

Russell Ernest Leed, Doctor of Philosophy, 1941
Major: Physical Chemistry
Title of Thesis: The Solubility of Mercurous Iodate
Directed by Dr. M. N. Haring
Pages in thesis, 28.

Words in abstract, 107.

ABSTRACT

The solubility of mercurous iodate in varying concentrations of potassium nitrate, magnesium nitrate, and lanthanum nitrate was studied in an effort to confirm the standard electrode potential for the mercurous iodate mercury electrode as measured by Haring and Zappeni (1).

The mean activity product, 9.96×10^{-14} , as extrapolated from figures 1, 2, and 3 was found to be somewhat different than that calculated by Haring and Zappeni (2.07×10^{-14}).

A close survey of figures 1, 2, and 3 shows that the point of solubility of the mercurous iodate in pure water is far off the extrapolated curve. This phenomenon appears to be real and not accidental, since repeated trials on three different occasions showed a similar titration value.

The mean activity product as extrapolated from figures 1, 2, and 3 was found to be 9.96×10^{-14} .

The solubility of mercurous iodate in water was calculated to be 2.15×10^{-5} moles per liter.

The standard electrode potential of the mercurous iodate electrode was calculated to be 0.4022 volt.

The activity coefficients of the mercurous iodate in the various salt solutions were calculated. These values are found on tables I, II, and III.

THE SOLUBILITY OF NEPOTROUS IODATE

By

Russell E. Lead

**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**

1941

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

TABLE OF CONTENTS

	Page
I. Introduction	1
II. Theoretical Discussion.....	2
III. Materials and Methods	9
A. Reagents.....	9
B. Apparatus, Method and Techniques.....	11
IV. Results.....	16
A. Calculations of Standard Electrode Potential	16
B. Tabulation of Results.....	19
V. Discussion of Results.....	22
VI. Discussion of Errors.....	25
VII. Summary.....	26
VIII. Bibliography.....	27

INTRODUCTION

The importance of solubility data as a check on standard electrode potentials is being realized today. The field is comparatively new and very little literature is available at the present time.

However Kolthoff and Lingane (2) carried out a very interesting piece of work in which they checked the $\text{IO}_3^-/\text{AgIO}_3(\text{s})/\text{Ag}$ standard electrode potential by solubility data. The results appeared to be successful in that the standard potential of the $\text{IO}_3^-/\text{AgIO}_3(\text{s})/\text{Ag}$ electrode as computed from the activity product of AgIO_3 was found to be 0.3551 ± 0.0007 volts at 25°C . This result is 1.0 mV. less than the value 0.3569 volt obtained by Pearce and Wirth. (3) However, due to a liquid junction potential uncertainties were involved in the measurements of Pearce and Wirth, and it is believed that the value 0.3551 volt is the more reliable for E° .

Other work involving solubility data was carried out by Pearce and Celko (4) who measured the solubility of lanthanum iodate in varying concentrations of potassium chloride, magnesium chloride, magnesium sulfate, and potassium sulfate solutions.

Recently Haring and Zapponi (loc. cit.) established the standard electrode potential of the $\text{IO}_3^-/\text{Hg}_2(\text{IO}_3)_2(\text{s})/\text{Hg}$ electrode at 0.394 ± 0.001 volt. It was the object of the writer to confirm the above standard potential in a manner similar to the work completed by Kolthoff and Lingane.

THEORETICAL DISCUSSION

The solubility of difficultly soluble salts can be measured by several methods.

Conductance Measurements

The solubilities of slightly soluble salts can, in many cases, be obtained from determinations of the specific conductance, L , of their saturated solutions. These solutions are so dilute that the equivalent conductance is practically the same as the equivalent conductance at infinite dilution, that is

$$\lambda = \lambda_0 = \frac{1000L}{C}$$

$$\text{or } C = \frac{1000L}{\lambda_0}$$

where C denotes the solubility of the substance in equivalents per liter and λ_0 is the equivalent conductance at infinite dilution. The specific conductance of the water is no longer negligible, and the following equation must be considered

$$L = L^1 - L_{H_2O}$$

where L^1 is the specific conductance of the solution.

Electromotive Force Method

The determination of the solubilities of sparingly soluble salts can also be carried out by e. m. f. measurements. This method can best be described by a specific example (5). Suppose that two silver electrodes are arranged in a concentration cell using potassium nitrate as the salt bridge. In one part are silver ions of known concentration, and in the other part are silver ions in equilibrium with solid silver chloride.



The voltage E can then be measured, and by proper substitution in the following equation, the A_{Ag^+} can be calculated.

$$E = -0.05915 \log \frac{A_1}{A_2} = -0.05915 \log \frac{m_1 \gamma_1}{m_2 \gamma_2}$$

The voltage E of this cell is 0.450 volt at 25° C. and the activity coefficient, γ , of the 0.1 molal AgNO_3 is 0.82. From the above equation

$$0.450 = -0.05915 \log \frac{m_1 \gamma_1}{0.1 \times 0.82}$$

$$m_1 \gamma_1 = 1.94 \times 10^{-9}$$

This solution of silver chloride in equilibrium with solid silver chloride is very dilute and the activity coefficient of the chloride ion is practically the same as that of the 0.1 molal solution of potassium chloride, namely, 0.76. The activity product is then

$$K_{\text{AgCl}} = A_{\text{Ag}^+} \times A_{\text{Cl}^-} = (1.94 \times 10^{-9}) \times (0.1 \times 0.76)$$

$$K_{\text{AgCl}} = 1.48 \times 10^{-10}$$

When silver chloride is dissolved in water, the concentrations of the silver ions and chloride ions are the same, and thus the solubility of the silver chloride = $\sqrt{1.48 \times 10^{-10}} = 1.22 \times 10^{-5}$ (assuming the activity coefficient to be one).

Direct

The method involves the measurement of the solubility of a sparingly soluble salt in varying concentrations of a salt solution, with or without a common ion. One or both ions may be determined (the latter if there is a common ion).

The solubility products are calculated and plotted against the square root of the ionic strengths of the solutions. By extrapolation of the curve to zero ionic strength the activity product can be obtained from which the solubility can be computed.

It is assumed that in exceedingly dilute solutions the ions are practically ideal solutes, and it is found that the activity product equals

the solubility product, in which case the activity coefficient is assumed to be one.

This method was used by the writer and the method of calculation will be reviewed briefly.

Activity Product

The solubility product, L , was obtained by the following equation

$$L = m_{\text{Hg}_2^{++}} \times m_{\text{IO}_3^-}^2 \quad (1)$$

where m represents the molalities of the respective ions.

The ionic strength was calculated in the following manner

$$\mu = 1/2 \sum m_i z_i^2 \quad (2)$$

where μ is the ionic strength, m_i is the molality of the ion in question and z_i is its valence. Substituting the values of saturated mercurous iodate in potassium nitrate solutions, the above equation would be

$$\mu = 1/2 \left[(m_{\text{Hg}_2^{++}} \times 2^2) + 2 (m_{\text{IO}_3^-} \times 1^2) + (m_{\text{K}^+} \times 1^2) + (m_{\text{NO}_3^-} \times 1^2) \right]$$

in magnesium nitrate, the above equation would be

$$\mu = 1/2 \left[(m_{\text{Hg}_2^{++}} \times 2^2) + 2 (m_{\text{IO}_3^-} \times 1^2) + (m_{\text{Mg}^{++}} \times 2^2) + 2 (m_{\text{NO}_3^-} \times 1^2) \right]$$

in lanthanum nitrate, the above equation would be

$$\mu = 1/2 \left[(m_{\text{Hg}_2^{++}} \times 2^2) + 2 (m_{\text{IO}_3^-} \times 1^2) + (m_{\text{La}^{3+}} \times 3^2) + 3 (m_{\text{NO}_3^-} \times 1^2) \right]$$

As stated above, extrapolation of the curves yields the activity product K which is represented as

$$K = A_{\text{Hg}_2^{++}} \times A_{\text{IO}_3^-}^2 \quad (3)$$

where A is the activity.

