

1955

# Iodato-silver complexing equilibria

James Joseph Renier  
*Iowa State College*

Follow this and additional works at: <https://lib.dr.iastate.edu/rtd>

 Part of the [Physical Chemistry Commons](#)

## Recommended Citation

Renier, James Joseph, "Iodato-silver complexing equilibria" (1955). *Retrospective Theses and Dissertations*. 15140.  
<https://lib.dr.iastate.edu/rtd/15140>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact [digirep@iastate.edu](mailto:digirep@iastate.edu).

**UNCLASSIFIED**

---

Title: "Iodato-Silver Complexing Equilibria"

13 /

---

Author: James Joseph Renier

(Official certification of the classification shown is filed in the  
Ames Laboratory Document Library)

Signature was redacted for privacy.

---

W. E. Dreeszen

Secretary to Declassification  
Committee

**UNCLASSIFIED**

---



IODATO-SILVER COMPLEXING EQUILIBRIA

by

James J. Renier

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1955

UMI Number: DP12925

### INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

**UMI**<sup>®</sup>

---

UMI Microform DP12925

Copyright 2005 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company  
300 North Zeeb Road  
P.O. Box 1346  
Ann Arbor, MI 48106-1346

## TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. EXPERIMENTAL	7
A. Material	7
1. Reagents	7
2. Analytical standards	8
3. Radioactive silver	8
4. Tagged silver iodate	9
B. Analyses	10
C. Apparatus	17
D. Procedure	26
III. RESULTS	29
A. Results from the Solubility Determinations	29
B. Description of the Complexing Equilibria	37
C. Determination of the Equilibrium Solubility Product Constants	39
D. Evaluation of the Formation Equilibrium Constants	41
E. Thermodynamic Properties	46
IV. DISCUSSION	49
V. SUMMARY	53
VI. LITERATURE CITED	54
VII. ACKNOWLEDGMENTS	57

## I. INTRODUCTION

A class of chemical systems which has not been extensively investigated by conventional chemical analysis is one composed of a sparingly soluble salt and an aqueous solution of a soluble salt containing a common anion. The nature of this category requires that the common-ion effect be operative. The limited applicability of ordinary techniques is primarily due to the reduced solubility of the sparingly soluble salt. To ascertain the various equilibria established, a means of obtaining accurate data in the concentration range below  $10^{-5}$  M must be available. At the present time, a radiotracer technique is the method which most generally can meet this stringent requirement.

The fundamental operations of the radiotracer technique are two in number. The cation of the saturating salt is tagged with a radioactive nuclide. A solution of a soluble salt containing the common anion is equilibrated with the tagged salt and the total concentration of the free and complexed cation is determined radiochemically.

In procedures employing radiotracers for radioassay purposes, certain precautions must be taken in order to insure consistent analyses. The accuracy attainable is usually governed by the reproducibility of the sample preparation and counting technique. To achieve a precise radioassay of the equilibrium samples, the active material must be deposited and mounted in such a way that the geometry and backscattering are uniform for all samples. If the thickness of an active deposit varies, a self-absorption curve must be obtained for use as a reference standard. Counting rates should be held to values at which coincidence

losses are unimportant. All samples should be counted for a length of time sufficient to insure good statistics. The greatest error may be encountered if a representative sample of the equilibrium solution phase were not obtained. Zimmerman (1) has written an excellent review on the latter subject.

The application of radioactivity to the determination of solubility product constants was originally demonstrated by Paneth and Hevesy (2). They used Radium D to measure the solubility product of lead chromate. This measurement was subsequently refined by Hevesy and Róna (3) using Thorium B. Following these classic experiments, the method was not frequently employed because of the limited availability of suitable radioisotopes. However, nuclear piles and particle accelerators have provided useful tracers for many of the elements. Ishibashi and Funahashi (4), Ferla et al. (5, 6), Ruka and Willard (7), and many others (8-13) have radiochemically determined the solubilities of very insoluble salts in solutions of various compositions. Neiman et al. (14) and Jordan (15) have recently suggested additional methods of approach. Relatively few investigators have used radiotracers to resolve systems containing a range of common ion concentrations. Rare earth oxalate ion equilibria were studied by Crouthamel and Martin (16, 17). Work on the thorium iodate-iodate ion-water system was performed by Fry et al. (18). The silver chloride-chloride ion-water system was examined by Barney et al. (19) at one temperature. Martin and Jonte (20) in another investigation, obtained data which indicated the existence of  $\text{AgCl (aq.)}$  and  $\text{Ag(Cl)}_2^-$  species. They reported thermodynamic properties obtained from the solubility and its temperature coefficient. These species, and



higher chloro-complexes of silver were reported by Leden and Berne (21). Agreement between the results of the separate radiochemical investigations of the silver chloride systems was poor. The silver bromide-bromide ion-water system, and the silver azide-azide ion-water system have also been studied by Leden et al. (22, 23) in this manner. Certainly possibilities exist for improvement and further application of the method.

The work presented in this thesis is aimed at obtaining a definitive thermodynamic description of the silver iodate-iodate ion-water system. Included within the objective is the study of the iodato-silver complexing equilibria. An intelligible achievement of this end is impossible unless existing tracer techniques are improved. Consequently, an additional objective is of necessity the refinement of the radiochemical procedure.

The solubility of silver iodate has frequently been determined in pure water and in solutions of diverse ions, however, there has been only one quantitative report of its solubility in a solution containing a common ion (24). In order to facilitate the presentation, various reported data have been included in Table 1. Values are reported only for the cases in which the dissolving medium was pure water since the present work is not concerned with the solubility in solutions containing diverse ions.

Ricci and Amron (41) studied the aqueous ternary systems of silver iodate with each of the following salts at 25°C:  $\text{LiIO}_3$ ,  $\text{NaIO}_3$ ,  $\text{KIO}_3$ , and  $\text{NH}_4\text{IO}_3$ . Isotherms obtained for these systems were all of the simplest type with no evidence of either compound formation or solid solution and qualitative tests for silver in the solutions containing silver iodate

Table 1. Previous Solubility Determinations of Silver Iodate in Water

Investigators	Date	Method	Temperature °C.	Solubility mmol./l.
Longi (25)	1883	Chemical Analysis	25	0.127
Noyes and Kohr (26)	1902	Chemical Analysis	25	0.189
Böttger (27)	1903	Conductivity	19.95	0.154
Kohlrausch (28)	1905	Conductivity	18	0.138
Sammet (29)	1905	Cell	25	0.216
Sammet (29)	1905	Cell	60	0.654
Kohlrausch (30)	1908	Conductivity	9.43	0.0972
Kohlrausch (30)	1908	Conductivity	18.37	0.138
Kohlrausch (30)	1908	Conductivity	26.60	0.190
Hill and Simmons (31)	1909	Chemical Analysis	25	0.178
Whitby (32)	1910	Colorimetry	20	0.138
Roth (33)	1921	Conductivity	12.55	0.107
Roth (33)		Conductivity	16.35	0.126
Roth (34)	1921	Cell	16.2	0.136
Baxter (35)	1926	Chemical Analysis	75	0.840
Roth (36)	1928	Conductivity	18.00	0.138
Kolthoff and Lingane (37)	1938	Chemical Analysis	25	0.1771
Li and Lo (38)	1941	Chemical Analysis	10	0.0970
Li and Lo (38)	1941	Chemical Analysis	20	0.1463
Li and Lo (38)	1941	Chemical Analysis	25	0.1785
Li and Lo (38)	1941	Chemical Analysis	30	0.2152
Li and Lo (38)	1941	Chemical Analysis	35	0.2587
Keefer and Reiber (39)	1941	Chemical Analysis	25	0.1794
Derr, Stockdale and Vosburgh (40)	1941	Chemical Analysis	25	0.1772
Ricci and Amron (41)	1951	Chemical Analysis	25	0.1794
Ricci and Amron (41)	1951	Chemical Analysis	45	0.352

and the dissolved salt were negative.

Shchigol (24) reported the solubility of silver iodate at 20-22°C. in aqueous solutions for three concentrations of potassium iodate. Equilibrium mixtures were prepared by contacting an excess of silver iodate with 100 ml. of a solution of potassium iodate which had been prepared by weighing the salt directly. They were agitated for twenty-four hours and filtered. The saturation concentrations of silver iodate in the filtrates were determined volumetrically using the standard iodometric method for iodate analysis. The concentrations of iodate at which solubilities were measured were 0.005 M, 0.025 M and 0.50 M. The final molarities of iodate found in the 100 ml. filtrates were reported to be 0.005060 M, 0.0255000 M, and 0.500830 M which implies that percentage increases in the iodate concentrations of 1.2, 2, and 0.2 were determined with an accuracy as great as that contained in the concentrations stated above. This investigator considered that silver was present in the equilibrium solution phases only in the form of the  $\text{Ag}^+$  and  $\text{Ag}(\text{IO}_3)_2^-$  ions. From the data, a calculated instability constant ( $K_1$ ) for the latter species was reported as  $2.22 \times 10^{-6}$ . In the calculations, a value of the thermodynamic solubility product for silver iodate at 20-22°C. of  $3.5 \times 10^{-8}$  was used without reference to its origin. This value was not in agreement with the value of  $2.078 \times 10^{-8}$  obtained in the careful work of Li and Lo (36) at 20°C. It was also apparent that the values 0.960, 0.920 and 0.900, which were used as mean ionic activity coefficients in the calculations of the iodate ion activities at the ionic strengths of 0.00506, 0.02550, and 0.50083 were not in accord with the experimentally determined values for silver

iodate in solutions of potassium nitrate (36). Accordingly, the information on equilibria in the silver iodate-iodate ion-water systems is limited by the inherent uncertainties caused by determining differences between nearly like quantities, the few iodate concentrations studied, the neglect of the  $\text{AgIO}_3$  (aq.) species, and the questionable parameters used in the calculations.

