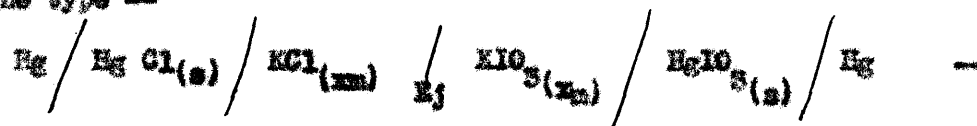


### ABSTRACT

Various cells were studied in an effort to establish the  $E^0$  value for the mercurous iodate-mercury electrode. An arrangement of the type —



was found to be quite satisfactory.

This cell included a liquid-junction potential ( $E_j$ ), and considerable study was given to this phase of the problem. The junction type finally chosen conformed for the most part to the "force diffusion" type of Guggenheim. Its design permitted the ready establishment of the junction whenever necessary. Its characteristics included stability as well as reproducibility; and more important - the measured  $E_j$  agreed well with the calculated value obtained from the Lewis and Sargent equation.

The mercurous iodate electrode was found to be quite constant and reproducible. Measurements indicated slight ageing effects, ease of polarization, negligible oxygen effect, difficulty of reproducing the mercurous iodate, and the gradual diminution of  $E^0$  with an increase in concentration of potassium iodate.

The arithmetical mean value of  $E^0$  for about fifty electrodes over a concentration range of 0.01 to 0.10 molar was calculated as  $0.3923 \pm 0.0005$  volts. From this value were computed the following data:

For the reaction -  $(\text{HgIO}_3)_2(s) + 1e \rightleftharpoons \text{Hg}(l) + \text{IO}_3^-(a=1)$

$$\Delta F_{298}^{\circ} = -9040 \text{ cal. / gram mol}$$

For the reaction -  $\text{HgIO}_3(s) \rightleftharpoons \text{Hg}(a=1) + \text{IO}_3^-(a=1)$

$$\Delta F_{298}^{\circ} = +9400 \text{ cal. / gram mol}$$

The activity product,  $K = 1.50 \times 10^{-7}$

The solubility,  $s_{298} = 3.6 \times 10^{-4}$  moles / 1000 grams water

## BIOGRAPHY

Faschal Philip Zapponi was born in Iron Mountain, Michigan, January 20, 1912.

Graduated from Wooster High School, Wooster, Ohio, in June, 1929.

Matriculated at Fern College in Cleveland, Ohio, in September, 1930, for one semester; after which he transferred to Wooster College, where he received a B.A. degree with distinction and special honors in Chemistry in June, 1934.

Employed as a graduate assistant at the University of Maryland from September, 1934, to September, 1938; from which institute he received M.Sc. (1936), and Ph.D. (1938).



THE STANDARD ELECTRODE POTENTIAL OF THE  
MERCURI-MERCUROUS IODATE ELECTRODE

BY

P. P. ZAPPONI

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Zapponi,  
P.P.  
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Thesis submitted to the Faculty of the Graduate School  
of the University of Maryland in partial fulfillment  
of the requirements for the degree of  
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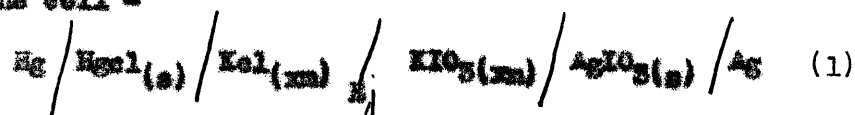
## INTRODUCTION

Standard electrode potentials have been determined for most of the common metals from electrodes of high constancy and reproducibility. Many of these values have been tabulated by Gerke in International Critical Tables.

The importance of determining precise  $E^0$  values cannot be overemphasized; since a knowledge of this constant permits the evaluation of many physico-chemical quantities, such as - heat of reaction ( $\Delta H$ ), free energy ( $\Delta F$ ), and equilibrium constants. In general, the precision of electromotive force measurements is superior to thermal measurements, so that indirect calculation of these quantities frequently leads to a more precise value than its direct experimental determination.

An extensive search of the literature revealed that the iodate ion forms, in addition to others, insoluble salts with the commonly occurring ions  $Pb^{++}$ ,  $Ag^+$ , and  $Hg_2^{++}$ . Of these only the standard Electrode potential for the silver - silver iodate electrode<sup>1</sup> has been determined.

The  $E^0$  value for the latter electrode was obtained from a study of the cell -



This cell included a liquid junction potential,  $E_j$ , which introduced an uncertainty of unknown magnitude. Pearce and Wirth calculated  $E^0$  on the basis of the geometrical mean activity coefficients ( $\gamma^2$ ) for potassium iodate; however, theory demands the employment of ionic activ-

ity coefficients for the iodate ion ( $\gamma_{\text{IO}_3^-}$ ). Moreover, in the calculation of  $E_j$ , these investigators assumed that the ratio of equivalent conductances ( $\Lambda$ ) of the two salts was the same at 25°C as at 15°C. This latter assumption was unnecessary, since the temperature coefficients for  $\Lambda$  of the salts in question were available.

In Table I the writer has tabulated the necessary data for comparing the results obtained with and without the previously mentioned assumptions.

Table I

m	$\gamma_{\text{KIO}_3}$	$\gamma_{\text{IO}_3^-}$	$E_c$	$E_j(\text{P-W})$	$E_j(\text{H-Z})$	$E^{\circ}(\text{P-W})$	$E^{\circ}(\text{H-Z})$
0.1000	0.692	0.637	0.0833	0.0037	0.0030	0.3571	0.3537
0.0500	.765	.718	.0825	.0032	.0077	.3567	.3545
0.0200	.832	.865	.0810	.0075	.0073	.3552	.3559

In this table, m is the molality;  $E_c$  is the measured potential in volts of the cell;  $E_j(\text{P-W})$  and  $E_j(\text{H-Z})$  are the junction potentials and standard electrode potentials evaluated by Pearce and Wirth, and Haring and Zayponi, respectively.

The large variation in  $E^{\circ}$  indicates that the  $\text{IO}_3^- / \text{AgIO}_3(\text{s}) / \text{Ag}$  electrode would not furnish a suitable reference electrode for the  $E^{\circ}$  determination of other insoluble iodate electrodes. We have chosen the mercurous iodate electrode for our research problem in order to establish, if possible, a reproducible reference electrode; preferably one that is easy to prepare. Such an electrode would facilitate the  $E^{\circ}$  determination of other metal-insoluble iodate electrode from a study of cells of the type represented in (2).

$$K / M(\text{IO}_3)_2(s) / \text{KIO}_3 / \text{HgIO}_3 / \text{Hg}(a)$$

Cell (3) does not involve a liquid-junction; moreover, its potential is independent of the concentration of the electrolyte.

Recently, Kohlhorst and Ludwig<sup>8</sup> have reported

$$E^{\circ} \text{IO}_3^-(a=1) / \text{AgIO}_3 / \text{Ag} \text{ as } 0.1551 \pm 0.0002 \text{ volts. Their value was in-}$$

directly calculated from the Debye-Hückel equation employing their experimentally determined solubility data and a knowledge of the  $E^{\circ} \text{Ag}^+(a=1) / \text{Ag}$  value.