Activity

The term activity may be defined as that quantity which, when substituted for the concentration in the mass action equation, will express its effect in determining the equilibrium. More simply, activity has been defined as an "as if concentration" or the ratio

$$A = \frac{f}{f^0}$$

between the fugacity f of a substance in some given state, and its fugacity f^0 in some state which, for temporary convenience, is chosen as its standard state.

The activity of a uni-univalent electrolyte may be defined as the product of the ionic activities.

$$A_+ \times A_- = A_0$$

The mean activity, $A_{\pm} = (A_+ \times A_-)^{1/2}$

Then we treat more complicated types such as potassium sulfate, potassium ferrocyanide, etc. our equations become a bit more complicated (6). If an electrolyte dissociates into ν ($=\nu^+ + \nu^-$) ions according to the equation $X = \nu^+ X^+ + \nu^- X^-$ we write for the equilibrium

$$A_+^{\nu^+} A_-^{\nu^-} = A_0; (A_{\pm})^{\frac{1}{\nu}} = A_+$$

Furthermore, if we define the mean molality of the ions, as we have their mean activity, then it is seen that

$$m_{\pm} = m (\nu_+^{\nu^+} \nu_-^{\nu^-})^{\frac{1}{\nu}}$$

From the same analogy, γ , the activity coefficient is

$$\gamma_{\pm} = (\gamma_+^{\nu^+} \gamma_-^{\nu^-})^{\frac{1}{\nu}}$$

Also

$$\gamma_{\pm} = \frac{A_{\pm}}{m (\nu_+^{\nu^+} \nu_-^{\nu^-})^{\frac{1}{\nu}}}$$

From which

$$\gamma_{\pm} = \frac{A_{\pm}}{m_{\pm}}$$

In dilute solutions of symmetrical electrolytes it may be considered that

$$A_+ = A_- = A_{\pm}$$

and the ionic activities may be approximated by the relation

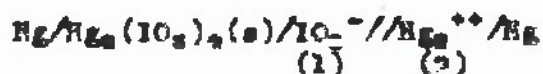
$$A_{\pm} = m \gamma_{\pm} \quad (4)$$

Calculation of the Activity Product from the Standard Electrode Potential

As stated in the early part of this paper, the object of this research was to calculate the standard electrode potential of the mercurous iodate electrode by solubility measurements.

The procedure is as follows:

Consider the cell (7).



$$L = m_{\text{Hg}_2^{++}} \times m_{\text{IO}_3^-}^2 \quad (5)$$

$$K = A_{\text{Hg}_2^{++}} \times A_{\text{IO}_3^-}^2 \quad (6)$$

$$A_1 = \gamma_{\pm} m_{\pm} \quad (4)$$

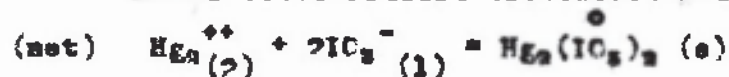
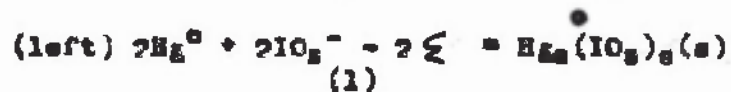
Substituting (4) in (6)

$$K = (\gamma_{\text{Hg}_2^{++}} m_{\text{Hg}_2^{++}}) \times (\gamma_{\text{IO}_3^-}^2 m_{\text{IO}_3^-}^2) \quad (7)$$

Hence

$$K = \gamma_{\text{Hg}_2^{++}} \gamma_{\text{IO}_3^-}^2 L = \gamma_{\pm}^3 L \quad (8)$$

The electrode reactions of the cell are:



The equilibrium constant K^1 is then:

$$K^1 = \frac{A_{\text{Hg}_2(\text{IO}_3)_2(s)}}{A_{\text{Hg}_2^{++}} \times A_{\text{IO}_3^-}^2} \quad (1)$$

Since $\text{Hg}_2(\text{IO}_3)_2$ is in its standard state $A_{\text{Hg}_2(\text{IO}_3)_2(s)} = 1$.

Hence

$$K^1 = \frac{1}{A_{\text{Hg}_2^{++}}(?) \times A_{\text{IO}_3^-}^2(1)} = \frac{1}{K} \quad (\text{at equilibrium})$$

$$E_{\text{cell}} = E^0 - \frac{0.05915}{2} \log \frac{1}{A_{\text{Hg}_2^{++}}(?) \times A_{\text{IO}_3^-}^2(1)}$$

$$E^0 = \frac{0.05915}{2} \log K^1 = \frac{0.05915}{2} \log \frac{1}{K} \quad (9)$$

$$E_{\text{cell}} = \frac{0.05915}{2} \log \frac{1}{K} - \frac{0.05915}{2} \log \frac{1}{A_{\text{Hg}_2^{++}}(?) \times A_{\text{IO}_3^-}^2(1)}$$

$$E_{\text{cell}} = \frac{0.05915}{2} \log \frac{A_{\text{Hg}_2^{++}}(?) \times A_{\text{IO}_3^-}^2(1)}{K} \quad (10)$$

Substitution (4) in (10)

$$E_{\text{cell}} = \frac{0.05915}{2} \log \frac{(Y_{\text{Hg}_2^{++}} \text{Hg}_2^{++})_{(2)} (Y_{\text{IO}_3^-} \text{IO}_3^-)_{(1)}^2}{K} \quad (11)$$

If both $A_{(1)}$ and $A_{(2)} = 1$, then equation (11) becomes equation (9)

E^0 for $\text{IO}_3^-/\text{Hg}_2(\text{IO}_3)_2/\text{Hg}$ (Haring and Zapponi) loc. cit. = +0.3939 volt.

E^0 for $\text{Hg}_2^{++}/\text{Hg}$ (3) = +0.7986 volt.

$$E_{\text{cell}} = E_{\text{left}} + E_{\text{right}}$$

$$E_{\text{cell}} = -0.3939 + 0.7986 = +0.4047 \quad (12)$$

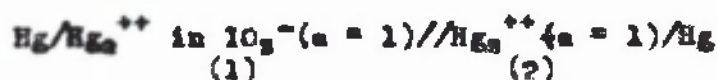
substituting (12) in (9)

$$+0.4047 = \frac{0.05915}{2} \log \frac{1}{K}$$

whence

$$K = 2.070 \times 10^{-14}$$

An alternate method for the calculation of the activity product may be approached in the following manner.



$$E = \frac{0.05915}{2} \log \frac{A_{\text{Hg}_2^{++}}(?) }{A_{\text{Hg}_2^{++}}(1)} \quad (13)$$

$${}^2H_{63}^{++}({}^2I_{63}^-) = 3 \quad (9)$$

shows

$${}^2H_{63}^{++}(1) = \frac{F}{({}^2I_{63}^-)(1)} = 3 \quad (10 \text{ if } {}^2I_{63}^- = 1)$$

Therefore

$$C = \frac{5.66915}{3} \log \frac{1}{3} \quad (14)$$

One can see that C is identical with C^0 of equation (9)

MATERIALS AND METHOD

A. Reagents

1. Mercury

An ordinary good grade of mercury was passed through a long column of normal nitric acid and mercurous nitrate in the form of a fine spray several times. This was dried and distilled in a current of air under reduced pressure in a special pyrex apparatus. This method was used by Hulett and Winchin (9).

2. Mercurous Nitrate

In a crystallizing dish were placed 50 cc. of water and 77 cc. of nitric acid (69%), and 204 grams of mercury. The reaction was permitted to go to completion, care being taken to maintain mixture at the temperature of ice. Since mercury was always present in excess, frequent stirring was necessary to prevent local formation of yellow basic nitrate. The crystals of $Hg_2(NO_3)_2 \cdot H_2O$ which separate are sucked dry as possible on a Buchner funnel. Analysis by Murray's (10) method proved the extreme purity of the crystals.