It is hoped that the present work will assist in the evaluation of the radiotracer method and give impetus to the elucidation of the various phenomena which underly complex ion formation.

## II. EXPERIMENTAL

## A. Material

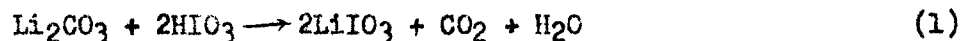
1. Reagents

All water that was used in this work was prepared by redistilling distilled water from alkali permanganate solutions. Its specific conductance was found to be  $2.5 \times 10^{-6}$  mho. cm.<sup>-1</sup>.

The lithium hydroxide, iron (III) nitrate, perchloric acid, borax, sodium thiosulfate, acetone, potassium nitrate, potassium hydroxide, carbon tetrachloride, sodium hydroxide, potassium iodide, hydrochloric acid, 37 percent formaldehyde solution, ammonium hydroxide, nitric acid, and iodic acid that were used were reagent grade chemicals. Potassium cyanide was C. P. grade. These reagents were obtained from the J. T. Baker Chemical Company, and were used without further purification. Lithium carbonate and lithium perchlorate were also reagent grade; the former being supplied by the Mallinckrodt Chemical Works, and the latter by the G. Frederick Smith Chemical Company. Solutions of lithium perchlorate were filtered before being used in order to remove any insoluble matter which was present.

The platinum used in the plating procedure was 1 mil sheet stock supplied by the American Platinum Works.

Lithium iodate was prepared by means of the following reaction:



A stoichiometric amount of iodic acid was added to an aqueous solution of lithium carbonate. The salt was allowed to crystallize after the carbon

dioxide formed in the reaction had been driven off by heating. The product was filtered, recrystallized twice from water, refiltered, washed, dried at 120°C. for twenty-four hours, and stored in a desiccator over anhydrous magnesium perchlorate. Analyses of the salt for total iodate content were consistent with the theoretical composition.

## 2. Analytical standards

The primary standards used were silver nitrate, potassium acid phthalate, and doubly recrystallized potassium iodate. These were reagent grade chemicals, purchased from the J. T. Baker Chemical Company. All standardized solutions of sodium thiosulfate contained a borax preservative.

## 3. Radioactive silver

Silver  $^{110m}$ , which decays with a half-life of 270 days (42, 43), was used throughout the experiments. It was obtained from the Oak Ridge National Laboratory in a ten millicurie shipment. The irradiated silver had been dissolved in 1.4 ml. of 2 N nitric acid, and was reported to have a radiochemical purity in excess of 98 percent.

Stock solutions containing silver of a definite specific activity were prepared in the following manner. An aliquot of the ten millicurie source was added to a dilute nitric acid solution containing an amount of inactive silver nitrate. A sample of 50 mg. of iron (III) carrier was added, and the solution was scavenged by precipitation of the iron with an excess of aqueous ammonia. The iron hydroxide was filtered from the solution with S&S black ribbon filter paper and pulp leaving a clear filtrate which was taken to dryness with an excess of nitric acid.

The residue was dissolved in dilute nitric acid, and the silver was quantitatively precipitated as the chloride. This precipitate was digested, and filtered through S&S blue ribbon filter paper; subsequently, it was dissolved from the filter with concentrated ammonia. Potassium cyanide was added, and the silver was electroplated on a platinum gauze cathode according to a method proposed by Slomin (44). Following this operation, the silver was dissolved from the electrode with 10 N nitric acid, and the entire purification cycle was repeated. The final electroplating was performed using a carefully weighed electrode, and the amount of pure silver was determined gravimetrically. The remainder of the procedure merely involved dissolution of the weighed silver in nitric acid, fuming with perchloric acid, and dilution in a volumetric flask. Two stock solutions containing silver of different specific activities were prepared.

#### 4. Tagged silver iodate

An aliquot of the stock solution prepared by the method of Part 3 above, and containing approximately 10 mg. of radioactive silver, was added to a heavy glass centrifuge tube. Lithium hydroxide was added in sufficient quantity to neutralize excess acid; however, the final pH was kept below the value at which hydrous silver oxide appears. A solution of lithium iodate was now added slowly, with constant stirring, and a copious precipitate of silver iodate was formed which was centrifuged and washed repeatedly with 10 ml. portions of warm water. The wet mass of crystals was finally washed, slurried, and transferred to the equilibrium flask using many small portions of the solution

phase with which they were to be equilibrated. Two groups of silver iodate precipitates containing silver of different specific activities were prepared from the two stock solutions described in the previous section.

#### B. Analyses

The equilibrated mixtures contained tagged silver iodate in contact with an aqueous solution of lithium iodate. In cases where measurements were performed at constant total ionic strength, lithium perchlorate was also present. Therefore, a previous knowledge of the concentration of lithium perchlorate in a given solution would allow for a complete description of all solutions with but two analyses, total iodate, and total silver.

The main stock solution of lithium perchlorate was analyzed by passing aliquots of it through a column of Dowex-50 cation exchange resin in the acid form. The equivalent acid liberated by the lithium ion was titrated with an aqueous solution of sodium hydroxide which had been standardized against pure potassium acid phthalate. The sodium hydroxide solution was prepared by filtering a saturated aqueous solution of sodium hydroxide into hot, boiled, doubly distilled water, and stored in a bottle equipped with an ascarite-magnesium perchlorate trap to exclude carbon dioxide from the air entering the bottle.

Analyses for iodate ion were performed volumetrically. An iodometric procedure was employed in which iodate ion was reduced to iodine in dilute hydrochloric acid solution by an excess of iodide ion. The liberated iodine was titrated with sodium thiosulfate which had been



standardized against doubly recrystallized potassium iodate. The normalities of the sodium thiosulfate solutions were periodically checked.

A radioassay technique was employed to determine the concentration of silver in a given equilibrium sample. In principle the analysis was simple. Once the specific activity of the radioactive silver in the solid phase was known, a determination of the activity contained in a definite volume of the solution phase gave the concentration of silver contained therein. However, due to the problems encountered in obtaining a reproducible set of counting conditions from one sample to the next, the procedure was made rather difficult.

Previous experiments on sparingly soluble silver salts have been enumerated. In the work of Jonte and Martin (20), the concentration of silver was determined by counting the silver contained in an aliquot of the equilibrium solution after evaporation on a copper disc. By employing uniform copper discs, and a careful evaporation technique, geometry and backscattering factors were held quite constant. As the ionic strength of an aliquot increased, the bulk of the sample also increased, consequently, self absorption factors were not held constant from one sample to the next. Because of this feature, a series of solutions having identical concentrations of radioactive silver, but containing different quantities of dissolved solid were used to prepare standards for comparison. The method is adequate for systems in which the ionic strength of the equilibrium solution phase is low; however, if samples of considerable thickness are obtained, an accurate comparison is very difficult to obtain. This factor alone was sufficient to exclude the possibility of using such a procedure in the present work since many

measurements were made at ionic strengths as high as 1 M. Leden et al. (21, 22, 23) employed a dipping counter for counting radiosilver present in aliquots of the equilibrium solution phases. The counting rates obtained were directly proportional to the concentrations of the silver in the aliquots. This technique allows for a greater reproducibility of geometry and self-absorption effects than do most procedures in which solid materials are counted, however, it possesses two distinct disadvantages. The counting geometry, thickness of the counter window, and the necessity for isotopic dilution to insure negligible adsorption of activity on the apparatus require that tracers of very high specific activities be used. If cumbersome shielding is to be avoided, this factor also imposes definite limits on the amount of active material that may be used to prepare samples of the solid phase. The other factor, which plays an important role in the accuracy of the determinations, is the density of the equilibrium solutions. To apply the method with rigor, especially at high ionic strengths, only solutions of approximately the same density may be compared. In research of the type described in this thesis, the densities of the equilibrium solution phases were not uniform. Therefore it would have been necessary to investigate the variation of counting rate with density for the ranges over which the concentrations of common and diverse ions were varied. A procedure in which liquid samples are directly counted is obviously capable of giving accurate results only at a great expense of convenience. This highly undesirable feature mitigated against the use of this procedure in this present work and initiated a search for a technique which embodied both ease of operation and accuracy for all equilibrium solution

concentrations and densities.