### THEORETICAL DISCUSSION

The Nernst mechanism for the development of a potential difference at phase boundaries was of great importance in the early development of electrochemistry. According to his theory, the e.m.f. resulting from the contact of a metal with solution of its ions was the result of two opposing forces. One of these forces was the tendency of the metal to send ions into solution in opposition to the other which tended to deposit metal ions from the solution upon the metal. The magnitude of the former force was expressible in terms of a hypothetical concept electrolytic solution pressure ( $P$ ), and the latter in terms of the osmotic pressure ( $p$ ) of the metallic ions in solution.

From purely theoretical considerations Nernst derived relationship ( $S$ ), in which

$$E = \frac{RT}{nF} \ln \frac{p}{P} (S)$$

$N$  is the number of faradays transferred through the cell by the electrode reactions,  $F$  is the faraday constant, and  $R$  and  $T$  have their usual significance. Now, for a given metal at constant  $T$ ,  $P$  may be regarded as a constant. Thus it is evident that the single electrode potential of a metal is a function of the concentration of the metal ions in the solution in which the metal is immersed. Then, to provide a uniform basis of comparison of potentials, it is necessary to select one ion concentration as a standard. This latter quantity was chosen as one gram atomic weight of ion per 1000 grams of solvent; in other words, the potential exhibited by a metal when in equilibrium with its ions

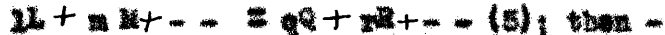
at one molar concentration.

The concept of activity was introduced by Lewis in 1908. By its use simple equations which apply to dilute solutions may be made applicable to concentrated solutions; i.e., the activity was until recently an empirical quantity which, when substituted for the concentration in the mass-action expression, expressed its effect in determining the position of equilibrium. In a sense it is an "effective concentration". In recent years it has been found possible to calculate activities in dilute solutions of electrolytes on purely theoretical bases so that this quantity acquires a definite physical significance. Mathematically - activity has been defined by equation (4).

$$\Delta F = RT \ln \frac{a_2}{a_1} \quad (4)$$

In this expression  $\Delta F$  represents the change in free energy when one gram mol of an ion or compound is transferred reversibly from a solution in which its concentration is  $n_1$  to one in which its concentration is  $n_2$ ; whence  $a_1$  and  $a_2$  are the corresponding activities. Expression (4) indicates that the activities are merely relative quantities, and hence numerical values can only be obtained with reference to a standard. For convenience the actual standard chosen may be varied; but for strong electrolytes the activity of a solute at infinite dilution is defined as equal to its concentration under the same condition. At other dilutions  $a/n$  is not unity, and this ratio has been called the "activity coefficient ( $\gamma$ )". This quantity is called by many the "thermodynamic degree of dissociation", and may be regarded as a measure of the extent to which an ion or molecule approaches ideal behavior.

The standard electrode potential of a metal may be determined from a measurement of the electromotive force of a suitable voltaic cell. Let us assume the cell reaction to be -



if  $\Delta F$  represents the change in free energy in this reaction under the conditions of the experiment, its value would be given by (6).

$$\Delta F = (qF_Q + rF_R + \dots) - (lF_L + mF_M + \dots) \quad (6)$$

Similarly, if the substances are in their standard states,  $\Delta F^\circ$  is given by expression (7).

$$\Delta F^\circ = (qF_Q^\circ + rF_R^\circ + \dots) - (lF_L^\circ + mF_M^\circ + \dots) \quad (7)$$

Proper combination of equations (4), (6) and (7) yields -

$$\Delta F - \Delta F^\circ = RT \ln \left( \frac{a_Q^q a_R^r \dots}{a_L^l a_M^m \dots} \right) \quad (8)$$

However, for a system in equilibrium at constant temperature,  $F$  is zero. Hence it follows that -

$$\Delta F^\circ = -RT \ln \left( \frac{a_Q^q a_R^r \dots}{a_L^l a_M^m \dots} \right) \quad (9)$$

Moreover, at a given  $T$ ,  $\Delta F^\circ$  is constant so that under conditions of equilibrium the quantity in parenthesis (called "activity quotient,  $K$ ") is also a constant; i.e. (9) may be rewritten -  $\Delta F^\circ = -RT \ln K$  (10).

The constant,  $K$ , is frequently termed the equilibrium constant. Substitution of (10) in (8) yields (11).

$$\Delta F = -RT \ln K + RT \ln \left( \frac{a_Q^q a_R^r \dots}{a_L^l a_M^m \dots} \right) \quad (11)$$

Furthermore, in a voltaic cell  $\Delta F$ , which is a measure of the electrical work done, is given by equation (12).

$$F = -nFE \quad (12)$$

Finally, if  $E$  represents the voltage under the given conditions, and  $E^0$  the voltage under standard conditions, we obtain by substituting (12) in (11) formula (13).

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_0^0 a_2^r}{a_1^i a_3^m} \quad (13)$$

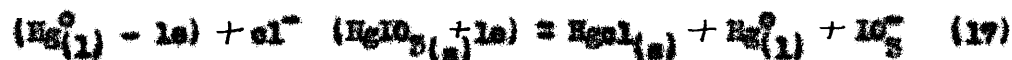
The cell measured in this research was



This cell includes a liquid-junction potential, theoretical treatment of which will be deferred until later. When this cell operates to produce one equivalent of electricity, the following reactions occur at the electrodes:



However, the total cell reaction is a summation of the half-cell reactions, so that the overall reaction is given by (17), and the total cell potential by (18).



$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{HgCl}_{(s)}} a_{\text{Hg}_{(l)}}^0 a_{\text{IO}_3^-}}{a_{\text{Hg}_{(l)}}^0 a_{\text{cl}^-} a_{\text{HgIO}_{3(s)}}} \quad (18)$$

Now -  $a_{\text{HgCl}_{(s)}}$ ,  $a_{\text{Hg}_{(l)}}^0$  and  $\text{HgIO}_{3(s)}$  are all equal to unity, since these substances are in their standard states. Hence, expression (18) reduces to (19).

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{IO}_3^-}}{a_{\text{cl}^-}} \quad (19)$$

The generally accepted convention requires that the cell, or half-cell, reaction be written as that reaction which results in the flow of negative electricity from right to left within the cell as written. Measurement of the potential of this cell indicated that the calomel electrode was negative to the mercurous iodate electrode. By convention, this means that the overall potential is positive; since the potential is considered to be positive if negative electricity flows from right to left within the cell.

The actual standard electrode potential of the cell is generally referred to the standard hydrogen electrode. The latter electrode, which consists of platinized - platinum dipping into an aqueous solution of hydrogen ions at unit activity and bathed in hydrogen gas at one atmosphere pressure, is considered to be zero at all temperatures. For reference the standard is always placed on the left so that the sign of the cell voltage gives the sign of the charge of the electrode against the solution.