3. Mercurous Iodate

To a well stirred puddle of mercury, which was covered with 400 cc. of distilled water, was rapidly 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.

The rapid addition procedure was carried out in order to eliminate the presence of colloids. The time for the addition of 150 cc. of each solution was fifteen minutes as compared with a thirty minute addition as used by Haring and Kraybill (11). The worker cited learned that a change

of only 0.24 millivolt was observed when the two procedures were compared.

After the addition of 150 cc. of each solution, the stirrer was stopped; the mercurous iodate permitted to settle; and 500 cc. of the supernatant solution siphoned off, and replaced with 400 cc. of distilled water. 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 N potassium iodate, and the mixture stirred for one hour. This was repeated until 2 liters of 0.005 N potassium iodate had been used in portions of 500 cc. each. The prepared salt was then stored in 0.005 N potassium iodate for six months.

4. Sodium Thiosulphate

2.50 grams of Baker and Adamson reagent sodium thiosulphate was dissolved in a liter of freshly distilled conductivity water, and 0.01 gram of sodium carbonate was added to the solution. The solution was then allowed to stand three weeks before standardizing.

5. Potassium Iodate

Once recrystallized from conductivity water G. Frederick Smith special analytical reagent grade of potassium iodate was employed throughout the research. The salt was dried for three hours at 135° C.

6. Potassium Nitrate

Merck's reagent salt was recrystallized three times from conductivity water. The mother liquor from the second recrystallization was free of chloride. The salt was dried for three hours at 150° C.

7. Magnesium Nitrate

Baker's analyzed reagent magnesium nitrate hexahydrate was used. To test the degree of hydration an analysis for magnesium was carried out (12). The analysis showed 9.458 percent magnesium as compared to 9.434,

the theoretical value.

8. Lanthanum Nitrate

C. P. quality of Eimer and Amend Co. lanthanum nitrate was used in this research.

9. Potassium Iodide

Baker and Adamson reagent potassium iodide was used in the titrations.

10. Starch Solution

A paste of 2 grams of powdered corn starch and a little water was added slowly to a liter of boiling water. It was allowed to cool, and the clear solution was decanted and put in a glass stoppered bottle. Freshly distilled mercury was added to preserve the suspension.

11. Water

Conductivity water was used in the preparation of all solutions.

B. Apparatus, Method, and Technique.

1. Apparatus

All weights and glassware were calibrated before use.

One of the important problems in the research was the successful shaking of the bottles containing mercurous iodate in the various salt solutions. This was overcome very easily by the apparatus shown in Plate I.

It can be noted that the motor below the thermostat is connected to a basket 15" x 9" x 9" constructed of paraffined wood and wire. The shaker is immersed in the bath and is firmly set on a rod extended across the center of the thermostat by means of a hinged bearing. A paraffined cord is connected to the basket and is extended to a point off center of the rotating wheel of the motor by means of a pulley mounted on the front steel frame of the thermostat. By means of the off center connection of

