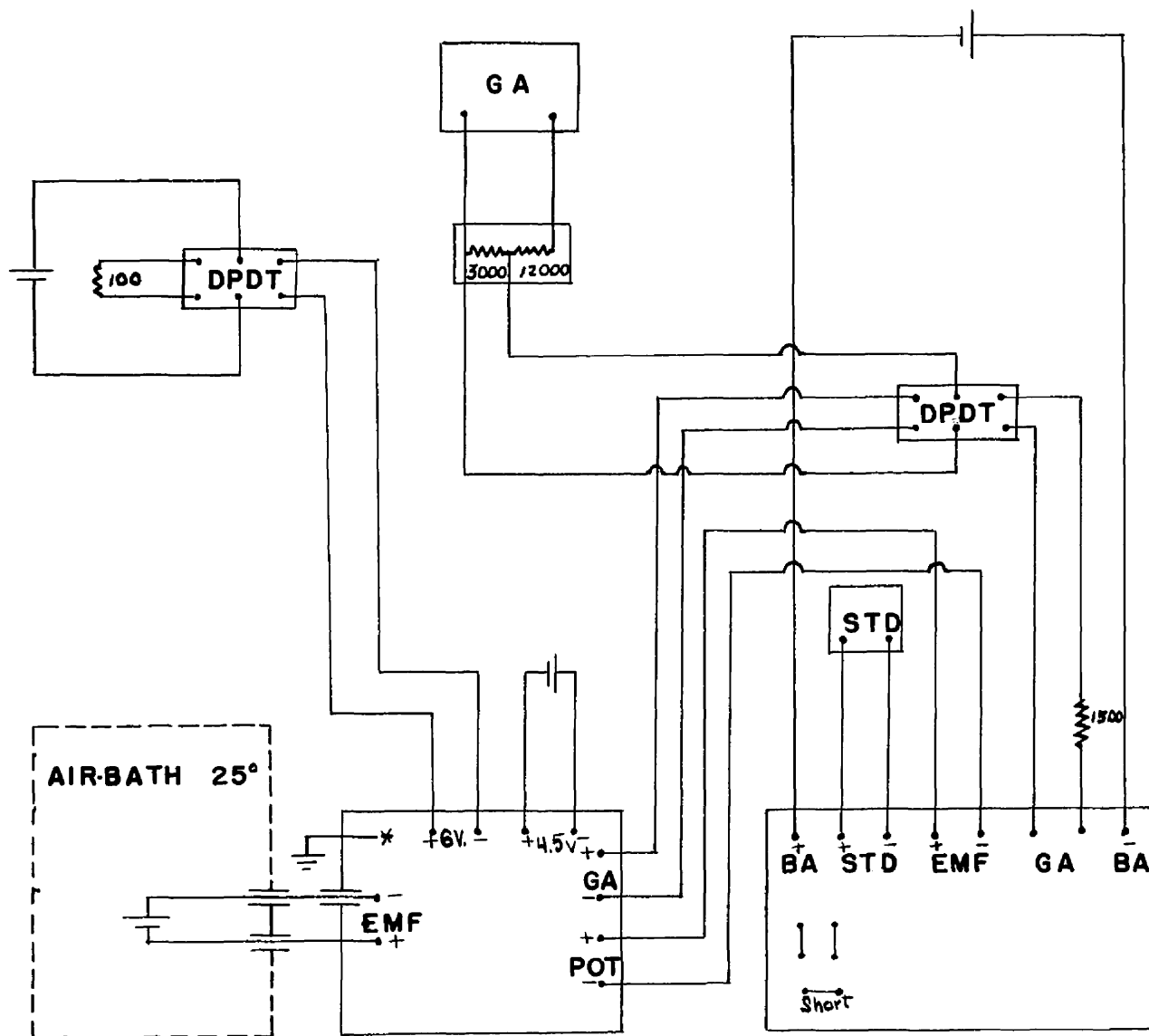
FIGURE III

E.M.F. CIRCUIT

Reagents

Water

Conductivity water of 1.5 micromhos was used in the preparation of all solutions.

Sodium Carbonate

The sodium carbonate used in the standardization of the acid solutions was of reagent quality. It was prepared for use by heating to a temperature of 270° to 280° C., at which temperature it was maintained for 1 1/2 hours. Titrations were run in triplicate using methyl orange as the indicator. The desired concentrations were prepared from the standard acid solutions by dilution on a weight basis. All concentrations are expressed on a molal basis.

Mercurous Sulfate

The mercurous sulfate used in the study of the electrode, $SO_4^= | Hg_2SO_4 | Hg$, was prepared by the electrolytic method of Clark and Weston[13].

Mercury

The mercury used was cleaned and treated according to the method of Hulett and Minchin[14].

Other Reagents

All other reagents employed were of reagent quality.

## Preparation of Electrodes

### Calomel Electrodes

The calomel electrodes used were prepared in the following manner. The electrode compartment was thoroughly cleaned and rinsed with acid of the concentration to be used in the half-cell. The bottom of the compartment was dried in the vicinity of the platinum contact and mercury added to a depth of about 0.5 to 0.7 centimeter. Over the mercury was placed about the same depth of paste prepared from calomel, mercury, and acid of the concentration to be used. The cell was then filled with hydrochloric acid of the proper concentration. The electrode used as a reference was prepared in compartment B of Figure I. Half-cells to be measured were prepared in units corresponding to compartment A of Figure I. For measuring the asymmetry potential, the electrodes in A and B were of the same composition.

### Mercury-Mercurous Sulfate-Sulfate-ion Electrodes

These electrodes were prepared in a manner similar to the above, first cleaning the units, rinsing with acid of the proper concentration, then drying the part of the electrode which was to hold the mercury. In this case, the layer of mercury was covered with a layer of mercurous sulfate previously rinsed six times with sulfuric acid of the concentration used in the cell. The rinsing was done just before use of the mercurous sulfate.

### Quinhydrone Electrodes

Hydrochloric acid of various concentrations was freed from dissolved air by heating to boiling in a long necked flask. After cooling to room temperature the acid was saturated with quinhydrone in a glass stoppered flask. Cells were made up by placing this saturated solution in the

electrode vessels and inserting a platinum spiral electrode previously cleaned in dichromate cleaning solution. To insure saturation some solid quinhydrone was added to each half-cell prepared. This solution was freshly prepared for each measurement employing quinhydrone either as a reference or as an unknown cell.