By substituting in expression (19) the ionic activity of the iodate and chloride ions, we obtain (20). From a study of the

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{\gamma_{IO_3^-} a_{IO_3^-}}{\gamma_{Cl^-} a_{Cl^-}} \quad (20)$$

half-cell reactions and expression (20), we find that individual ionic activity coefficients are necessary for the evaluation of  $E^{\circ}$ . However, Guggenheim<sup>5</sup> and Harned<sup>4</sup> are convinced that it is not possible to determine individual ionic activity coefficients free from any assumptions. On the basis of the similarity in weight and mobility of potassium and chloride ions, MacInnes made the highly plausible assumption that in



dilute solutions of potassium chloride the two ions have the same activities, and consequently - the same activity coefficients. Having established the individual ionic activity coefficient for the potassium ion, it is a very simple procedure to calculate the ionic activity coefficient for any other ion. The generally accepted values for  $\gamma_{\pm \text{KCl}}$  are those of Harned<sup>5</sup>. For example, accepting MacInnes' assumption, we have

$$\gamma_{\pm \text{KCl}} = (\gamma_{\text{K}^+} \gamma_{\text{Cl}^-})^{1/2} = \gamma_{\text{K}^+} = \gamma_{\text{Cl}^-} \quad (21)$$

Then, to evaluate the activity coefficient for the iodate ion, we need only to square the geometrical mean activity coefficient for potassium iodate, and divide this quantity by  $\gamma_{\text{K}^+}$ . Thus -

$$\gamma_{\text{KIO}_3}^{\pm} = \gamma_{\text{K}^+} \gamma_{\text{IO}_3} \quad (22)$$

$$\gamma_{\text{IO}_3} = \frac{(\gamma_{\pm \text{KIO}_3})^2}{\gamma_{\text{K}^+}} \quad (23)$$

Finally, the potential (E) of the cell having been measured, allowances are made for the junction potential, and the proper values are substituted in (20). Its solution leads to  $E^0$  for the complete cell. However,  $E^0$  for the calomel electrode is known; hence the  $E^0$  value for the mercury-mercurous iodate electrode is established.

Since our cell involves a liquid-junction potential, it would be well at this time to consider briefly the nature of these troublesome points of contact. When two solutions are brought together so as to avoid mechanical mixing, the more concentrated solution tends to diffuse into the more dilute, and the rate of diffusion of each ion is roughly proportional to its speed in an electrical field. Because of the different mobilities of the ions, an electrical double layer is established at the junction of the two solutions. However, no ex-

possible separation of anions from cations results because of the presence of electrostatic forces. Therefore, at the junction of two solutions differing in environment there must exist a potential difference, and its magnitude is a function of the relative speeds of the ions; moreover, its direction is such that the more dilute solution always assumes the charge of the faster moving ion.

In the evaluation of the junction potential we have employed the Lewis and Sargent equation which is given by equation (24).

$$E_j = \pm \frac{RT}{N} \ln \frac{\sqrt{1}}{\sqrt{2}} \quad (24)$$

This equation is only applicable to junctions with a common ion, and with salts of the same concentration. In (24) the actual values for  $\sqrt{1}$  and  $\sqrt{2}$  are substituted.  $\sqrt{1}$  always refers to the electrolyte on the left, and  $\sqrt{2}$  to the one on the right. The junction potential is negative when cation and positive when anion is common.

At present it is a perplexing problem to decide the proper method for establishing the junction. Guggenheim<sup>6</sup> favors the "continuous mixture junction", because the Henderson equation, from which the Lewis and Sargent equation is derived, assumes this type of junction. According to Guggenheim, a "continuous mixture junction" exists when "the composition at any point of the transition layer is a linear combination of the compositions of the extreme liquids". Although it is the junction most readily treated mathematically, nevertheless it is extremely difficult to obtain experimentally.

In our research we have employed a junction that conforms, with certain restrictions, to the "free diffusion junction" of Guggenheim. In this type, the transition layer is initially short compared

to the distance between the electrodes, and unconstrained diffusion is permitted to take place. The length of the transitional layer is always increasing, but there is "cylindrical symmetry", i.e. the potential and concentration gradients are parallel to some fixed straight line. It is with respect to "cylindrical symmetry" that our junction compartment differs from that of Guggenheim's. Taylor<sup>7</sup> believes that this is the true method for establishing the junction. We have chosen this type of junction for four reasons. First - Guggenheim's results indicated definitely that for junctions of the type considered in this research,  $E_j$  was practically independent of the mode of establishing it. Second - it was quickly recognized that this type of junction, although mathematically unsound, yielded potentials of high constancy and reproducibility. Third - our measurements have shown that the experimentally determined  $E_j$  values conformed to those calculated by the Lewis and Sargent equation. Fourth - our design made possible the frequent renewal of the junction.

\*

## EXPERIMENTAL DETAILS

### A. Reagents

#### 1. Mercury

This element was purified by the method of Halsett and Minchin<sup>8</sup>. It consists in passing mercury in the form of a fine spray through a long, glass column containing a solution which is normal with respect to nitric acid and mercurous nitrate. The mercury is dried, and then distilled in a current of air under reduced pressure.

#### 2. Mercurous Nitrate

In a crystallizing dish were placed 50 cc. of water, 72 cc. of nitric acid (69%), and 204 grams of Hg. The reaction was permitted to go to completion, care being taken to maintain the mixture at the temperature of ice. Since Hg was always present in excess, frequent stirring was necessary to prevent local formation of the yellow basic nitrate. The crystals of  $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ , which separate, are sucked dry as possible on a Buchner funnel, which is free from filter paper or asbestos. Analysis by Murray's<sup>9</sup> method proved the extreme purity of the crystals.

#### 3. $\text{KIO}_3$

The source of  $\text{KIO}_3$  were employed in this research. The first was prepared according to the method outlined in Miller, Hall and Blanchard<sup>10</sup>. Repeated recrystallizations yielded a product whose analysis conformed to Murray's reagent grade for this compound. Sorek's

reagent grade was used directly as such without preliminary recrystallization or drying for the second source of this salt.

#### 4. $HgIO_3$

We have prepared  $HgIO_3$  by two distinct methods - the electrolytic and the double decomposition method. In the former, a solution 0.05 N with respect to potassium iodate and 0.02 N to acetic acid was used as electrolyte in a cell composed of a well-stirred mercury anode and a platinum cathode. The latter electrode was placed in a second beaker, connection with first being made by means of a U-tube containing the electrolyte as a bridge. The anodic current density was maintained at approximately 5.0 amperes per square decimeter. Electrolytic  $HgIO_3$  was only used to check the constancy and reproducibility of the electrode by "backing" several of these electrodes against each other.

The double decomposition method for preparing  $HgIO_3$  yielded electrodes of high constancy and reproducibility for a given sample. However, measurements soon indicated that great care must be exercised in its preparation. A research in now being conducted in this laboratory to ascertain the best conditions for producing  $HgIO_3$  of definite crystalline size, and hence - solubility.