A radioassay method which possessed the desired attributes was based upon an electrodeposition procedure for mounting samples for counting. Samples of 2.00 ml. of the equilibrium solution phases were carefully added to 5 ml. portions of strong nitric acid solutions which contained a predetermined amount of silver carrier (usually 10 mg.). To insure complete exchange between the tracers and the carriers, the solutions were evaporated to dryness. The residues were subsequently dissolved in 25 ml. portions of concentrated ammonium hydroxide, and the following ingredients were added in the amount and order stated below to convert the solutions into suitable silver plating baths.

0.3 g. KCN

9 g.  $\text{KNO}_3$

1 g. KOH

3/4 ml. 37% formaldehyde solution

5 ml.  $\text{H}_2\text{O}$

For solutions in which iodate ion concentrations were high and perchlorate ions were present, approximately one-half of the potassium nitrate was replaced with ammonium nitrate. In every case in which perchlorate ion was present the quantity of potassium nitrate added was sufficient to precipitate most of it since high concentrations of perchlorate ions interfered with the electrolysis. The plating baths were heated and separated from the undissolved solids by decantation.

They were subsequently transferred into electrolysis cells, heated nearly to their boiling temperatures, and a current of 0.2 amp. was passed through them for a period of thirty-five minutes. In all the

electrolyses, the baths were stirred constantly. The plates obtained were thoroughly washed with many small portions of water and acetone and dried in an oven for ten minutes at 120°C. The silver that was uniformly deposited was determined gravimetrically and was counted to determine its activity. From these data the activities corresponding to 100 percent recovery of the carriers were computed. The application of corrections for self-absorption and radioactive decay converted the observed activities to ones which were proportional to the tracer concentrations in the various aliquots of the equilibrium solution phases. A knowledge of the specific activity of the silver used in the experiments made the radioassay complete.

The specific activities of the silver contained in the two stock solutions mentioned in Part 3 of A above, were determined in the course of experiments on the effect of self-absorption in the analysis. This effect was studied by counting a series of samples of different thicknesses that had been prepared from 2.00 ml. aliquots of the stock solutions in the manner prescribed for treating samples of the equilibrium solution phases. The variation of the measured activity, corrected for the fraction of recovery of the silver carrier, with plate thickness has been plotted in Figure 1. The reproducibility of the plating method is amply demonstrated by the good fit of the experimental points to smooth curves, and by the fact that the two curves corresponding to two different specific activities are strictly parallel. Curve I was used to obtain correction factors which were used to normalize all counting data to a thickness of 1.4 mg./cm.<sup>2</sup>. These factors have been plotted as a function of the plate thickness in Figure 2. The

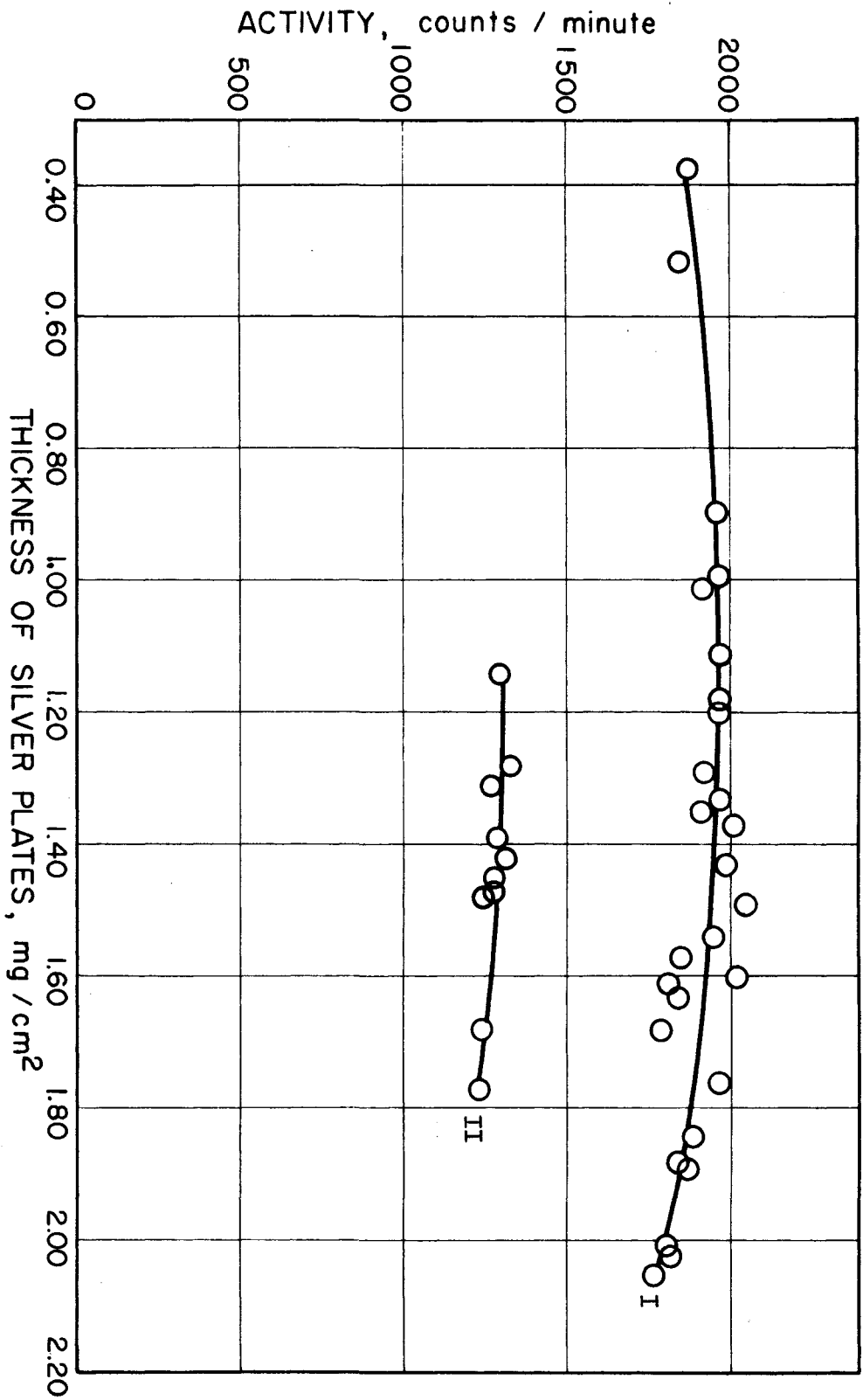
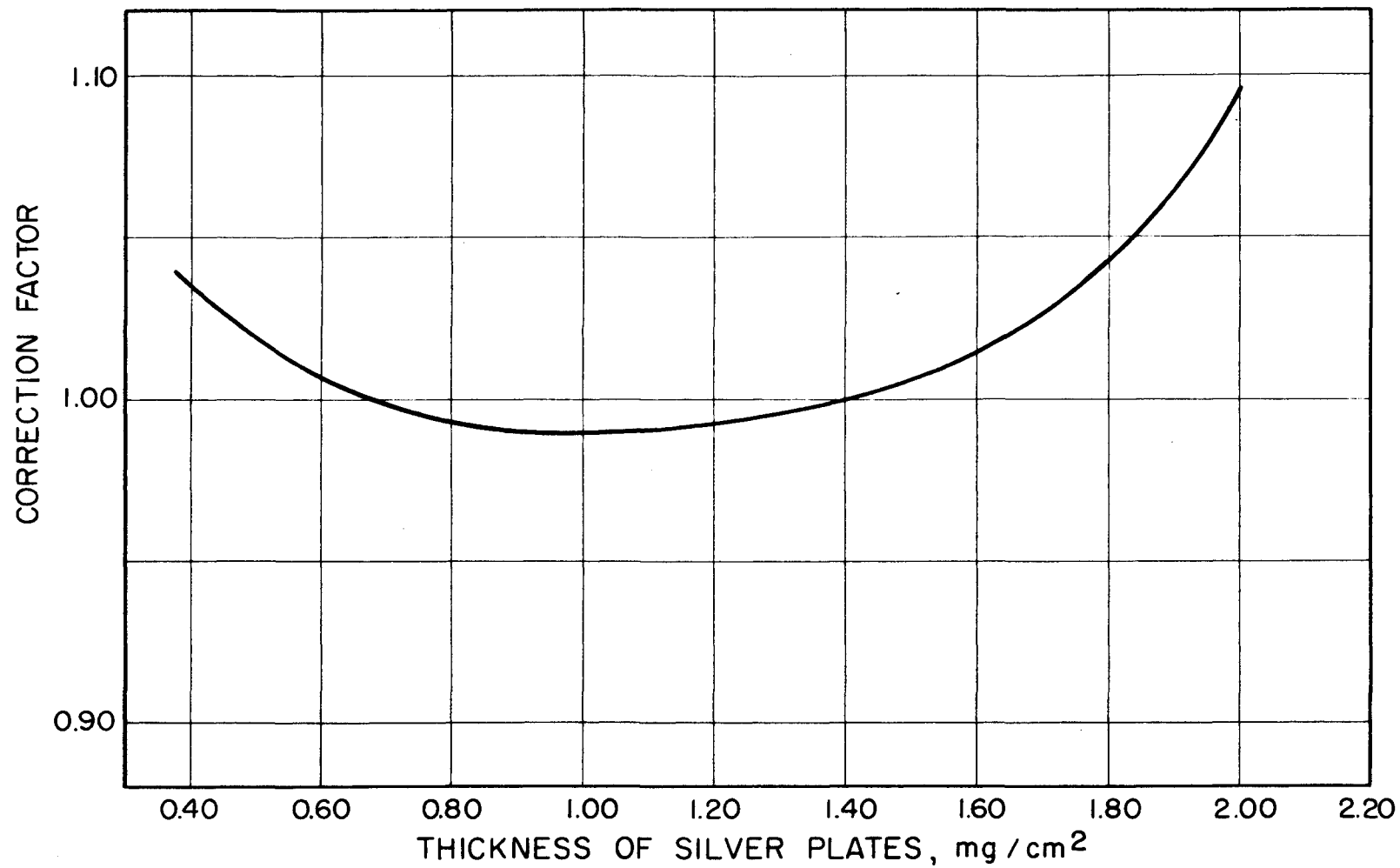


Figure 1. Experimentally determined self-absorption curves for  $Ag^{110m}$  of different specific activities.