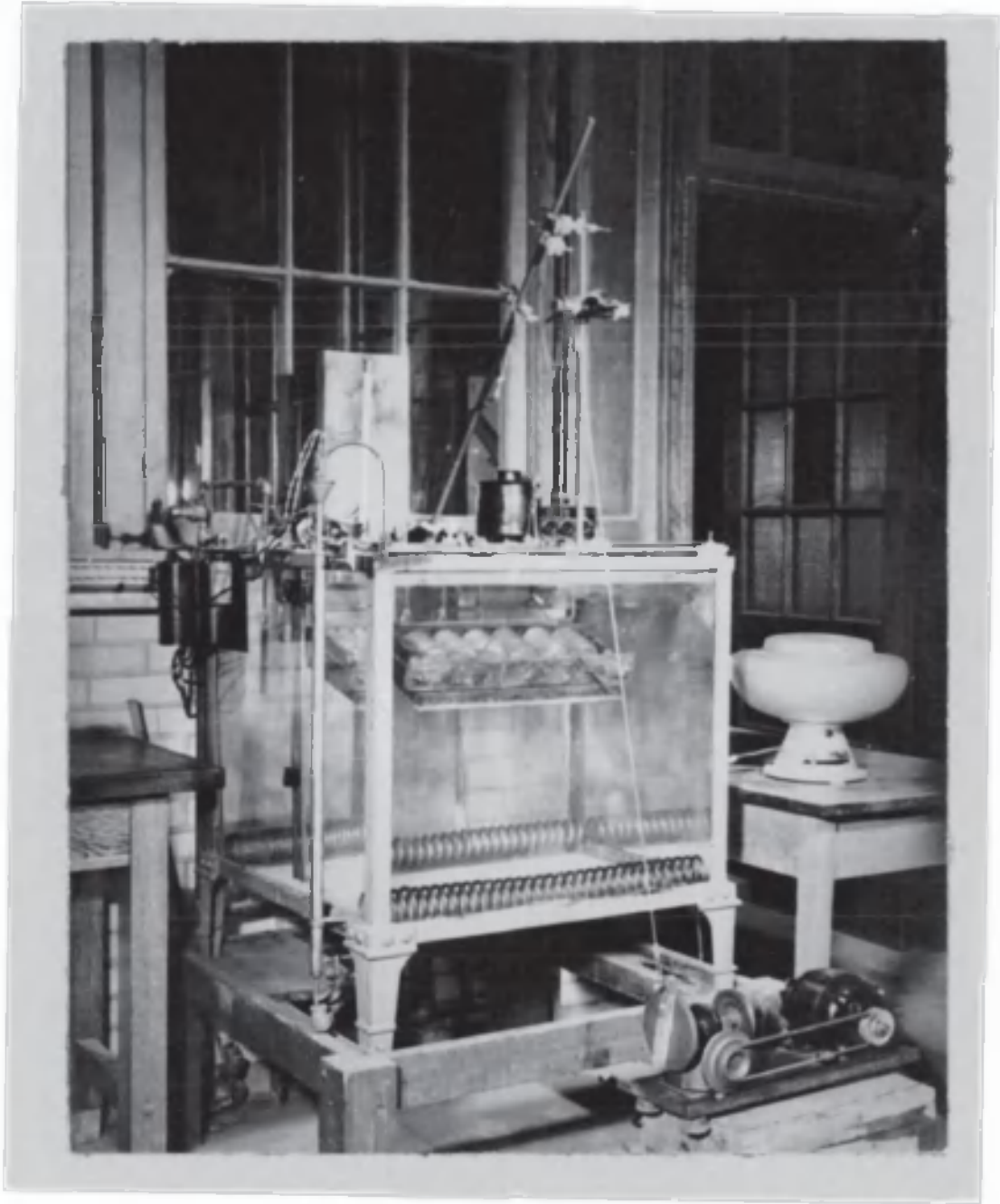


PLATE I

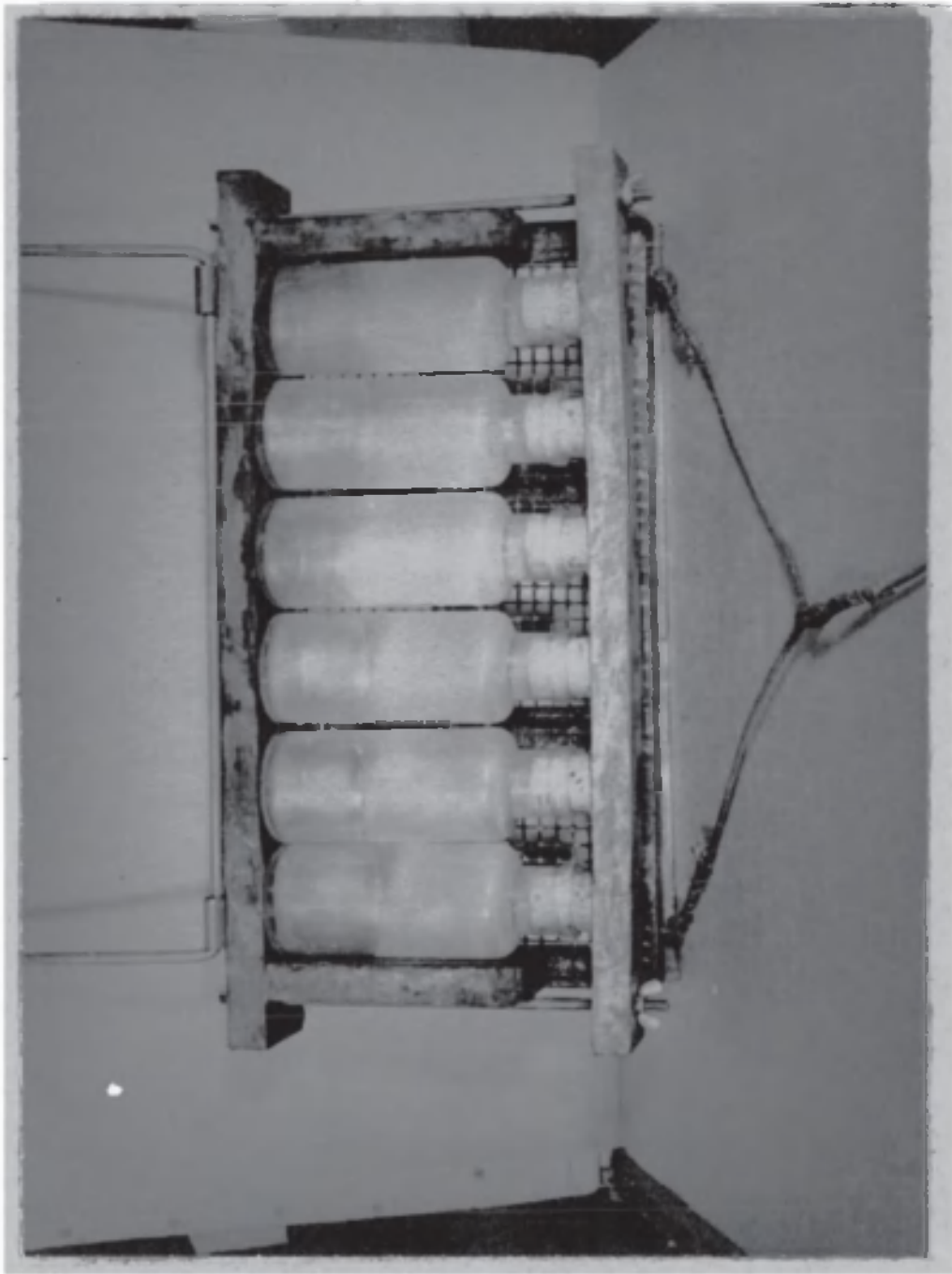


PLATE II

the cord to the motor a lifting and lowering motion of the basket is carried out. The latter motion is aided by a lead strip placed on the front of the basket.

The shaker is of such dimensions that six 250 cc. wide mouth or three 500 cc. narrow mouth bottles can be tightly inserted. The front of the basket consists of a movable bar (wood paraffined) which can be firmly bolted, wedging the bottles therein.

The apparatus as constructed in this manner produced a tilting effect on the bottles. The total upward and downward motion on the forepart of the basket might be estimated as 8 or 9 inches. The salt in the solutions is swirled about and it appears that effective shaking is produced.

Titrations were carried out on a special titration stand which consisted of a frosted glass base beneath which was a fluorescent lamp. This constant light source greatly facilitated precise titration. The 10 cc. micro burettes used were made and calibrated by the Arthur H. Thomas Company.

2. Method and Technique

(a) Standardization of Sodium Thiosulphate

The sodium thiosulphate solution was prepared as directed under "Materials" and allowed to stand for three weeks. The reason for this is that the standardization value remained fairly constant for a long time after such aging.

A number of methods of standardization were studied in a previous research (13) and it was learned that analytical reagent potassium iodate produced the best results (14). The approximate value of the sodium thiosulphate solution was (0.0075-0.010) N which in turn required precise analytical technique. A calibrated micro burette was employed, which could be read to 0.005 cc.

The reactions involved are:



To 6 cc. of the potassium iodate solution diluted to 100 cc. were added 10 cc. of freshly prepared 10 percent potassium iodide and 10 cc. of 6 N hydrochloric acid and then swirled for 30 seconds. The sodium thiosulphate was then rapidly titrated to the disappearance of the yellow color and 2 cc. of starch solution were added. The titration was then continued to the disappearance of the blue color. The total titration time was two minutes. The final volume was about 150 cc.

(b) Preparation of Saturated Mercurous Iodate in the Various Salt Solutions.

The mercurous iodate after preparation was stored in 0.005 N potassium iodate. To remove the latter solution about 2 grams of the wet salt were centrifuged. After each treatment the liquid was decanted and conductivity water added with vigorous shaking. This procedure was repeated twenty times and the salt was centrifuged thrice in the presence of the salt solution in which it was to be dissolved. After the last treatment the mercurous iodate (2 grams) was distributed between three 500 cc. pyrex bottles, which were paraffined inside, containing the same molar concentration of the dissolved salt.

The paraffining procedure was employed to prevent the adsorption of the extraneous ions (11). The worker cited has shown that there is an exchange between the lattice cations and the cations in the surface of the glass container. If this occurred, the actual concentration of mercurous ions would be smaller than that of the iodate. However, error is eliminated by coating the inside of the bottle with paraffin.

The corks were also carefully coated with paraffin to prevent similar adsorption taking place. The salt solutions, as already mentioned, were prepared on a molar basis.

After the addition of the mercurous iodate to the salt solution, the corks were tightly inserted, and the bottles wedged in the shaker.

(a) Shaking

The solutions as prepared above were then shaken for four hours in a thermostat regulated at $25.00 \pm 0.02^\circ \text{C}$. This time was found to be sufficient for equilibrium to be established (13). Analysis of a saturated solution of mercurous iodate in water showed that two hours only were necessary. After shaking, the bottles were clamped in an upright position and allowed to stand for 24 hours in the thermostat.

(d) Filtration and Centrifuging

The solutions in each of the bottles were then filtered by a rubber tube, previously boiled, plugged with pyrex glass wool and attached to a pipette. A rubber tube was connected to the upper part of the pipette so that the supernatant liquid could be sucked out slowly by an aspirator.

This procedure appeared slow and tedious, but it seemed to be the only method by which the colloid, whose presence could be demonstrated by a Tyndall cone, could be removed. However, even with this procedure some solutions still showed a trace of colloid. This was often the case with the dilute solutions.

After sucking out approximately 150 cc. of the liquid, the solution was quickly put into three 50 cc. centrifuge tubes and centrifuged for ten minutes. Following this procedure 99.70 cc. of the supernatant liquid was pipetted into a 250 cc. Erlenmeyer flask. Observations showed a slight Tyndall effect in some cases, i. e. low concentrations of the

salt solutions.

(e) Titration

The mercurous iodate solution transferred into the Erlenmeyer was titrated in the same manner as described under "Standardization of Sodium Thiosulphate."

RESULTS

The solubilities and solubility products of mercurous iodate in varying concentrations of potassium nitrate as calculated are tabulated in table I.

Similar results, as indicated above, for magnesium and lanthanum nitrate are tabulated in tables II and III respectively.

The degree of hydration of the magnesium nitrate was in doubt so it was analyzed for magnesium. The pyrophosphate method (12) was used with the following results:

Run	Percent Magnesium
1	9.568
2	9.550

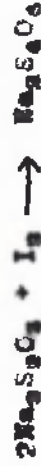
The theoretical value is 9.464 percent magnesium.