Silver-Silver Chloride-Chloride-ion Electrodes

These electrodes were prepared on a roll of platinum gauze welded to a platinum wire sealed in soft glass. The total area of four of these electrodes was calculated to be 27 square centimeters. The gauze after thorough cleaning was silver plated in a bath containing 34 grams of sodium cyanide and 24 grams of silver (from silver nitrate) in a liter of water. This bath is of the composition recommended by Blum and Hogaboom[15]. Four electrodes were plated simultaneously using a silver anode.

The electrodes were connected in parallel, symmetrically arranged about the anode, and plated for six hours at a current density of four milliamperes per square centimeter. The plating was done at room temperature with occasional stirring.

After plating the electrodes were washed over a period of four days using 12 changes of distilled water. Each change of water was heated to boiling with the electrodes immersed in an attempt to increase the rate of washing.

After this thorough cleaning the electrodes were chloridized in a 0.1 molal HCl solution using the same current density as before. The electrodes were connected in parallel, and treated simultaneously. The cathode was platinum.

The preparation was completed by washing in distilled water for two days, then putting the electrodes to soak in acid of the concentration

to be used in their measurement. The time of soaking of each electrode
before measuring against the various references is given in the following
table.

| Conc. of HCl on Electrode | Time of soaking (in days) before measurement | | |
|---|---|---|---|
| | Against $Hg\|Hg_2Cl_2\|Cl^-$ | Against $Hg\|Hg_2SO_4\|SO_4^{--}$ | Against $Pt\|H_2Q,Q\|H^+$ |
| 0.20m | 7 | 10 | 33 |
| 0.10m | 6 | 1 | 34 |
| 0.05m | 12 | 14 | 17 |
| 0.01m | 12 | 14 | 17 |

Table I - A

For measurement these electrodes were placed in small electrode
vessels with side-arm dipping into cup C, of Figure I.

In all cases the electrode used as a reference was placed in
the permanent electrode compartment, represented by B of Figure I. The
electrodes measured were run in duplicate in units corresponding to A
of Figure I. In the cases of the quinhydrone electrode, and the silver-
silver chloride electrode contact was not made through the metal contact
at the bottom of the electrode vessel, but through a wire dipping into
mercury in the glass tube holding the platinum.

The reference electrode compartment, B of Figure I, was always
rinsed at least six times with the appropriate solution before assembling
the electrode.

Measurement of the E. M. F. of Cells

The complete cell for measurement was assembled as follows. Referring to Figure I, the stopcock D was first opened and the lower end of the tube, I, placed in cup C, containing acid of the concentration to be used in a particular cell. By pressing bulb E, acid was drawn up inside the glass electrode membrane. In this manner the inner surface of the electrode was rinsed with several portions of the appropriate acid before measuring a cell. Finally a portion of acid was drawn up inside the membrane to the height of the surrounding jacket and the stopcock closed. Electrodes in units corresponding to A of Figure I were placed in position with the side-arms dipping into cup C. The acid in these electrodes was of the same concentration as that in the cup. Electrodes were measured in duplicate.

To obtain the overall E. M. F. of any cell three measurements were necessary. Using, for example, measurement of the $E^o$ for the $SO_4^-|Hg_2SO_4|Hg$ electrode employing 0.1 molal $H_2SO_4$ against a calomel reference, the three measurements are:

1) Measurement of the asymmetry potential of the glass electrode using the same half-cell on each side of the membrane:

$$Hg|Hg_2Cl_2|HCl\ (0.1m)|Glass|HCl\ (.1m)|Hg_2Cl_2|Hg$$
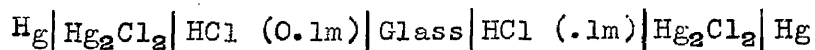
Any E. M. F. observed here would be due to a difference in behavior of the glass membrane on the two sides. This cell was allowed about one hour to come to temperature equilibrium.

2) Measurement of the unknown E. M. F. of the cell:

$$Hg|Hg_2Cl_2|HCl\ (.1m)|Glass|H_2SO_4\ (.1m)|Hg_2SO_4|Hg$$
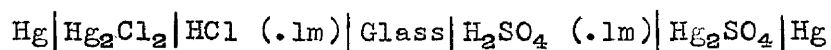
The unknown cells were allowed an hour to reach temperature equilibrium, then readings taken until constant within 0.1 millivolt. This usually

required a period of from 3 to 7 hours. The quinhydrone cells reached equilibrium most rapidly. The calomel cells required at least a day to reach the desired constancy.

3) Remeasurement of the asymmetry potential using the same cell as in the first measurement.

## IV. RESULTS

Calculation

For calculation of the $E^o$ values measured, equations 27) to 37) were used together with the data of the tables which follow. From tables I-B and I-C the $\gamma m$ values were obtained; from I-D, the $E^o$ values of the reference electrodes employed; and from tables I to XI, the cell E. M. F. values. Tables I to XI correspond to equations I to XI (these equations are 27) to 37) but were given Roman numerals to correspond to the tables assembled by their use.)

Taking for example the calculation of $E^o$ for the half-cell $SO_4^{--}|Hg_2SO_4|Hg$ using 0.1 molal $H_2SO_4$ and measured against a calomel reference the following calculation results.

Equation 27) (or I) is used:

$$E_d^o = E_{cell} - E_a^o + .1183 \log \frac{1}{\gamma m_{HCl}} + .02958 \log 4(\gamma m_{H_2SO_4})^3$$

Substituting the values

$$E_{cell} = 0.3390 \text{ (Table I)}$$

$$E_a^o = -0.2676 \text{ (Table I-D)}$$

$$.1183 \log \frac{1}{\gamma m_{HCl}} = 0.1300 \text{ (Table I-B)}$$

$$.02958 \log 4(\gamma m_{H_2SO_4})^3 = -0.1221$$

$$E_d^o = 0.3390 - (-0.2676) + 0.1300 + (-0.1221)$$

$$E_d^o = 0.6145$$

The $E^o$ values for all electrodes measured are calculated in the same manner using data from the appropriate tables. These results are listed in the last column of each table from table I to table XI. These tables include also the cell measured, the sign of the E. M. F. (found experimentally), and the asymmetry potentials. The average asymmetry

potential was used in calculating all $E^o$ values listed.