**Figure 2.** Calculated correction factor curve for normalizing all counting data to a sample thickness of  $1.40 \text{ mg}/\text{cm}^2$ .

thicknesses of all the samples that were assayed is covered by the range of thickness reported. Specific activities calculated from the counting rates at a thickness of  $1.4 \text{ mg./cm.}^2$  were consequently employed as standards throughout this work. These quantities for the silver contained in the two stock solutions that were prepared are listed below in Table 2.

Table 2. Specific Activities of Silver in Stock Solutions

Solution No.	Concentration of Silver mg./ml. $\times 10^3$	Specific Activity ( $1.4 \text{ mg./cm.}^2$ thickness) cts./min. mg. $\times 10^{-5}$
I	4.92	1.98
II	2.25	2.89

Backscattering of radiation from the samples was held constant by mounting all the plates on a sufficient thickness of tantalum to insure infinite backscattering characteristics.

The accuracy with which samples were analyzed was achieved with little expense in convenience and was uniformly obtained for all samples regardless of the composition, or density of the equilibrium solutions.

### C. Apparatus

All mixtures were allowed to equilibrate in Precision Scientific Company water baths in which the temperatures were held constant to  $\pm 0.1^\circ\text{C}$ .

Erlenmeyer flasks having ground glass stoppers were used exclusively to contain the equilibrium mixtures. Some were Corning Glass Works pyrex Low Actinic, red variety glass, while others were standard pyrex flasks which had been wrapped with a black plastic adhesive tape to exclude light. The flasks were sealed with paraffin wax before being placed in the constant temperature baths, and were agitated with the aid of two Burrell Model CC shakers. Caps for the flasks were made from pyrex male 24/40 standard tapers.

Separations of representative samples of the equilibrium solution phases from the various mixtures were accomplished by filtration through "fine" fritted glass discs having nominal maximum pore sizes of five microns. A simple apparatus was designed which permitted the filtrations to be performed under pressure in the thermostatted baths. It was found that suction applied to a filter of this pore size caused considerable cooling of the equilibrium solution samples.

The fritted filters were 10 mm. in diameter and were mounted in the end of 13 mm. pyrex glass tubes. The filter tubes were sealed through standard taper caps for the equilibrium flasks and were sufficiently long to allow for insertion of the fritted discs to a distance of 3 mm. above the bottom of the flasks. A 5 mm. glass tube was also sealed to the caps to provide the connection through which pressure could be applied with a 30 cc. glass tip hypodermic syringe. During the sampling operation all caps were held in place by rubber bands which extended from glass hooks on the caps to the clamps on the shaker. When pressure was applied with the syringe, the equilibrium solution was forced through the filter into the filter tube from which samples were withdrawn with the aid of



pipettes.

The necessity for obtaining true samples of the equilibrium solutions has been stressed. Before the filtering medium mentioned was adopted for use in this work, a study was carried out to determine its effectiveness. Four different fritted glass filters having the nominal maximum pore sizes of 30, 14, 5 and 1.2 microns were examined. It was thought that if samples of an equilibrium solution were passed through these filters, and radioassays of definite volumes of the filtrates were identical, all filters would be suitable for obtaining representative equilibrium solution samples. The results of the first experiment are given in Table 3. The amount of the filtrate that was assayed in each case was exactly 2.00 ml. The solution sampled was 0.005 M with respect to lithium iodate. Each assay value is an average of two determinations.

Table 3. Assays of Filtrates from Equilibrium Solution of pH 5-6 and 0.005 M with Respect to  $\text{LiIO}_3$ , for Various Filters

Filter name	Nominal Maximum Pore Size microns	Counting Rate of 2 ml. Portion counts/minute	Time Needed to Obtain Sample minutes
Coarse <sup>a</sup>	40	1458	2
Medium	14	522	10
Fine	5	463	30
Ultra fine	1.2	372	250

<sup>a</sup>This filtration was performed with suction.

The results listed in Table 3 certainly indicated that all of the filters were not usable. The high assay value obtained in the case of the coarse filter was caused by a small portion of the solid phase passing through the filter into the filtrate. The reason for the differences obtained with the other filters were not immediately clear. It was considered possible that particles approaching colloidal dimensions were not being filtered effectively, or that silver was being adsorbed on the fritted glass. The latter notion seemed to be more compatible with the trend of the assay values given in Table 1. In either case, a decrease in the pH of the equilibrium solution should have produced a marked effect on the discrepancies since radiocolloid formation is reduced in acid solutions, and adsorption sites would be occupied by excess hydrogen-ion present. The results of an experiment in which the pH of the same equilibrium solution was adjusted to a value of 2 are given in Table 4. In this and all subsequent experiments the coarse filter was not used.

Table 4. Assays of Filtrates from Equilibrium Solution of pH 2 and 0.005 M with Respect to  $\text{LiIO}_3$ , for Various Filters

Filter name	Normal Maximum Pore Size microns	Counting Rate of 2 ml. Portion counts/minute
Medium	14	559
Fine	5	523
Ultra fine	1.2	472

An increase in the hydrogen ion concentration caused the difference between the assay values to narrow. This fact was taken as evidence that adsorption rather than radiocolloid formation was the cause of the disagreement. A trend was also present in the assay values obtained in this experiment. It was calculated that an increase of approximately 4% in the counting rates over those obtained in the first experiment was due to the increase in ionic strength caused by the addition of the perchloric acid. However, in each case there was at least an equal, or substantially greater increase in the assay values due to the suspected decrease in the number of available adsorption sites. To further eliminate the possibility of the existence of a radiocolloid of silver, a third experiment was performed using an equilibrium solution which was nearly neutral and was 0.10 M with respect to lithium iodate. The increase in the lithium ion concentration by a factor of twenty was expected to decrease adsorption of silver if it were taking place, but to have little effect if a radiocolloid was present. The results again suggested that the observed effect was the consequence of adsorption.

Table 5. Assays of Filtrates from Equilibrium Solution of pH 5-6, and 0.1 M with Respect to  $\text{LiIO}_3$ , for Various Filters

Filter name	Normal Maximum Pore Size microns	Counting Rate of 2 ml. Portions counts/minute
Medium	14	186
Fine	5	174
Ultra fine	1.2	150

To prove in a more convincing manner that adsorption of silver in the fritted discs was taking place, the following experiment was conducted. A clear solution of radioactive silver was prepared which was 1 M with respect to perchloric acid and contained approximately the same concentration of silver as the one employed in the first two experiments. Portions were subjected to the same procedure as that previously employed with one exception; 2.00 ml. samples of the solution were assayed before the filtration as well as after the filtration. The results are given in Table 6.

Table 6. Assays of a  $\text{AgClO}_4$  Solution 1 M with Respect to  $\text{HClO}_4$ , and Filtrates for Various Filters

Filter name	Normal Maximum Pore Size microns	Counting Rate of 2 ml. Portions of Filtrate counts/minute	Counting Rate of 2 ml. Portions of Solution counts/minute
Medium	14	646	659
Fine	5	616	648
Ultra fine	1.2	596	652

The possibility of a radiocolloid of silver existing in 1 M perchloric acid solution of silver perchlorate is remote, however, the results of Table 6 indicated that the differences, although smaller than in previous experiments, still existed and the trend of assay values originally found had not disappeared. On the basis of the above results the colloid hypothesis was abandoned, and the adsorption hypothesis was

considered to be well substantiated. Another experiment was performed to see if the "medium" and "fine" filters could be saturated with silver. Two 3 ml. portions of the perchlorate solution were drawn through each of the filters and discarded before a sample was taken for assay purposes. Indeed, Table 7 indicates that they were saturated.