A. Calculation of Standard Electrode Potential

1. Solubility of Mercurous Iodate

Sample calculation:

$$M_{\text{Hg}_2\text{S}_2\text{O}_3} = 0.009410$$



$$\text{Hence } 1 \text{ mol } \text{Hg}_2\text{S}_2\text{O}_3 = 1/12 \text{ mol } \text{Hg}_2(\text{IO}_3)_2$$

Therefore

$$1 \text{ cc. of } 0.009410 \text{ M } \text{Hg}_2\text{S}_2\text{O}_3 \text{ solution} = \frac{0.009410}{1000 \times 12}$$

$$1 \text{ cc. of } 0.009410 \text{ M } \text{Hg}_2\text{S}_2\text{O}_3 \text{ solution} = 7.841 \times 10^{-7} \text{ mols } \text{Hg}_2(\text{IO}_3)_2$$

Then:

$$M_{\text{Hg}_2(\text{IO}_3)_2} = \frac{0.009410 \times 7.841 \times 10^{-7}}{0.09970} \quad (15)$$

where $m_{\text{Hg}_2(\text{IO}_3)_2}$ is the solubility of the mercurous salt and $cc \cdot \text{Na}_2\text{S}_2\text{O}_3$ is the volume of the standard thiosulphate necessary for a complete titration. The value .69970 represents the volume of the pipette used in the experiment.

2. Solubility Product of Mercurous Iodate

L, the solubility product, is calculated as follows:

$$L = m_{\text{Hg}_2^{++}} \times m_{\text{IO}_3^-}^2 \quad (1)$$

$$L = 4m_{\text{Hg}_2^{++}}^3 \quad (\text{if there is no common ion}) \quad (16)$$

3. Ionic Strength

$$\mu = 1/2 \left[(m_{\text{Hg}_2^{++}} \times 2^2) + 2(m_{\text{IO}_3^-} \times 1^2) + (m_{\text{I}^+} \times 1^2) + (m_{\text{IO}_3^-} \times 1^2) \right]$$

$$\mu = 1/2 \left[(m_{\text{Hg}_2^{++}} \times 2^2) + 2(m_{\text{IO}_3^-} \times 1^2) + (m_{\text{Hg}_2^{++}} \times 2^2) + 2(m_{\text{IO}_3^-} \times 1^2) \right]$$

$$\mu = 1/2 \left[(m_{\text{Hg}_2^{++}} \times 2^2) + 2(m_{\text{IO}_3^-} \times 1^2) + (m_{\text{I}_2^{++}} \times 3^2) + 3(m_{\text{IO}_3^-} \times 1^2) \right]$$

where μ is the ionic strength, and m is the concentration expressed in molality.

4. Activity Product

The weighted mean activity product as extrapolated from the curves in figs. 1, 2, and 3 is 3.955×10^{-14}

5. Standard Electrode Potential

$$\text{Hg}/\text{Hg}_2^{++} (a = 1) // \text{Hg}_2^{++} (a = 1)/\text{Hg}$$

$$E = \frac{RT}{2F} \ln K \quad (17)$$

$$E = \frac{0.05915}{2} \log 3.955 \times 10^{-14}$$

$$E = -0.3964 \text{ volt}$$

$$E_{\text{cell}} = E_{\text{left}} + E_{\text{right}}$$

$$-0.3964 = -0.7986^{(8)} + E_{\text{IO}_3^-/\text{Hg}_2(\text{IO}_3)_2(s)/\text{Hg}}$$

$$E_{\text{IO}_3^-/\text{Hg}_2(\text{IO}_3)_2(s)/\text{Hg}} = 0.4022 \text{ volt}$$

C. Activity Coefficient

Previously it has been shown that

$$K = \gamma_{\pm}^3 L \quad (5)$$

Hence

$$\gamma_{\pm} = \frac{K}{L}^{1/3} \quad (18)$$

The activity coefficients are tabulated in tables I, II, and III and plotted in Fig. 8. The activity product used in the calculation of the activity coefficients was not the mean value, but each extrapolated value found on figures 1, 2, and 3. The activity product used for potassium nitrate was 2.90×10^{-14} ; for magnesium nitrate, 5.01×10^{-14} ; for lanthanum nitrate, 5.01×10^{-14} .

Table 1

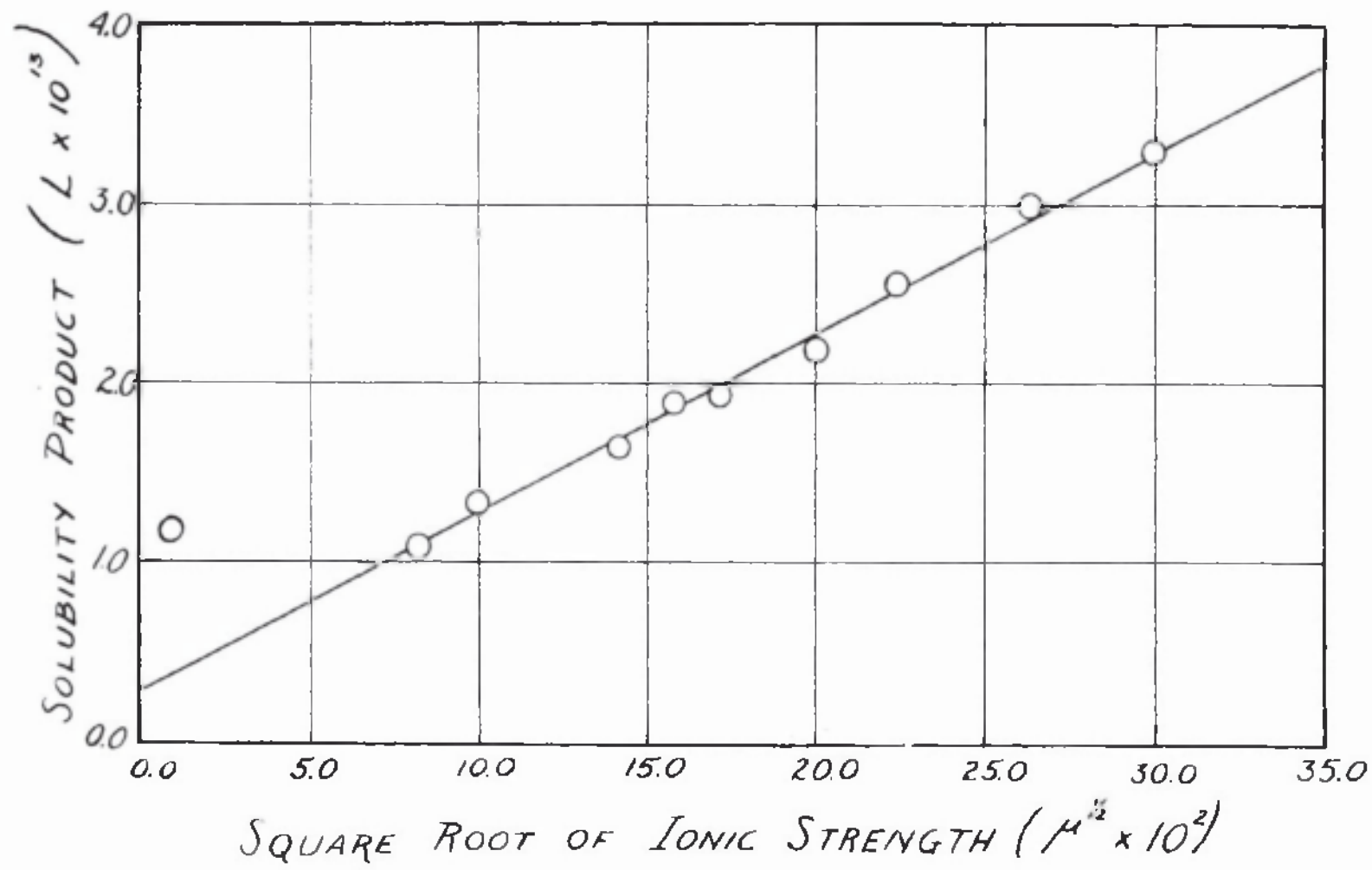
Solubility $K_{sp}(IO_3)_2$ mols/l.	Solubility Product $K_{sp}(IO_3)_2$	Molality KNO_3	Ionic Strength μ	$\mu^{1/2}$	Activity Coefficient γ_{\pm}
3.105×10^{-5}	1.197×10^{-13}	0.000000	9.315×10^{-3}	0.965×10^{-2}	0.629
3.015×10^{-5}	1.096×10^{-13}	0.006698	0.6728×10^{-2}	8.203×10^{-3}	0.642
3.229×10^{-5}	1.999×10^{-13}	0.009832	0.9932×10^{-2}	9.966×10^{-3}	0.600
3.457×10^{-5}	1.652×10^{-13}	0.01976	1.986×10^{-2}	14.09×10^{-3}	0.560
3.617×10^{-5}	1.894×10^{-13}	0.02480	2.491×10^{-2}	15.78×10^{-3}	0.535
3.649×10^{-5}	1.949×10^{-13}	0.02939	2.944×10^{-2}	17.16×10^{-3}	0.530
3.800×10^{-5}	2.195×10^{-13}	0.03399	4.011×10^{-2}	20.09×10^{-3}	0.509
4.001×10^{-5}	2.562×10^{-13}	0.04989	4.995×10^{-2}	22.35×10^{-3}	0.487
4.199×10^{-5}	2.829×10^{-13}	0.06891	6.903×10^{-2}	26.27×10^{-3}	0.468
4.259×10^{-5}	3.090×10^{-13}	0.08921	8.934×10^{-2}	29.89×10^{-3}	0.454