Activity Coefficients for Hydrochloric Acid

| Molality of HCl | Activity (16) Coefficient | Value of .1183 log $\gamma m_{HCl}$ |
|---|---|---|
| 0.20 molal | 0.766 | -0.0964 |
| 0.10 " | 0.796 | -0.1300 |
| 0.05 " | 0.829 | -0.1636 |
| 0.01 " | 0.904 | -0.2418 |

Table I-B

Activity Coefficients for Sulfuric Acid

| Molality of $H_2SO_4$ | Activity (17) Coefficient | .02958 log $4(\gamma\, m_{H_2SO_4})^3$ |
|---|---|---|
| 0.30 molal | 0.180 | -0.0947 |
| 0.20 " | 0.209 | -0.1045 |
| 0.10 " | 0.265 | -0.1221 |
| 0.05 " | 0.340 | -0.1392 |
| 0.02 " | 0.453 | -0.1635 |
| 0.01 " | 0.544 | -0.1831 |

Table I-C

$E^o$ Values for Reference Electrodes

| Reference Electrode | $E^o$ Value | |
|---|---|---|
| $Hg\,\vert\,Hg_2Cl_2\,\vert\,Cl^-$ | -0.2676 | (18) |
| $Hg\,\vert\,Hg_2SO_4\,\vert\,SO_4^{--}$ | -0.6152 | (19) |
| $Ag\,\vert\,AgCl\,\vert\,Cl^-$ | -0.2223 | (20) |
| $Pt\,\vert\,(H_2Q,Q)\,\vert\,H^+$ | -0.6990 | (21) |

Table I-D
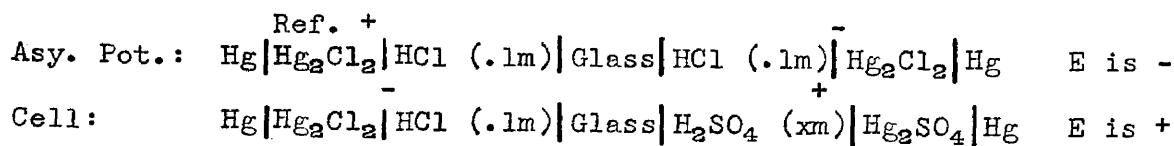
Asy. Pot.:  Hg|Hg$_2$Cl$_2$|HCl (.1m)|Glass|HCl (.1m)|Hg$_2$Cl$_2$|Hg    E is -

Ref. +                                          -

Cell:      Hg|Hg$_2$Cl$_2$|HCl (.1m)|Glass|H$_2$SO$_4$ (xm)|Hg$_2$SO$_4$|Hg    E is +

-                                          +

Overall E is sum of two potentials.

| Conc. of H$_2$SO$_4$ | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E$_{cell}$ Measured | Overall E of Cell | E$^o$ of Cell Eq. 27 |
|---|---|---|---|---|---|---|
| 0.30 m | -0.0088 | -0.0091 | -0.0090 | 0.3022 | 0.3112 | 0.6141 |
| 0.20 | -0.0091 | -0.0094 | -0.0093 | 0.3119 | 0.3212 | 0.6143 |
| 0.10 | -0.0094 | -0.0093 | -0.0094 | 0.3296 | 0.3390 | 0.6145 |
| 0.05 | -0.0090 | -0.0091 | -0.0091 | 0.3475 | 0.3566 | 0.6150 |
| 0.02 | -0.0091 | -0.0093 | -0.0092 | 0.3715 | 0.3807 | 0.6148 |
| 0.01 | -0.0091 | -0.0092 | -0.0092 | 0.3906 | 0.3998 | 0.6143 |

Table I
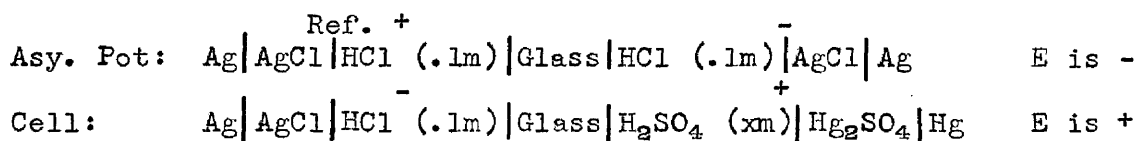
Asy. Pot:  Ag|AgCl|HCl (.1m)|Glass|HCl (.1m)|AgCl|Ag    E is -

Ref. +                                          -

Cell:      Ag|AgCl|HCl (.1m)|Glass|H$_2$SO$_4$ (xm)|Hg$_2$SO$_4$|Hg    E is +

-                                          +

Overall E is sum of two potentials.

| Conc. of H$_2$SO$_4$ | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E of Cell Measured | E of Cell Overall | E$^o$ of Cell Eq. 28 |
|---|---|---|---|---|---|---|
| 0.30 m | -0.0079 | -0.0071 | -0.0075 | 0.3491 | 0.3566 | 0.6142 |
| 0.20 | -0.0078 | -0.0079 | -0.0079 | 0.3596 | 0.3675 | 0.6153 |
| 0.10 | -0.0079 | -0.0069 | -0.0074 | 0.3764 | 0.3838 | 0.6140 |
| 0.05 | -0.0073 | -0.0078 | -0.0076 | 0.3941 | 0.4017 | 0.6148 |
| 0.02 | -0.0078 | -0.0052 | -0.0065 | 0.4171 | 0.4236 | 0.6124 |
| 0.01 | -0.0032 | -0.0056 | -0.0044 | 0.4358 | 0.4402 | 0.6094 |

Table II

Ref. +
Asy. Pot.: $Pt|(H_2Q,Q)|HCl$ (.1m) $|Glass|HCl$ (.1m) $\overline{|H_2Q,Q|}Pt$    E is -

Cell:    $Pt|(H_2Q,Q)|HCl$ (.1m) $|Glass|H_2SO_4$ (xm) $\overset{+}{Hg_2SO_4}|Hg$    E is +

Overall E is sum of two potentials.

| Conc. of $H_2SO_4$ | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E of Cell Measured | E of Cell Overall | $E^\circ$ of Cell Eq. 29 |
|---|---|---|---|---|---|---|
| 0.30 m | -0.0064 | -0.0060 | -0.0062 | 0.0038 | 0.0100 | 0.6144 |
| 0.20 | -0.0065 | -0.0064 | -0.0065 | 0.0144 | 0.0209 | 0.6154 |
| 0.10 | -0.0065 | -0.0065 | -0.0065 | 0.0315 | 0.0380 | 0.6149 |
| 0.05 | -0.0060 | -0.0067 | -0.0064 | 0.0488 | 0.0552 | 0.6150 |
| 0.02 | -0.0068 | -0.0058 | -0.0058 | 0.0730 | 0.0788 | 0.6143 |
| 0.01 | -0.0055 | -0.0048 | -0.0052 | 0.0928 | 0.0980 | 0.6139 |