Table 7. Saturation of Medium and Fine Filters

Filter name	Normal Maximum Pore Size microns	Counting Rate of 2 ml. Portions of Filtrate After Saturation counts/minute	Counting Rate of 2 ml. Portions of Solutions <sup>a</sup> counts/minute
Medium	14	645	659
Fine	5	641	648

<sup>a</sup>These values were obtained from Table 6.

The preceding series of investigations indicated that "fine" filters could be employed if precautions were taken to saturate the filters before drawing samples for radioassay.

In the course of the study mentioned above, the effectiveness of centrifugation as a means of separating equilibrium solutions from the equilibrated mixtures was also investigated. It was found that occasionally this method was not completely effective in separating the solid from the solution phases, however, contaminated samples were easily discovered since inclusion of small particles of the solid caused great increases in the counting rates of the samples. The method also

possessed the disadvantage of having to remove mixtures from the constant temperature baths for separation of the equilibrium solution phases.

The electrolysis cells which were used to contain the silver plating baths were similar to Tracerlab E-16 Electroplating Cells in all respects except one. Non-magnetic stainless steel was used in their construction rather than chrome-plated brass because of the highly corrosive nature of the ammoniacal cyanide bath. Electrodes were made from 1 mil platinum stock. Cathodes were cut in the form of discs having a diameter of 1 inch. Anodes were 0.5 x 0.7 cm. rectangles, and were spot welded to platinum wires which were sealed into glass tubes 4 inches in length. Electrical contacts to the cathodes were made directly with the frame of the apparatus; whereas the anode contacts were made through the anode tubes filled with mercury. The necessary plating voltage was supplied by a Sargent-Slomin Electroanalyzer. Rubber gaskets used to prevent leaking around the cathodes had outside diameters of 1 inch and inside diameters of 7/8 inch. A platinum surface of 3.47 cm.<sup>2</sup> was exposed for silver plating after the apparatus was assembled and the gaskets were secured against the cathodes. Anodes were stationary during the electrolyses, and stirring was accomplished with motor driven glass stirrers having two small blades at right angles. A rheostat was provided to control the speed of the stirring motor.

For the purpose of avoiding needless repetition, the procedure for plating silver samples was merely stated in Part B above. The actual precautions taken to insure smooth, bright, and reproducible plates were not discussed at any length. Plating without stirring was tedious, and bulky, non-reproducible plates were obtained from which particles of

silver were disengaged by the slightest provocation. Because of the health hazard involved in such a technique, and the difficulty with which plates were reproduced, stirring had to be used. For the best results, the anode was mounted at the side of the cell and 1 inch above the cathode at the bottom of the cell. The glass stirrer was inserted to a position immediately above the anode flag. Strong vortex motion induced by the stirrer on the solution near the cathode was easily controlled by using the anode as a baffle. Various degrees of baffling were obtained by merely rotating the anode flag. This control was necessary to prevent the appearance of a bald spot at the center of the plate. Convection was found to be helpful in increasing the rate of deposition and consequently the fineness of the plate. For this reason the baths were maintained near to their boiling temperatures during the electrolyses. To provide uniform convection over the whole of the cathode surface, a stainless steel plug had to be inserted at the bottom of the commercial cell where thermal contact was made with the hot plate.

To prevent the ammoniacal cyanide baths from attacking the silver plates at the terminations of the plating periods, carbon tetrachloride was added to the electrolysis cells in sufficient quantities to lift the plating baths from the plates. The current immediately fell to an insignificant value but the plates were protected from the corrosive action of the bath. The bath was subsequently removed from above the carbon tetrachloride by means of a pipette equipped with a syringe.

Potassium nitrate that was added to the plating baths served two purposes, elimination of the major portion of the perchlorate ion present and reduction of the internal resistance of the bath. At high

voltages the cathodes were etched, and at high current densities the silver plates were burned. Inclusion of this salt with a little 37% formaldehyde solution enabled bright and clean plates to be obtained at current densities in the range 0.05 - 0.10 amp./cm.<sup>2</sup> under an applied voltage in the range 2.5 - 5 volts. Experiments with blanks demonstrated that there was no dissolution of the anode at these operating values of current and voltage.

The mass of most of the silver plates was in the range 3 to 5 mg. To keep the errors in weighings below a nominal value of 1%, samples were weighed with an Ainsworth analytical balance capable of determining masses with an accuracy of  $\pm 0.03$  mg.

A Tracerlab Geiger-Mueller counter with an end mica window of thickness 1.8 mg./cm.<sup>2</sup> was used in conjunction with a Nuclear Instrument and Chemical Corporation Model 165 scaling unit for the counting of radioactive samples. Counting data were taken using the same aluminum sample holder, tantalum backing, lead housing, and commercial plastic counter mount for all samples.

#### D. Procedure

To prepare a mixture for equilibration, tagged silver iodate was slurried with a portion of a 50 ml. solution that contained the concentration of lithium iodate for which the solubility was to be measured. The slurry was transferred to an equilibrium flask and the remainder of the 50 ml. was used to completely transfer the residues. The flask was subsequently sealed with paraffin wax, inserted into a constant temperature bath, and clamped to the shaking mechanism. Mixtures which



contained silver of the lower specific activity were prepared with 25 mg. of solid phase, whereas those which had the higher specific activity silver contained 12.5 mg. For measurements at constant ionic strength, the mixtures were made from solutions containing both lithium iodate and lithium perchlorate in the proper proportions. These solutions had been prepared by adding an accurately weighed quantity of pure lithium iodate to an appropriate amount of 1.000 M lithium perchlorate solution in a volumetric flask. The desired ionic strength of 1.00 M was obtained by dilution to the mark.

Mixtures were allowed to equilibrate for a period of at least one week. Samples of the solution phase obtained after two weeks of equilibration gave the same results as those which had been taken after an interval of one week. In some cases saturation equilibrium was approached from both below and above the bath temperatures. Differences in the observed solubilities for seven experiments at different temperatures, and concentrations of salts, were not obtained by either of the procedures, and data obtained by approaching saturation only from supersaturation were on a smooth curve with those obtained by approaching from unsaturation.

To sample an equilibrium solution phase, the filtering apparatus was brought to the equilibrium temperatures, inserted into the mixture, and pressure was applied until a suitable amount of clear filtrate resided in the filter tube. The level of the solution in the tube was never allowed to reach the neck of the flask. Pipettes were rinsed with small portions of the filtered solution and in most cases two 5 ml. samples were taken for iodate analysis. For solution phases in which

the concentration of iodate ion was very high 2 ml. samples were taken for analysis. Pressure was applied again and two 2 ml. samples were taken for radioassay of the silver present. To insure that all filters were completely saturated with silver ion before samples were taken for radioassay, the first portions of the equilibrium solution phase were always taken for the iodate analysis.

## III. RESULTS

## A. Results from the Solubility Determinations

Results of the analysis of the equilibrium solutions containing only lithium iodate have been listed in Table 8 for 25.0°C., 35.0°C. and 50.0°C. Instances in which solubility data were obtained with silver of different specific activities have been indicated. Assays of the equilibrium solutions in which ionic strengths were fixed at 1.00 M have been presented in Table 9. The range of iodate concentrations studied was greater in these solutions.

Plots of the logarithms of the total silver concentrations have been presented in Figures 3 and 4. An examination of these plots indicated an important feature of the equilibrium systems. In every case it appeared that the slopes of the curves in the region of high iodate ion activities or concentrations were not greater than 1.0, consequently there was no evidence for significant formation of complex species containing more than two iodate ligands per central silver atom in the range of concentrations studied.

For Figure 3, iodate activities were computed from the concentrations by employing activity coefficients,  $\gamma_{\pm}$ , for a singly charged ion. These were interpolated from the tabulation of  $\gamma_{\pm}$ , presented by Crouthamel and Martin (17). The same activity coefficients were used for all equilibrium temperatures since  $\gamma_{\pm}$  is virtually independent of temperature in a small range of temperature. Activity coefficients applied to iodate concentrations in the range  $0.1 \leq [\text{IO}_3^-]_{\text{tot}} \leq 0.27$  moles/liter were used with the reservation that they represented only

Table 8. Results from Solubility Experiments of  $\text{AgIO}_3$  in Aqueous Solutions of  $\text{LiIO}_3$

Temperature °C.	$[\text{Ag}]_{\text{tot}}$ <sup>a</sup> Observed moles/liter x 10 <sup>6</sup>	$[\text{IO}_3^-]_{\text{tot}}$ <sup>b</sup> Observed moles/liter	$\gamma_{\pm}$ <sup>c</sup>	$-\log_{10}([\text{Ag}]_{\text{tot}} [\text{IO}_3^-]_{\text{tot}})^{1/2}$ <sup>d</sup>	$[\text{Ag}]_{\text{tot}}$ Calculated moles/liter x 10 <sup>6</sup>
25.0	37.0 <sup>d</sup>	0.000722	0.968	3.80	45.2
	18.1 <sup>d</sup>	.00187	.951	3.76	18.2
	7.03 <sup>d</sup>	.00421	.933	3.79	8.46
	6.85 <sup>d</sup>	.00493	.928	3.77	7.34
	4.29 <sup>d</sup>	.0101	.903	3.72	3.86
	3.30	0.0110	0.899	3.77	3.59
	3.05	.0151	.887	3.72	2.73
	2.12	.0249	.863	3.70	1.84
	1.13	.0353	.845	3.77	1.43
	1.11	.0848	.795	3.61	1.00
	0.978	0.1023	0.782	3.61	0.865
	.993	.1180	.776	3.58	.845
	.835	.1540	.761	3.57	.849
	.915	.2042	.747	3.49	.892
	1.04	.2580	.733	3.43	.975

<sup>a</sup> $[\text{Ag}]_{\text{tot}}$  is the total concentration of silver obtained by radioassay.