Table II

Solubility $Hg_2(10_2)_2$ mols/l.	Solubility Product $Hg_2(10_2)_2$	Molality $Hg_2(NO_3)_2$	Ionic Strength μ	$\mu^{\frac{1}{2}}$	Activity Coefficient γ_{\pm}
2.105×10^{-5}	1.197×10^{-19}	0.0000000	9.215×10^{-2}	0.965×10^{-2}	0.748
2.580×10^{-5}	1.411×10^{-19}	0.0007459	0.2226×10^{-2}	4.729×10^{-2}	0.708
2.295×10^{-5}	1.431×10^{-19}	0.001050	0.2250×10^{-2}	5.701×10^{-2}	0.705
2.402×10^{-5}	1.575×10^{-19}	0.001496	0.4590×10^{-2}	6.775×10^{-2}	0.689
2.250×10^{-5}	1.504×10^{-19}	0.002091	0.6194×10^{-2}	7.870×10^{-2}	0.693
2.561×10^{-5}	1.806×10^{-19}	0.002361	0.7191×10^{-2}	8.480×10^{-2}	0.652
2.612×10^{-5}	1.885×10^{-19}	0.002667	1.111×10^{-2}	10.54×10^{-2}	0.643
2.712×10^{-5}	2.047×10^{-19}	0.005237	1.582×10^{-2}	12.29×10^{-2}	0.626
2.803×10^{-5}	2.200×10^{-19}	0.006252	1.887×10^{-2}	13.74×10^{-2}	0.611
2.912×10^{-5}	2.395×10^{-19}	0.008596	2.591×10^{-2}	16.10×10^{-2}	0.594
4.116×10^{-5}	2.784×10^{-19}	0.01267	4.076×10^{-2}	20.19×10^{-2}	0.564
4.136×10^{-5}	2.821×10^{-19}	0.01591	4.605×10^{-2}	21.46×10^{-2}	0.560
4.172×10^{-5}	2.904×10^{-19}	0.01856	5.581×10^{-2}	23.62×10^{-2}	0.557
4.248×10^{-5}	3.066×10^{-19}	0.02236	7.021×10^{-2}	26.50×10^{-2}	0.547
4.295×10^{-5}	3.172×10^{-19}	0.02605	9.023×10^{-2}	30.09×10^{-2}	0.540
4.471×10^{-5}	2.576×10^{-19}	0.02586	10.77×10^{-2}	32.83×10^{-2}	0.519