Table III

Ref. +
Asy. Pot: $Hg|Hg_2Cl_2|HCl$ (.1m) $|Glass|HCl$ (.1m) $\overline{|Hg_2Cl_2|}Hg$    E is -

Cell:    $Hg|Hg_2Cl_2|HCl$ (.1m) $|Glass|HCl$ (xm) $\overline{|AgCl|}Ag$    E is -

Overall E is difference of two potentials.

| Conc. of HCl | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E of Cell Measured | E of Cell Overall | $E^\circ$ of Cell Eq. 30 |
|---|---|---|---|---|---|---|
| 0.20 m | -0.0087 | -0.0087 | -0.0087 | -0.0893 | -0.0806 | 0.2206 |
| 0.10 | -0.0087 | -0.0089 | -0.0088 | -0.0557 | -0.0469 | 0.2207 |
| 0.05 | -0.0059 | -0.0061 | -0.0060 | -0.0192 | -0.0132 | 0.2208 |
| 0.01 | -0.0061 | -0.0061 | -0.0061 | +0.0578 | +0.0639 | 0.2197 |

Table IV

Asy. Pot.:  $Hg \mid Hg_2SO_4 \mid H_2SO_4$ (.1m) $\mid$ Glass $\mid$ $H_2SO_4$ (.1m) $\mid Hg_2SO_4 \mid Hg$   E is $-$

Ref. $+$    $+$                              $-$

Cell:  $Hg \mid Hg_2SO_4 \mid H_2SO_4$ (.1m) $\mid$ Glass $\mid$ HCl (xm) $\mid$ AgCl $\mid$ Ag   E is $-$

Overall E is difference of two potentials.

| Conc. of HCl | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E of Cell Measured | E of Cell Overall | $E^o$ of Cell Eq. 31 |
|---|---|---|---|---|---|---|
| 0.20 m | -0.0077 | -0.0079 | -0.0078 | -0.4266 | -0.4188 | 0.2210 |
| 0.10 | -0.0084 | -0.0078 | -0.0081 | -0.3944 | -0.3863 | 0.2221 |
| 0.05 | -0.0065 | -0.0069 | -0.0067 | -0.3591 | -0.3524 | 0.2213 |
| 0.01 | -0.0069 | -0.0069 | -0.0069 | -0.2805 | -0.2736 | 0.2219 |

Table V

Asy. Pot.:  $Pt \mid (H_2Q,Q) \mid HCl$ (.1m) $\mid$ Glass $\mid$ HCl (.1m) $\mid (H_2Q,Q) \mid Pt$   E is $-$

Ref. $+$    $+$                              $-$

Cell:  $Pt \mid (H_2Q,Q) \mid HCl$ (.1m) $\mid$ Glass $\mid$ HCl (xm) $\mid$ AgCl $\mid$ Ag   E is $-$

Overall E is difference of two potentials.

| Conc. of HCl | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E of Cell Measured | E of Cell Overall | $E^o$ of Cell Eq. 32 |
|---|---|---|---|---|---|---|
| 0.20 m | -0.0059 | -0.0007 | -0.0033 | -0.3846 | -0.3813 | 0.2225 |
| 0.10 | -0.0069 | -0.0042 | -0.0056 | -0.3521 | -0.3465 | 0.2225 |
| 0.05 | -0.0083 | -0.0071 | -0.0077 | -0.3205 | -0.3128 | 0.2226 |
| 0.01 | -0.0076 | -0.0082 | -0.0079 | -0.2435 | -0.2356 | 0.2216 |

Table VI

Ref. +

Asy. Pot: $Hg \mid Hg_2Cl_2 \mid HCl$ (.1m) | Glass | HCl (.1m) | $Hg_2Cl_2 \mid Hg$    E is −

Cell: $Hg \mid Hg_2Cl_2 \mid HCl$ (.1m) | Glass | HCl (xm) | $(H_2Q,Q)$ | Pt    E is +

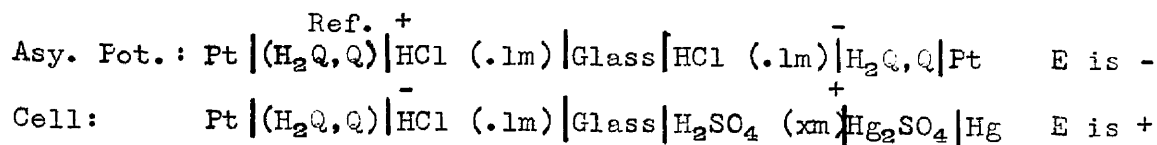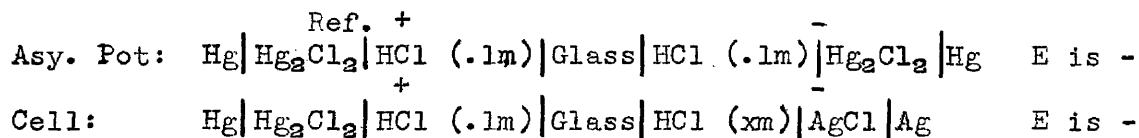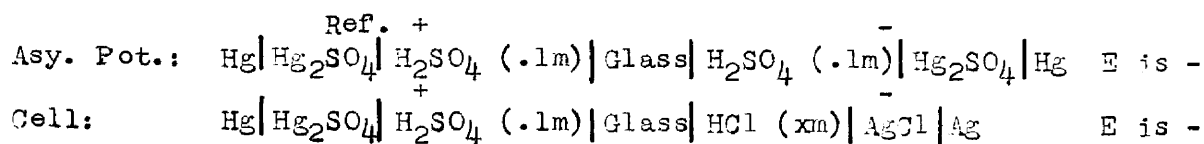Overall E is sum of two potentials.