<sup>b</sup> $[\text{IO}_3^-]_{\text{tot}}$  is the total concentration of iodate obtained by iodometric analysis.

<sup>c</sup> These values are mean ionic activity coefficients for singly charged ions obtained by interpolation from the table of  $\gamma_{\pm}$  values presented by Crouthamel and Martin (17).

<sup>d</sup> These values were obtained with silver of specific activity  $1.98 \times 10^5$  counts/minute mg. All other values were obtained with silver of specific activity  $2.89 \times 10^5$  counts/minute mg.

Table 8. Continued

Temperature °C.	$[\text{Ag}]_{\text{tot}}$ <sup>a</sup> Observed moles/liter x 10 <sup>6</sup>	$[\text{IO}_3^-]_{\text{tot}}$ <sup>b</sup> Observed moles/liter	$\gamma_{\pm}$ <sup>c</sup>	$-\log_{10}([\text{Ag}]_{\text{tot}} [\text{IO}_3^-]_{\text{tot}})^{1/2} \gamma_{\pm}$	$[\text{Ag}]_{\text{tot}}$ Calculated moles/liter x 10 <sup>6</sup>
35.0	87.5	0.000693	0.970	3.62	99.7
	23.0	.00272	.943	3.59	27.2
	15.1	.00435	.932	3.62	17.5
	8.66 <sup>d</sup>	.00780	.914	3.63	10.4
	7.68	.0114	.900	3.58	7.58
	4.09	0.0266	0.860	3.55	3.80
	2.71	.0398	.837	3.56	2.90
	2.46	.0520	.821	3.54	2.48
	1.99	.0836	.795	3.49	1.99
	1.73	.1023	.782	3.49	1.88
	1.89	0.1068	0.781	3.46	1.86
	1.69	.1279	.771	3.44	1.81
	1.80	.1682	.757	3.38	1.80
	1.74	.2292	.740	3.33	1.91
	1.66	.2523	.737	3.32	1.96
	1.97	.2700	.732	3.28	2.01

<sup>a</sup> $[\text{Ag}]_{\text{tot}}$  is the total concentration of silver obtained by radioassay.

<sup>b</sup> $[\text{IO}_3^-]_{\text{tot}}$  is the total concentration of iodate obtained by iodometric analysis.

<sup>c</sup> These values are mean ionic activity coefficients for singly charged ions obtained by interpolation from the table of  $\gamma_{\pm}$  values presented by Crouthamel and Martin (17).

<sup>d</sup> These values were obtained with silver of specific activity  $1.98 \times 10^5$  counts/minute mg. All other values were obtained with silver of specific activity  $2.89 \times 10^5$  counts/minute mg.

Table 8. Continued

Temperature °C.	[Ag] <sub>tot</sub> <sup>a</sup> Observed moles/liter x 10 <sup>6</sup>	[IO <sub>3</sub> <sup>-</sup> ] <sub>tot</sub> <sup>b</sup> Observed moles/liter	$\gamma_{\pm}$ <sup>c</sup>	$-\log_{10}([Ag]_{tot}[IO_3^-]_{tot})^{\frac{1}{2}}$	[Ag] <sub>tot</sub> Calculated moles/liter x 10 <sup>6</sup>
50.0	217	0.00914	0.966	3.37	206
	65.6	.00283	.942	3.40	70.9
	23.0 <sup>d</sup>	.00800	.911	3.40	27.8
	19.9 <sup>d</sup>	.0109	.899	3.38	21.5
	13.7	.0177	.880	3.37	14.4
	7.26	0.0395	0.837	3.35	8.15
	3.64	.1008	.783	3.33	5.12
	4.05	.1317	.770	3.25	4.75
	4.24	.1580	.760	3.21	4.62
	4.34	.2660	.732	3.11	4.70

<sup>a</sup>[Ag]<sub>tot</sub> is the total concentration of silver obtained by radioassay.

<sup>b</sup>[IO<sub>3</sub><sup>-</sup>]<sub>tot</sub> is the total concentration of iodate obtained by iodometric analysis.

<sup>c</sup> These values are mean ionic activity coefficients for singly charged ions obtained by interpolation from the table of  $\gamma_{\pm}$  values presented by Crouthamel and Martin (17).

<sup>d</sup> These values were obtained with silver of specific activity  $1.98 \times 10^5$  counts/minute mg. All other values were obtained with silver of specific activity  $2.89 \times 10^5$  counts/minute mg.

Table 9. Results from Solubility Experiments of  
 $\text{AgIO}_3$  in Aqueous Iodate Solutions of  
 Constant Ionic Strength 1.00 M

Temperature °C.	$[\text{Ag}]_{\text{tot}}^{\text{a}}$ Observed moles/liter x $10^6$	$[\text{IO}_3^-]_{\text{tot}}^{\text{b}}$ Observed moles/liter	$[\text{Ag}]_{\text{tot}}$ Calculated moles/liter x $10^6$	
25.0	90.2	0.000940	89.5	
	35.4	.00248	34.0	
	14.5	.00540	15.6	
	9.05	.0103	8.30	
	1.96	.0501	1.93	
	1.68	0.0634	1.60	
	1.38	.1001	1.21	
	0.885	.2000	1.04	
	1.04	.298	1.13	
	1.14	.400	1.31	
	1.33	0.492	1.49	
	1.44	.596	1.71	
	2.27	.699	1.94	
	2.48	.754	2.06	
	2.30	.998	2.63	
	35.0	198	0.000900	193
		64.3	.00265	66.1
		34.4	.00544	32.4
15.9		.0110	16.3	
6.52		.0263	7.13	
4.65		0.0400	4.93	
4.15		.0505	4.06	
3.30		.0659	3.33	
2.58		.101	2.56	
2.52		.200	2.14	
2.43		0.305	2.28	
2.21		.404	2.57	
2.50		.501	2.81	
3.67		.605	3.29	
4.19		.707	3.78	
3.48		.772	3.95	

<sup>a</sup> $[\text{Ag}]_{\text{tot}}$  is the total concentration of silver obtained by radioassay.

<sup>b</sup> $[\text{IO}_3^-]_{\text{tot}}$  is the total concentration of iodate obtained by iodometric analysis.