Our method was essentially as follows: To a well-stirred puddle of Hg, which was covered with 400 cc. of distilled water, was added dropwise from two dropping funnels two solutions of equivalent concentrations. One of these was 0.05 N in mercurous nitrate and 0.05 N in nitric acid; while the other was a 0.05 N potassium iodate

solution. After the addition of 150 cc. of each solution, the stirrer was stopped; the  $\text{HgIO}_3$  permitted to settle; and about 500 cc. of the supernatant solution was siphoned off, and replaced with 400 cc. of distilled water. This procedure generally required about one and a half hours, and was repeated after additions of 150, 100 and 100 cc. of the equivalent solutions; i.e. until 500 cc. of each solution had been used. The final supernatant solution was replaced with 500 cc. of 0.005  $\text{KIO}_3$ , and the mixture was stirred vigorously for at least one hour. This was repeated until 2 liters of 0.005  $\text{KIO}_3$  had been used in portions of 500 cc. each. The total time for the preparation was about 12 hours. Because of the finely-divided character and the poor settling properties of the  $\text{HgIO}_3$ , it was found necessary to centrifuge the solution from the crystals. This procedure was repeated five times employing  $\text{KIO}_3$  of the concentration to be studied in the cell. Finally, the  $\text{HgIO}_3$  was mixed with a little  $\text{Hg}$ , and stored for aging purposes under a  $\text{KIO}_3$  solution of the same concentration that was used in the centrifuging process.

### 5. $\text{HgCl}$

The reagent grade was repeatedly washed with distilled water, and the  $\text{KCl}$  solution of concentration to be studied. The moist mixture was then mixed with a little  $\text{Hg}$ , and permitted to age under the  $\text{KCl}$  solution.

### 6. $\text{KCl}$

This chemical was of reagent quality, and was weighed directly

as such.

7.  $H_2O$

Conductivity water was employed in the preparation of all solutions.

## B. Apparatus, Method and Technique

### 1. Preparation of the half-cells

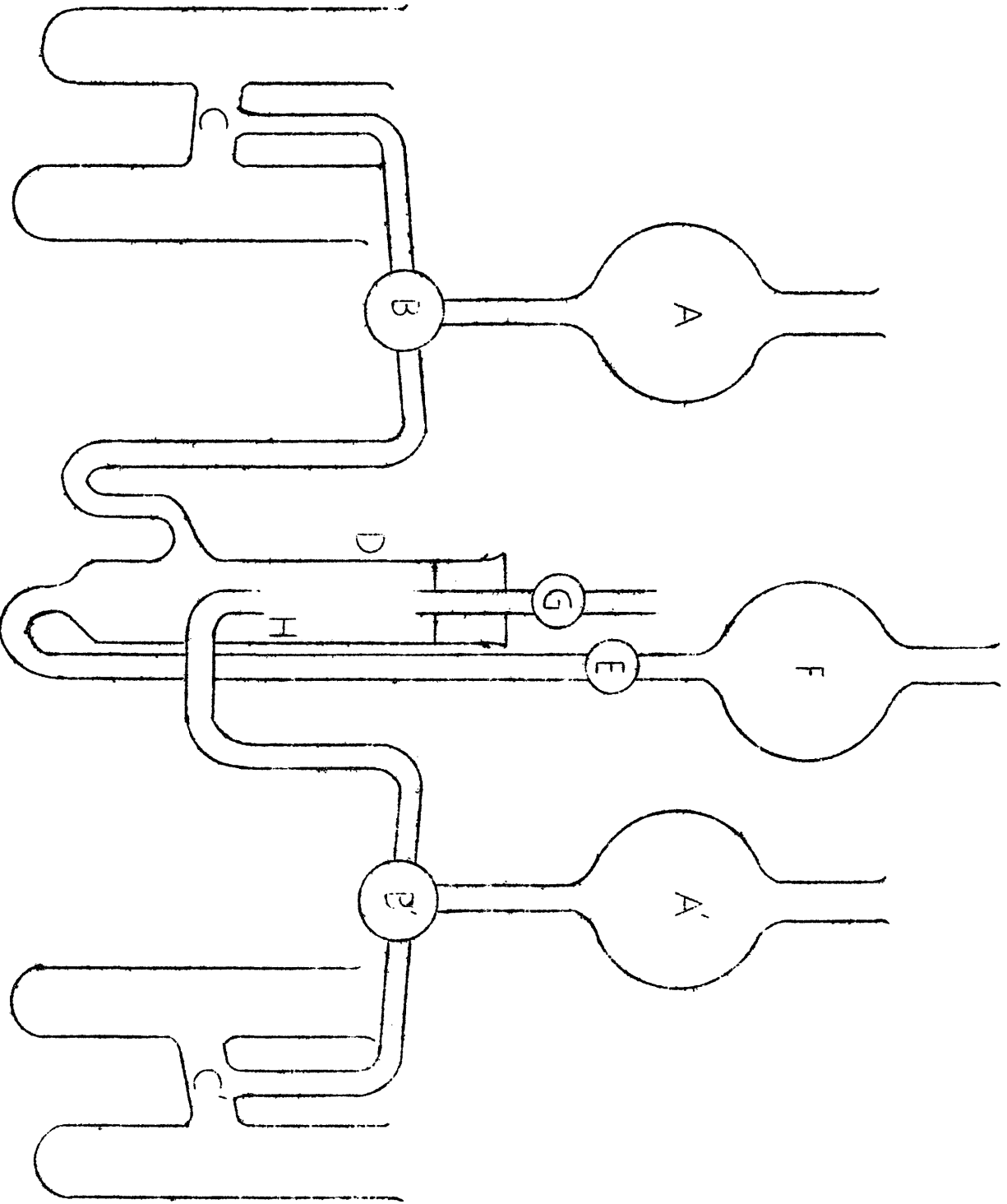
The iodate and calomel half-cell electrodes were specially designed, and are shown in Fig. 1(a). Care must be taken to prevent excess glass from accumulating at the inner seal. This may be prevented by careful blowing and annealing. Failure to observe this precaution invariably leads to a cracking of the electrode at this point. Although the electrode vessel is made entirely from pyrex glass, the extreme fineness of the sealed-in platinum produces a leak-proof union.

The calomel and mercurous iodate electrodes were prepared as follows: The electrode cups were half-filled with mercury, care being taken to eliminate air bubbles, and to have the platinum wire well-covered with the metal. The aged mercury-mercurous iodate mixture was then centrifuged from the potassium iodate solution under which it had been stored; and the moist paste was prepared by vigorous shaking and grinding of the components. The paste was finally placed above the mercury to a depth of approximately one centimeter. Electrodes prepared in this manner were stored in test tubes under solutions of the salts of the concentrations to be studied in the cell.