| Conc. of HCl | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E of Cell Measured | E of Cell Overall | $E^o$ of Cell Eq. 33. |
|---|---|---|---|---|---|---|
| 0.20 m | −0.0060 | −0.0060 | −0.0060 | 0.2918 | 0.2978 | 0.6954 |
| 0.10 | −0.0060 | −0.0060 | −0.0060 | 0.2919 | 0.2979 | 0.6955 |
| 0.05 | −0.0060 | −0.0060 | −0.0060 | 0.2918 | 0.2978 | 0.6954 |
| 0.01 | −0.0060 | −0.0052 | −0.0056 | 0.2923 | 0.2979 | 0.6955 |

Table VII

Ref. +

Asy. Pot: $Hg \mid Hg_2SO_4 \mid H_2SO_4$ (.1m) | Glass | $H_2SO_4$ (.1m) | $Hg_2SO_4 \mid Hg$   E is −

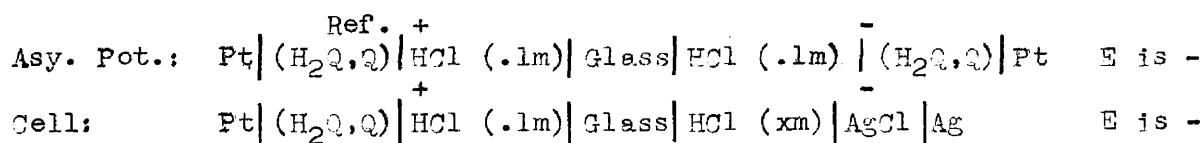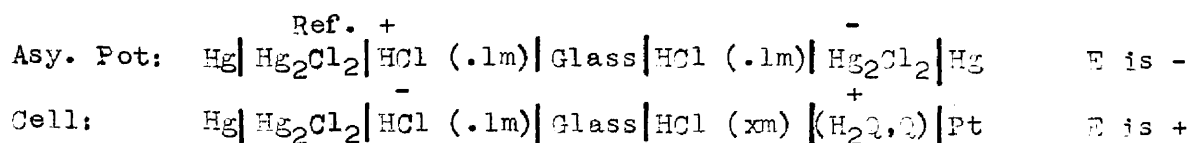Cell: $Hg \mid Hg_2SO_4 \mid H_2SO_4$ (.1m) | Glass | HCl (xm) | $(H_2Q,Q)$ | Pt   E is −

Overall E is difference of two potentials.

| Conc. of HCl | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E of Cell Measured | E of Cell Overall | $E^o$ of Cell Eq. 34 |
|---|---|---|---|---|---|---|
| 0.20 m | −0.0069 | −0.0070 | −0.0070 | −0.0467 | −0.0397 | 0.6976 |
| 0.10 | −0.0070 | −0.0069 | −0.0070 | −0.0469 | −0.0399 | 0.6974 |
| 0.05 | −0.0069 | −0.0067 | −0.0068 | −0.0466 | −0.0398 | 0.6975 |
| 0.01 | −0.0067 | −0.0068 | −0.0068 | −0.0468 | −0.0400 | 0.6973 |

Table VIII

Asy. Pot.:    Ag | AgCl | $\overset{\text{Ref. +}}{\text{HCl}}$ (.05m) | Glass | HCl (.05m) | $\overset{-}{\text{AgCl}}$ | Ag         E is -

Cell:    Ag | AgCl | $\overset{-}{\text{HCl}}$ (.05m) | Glass | HCl (xm) | $\overset{+}{(\text{H}_2,\text{Q})}$ | Pt         E is +
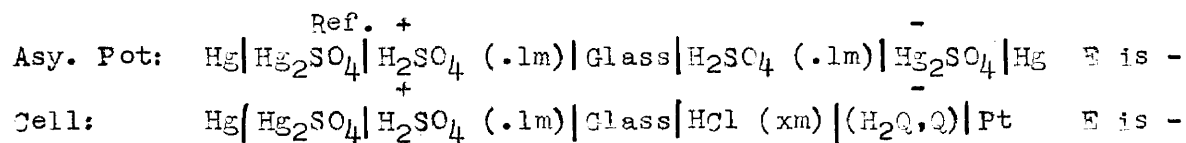
Overall E is sum of two potentials

| Conc. of HCl | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E of Cell Measured | E of Cell Overall | E° of Cell Eq. 35 |
|---|---|---|---|---|---|---|
| 0.20 m | -0.0077 | -0.0068 | -0.0073 | 0.3045 | 0.3118 | 0.6977 |
| 0.10 | -0.0068 | -0.0075 | -0.0072 | 0.3025 | 0.3097 | 0.6956 |
| 0.05 | -0.0075 | -0.0079 | -0.0077 | 0.3029 | 0.3106 | 0.6965 |
| 0.01 | -0.0079 | -0.0083 | -0.0081 | 0.3025 | 0.3108 | 0.6965 |

Table IX

Asy. Pot:    Ag | AgCl | $\overset{\text{Ref. +}}{\text{HCl}}$ (.05m) | Glass | HCl (.05m) | $\overset{-}{\text{AgCl}}$ | Ag         E is -

Cell:    Ag | AgCl | $\overset{-}{\text{HCl}}$ (.05m) | Glass | HCl (xm) | $\overset{+}{\text{Hg}_2\text{Cl}_2}$ | Hg         E is +
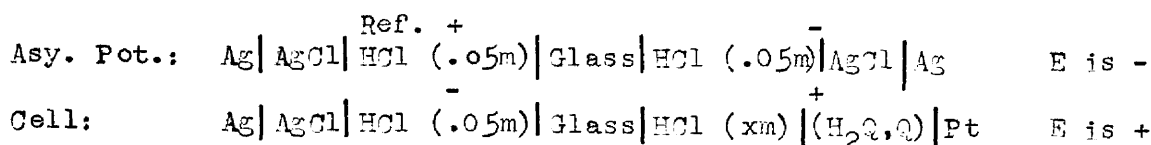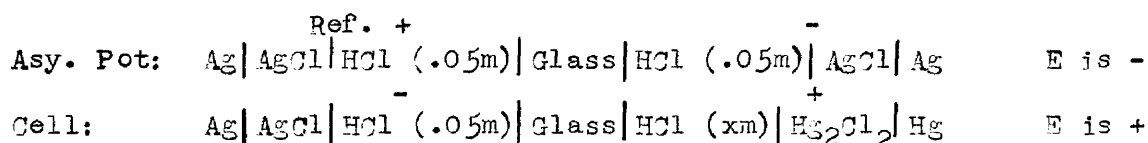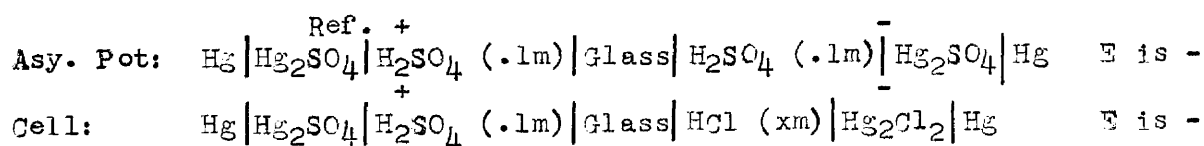
Overall E is sum of two potentials