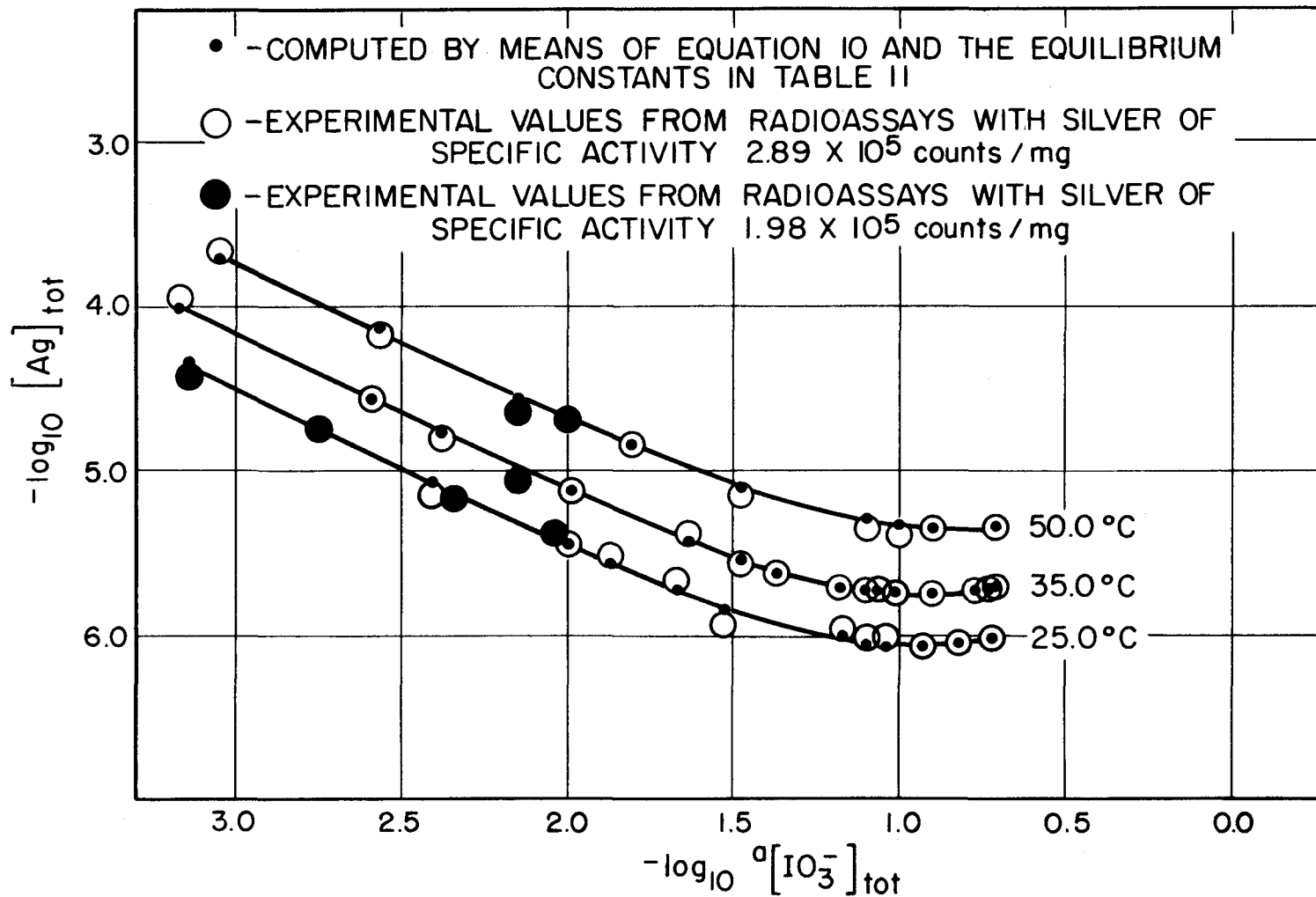
Table 9. Continued

Temperature °C.	[Ag] <sub>tot</sub> <sup>a</sup> Observed moles/liter x 10 <sup>6</sup>	[IO <sub>3</sub> <sup>-</sup> ] <sub>tot</sub> <sup>b</sup> Observed moles/liter	[Ag] <sub>tot</sub> Calculated moles/liter x 10 <sup>6</sup>
50.0	4.09	0.00107	4.00
	14.6	.00285	15.1
	71.5	.00583	74.7
	40.1	.0110	40.4
	18.3	.0253	18.6
	11.3	0.0414	12.1
	9.72	.0515	10.2
	7.95	.0694	8.22
	6.21	.1030	6.22
	5.31	.207	5.12
	6.35	0.322	5.21
	5.73	.412	5.56
	5.96	.507	6.05
	7.30	.745	7.49
	8.35	.800	7.84
	7.34	0.810	7.91
	8.96	.998	9.16

<sup>a</sup>[Ag]<sub>tot</sub> is the total concentration of silver obtained by radioassay.

<sup>b</sup>[IO<sub>3</sub><sup>-</sup>]<sub>tot</sub> is the total concentration of iodate obtained by iodometric analysis.





**Figure 3. Graphs of solubilities of AgIO<sub>3</sub> for equilibrium solutions of low, variable ionic strengths.**

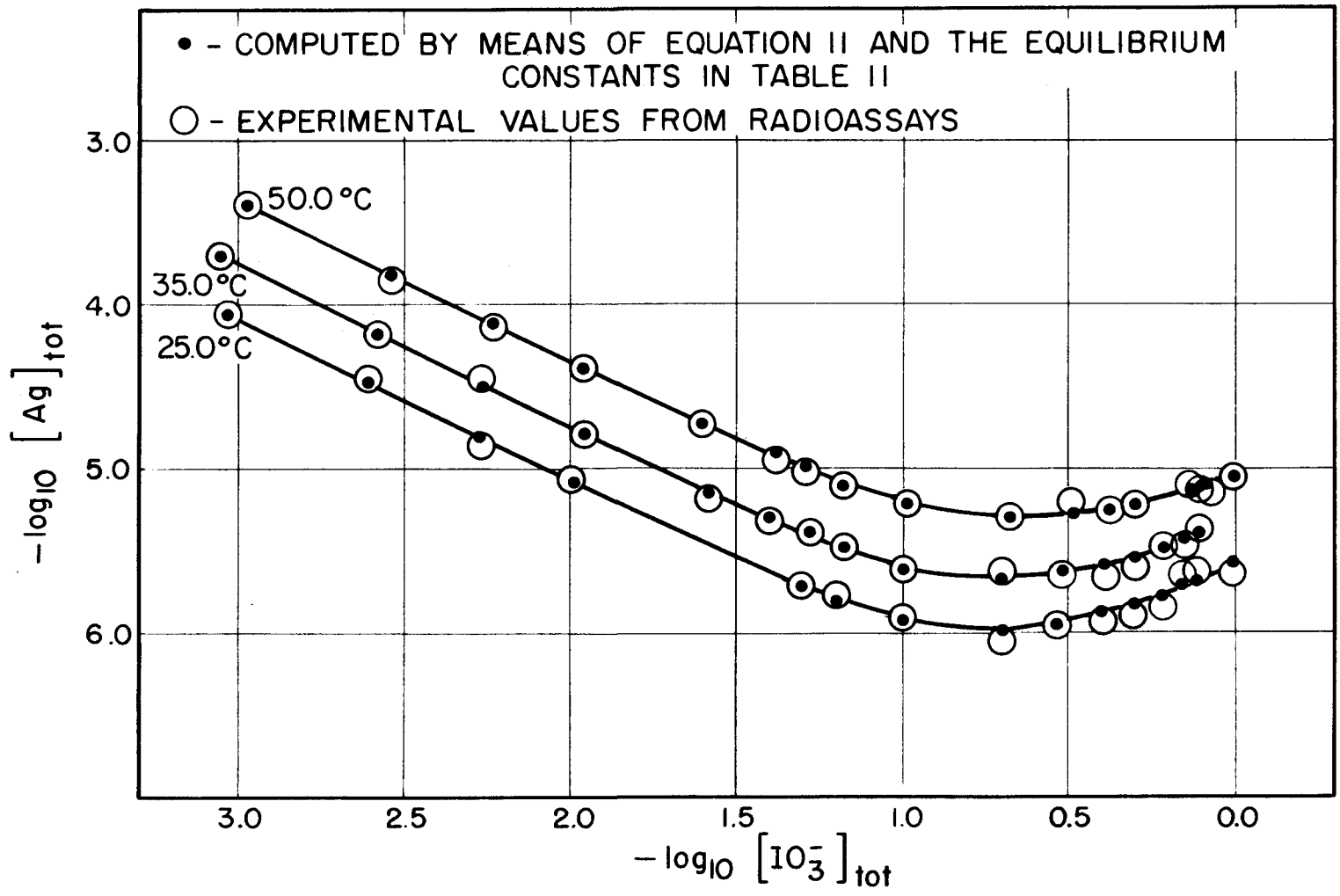


Figure 4. Graphs of solubilities of  $\text{AgIO}_3$  for equilibrium solutions in which ionic strengths were fixed at 1.00 M.

a fair approximation to the true values for silver iodate in aqueous solutions of lithium iodate. In all calculations it was assumed that only a negligible fraction of the total iodate was supplied by dissolution of silver iodate or removed by the formation of iodate complexes; i.e.

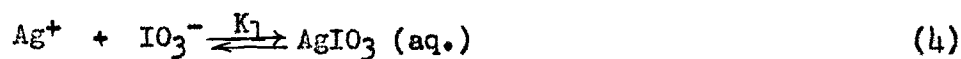
$$[\text{IO}_3^-] \approx [\text{IO}_3^-]_{\text{tot}} \quad (2)$$

where:  $[\text{IO}_3^-]$  = molar concentration of free iodate ion

$[\text{IO}_3^-]_{\text{tot}}$  = observed total molar concentration of iodate  
in the equilibrium solutions.

#### B. Description of the Complexing Equilibria

The equilibrium state of the system was successfully described by the following three chemical equilibria:



Formation equilibrium constants for the two iodate complexes and the equilibrium solubility product constant were defined according to the following scheme:

$$K_{\text{sp}} = [\text{Ag}^+][\text{IO}_3^-] \gamma_{\pm}^2 \quad (6)$$

$$K_1 = \frac{[\text{AgIO}_3(\text{aq.})] \gamma_0}{[\text{Ag}^+][\text{IO}_3^-] \gamma_{\pm}^2} \quad (7)$$

$$K_2 = \frac{[\text{Ag}(\text{IO}_3)_2^-] \gamma_2}{[\text{Ag}^+][\text{IO}_3^-]^2 \gamma_{\pm}^2 \gamma_-} \quad (8)$$

where:  $\gamma_-$  = activity coefficient for  $\text{IO}_3^-$   
 $\gamma_0$  = activity coefficient for  $\text{AgIO}_3$  (aq.)  
 $\gamma_2$  = activity coefficient for  $\text{Ag}(\text{IO}_3)_2^-$   
 $\gamma_{\pm}$  = mean ionic activity coefficient for  $\text{AgIO}_3$  in the  
 equilibrium solutions.

Brackets denote concentrations in moles/liter.