### 2. The Cell-Vessel

A diagrammatic representation of the cell vessel is shown in Fig. 1(b). In this diagram A and A<sup>1</sup> represent storage reservoirs for the chloride and iodate salt solution, respectively. B and B<sup>1</sup> are three-way stopcocks, which permit the filling of the junction compart-





ment (D), as well as the flushing of the electrodes in the H-cells, C and C<sup>1</sup>. The junction compartment is closed with a one-hole rubber stopper into which is inserted a two-way stopcock (G) that can be opened to the atmosphere. The sealed-in tip (H) is bent to facilitate the establishment of the junction. By opening stopcock(H), it is possible to draw up the contents of (D) into storage reservoir (F). In this way it was possible to renew the junction as frequently as necessary. The apparatus is entirely of pyrex glass, and measures about 75 mm. from C to C<sup>1</sup>. However, due to its triangular form, it is quite compact and strong. The whole cell is supported from its approximate center of gravity by means of a copper bar which is firmly screwed to a wooden support that is wired to the cell.

### B. Filling the Cell Vessel

The cell was clamped rigidly to a ring stand. With stopcock B<sup>1</sup> in such a position so as to be opened to C<sup>1</sup> and A<sup>1</sup>, but closed to (D), the iodate solution was poured into C<sup>1</sup> until the solution had reached the horizontal, glass tubing leading to B<sup>1</sup>. The two iodate electrodes were then simultaneously inserted into C<sup>1</sup>. This procedure forced the iodate solution into reservoir A<sup>1</sup>. In this way air bubbles could be eliminated. The calomel half-cell was filled in an identical manner; after which both A and A<sup>1</sup> were filled with the chloride and iodate solutions, respectively.

With (G) opened to the atmosphere, B<sup>1</sup> was turned so as to connect reservoir A<sup>1</sup> with the junction compartment. Then, the iodate solution was permitted to fill the side tube just level to the tip; and

$B^1$  was closed to  $A^1$ , but opened to  $C^1$  and (D). For the calomel side, the chloride solution was allowed to rise in (D) to within about a quarter of an inch of the tip; (B) was turned similarly to  $B^1$ , and (C) was closed to the atmosphere.

The entire apparatus was suspended by clamping the copper bar in a water thermostat which was maintained at  $25.00^{\circ} \pm 0.05^{\circ}\text{C}$ . Care was taken to have the water level in the thermostat above the electrodes and the junction tip. After the attainment of temperature equilibrium, the junction was made. This was accomplished by opening (C) to the air, and turning (B) so as to permit the chloride solution to flow from (A) into (D) to a height of one-half inch above the tip. Finally, (C) was closed and (B) was turned to its previous position, i.e., closed to (A) but open to both (C) and (D).

The potentials were measured ten minutes after establishing the junction by means of a Rubicon potentiometer, which could be readily estimated to  $\pm 0.02$  mv. A Leeds and Northrup type R galvanometer, with a sensitivity of 7.5 microvolts per mm. and with an external damping resistance of 2000 ohms, was used as a mill indicator. The deflection of the galvanometer was determined by means of a lamp and scale reading device. For the 0.01 M solutions, it was found necessary to employ a Leeds and Northrup galvanometer with a sensitivity of 0.00039 microamperes per mm. with a damping resistance of 9000 ohms.

Each electrode in the H-cells had a separate lead to a switchboard. By a suitable arrangement of jacks, the potential of any pair could be measured. Each "set-up" made possible the measurement of six different e.m.f.s.; some of these being valuable merely in that they

afforded cross-checks.

To reestablish the junction, (G) was opened to the atmosphere, and the compartment's contents were sucked into (F). B<sup>1</sup> was opened in order to flush the junction tip, and this iodate solution was also drawn into (F). Finally, by opening (B), the compartment was repeatedly washed with the chloride solution until free from iodate. The junction was then established as described previously.

## PRELIMINARY EXPERIMENTS

### A. Consideration of Cells Without Liquid Junctions

In precise electromotive force measurements it is preferable, if possible, to eliminate the liquid junction. Cells without liquid junctions are thermodynamically exact; whereas cells with liquid junctions cannot be treated with the precision desired in electrochemistry.

In our preliminary measurements, cell (26) was studied,



This cell does not involve any appreciable junction potential, because the solutions have nearly identical composition. The potential for this cell was found to be highly erratic; so that this type of cell was abandoned. The cell was measured by employing the apparatus and technique of Hatfield<sup>11</sup>. The writer is firmly convinced that variability of the potentials was due to the solvent action on  $\text{HgIO}_3$  by the iodate-perchloric acid solution (it is a known fact that iodic acid dissolves  $\text{HgIO}_3$ ).

### B. Junction Types

Since the junction potential amounted to 6-7 per cent of the measured potential, it was important to give this phase of the problem considerable thought. Of course, the "flowing junction" method was considered first because of the high reproducibility and constancy of the junction potential. However, this type was not studied experimentally as other simpler types gave results in agreement with the Lewis and Dargent equation; moreover, nothing is known at present as to the conditions determining its steady state. In other words it cannot be

treated mathematically.

Considerable time was spent in working with the junction recommended by Lundberg, Vestling and Ahlberg<sup>13</sup>. These investigators formed the junction in an ungreased three-way stopcock which connected the electrode vessels. Our measurements failed to substantiate their claims of a highly constant and reproducible junction; even though our technique was varied frequently. The junction potential in every case increased steadily.

The third type of junction was merely used to study the reproducibility and constancy of the iodate electrodes. This junction was mentioned by Dale<sup>15</sup>, and consisted of side tubes dipping into a beaker containing a 50-50 mixture of the chloride and iodate solutions of concentrations to be studied in the cell. This type of junction gave surprisingly constant values, which agreed quite closely to the potentials obtained with our own junction.

Lewis, Brighton and Sebastian<sup>14</sup> employed a junction whose potentials agreed well with those predicted by the Lewis and Sargent equation. We have modified their junction slightly, and have determined its characteristics by studying the cell -

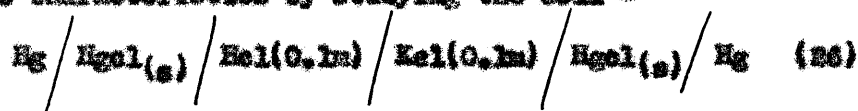


Table II

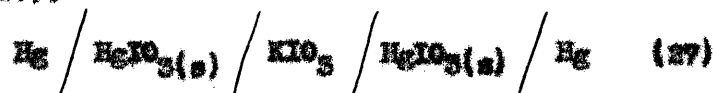
	$E_j(\text{L. \& Y.})^{15}$ :(Observed)	$E_j(\text{Taylor})^7$ :(Calculated)	$E_j(\text{L. B. \& S.})^{14}$ :(Observed)	$E_j(\text{L. \& Z.})$ :(Observed)	$E_j$ :(Calculated)
Junction:	Flowing-	Stationary	Stationary	Stationary	L. \& S. Equ-
	junction				tion
HCl(0.1)	0.0258	0.0276	0.0276	0.0277	0.0284
KCl(0.1)					

In Table II,  $E_j(\text{H. \& Z.})$  represents the arithmetical mean of sixteen junction measurements. A comparison of results indicates not only the better agreement of stationary junctions with the calculated values, but also the good agreement of  $E_j(\text{H. \& Z.})$  with other junctions of the same type. In many instances it is possible to devise cells in which  $E_j$  can be measured with the high precision required in electrochemistry.