| Conc. of HCl | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E of Cell Measured | E of Cell Overall | E° of Cell Eq. 36 |
|---|---|---|---|---|---|---|
| 0.10 m | -0.0092 | -0.0082 | -0.0087 | 0.0026 | 0.0113 | 0.2672 |
| 0.05 m | -0.0078 | -0.0076 | -0.0077 | 0.0367 | 0.0444 | 0.2667 |

Table X

Asy. Pot:    Hg | Hg$_2$SO$_4$ | $\overset{\text{Ref. +}}{\text{H}_2\text{SO}_4}$ (.1m) | Glass | H$_2$SO$_4$ (.1m) | $\overset{-}{\text{Hg}_2\text{SO}_4}$ | Hg         E is -

Cell:    Hg | Hg$_2$SO$_4$ | $\overset{+}{\text{H}_2\text{SO}_4}$ (.1m) | Glass | HCl (xm) | $\text{Hg}_2\text{Cl}_2$ | Hg         E is -

Overall E is difference of two potentials

| Conc. of HCl | Asy. Pot. Before | Asy. Pot. After | Asy. Pot. Average | E of Cell Measured | E of Cell Overall | E° of Cell Eq. 37 |
|---|---|---|---|---|---|---|
| 0.10 m | -0.0070 | -0.0069 | -0.0070 | -0.3473 | -0.3403 | 0.2670 |
| 0.05 m | -0.0074 | -0.0073 | -0.0074 | -0.3142 | -0.3068 | 0.2669 |

Table XI

Discussion of Results

For convenience all of the $E^\circ$ values determined have been grouped

together in tables XII to XV.  In tables XII and XIII have been placed

also the results obtained for the same electrodes in the preliminary

research.

## The $SO_4^= | Hg_2SO_4 | Hg$ Electrode

Referring to table XII in which are given the values found for $E^\circ$

of the $SO_4^= | Hg_2SO_4 | Hg$ electrode, it is seen that in each case the average

value for the electrode is nearly the same.  The values obtained using

the calomel reference are the most consistent showing an overall variation

of 0.9 millivolt.  With the silver-silver chloride reference (disregarding

the last two values) the overall variation is 1.3 millivolts, and with the

quinhydrone reference, 1.5 millivolts.  In all cases, the average value

is within 0.7 millivolt of the accepted value of 0.6152 v.  (See table

I-D)  This is an error of 0.11 percent.  The results found previously

gave an average value of .6134 V, nearly 2 millivolts from the accepted

value.  The improved results are believed due to better equipment for

E. M. F. measurement since the cells were prepared in the same manner.

The $SO_4^{--} | Hg_2SO_4 | Hg$ electrode was found to reach equilibrium quite

rapidly; constant readings were obtained within three hours.  Reproducible

results were obtained using freshly prepared electrolytic mercurous sulfate

and another sample which had been prepared for over a year.

The measurements were not carried to low acid concentrations since

it has been shown (22) that the values fall rapidly, due to hydrolysis

of the mercurous sulfate.

The last two values for this electrode measured against the silver-

silver chloride reference are disregarded in taking the average since they

$E^{o}$ For $SO_4^{=} | Hg_2SO_4 | Hg$ Electrode

| Conc. of $H_2SO_4$ | Calomel Reference 1938 | Calomel Reference 1939 | Silver Chloride Reference | Quinhydrone Reference |
|---|---|---|---|---|
| 0.30 m | 0.6128 | 0.6141 | 0.6142 | 0.6144 |
| 0.20 | 0.6140 | 0.6143 | 0.6153 | 0.6154 |
| 0.10 | 0.6139 | 0.6145 | 0.6140 | 0.6149 |
| 0.05 | 0.6141 | 0.6150 | 0.6148 | 0.6150 |
| 0.02 | 0.6130 | 0.6148 | 0.6124 | 0.6143 |
| 0.01 | 0.6127 | 0.6143 | 0.6094 | 0.6139 |
| | 0.6134 Average | 0.6145 Average | 0.6146 Average | 0.6147 Average |

Table XII

$E^{o}$ For $Cl^- | AgCl | Ag$ Electrode

| Conc. of HCl | Calomel Reference 1938 | Calomel Reference 1939 | Mercurous Sulfate Reference | Quinhydrone Reference |
|---|---|---|---|---|
| 0.20 m | | 0.2206 | 0.2210 | 0.2225 |
| 0.10 | 0.2197 | 0.2207 | 0.2221 | 0.2225 |
| 0.05 | 0.2191 | 0.2208 | 0.2213 | 0.2226 |
| 0.01 | 0.2196 | 0.2197 | 0.2219 | 0.2216 |
| | 0.2195 Average | 0.2205 Average | 0.2216 Average | 0.2223 Average |

Table XIII

$E^{o}$ For Quinhydrone Electrode

| Conc. of HCl | Calomel Reference | Mercurous Sulfate Reference | Silver Chloride Reference |
|---|---|---|---|
| 0.20 m | 0.6954 | 0.6976 | 0.6977 |
| 0.10 | 0.6955 | 0.6974 | 0.6956 |
| 0.05 | 0.6954 | 0.6975 | 0.6965 |
| 0.01 | 0.6955 | 0.6973 | 0.6965 |
| | 0.6955 Average | 0.6975 Average | 0.6966 Average |

$E^{\circ}$ For $Cl^- | Hg_2Cl_2 | Hg$ Electrode

| Conc. of HCl | Silver Chloride Reference | Mercurous Sulfate Reference |
|---|---|---|
| 0.10 m | 0.2672 | 0.2670 |
| 0.05 m | 0.2667 | 0.2669 |
| | 0.2670 Average | 0.2670 Average |

Table XV

are obviously considerably in error.