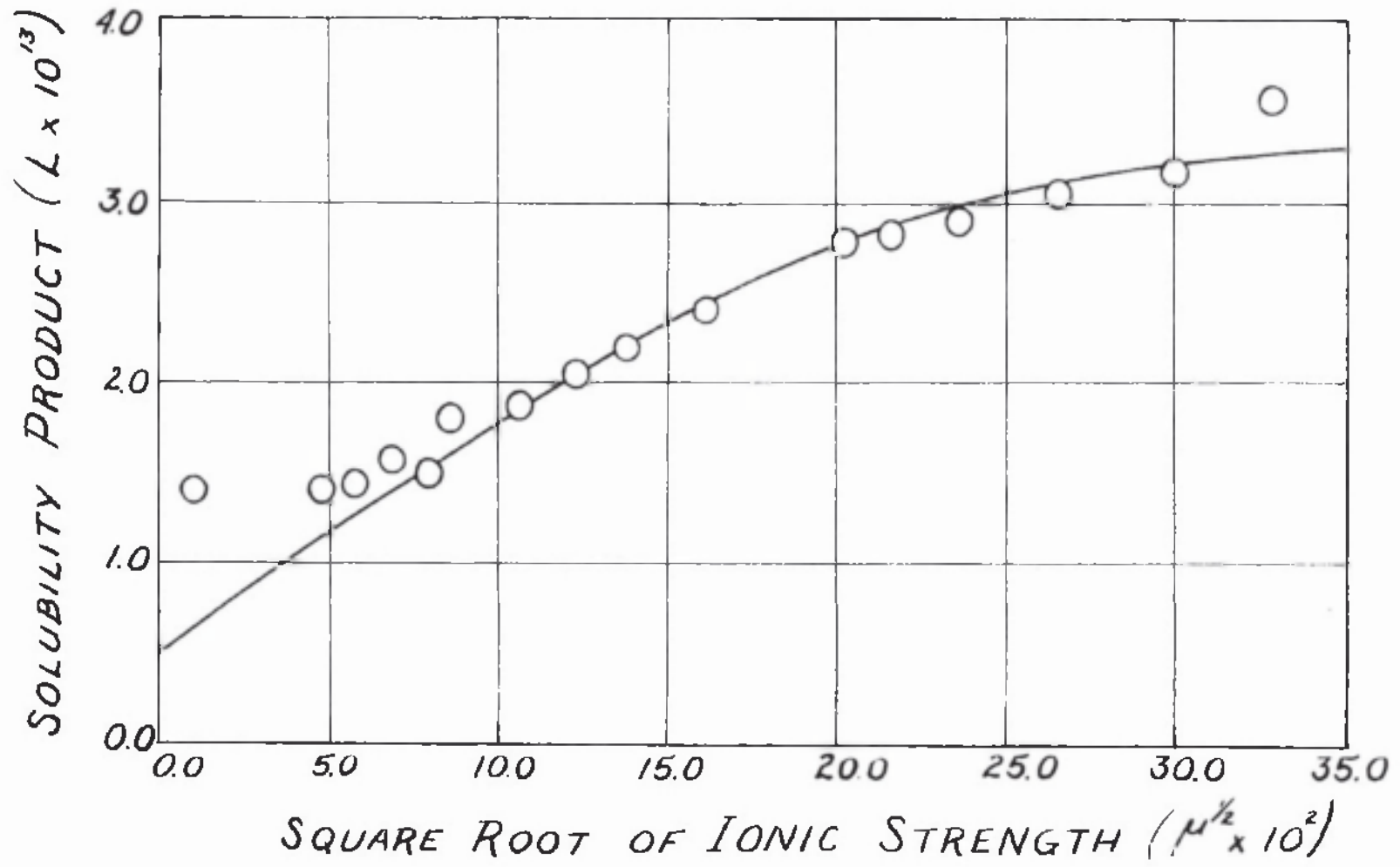
Table III

Solubility $Hg_2(10g)_2$ mols/l.	Solubility Product $Hg_2(10g)_2$	Molality $La(HCl)_2$	Ionic Strength μ	$\mu^{\frac{1}{2}}$	Activity Coefficient γ_{\pm}
3.105×10^{-5}	1.197×10^{-13}	0.000000	9.315×10^{-5}	0.965×10^{-2}	0.748
3.241×10^{-5}	1.962×10^{-13}	0.006346	0.3705×10^{-2}	6.249×10^{-2}	0.716
3.371×10^{-5}	1.573×10^{-13}	0.001077	0.6563×10^{-2}	8.101×10^{-2}	0.689
3.514×10^{-5}	1.795×10^{-13}	0.001466	0.8900×10^{-2}	9.434×10^{-2}	0.661
3.652×10^{-5}	1.948×10^{-13}	0.002150	1.306×10^{-2}	11.43×10^{-2}	0.636
3.852×10^{-5}	2.285×10^{-13}	0.003675	2.216×10^{-2}	14.89×10^{-2}	0.603
4.022×10^{-5}	2.601×10^{-13}	0.004850	2.922×10^{-2}	17.09×10^{-2}	0.586
4.108×10^{-5}	2.773×10^{-13}	0.006962	4.189×10^{-2}	20.47×10^{-2}	0.565