The variation of  $E_j(\text{H. \& Z.})$  with time was also studied by means of cell (26). It was observed that  $E_j$  decreased 0.5 to 0.4 mv. in the first five minutes; after which a steady state is reached in which  $E_j$  remained constant to 0.2 mv. for five to six hours. On this basis we have made all subsequent measurements ten minutes after forming the junction. This should allow ample time for the steady state to be reached.

### C. Characteristics of the Mercurous Iodate Electrode

We have studied the reproducibility of the electrode by means of cell (27).



During the course of the research about forty measurements of cell (27) were made. It was found possible to reproduce the potential to within 0.03 millivolts; provided a given source of mercurous iodate was employed. This reproducibility compared favorably with the calomel electrode with a corresponding value of about 0.05 millivolts. In other words, the e.m.f. of the mercury-mercurous iodate electrode using a definite source of the insoluble salt can be duplicated without difficulty.

The constancy of the electrode was abundantly verified throughout the research. Dry-old electrodes remained constant to 0.1 mv. indefinitely.

Careful study of aging of the salt indicated that this factor was of minor importance; thus, mercurous iodate that had been stored under 0.005m H<sub>2</sub>O for six months deviated only 0.2 mv. from the value obtained twenty-four hours after its preparation.

It was repeatedly evident that the mercurous iodate electrode polarized readily; however, they always returned to their initial values, which indicated conclusively that a state of equilibrium existed.

#### D. The Effect of Oxygen

In order to observe the effect of oxygen upon the potential of the electrode, a cell of type (26) was set up. One-half of the electrode apparatus was carefully filled under oxygen free conditions by employing a H<sub>2</sub> atmosphere; while the other half-cell consisted of the ordinary solution. Special attention was given to preparing HgI<sub>2</sub> in absence of air; however, it is doubtful that this procedure was of any particular value, since nitric acid was present during the preparation; moreover, the insoluble iodate came in contact with air during the centrifuging, paste-forming and electrode-preparing processes. The electrodes were then placed in the H-cell and the system repeatedly evacuated and filled with nitrogen. This procedure may have effected the concentration of the iodate solution. A potential of 0.5 mv. was obtained, which value could be easily accounted for by a slight change in concentration during evacuation.

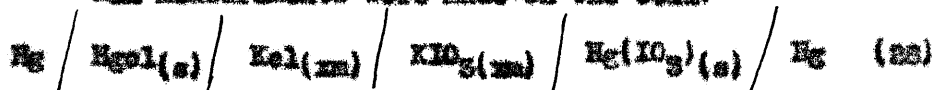


Other lines of evidence supporting our contention that oxygen has no effect on the potential are: First, if oxidation took place, we would be dealing with a  $\text{Hg}(\text{IO}_3)_2$  electrode. We have measured the e.m.f. of the mercuric iodate-mercury electrode, and have found its potential to be about 60 mv. more positive than the mercurous iodate electrode. Second, in the preparation of  $\text{HgIO}_3$  there was always present potassium iodate and nitric acid. Such a solution is a powerful oxidizing agent. However, the observed potential never approached that of mercuric iodate; hence we concluded that this solution, even though present in much higher concentration and being a more powerful oxidizing agent than oxygen, did not oxidize mercurous iodate to any appreciable degree. Third, we have never been able qualitatively to establish the presence of the reduction products of the iodate ion.

With respect to this point, Lundberg, Vestling and Ahlberg<sup>12</sup> have emphasized the fact that "as all of the substances reacting at any electrode are in chemical equilibrium, the measured potentials for the main reaction and all other secondary reactions are the same". If this contention were true, the  $E^0$  values, calculated on the basis of mercurous iodate, should increase with an increase in the concentration of potassium iodate; however, our results have shown the reverse effect.

DATA AND CALCULATIONS

All measurements were made on the cell:



In order to calculate  $E^0$  for the mercurous iodate electrode, we must know, not only the junction potential, but also  $\gamma_{\text{Cl}^-}$  and  $\gamma_{\text{IO}_3^-}$ . In Table III, we have recorded the best available data from which the  $E_j$  value has been calculated by employing the Lewis and Sargent equation.

Table III

Concentration C (Equivalent weights per liter of solution)	$\Delta$ KCl(298.1) † Shedlovsky- J.A.C.S., 54, 1429 (1932)	$\Delta$ KIO <sub>3</sub> (298.1) X International Critical Tables	$E_j =$ 0.0591 log $\frac{\Delta \text{KCl}}{\Delta \text{KIO}_3}$
0.0100	141	106	0.0073
.0300	136*	101*	.0076
.0500	132	98.6	.0077
.0750	131*	96.5*	.0078
.1000	129	94.3	.0080

† - Shedlovsky's highly precise values were rounded off to the nearest whole number.

X - These values were obtained by converting the  $\Delta$  291.1 given in reference cited to  $\Delta$  298.1 by means of the temperature coefficient  $(\frac{d\Delta}{dT})$ , which was given as 2.1 reciprocal ohms per degree in the same table.

\* - Obtained by graphical interpolation from a large-scale graph.