The $Cl^- | AgCl | Ag$ Electrode

In table XIII the results for the $Cl^- | AgCl | Ag$ electrode are given. Here again the more recent values are a millivolt nearer the accepted value of 0.2223 V (see table I-D) than the previous values. The agreement for different references is not good, the overall variation being 1.8 millivolts for the averages under each reference. This may be due, in part, to the fact that the electrodes were older (see table I-A) when measured with the quinhydrone reference than when measured with the calomel reference. The difference in the asymmetry potential seen in tables IV, V, and VI is not a sudden change, for the electrodes using 0.2 m and 0.1 m HCl were measured several weeks before those using 0.05 m and 0.01 m. Hence the lowering of the asymmetry potential occurred over a considerable period of time. When a quick change of asymmetry potential occurs, especially before and after a single cell, the results have been found to be unreliable.

The greatest deviation from the true $E^{\circ}$ value was found when using the calomel reference. Here the deviation was 1.8 millivolts from the true value of 0.2223 V, or a difference of 0.81%.

The period required for measurement of these electrodes was not long since they had been standing in the proper solution for several days before measurement.

## The Quinhydrone Electrode

Table XIV shows the $E^o$ values found for the quinhydrone electrode measured against different references. Agreement for different concentrations of acid is good for any one reference, but values found for $E^o$ of the quinhydrone electrode with different references are in poor agreement (see table). The value closest the correct value of 0.6990 V (table I-D) was obtained using the $Hg\left|Hg_2SO_4\right|SO_4^=$ electrode as a reference. An average value of 0.6975 was obtained. This is in error by 1.5 millivolts, or 0.21 percent. The poorest value is in error by 3.5 millivolts, or 0.5 percent.

Derivation of the equation for $E^o$ for the quinhydrone electrode shows that the measured E. M. F. should be the same for cells using different concentrations of acid with the quinhydrone. This was found to be the case in actual measurements. The values were erratic in the case of the $Ag\left|AgCl\right|Cl^-$ reference, but the calculated $E^o$ values were erratic to the same extent.

The quinhydrone electrodes were observed to reach equilibrium rapidly, most of the time being used to allow the electrodes to reach the correct temperature.

## The Calomel Electrode

Table XV gives the results for the measurements made to determine the $E^o$ value for the calomel electrode. This electrode comes to equilibrium much more slowly, at least a full day being required. Hence fewer measurements were made. Two concentrations were measured against each of two

references. The results agree well with each other, the average values being the same for the two references. This value of 0.2670 is 0.6 millivolt below the correct value of 0.2676 V (see table I-D). This is an error of 0.22%.

The calomel electrode gave some difficulty in measurement when used as an unknown since it requires more time to become constant. However, when used as a reference electrode it was kept assembled for longer periods and became very constant and reproducible. Reference to tables XII, XIII, and XIV, shows that the most consistent $E^o$ values were obtained by measurements against this electrode.

In order to determine the relative suitability of the various electrodes as references they were compared in the following manner. The deviations from the average $E^o$ value of each electrode measured against a given reference were added (without regard to sign) and the total divided by the number of measurements. The results were as follows.

$Hg|Hg_2Cl_2|Cl^-$ electrode varied by $\pm$ 0.2 millivolts

$Hg|Hg_2SO_4|SO_4^=$ electrode varied by $\pm$ 0.2 millivolts

$Ag|AgCl|Cl^-$ electrode varied by $\pm$ 0.5 millivolts

$Pt|(H_2Q,Q)|H^+$ electrode varied by $\pm$ 0.4 millivolts

This kind of comparison indicates that the first two electrodes listed are the most reliable, since they give more consistent results. Of these two, the $Hg|Hg_2SO_4|SO_4^=$ electrode gave results nearer to the correct $E^o$ value. Further these two electrodes are much easier to prepare. The quinhydrone electrode is not difficult to prepare, but its use involves changing frequently because of decomposition of the quinhydrone.

Although the calomel electrode does not reach equilibrium for a day or so, after once attaining equilibrium it remains true for a long time and does not need to be changed.

The $CrO_4^=|PbCrO_4|Pb$ Electrode

An attempt was made to determine the $E^o$ value for the electrode $CrO_4^=|PbCrO_4|Pb$ through measurement of cells of the type:

$$Hg|Hg_2Cl_2|HCl\ (.1m)|Glass|H_2CrO_4|PbCrO_4|Pb.$$
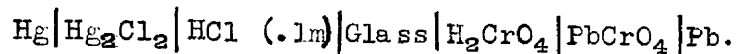
The glass electrode was found to behave quite as expected, but the cells studied did not reach, or approach equilibrium. Further, cells made up identically did not show agredment with each other.

Both platinum plated with lead (electrolytically) and lead wires were used, but neither type showed any consistency.

Because of the total lack of agreement among duplicates the results are not included in this thesis. The author believes the difficulty to lie in the chromate-acid chromate-dichromate equilibrium system. (23)

The Glass Electrode.

In the study of these electrodes several matters of interest have been learned about the glass electrode itself.

The electrode employed in this research was about three years old. Except for a considerable increase in asymmetry potential, the electrode behaved as well as when it was new. The asymmetry potential was usually constant though in several months it varied between 5 and 9 millivolts. The values are listed in tables I to XI.

It was observed that if the asymmetry potential varied more than a few tenths of a millivolt before and after measurement of a given cell, the $E^o$ calculated from the measurement could not be trusted. One series of measurements had to be discarded for this reason. Although some values showing this variation are included they are not reliable.

It was observed, also, that if there was a change of asymmetry potential, the change must have been immediate for there was no corresponding

drift in the E. M. F. of the cell being measured.

In every case the curved outer surface of the cylindrical glass membrane was found to be positive with respect to the inner surface when the same solution was on each side. The same was found true of another electrode of similar construction. Although it cannot be stated as proved, it seems true that the convex surface in a glass electrode is positive with respect to the concave surface. Haugaard[24] observed that there is a definite difference in behavior exhibited by the two sides of the membrane. He states, "the electrode function of the concave side of the glass membrane is more like the reversible hydrogen electrode than that of the convex side."

Haugaard also found a change in the asymmetry potential with a change in the pH of the solution. This was confirmed in the present research only in part. In table VII, for instance, the asymmetry potential remained constant for concentrations of hydrochloric acid from 0.2 molal to 0.01 molal. A statement more consistent with this research would be that the asymmetry potential changes with the nature of the liquid, although this change may not always be in the same direction.