SOLUBILITY OF MERCUROUS IODATE
IN
POTASSIUM NITRATE

FIGURE 1



SOLUBILITY OF MERCUROUS IODATE
IN
MAGNESIUM NITRATE

FIGURE 2

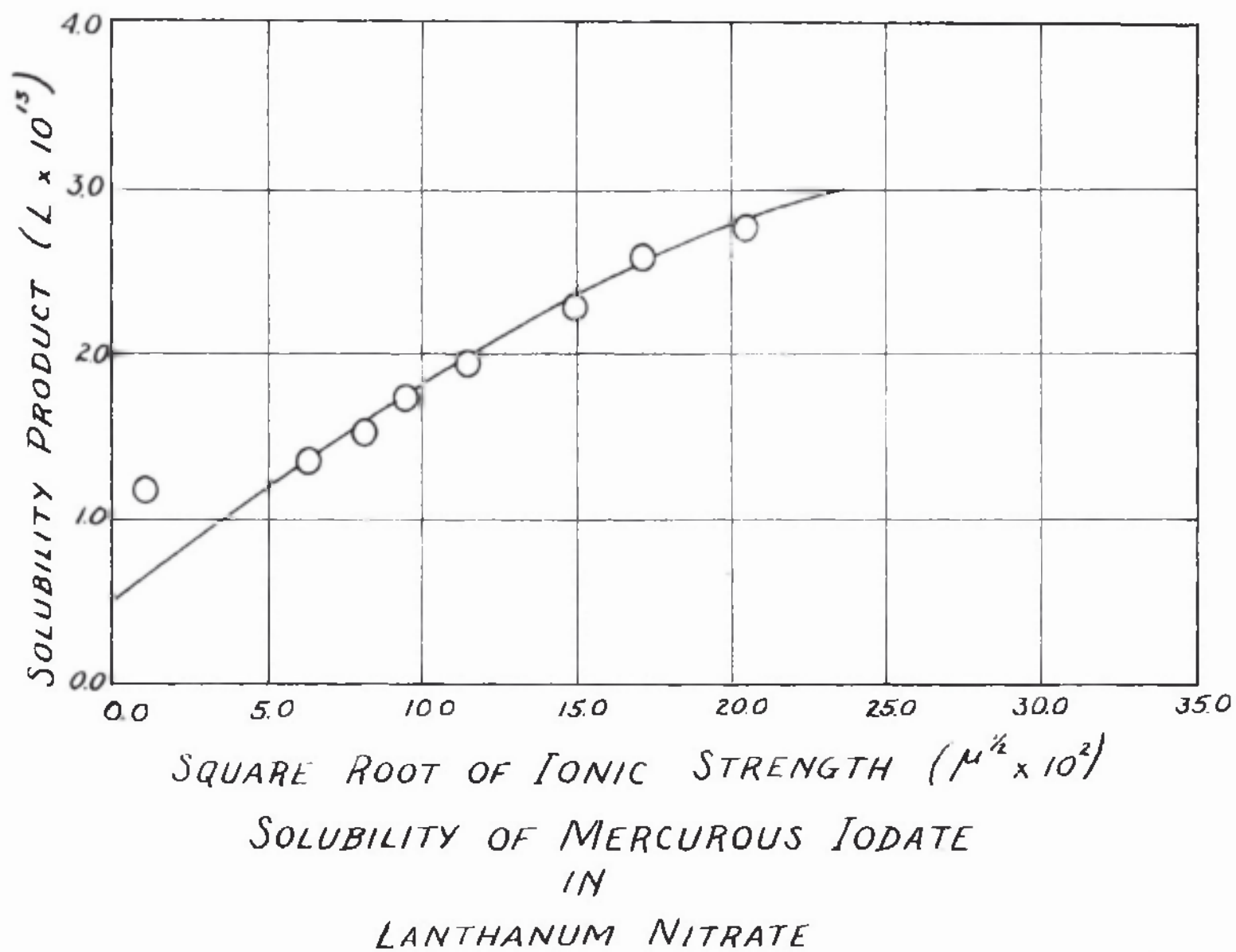


FIGURE 3

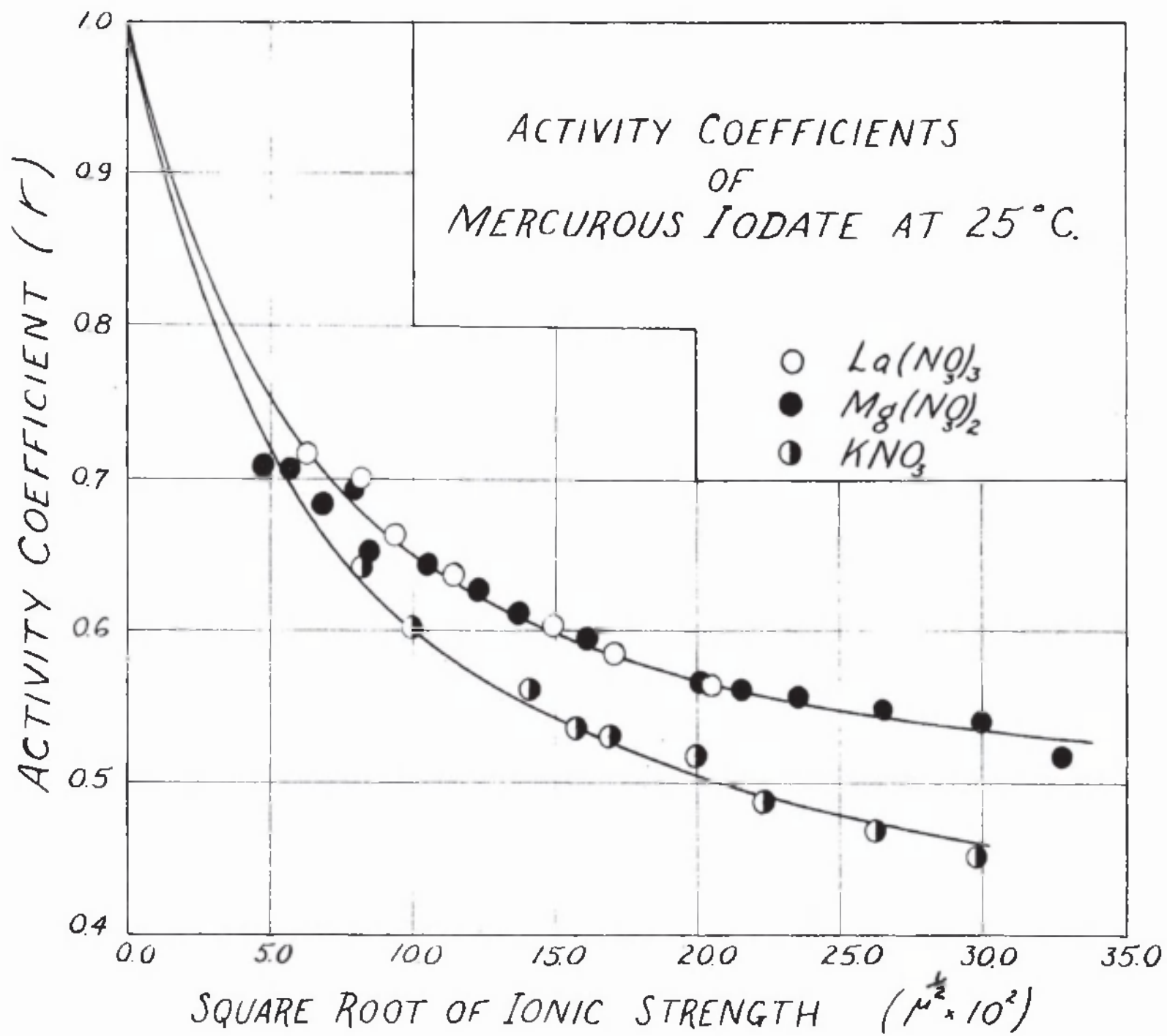


FIGURE 4

DISCUSSION OF RESULTS

The value, 0.4077 volt, of the standard electrode potential of the cell $\text{IC}_3^-/\text{Hg}_2(\text{IC}_3)_2(\text{s})/\text{Hg}$ as calculated from solubility data shows only fair agreement with the value 0.3939 (\pm 0.001) as obtained by Haring and Zapponi (loc. cit.). Possible causes for this deviation are as follows.

The activity product used in the calculation of the above standard electrode potential was obtained by a relative weight mean of the values of figures 1, 2, and 3. Since the writer was assured of the purity of the potassium nitrate used in figure 1, he gave that extrapolated value a weight of 2 in comparison with a weight of 1 given for each of the extrapolated values in figures 2 and 3.

It was observed by a Tyndall cone that a faint colloid was formed when the mercurous salt was dissolved in the various salt solutions. The quantity of the colloid was dependent on the concentration of the dissolved salt present. There was always more colloid the more dilute the salt solution. In a previous research (13) efforts were made to remove this colloid without any apparent success. However, the procedure used in this research gave much better results. Titration fluctuations of the sodium thiosulphate solutions were evident in the low concentration range of the dissolved salt. This can be illustrated by examining figure 2 where four points in the dilute range do not fall on the curve. For these points, duplicate titrations showed unusually large variations. For this reason, these four points are ignored in drawing the curve. It is interesting to note that the one point in the dilution range which falls on the curve gave two identical titration values. The point in the more concentrated portion on figure 2 is off the curve, but this is obviously due to an error

in method or technique.

An examination of the solubility of mercurous iodate in pure water in figures 1, 2, and 3 will show it to be far from the extrapolated curve. However, this deviation appears to be real, since repeated trials on three different occasions showed a similar titration value. The writer is unable to account for this.

The consideration of grain size may also be important in connection with these results. Previously (19) it was noted that three independent preparations of mercurous iodate gave three different activity products and correspondingly different slopes of the curves when the same dissolved salt was used; although an effort was made in each case to prepare the mercurous salt in exactly the same manner. In the preparation of the mercurous salt used in this research the writer attempted to eliminate grain size effect by the method of preparation and prolonged aging (6 months).

It is also possible that hydrolysis may have taken place, since the research was carried out in dilute solutions.



It is interesting to note that Haring and Zapponi did not report any e. m. f. measurements below 0.01 N KIO_3 which was practically the maximum concentration value in this research. Furthermore the common ion they used should suppress such hydrolysis.

Also in their research the activity coefficients used could be in error enough to cause a variation of 2-3 mve.

For these reasons the writer feels that the activity product as obtained in this research is as accurate as can be expected under the conditions of the experiment. However, it must be admitted that the standard electrode potential as published by Haring and Zapponi (loc. cit) is subject

to fewer sources of error. Accordingly, it is hoped that further work be done on this problem. Solubility measurements should be carried out in the presence of a common ion. This procedure would considerably reduce hydrolysis and a lower extrapolated activity product should be obtained. Such a result would certainly explain the variance in the results obtained by the writer and Haring and Zepponi. However, the writer believes the presence of colloid to be the most serious cause of the deviation between the two values. Attempts were not made in this research to use a common ion because no good micro method of determining mercury is available. The electrolytic method in a large volume of solution and the use of a micro balance appear the most hopeful.

The results obtained in this research were very much better than previously obtained (19). The use of a constant light source titration stand, special burettes, larger sample for titration, and an increased concentration of standardized thiosulphate seemed to improve the work considerably.

The writer has also noted that in a recent research (2) in which the standard electrode potential of the $\text{IO}_3^-/\text{AgIO}_3(\text{s})/\text{Ag}$ electrode was checked by solubility measurements with a deviation of only 1.3 mvs. the activity product of the AgIO_3 was 3.04×10^{-8} which is very much larger than that of mercurous iodate. Furthermore, the percentage error of a titration in this research would be multiplied three fold in the solubility product, whereas it would be doubled in the work on silver iodate. Also Pearce and Celke (5), who measured the solubility of lanthanum nitrate in varying concentrations of different salt solutions, did not check their results by s. m. f. measurements, so no evidence on the agreement to be expected between the two methods is possible.

DISCUSSION OF ERRORS

The largest error of the research was due to varying titration values of the sodium thiosulphate. This was encountered because of colloidal mercurous iodate present in the solutions. However, to be certain of the results as tabulated, three samples of the same salt concentration were titrated. Duplicate values accepted, except those cited in "Discussion of Results," were found to deviate from the average no greater than 0.5 percent. Titration errors may have also resulted from air oxidation of the potassium iodide added, but this was minimized by the rigidly standardized procedure followed.

Another error resulted from possible temperature changes of the mercurous iodate-dissolved salt solution while centrifuging for ten minutes. This process immediately followed the filtering of the solution from the paraffined bottles. This error is certainly small.

The instrumental errors, such as small temperature variations of the bath (0.05° C), precision of the reading of the burette (0.005 ml.), and errors in weighing can be entirely neglected in comparison to errors of method.

Uniform procedure was employed, whenever possible, throughout the research. The same solutions such as starch, 6 N acid, etc. were used to prevent any variation of results.

All solutions possible were made on a molal basis. It is to be noted that the concentration of the mercurous iodate is expressed as mols/liter; however, when dissolved salt solutions of 0.01 molal or less were used, this error should not become appreciable.

Use of paraffin coated bottles for storage of the preparation as well as their use in the shaking and standing of the solutions eliminated the error due to a variance in ratio of mercurous and iodate ions.

SUMMARY

1. The activity product, K , for mercurous iodate has been found to be 3.955×10^{-14} .
2. The standard electrode potential of the mercurous iodate electrode has been calculated. Its value is 0.4692 volt.
3. The activity coefficients of the mercurous iodate solutions in varying concentrations of potassium nitrate, magnesium nitrate, and lanthanum nitrate have been calculated. They are found on tables I, II, and III, and Fig. IV.
4. Suggestions have been offered to account for the difference between the K , E , K , and solubility value.

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