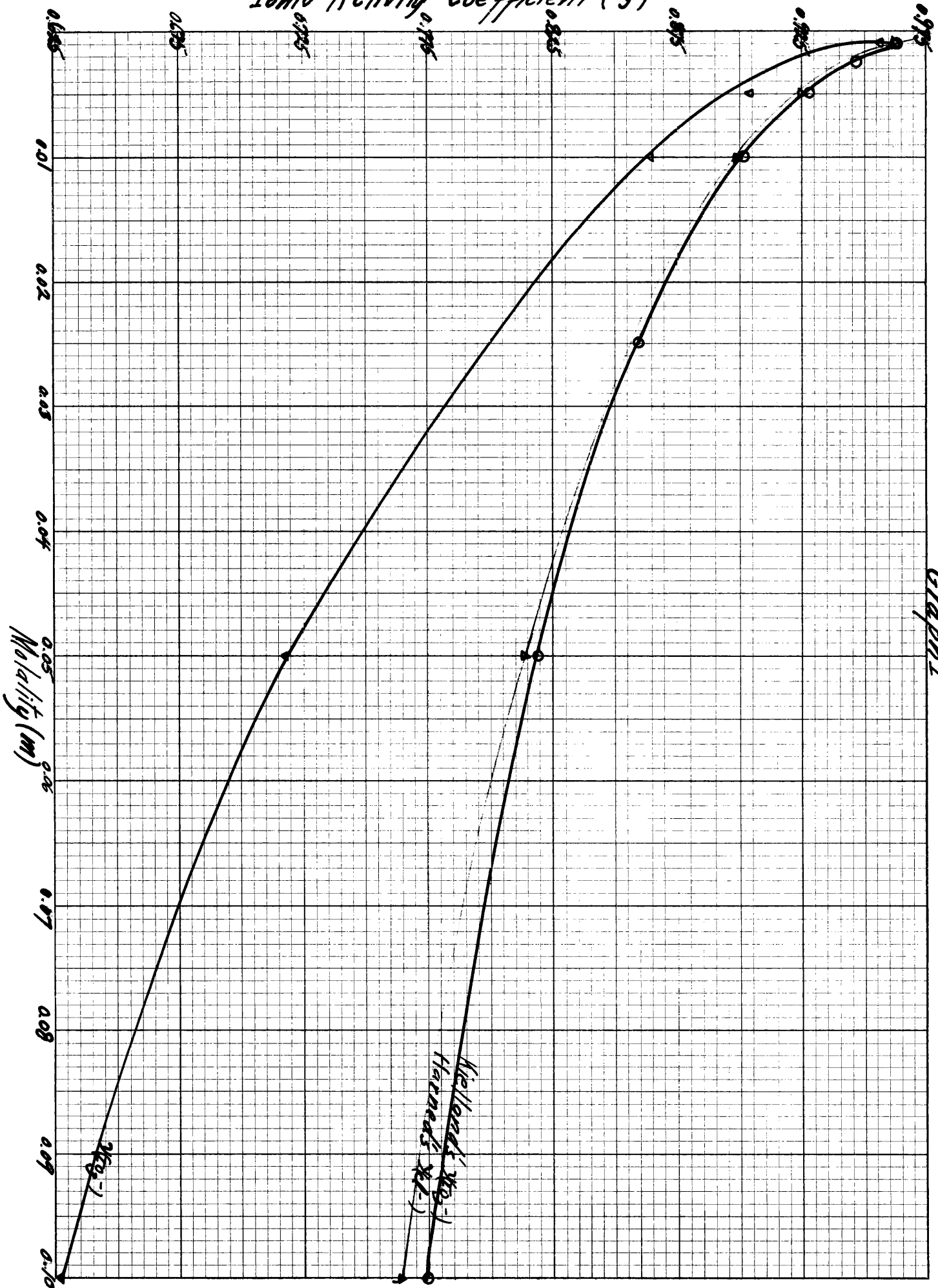
KClal, rather than normal, solutions were employed in all of

our measurements. Nevertheless, we have used the  $\gamma_j$  values based on the concentration expressed as normality. The error introduced by this procedure was negligible.

In the evaluation of  $\gamma_{\text{IO}_3^-}$ , it is necessary to accept MacInnes' assumption of equal ionic activity coefficients for the potassium and chloride ions. Values for  $\gamma_{\text{IO}_3^-}$ , which are computed as explained previously, and other data are listed in Table IV. We have plotted the known data in Graph I. The values of  $\gamma_{\text{LiCl}}$ ,  $\gamma_{\text{IO}_3^-}$  and  $\gamma_{\text{Cl}^-}$  at concentrations 0.05 and 0.075 molar were read directly from the curves and were included with the others in Table IV. For comparison we have tabulated and plotted Kielland's<sup>16</sup> ionic activity coefficients. His values were computed from the Debye-Hückel formula corrected for ion parameters.

Kielland's values for  $\gamma_{\text{IO}_3^-}$  are almost equal to Harstad's for the chloride ion (see Graph I). It is apparent that if the former's values were correct, the measured potential of cell (28) would depend upon the concentrations of the salts, only insofar that the junction potential changes with concentration. However, our research has definitely shown the dependence of the electromotive force with concentrations of the salts; from which we conclude that Kielland's values are incorrect.

Ionic Activity Coefficient ( $\gamma$ )



Graph I

Table IV

Molality (m)	$\gamma^{\pm} \text{KCl} =$ $\gamma_{\text{K}^+} \cdot \gamma_{\text{Cl}^-}$	$\gamma^{\pm} \text{KIO}_3$	$\gamma_{\text{IO}_3^-}$	Kjelland's $\gamma_{\text{IO}_3^-}$
0.01	0.892	0.892	0.895	0.902
.05	.846*	.812*	.780	—
.05	.815	.765	.718	.82
.075	.795*	.724*	.665	—
.10	.754	.692	.627	.775

\*obtained by graphical interpolation.

As the research progressed, it became evident that the preparation of the iodate was difficult to duplicate. Accordingly, it was advisable to study as many different preparations as possible. In Table V are recorded the measurements for six different preparations. P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub> were prepared with little or no precautions taken to regulate the rate of addition of the solutions, time of stirring, conditions of washing the reagent, etc. P<sub>4</sub>, P<sub>5</sub> and P<sub>6</sub>, on the other hand, were made under highly exacting conditions, which were reproduced as well as possible for these preparations. The disagreement in the potentials for the latter preparations was more marked than for P<sub>1</sub>, P<sub>2</sub>, and P<sub>3</sub>. Of course, some difficulty was anticipated in the reproduction of crystals of definite size because of the finely-divided state of the insoluble salt, so that aging of the salt was tried in order to form crystals of uniform size. However, potential measurements indicated that this factor was of minor importance.



Discarding the  $E^{\circ}$  values for  $P_4$  because of their disagreement with the other data (more than three times the average deviation), we have calculated the arithmetical mean value of  $E_{298.1}^{\circ} (Y_{IO_3^-})$  as 0.5923 with an average deviation of  $\pm 0.0005$  volts.

A research is now being conducted in our laboratory to determine the factors governing the preparation of mercurous iodate of definite solubility, and hence, of constant electromotive force. For some unknown reason,  $P_4$  exhibited, even visibly, a larger crystalline structure than the others. The potential measurements confirmed our belief. There is a possibility that the salt exists in polymorphic forms similar to  $Ag_2BrO_3$ . In any case, it is difficult to reproduce the solubility of compounds of this type; for, even the glassware, in which the salt is stored, might easily be a major factor<sup>2</sup>.

Each measured potential ( $E$ ) represents the arithmetical mean of about twenty values. Duplicate iodate electrodes were always observed against duplicate calomels. Generally, the cell was measured over a period of three or four days, the junction being reestablished whenever necessary. The average deviation from the arithmetical mean for a given measurement was of the order of 0.05 mv.

$\frac{1}{2}$  The values for  $E_{298.1}^{\circ}$  (calomel) were calculated from the formula -  $E \approx E^{\circ} - 0.05915 \log a_{Cl^-}$  (29), using Harned's  $E^{\circ}$  value of 0.2676 volts, and also his activity coefficients for potassium chloride.