## V. DISCUSSION OF ERRORS

In all cells measured, except those having the same concentration
of the same acid on each side of the glass membrane, there is a difference
in the activity of the water. According to Dole[25] an error is intro-
duced by this difference in activities. The magnitude of the error is
expressed by the equation

$$E = \frac{RT}{F} \ln \frac{c'_{H_2O} \cdot f'_{H_2O}}{c''_{H_2O} \cdot f''_{H_2O}} \qquad 38)$$

where R, T, and F have their usual significance.

c = concentration of water.

$f$ = activity coefficient.

This equation reduces to

$$E = .05915 \log \frac{a'_{H_2O}}{a''_{H_2O}} \qquad 39)$$

Using the equation in this form some calculations were made for
cells using 0.1 m HCl in the reference electrode and varying concentrations
of $H_2SO_4$ in the unknown cell. The activity of water in 0.1 m HCl is
taken as 1 as a first approximation (since activities were not available).
This will give the maximum error, for the true activity will be less than
1 and make the activity ratio more nearly 1 giving the log more nearly
equal to zero. The activity values for water in sulfuric acid solution
are those of Harned and Hamer[26]. Calculation gave for 0.3 m $H_2SO_4$ and
error of 0.3 millivolt, for 0.2 m $H_2SO_4$ an error of 0.2 millivolt, for
0.1 m $H_2SO_4$ an error of 0.1 millivolt which is within experimental error.
The lower concentrations give inconsequential errors. Application of
these corrections to the measured values would increase the $E^o$ value.

The increase would, however, scarcely change the average value for all concentrations measured.

For cells employing the same acid on each side of the membrane the errors would not be large for the range of concentrations is not great and the activity of water would be nearly the same.

The quinhydrone used in the various electrodes was prepared by the Eastman Kodak Company. This product was assumed to be sufficiently pure for use and was not recrystallized. There may have been impurities present in this reagent as used. However, electrodes measured against the quinhydrone reference gave in most cases as good or better $E^0$ values than the same electrodes measured against other references. On the other hand, in the determination of the $E^0$ value for the quinhydrone electrode the results were the poorest of any obtained, in one case being in error by 3.5 millivolts.

A possible additional source of error in the quinhydrone measurements is the fact that the reference electrodes used did not have as long to come to equilibrium as in measurements of other electrodes. The rapid establishment of equilibrium in the quinhydrone electrode made it possible to measure a series of these electrodes in a much shorter time. As a rule, the reference electrodes were used the day following their assembly, a complete series of cells being measured in one day. For other cells, the reference electrodes were in use for a week or more without changing. Hence, the establishment of equilibrium was more certain. The calomel reference, especially, requires time to become constant. It will be noted that the results were poorest for quinhydrone measured against calomel (see table XIV).

In the use of the $Ag|AgCl|Cl^-$ electrode the exclusion of air was

not attempted. This was believed to be unnecessary since according to Taylor the potential is not affected. Taylor[27] states: "After the experiments on aging of thermal-electrolytic electrodes were finished, a supplementary experiment was conducted to show that oxygen was not responsible for the aging effect. Several of these equilibrated electrodes were taken out of the cell and placed for four hours in an air saturated solution of the same composition as in the cell. They were then returned to the cell and compared with electrodes which had not been thus exposed. No significant changes in potential were observed." The electrodes used in this research were of different type, but would be expected to show the same behavior with respect to oxygen. Further, in the preliminary research air was removed from the acid solutions but the $E^o$ values found were not as good as the present ones.

By reference to tables XII to XV it can be seen that the results found for $E^o$ of the electrodes studied are below the correct values in practically every case. Having compared four different electrodes using each one as unknown and as reference, the writer feels that the error must lie somewhere in the glass electrode itself since it is the only part of the cell used in all measurements. The error is believed to be in the asymmetry potential for this potential was found to vary unpredictably at times. In the values used for calculation, the lowest recorded value for the asymmetry potential is 0.7 millivolts and the highest, 9.4 millivolts. The average value is about 7 millivolts for most of the measurements.

It seems much more likely that the error is here, rather than in impure reagents, or measuring equipment; otherwise the results would not be uniformly below the correct values.

That errors were introduced by temperature variations in the air bath is not likely. Except for a few times when it was necessary to place ice inside the bath, the temperature was maintained at $25^\circ$ C $\pm$ 0.1$^\circ$. The greatest variation even under the worst conditions was $\pm$ 0.15$^\circ$ C. Since the control was in an air bath, the cell would not undergo as great variation but remain close to $25^\circ$ after once reaching this temperature. Taking values from a Leeds and Northrup bulletin[28] for voltages for glass electrode and a saturated calomel cell, for 0.1 molal solution the E. M. F. at $20^\circ$ C is 0.3952 V and at $25^\circ$ C is 0.3943 V. This is a change of .0009 volts for $5^\circ$ change in temperature. For the maximum temperature change in the air bath, $\pm$ 0.15$^\circ$, the change would amount to .000027 V, which is well within the experimental error of measurement.

## VI. CONCLUSION

As a result of this research several facts have been established. First, the glass electrode has been shown to be applicable to the measurement of standard electrode potentials to an accuracy of one millivolt. The results are reproducible, but consistently below the true value.

Second, the glass electrode is still usable after a long period of time although its asymmetry potential is considerably higher than when the electrode is new.

The asymmetry potential changes with the nature of the solution, although the change is not always in the same direction. If, during a given cell measurement the asymmetry potential changes more than a few tenths of a millivolt, the measurement is not reliable.

Of the electrodes studied, the two found most suitable for this type of measurements were the $Hg|Hg_2Cl_2|Cl^-$ electrode and the $Hg|Hg_2SO_4|SO_4^=$ electrode. They are more reproducible and also easier to prepare and use.

The glass electrode should prove useful as a reference electrode in measuring standard potentials for electrodes not yet determined, and through its use the troublesome calculation of junction potentials may be avoided.

# VI. SUMMARY

The glass electrode has been shown useful as a reference electrode, especially for measuring standard electrode potentials. The method employed eliminates calculation of junction potentials.

A number of well-known electrodes have been studied, using the electrodes both as unknowns, and as references with cells involving the glass electrode. The most suitable of these have been pointed out.

Several features of the glass electrode have been studied.

The possible sources of error in the method have been discussed.

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