$E_{298.1}^{\circ}$  (iodate) was obtained by adding  $E_{298.1}^{\circ}$  (calomel) to the total cell potential without the liquid junction, i.e.  $E + E_j$ .  
(measured)

In order to evaluate  $E^{\circ} IO_3^- (a = 1) / HgIO_3(s) / Hg$ , two methods are available. In the first method the known values for

$\lambda_{298,1}(10_{3^{-}})$  and  $a_{10_{3^{-}}}$  are substituted in formula (28) and solving for  $\lambda^{\circ}$ . Briefly, the second method

$$\lambda_{298,1}(10_{3^{-}}) = \lambda^{\circ} - 0.05915 \log a_{10_{3^{-}}} \quad (28)$$

involves subtracting  $0.05915 \log a_{10_{3^{-}}}$  from both sides of expression (28), which yields (29)

$$0.05915 \log \frac{(a)}{(m)}_{10_{3^{-}}} = \lambda^{\circ} - (\lambda + 0.05915 \log a_{10_{3^{-}}}) \quad (29)$$

Now,  $\log \frac{(a)}{(m)}_{10_{3^{-}}}$  equals zero at infinite dilution, and hence

$$\lambda^{\circ} = \lambda + 0.05915 \log a_{10_{3^{-}}} \quad (30)$$

Then, plotting the quantity in parenthesis as ordinate against  $m \frac{1}{2}$ , and extrapolating to  $m \frac{1}{2} = 0$ , we obtain  $\lambda^{\circ}$  which corresponds to the ordinate value at this point. However, we have chosen the former method to evaluate  $\lambda^{\circ}$  due to the inability to reproduce measurements in solutions more dilute than 0.01 M. Precise e.m.f. measurements in dilute solutions are invariably difficult to obtain because they depend upon a relatively high percentage effect of small factors which may be negligible in more concentrated solutions.

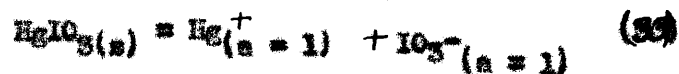
The activity product (K) for mercurous iodate has been computed by combining our value of 0.358 for  $\lambda^{\circ}_{HgIO_3}$  with the value 0.799 for  $\lambda^{\circ}_{Hg(a=1)} / Hg$  electrode in expression (29).

$$\lambda^{\circ}_{HgIO_3} = \lambda^{\circ}_{Hg(a=1)} / Hg + 0.0591 \log K \quad (31)$$

The value of K by this procedure was found to be  $1.50 \times 10^{-7}$ . The activity product (K) is a number which for all practical purposes may be considered to be equal to the solubility product constant (L); however, strictly speaking, its value in the previous calculation is based upon the  $a_{IO_3^{-}}$  being equal to unity. The solubility (s) of the insoluble salt is then calculated from the relationship  $s = \frac{1}{2} L^{\frac{1}{2}}$ , and



found to be  $3.6 \times 10^{-4}$  moles per 1000 grams of water @  $25^{\circ}$  C. Furthermore, from the value of K, the  $\Delta F^{\circ}_{298.1}$  for the reaction -



is readily computed from formula (31) to be +9400 calories per gram mol.

$$\Delta F^{\circ}_{(298.1)} = -2.303 RT \log K \quad (34)$$

On the basis of the equation  $\Delta F^{\circ} = -nFE^{\circ}$ , we have calculated the standard change in free energy for the reaction -



to be -9040 cal. per gram mol.

### DISCUSSION OF RESULTS

Two adverse effects are clearly evident from the experimental data: First, the difficulty encountered with respect to reproducing the insoluble salt; and second, the tendency of  $E^0$  to increase with a decrease in concentration. This latter effect was repeatedly verified throughout the course of the research for a given preparation of the insoluble salt.

Mr. Kraysill is now conducting a research to determine, if possible, the cause of the former difficulty. To account for the second effect, we are presenting two possible reasons; either one of which would explain the observed results. Careful study of Pezros and Wirth's data revealed that their results showed the same effect. This means that oxygen couldn't possibly cause this effect, since these investigators employed a nitrogen atmosphere. Moreover, theory demands an increase in  $E^0$  with an increase in concentration, if oxidation is a factor. This follows from the fact that  $E^0$  for the mercuric electrode is more positive than  $E^0$  for the mercurous electrode by, roughly, five or six centivolts.

Considerable thought was given as to whether we should employ  $\gamma_{\pm KIO_3}$  or  $\gamma_{IO_3^-}$ . True,  $E^0$  shows better agreement over the complete range of concentration for a given preparation; if we employ the former value. For comparison we have included in Table V the values for  $E^0$  based upon  $\gamma_{\pm KIO_3}$ . Definitely, we may say that if the fundamental idea of ionic activity coefficients is valid, then there is no doubt that  $E^0$  based upon  $\gamma_{IO_3^-}$  is to be preferred to  $E^0$  based upon  $\gamma_{\pm KIO_3}$ . Also, the  $\gamma_{\pm KIO_3}$  may be in error; however calculations indicated that an error of

three per cent in  $\gamma\text{HClO}_2$  would introduce an error in  $K^0$  of only 0.5 per cent.

The writer favors the second possible explanation - that of a hydrolytic reaction of type (31) -  $\text{HgClO}_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{HgOH} + \text{H}^+ + \text{ClO}_2^-$  (31).

This reaction is favored in the more dilute solutions; as a result the hydrogen ion concentration increases with dilution. In our preliminary study of the cell without liquid junction, it was shown that the hydrogen ion concentration affected the potential markedly, increasing this quantity. This factor could account for the observed variability of the  $K^0$  with a change in concentration of electrolyte.

### DISCUSSION OF ERRORS

The instrumental errors, such as the small temperature variation of the bath ( $0.05^{\circ}\text{C}$ ), precision of measuring the e.m.f. with the potentiometer (easily to  $\pm 0.0002$  volts), and errors in weighing can be entirely neglected in comparison to the errors of method.

Despite the simple salts employed in our junction and the low value of  $K_j$ , it is questionable whether the values calculated from the Lewis and Sargent equation are more precise than  $\pm 0.0004$  volts.

The method employed for the preparation of the insoluble salt introduced a deviation in the potential which on the average amounted to 0.2 millivolts. The electrodes themselves could be easily reproduced to a 0.1 millivolt. The inherent changes in the salt with a change in its ionic environment resulted in an average deviation of the order of 0.2 millivolts.

Confidently, we place the value of  $E^{\circ}_{\text{Hg}^{2+}(\text{aq})} / \text{Hg}$  at 0.392 with a precision of  $\pm 0.002$  volts.

APPENDIX

1. The standard electrode potential of the mercurous iodate electrode has been found to be  $0.392 \pm 0.001$  volts.
2. The activity product (K) for mercurous iodate has been calculated. Its value is  $1.30 \times 10^{-22}$ .
3. Assuming the equality of the solubility product with the activity product, we have calculated the solubility,  $s$ , as  $5.6 \times 10^{-6}$  moles per 1000 grams of water.
4. The standard change in free energy,  $\Delta F_{298}^{\circ}$ , for the reaction -  

$$\text{HgI}_2(s) + \text{Hg}(a=1) + \text{IO}_3^-(a=1) - \text{I}^-$$
 is calculated as  $+2400$  cal. per gram mol.
5.  $\Delta F_{298}^{\circ}$  for the reaction  $(\text{HgI}_2(s) + \text{I}_2) = \text{Hg}(l) + \text{IO}_3^-(a=1)$  is computed to be  $-3040$  cal. per gram mol.

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