The molar concentrations of the silver bearing species were formulated as a function of the total iodate concentration and the activity coefficients for the individual species. A summation of these molarities represented the total silver concentration in an equilibrium solution,  $[\text{Ag}]_{\text{tot}}$ , the quantity determined by the radioassay. In equation form these formulations are properly represented by:

$$[\text{Ag}]_{\text{tot}} = [\text{Ag}^+] + [\text{AgIO}_3(\text{aq.})] + [\text{Ag}(\text{IO}_3)_2^-] \quad (9)$$

$$\text{or: } [\text{Ag}]_{\text{tot}} = \frac{K_{\text{sp}}}{\gamma_{\pm}^2 [\text{IO}_3^-]_{\text{tot}}} + \frac{K_1 K_{\text{sp}}}{\gamma_0} + K_2 K_{\text{sp}} [\text{IO}_3^-]_{\text{tot}} \frac{\gamma_-}{\gamma_2} \quad (10)$$

Unfortunately the degree of iodate complexing in the concentration region for which it was valid to use the interpolated activity coefficients was not extensive. This fact caused the necessity for obtaining the values of  $K_1$  and  $K_2$  from experiments where the ionic strength was constant. It is important to note, however, that the equilibrium solubility product constants were conveniently secured from the data obtained for solutions in which the ionic strength varied.

Equation 5 was simplified for application to data taken for constant ionic strength by assuming that activity coefficients were effectively constant and could be included in the equilibrium constants to form a

set of three concentration equilibrium constants. The total silver was then given by:

$$[\text{Ag}]_{\text{tot}} = \frac{K_A}{[\text{IO}_3^-]_{\text{tot}}} + K_B + K_C [\text{IO}_3^-]_{\text{tot}} \quad (11)$$

$$\text{where: } K_A = \frac{K_{\text{sp}}}{\gamma_{\pm}^2} \quad (12)$$

$$K_B = \frac{K_1 K_{\text{sp}}}{\gamma_0} \quad (13)$$

$$K_C = K_2 K_{\text{sp}} \frac{\gamma_-}{\gamma_2} \quad (14)$$

Within the limits of error of the results, this assumption was validated in later calculations.

### C. Determination of the Equilibrium Solubility Product Constants

A form of Equation 10 that is convenient for determining equilibrium solubility product constants is given by Equation 15 below.

$$\log_{10}([\text{Ag}]_{\text{tot}} [\text{IO}_3^-]_{\text{tot}})^{\frac{1}{2}} \gamma_{\pm} = \log_{10} \left( K_{\text{sp}} + \frac{K_1 K_{\text{sp}}}{\gamma_0} [\text{IO}_3^-]_{\text{tot}} + K_2 K_{\text{sp}} \frac{\gamma_-}{\gamma_2} [\text{IO}_3^-]_{\text{tot}}^2 \right)^{\frac{1}{2}} \quad (15)$$

It predicts that a plot of  $\log_{10}([\text{Ag}]_{\text{tot}} [\text{IO}_3^-]_{\text{tot}})^{\frac{1}{2}} \gamma_{\pm}$  must approach  $\frac{1}{2} \log_{10} K_{\text{sp}}$  with a small slope as  $[\text{IO}_3^-]_{\text{tot}}^{\frac{1}{2}}$  approaches zero.

Plots of Equation 15 for the data at the three temperatures studied are given in Figure 5. Assay values obtained with silver of different specific activities have been indicated in these graphs also. The dashed lines indicate the extrapolations to zero ionic strength and values of the equilibrium solubility product constants are contained in

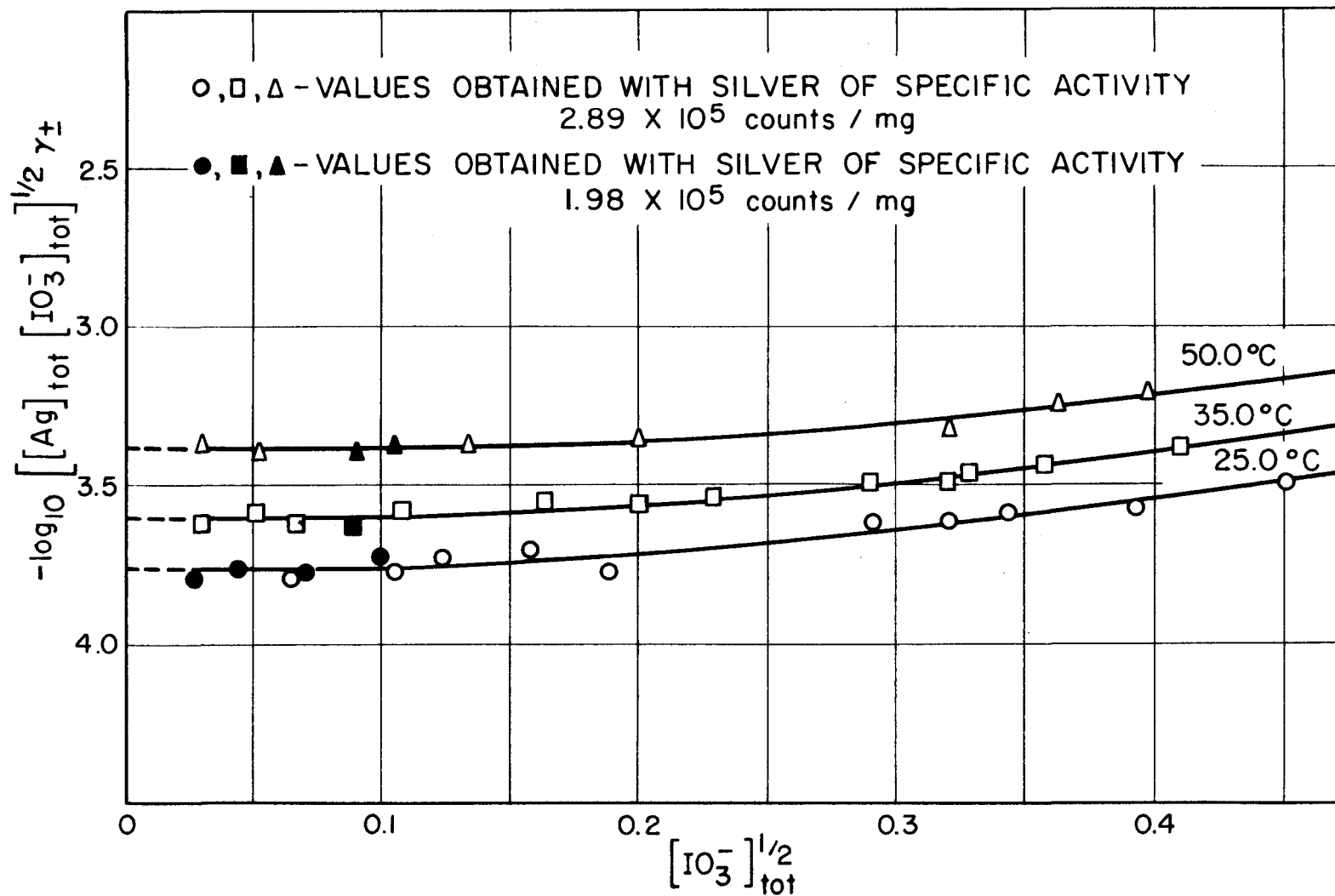


Figure 5. Experimental plots for the evaluation of equilibrium solubility product constants,  $K_{sp}$ , for zero ionic strength.

Table 10 below. For comparison, representative experimental values which were reported previously have been included.

Table 10. Equilibrium Solubility Product Constants for  $\text{AgIO}_3$  from Solubility Measurements in Aqueous Solutions of  $\text{LiIO}_3$

Temperature °C.	Intercept <sup>a</sup> $-\frac{1}{2}\log K_{sp}$	$K_{sp}$ Observed moles <sup>2</sup> x 10 <sup>8</sup>	$K_{sp}$ previously Determined moles <sup>2</sup> x 10 <sup>8</sup>
25.0 ± 0.1	3.76	3.0 ± 0.15	3.055 <sup>b</sup>
35.0 ± 0.1	3.60	6.3 ± 0.3	6.456 <sup>b</sup>
50.0 ± 0.1	3.38	17.4 ± 1.0	none

<sup>a</sup>From extrapolations in Figure 3.

<sup>b</sup>These values were taken from the work of Li and Lo (38).

#### D. Evaluation of the Formation Equilibrium Constants

Concentration equilibrium solubility product constants,  $K_A$ , were obtained from the data for constant ionic strength by plotting the quantity  $-\log [\text{Ag}]_{\text{tot}} [\text{IO}_3^-]_{\text{tot}}$  versus  $[\text{IO}_3^-]_{\text{tot}}^{\frac{1}{2}}$  and extrapolating to an iodate concentration of zero. These functions have been graphed in Figure 6. Good extrapolations were possible since the experimental curves approached the vertical axis at an extremely small angle from the horizontal.

Equation 11 was also employed for the evaluation of  $K_B$  and  $K_C$ . By subtracting the term containing  $K_A$  from  $[\text{Ag}]_{\text{tot}}$  for experimental values

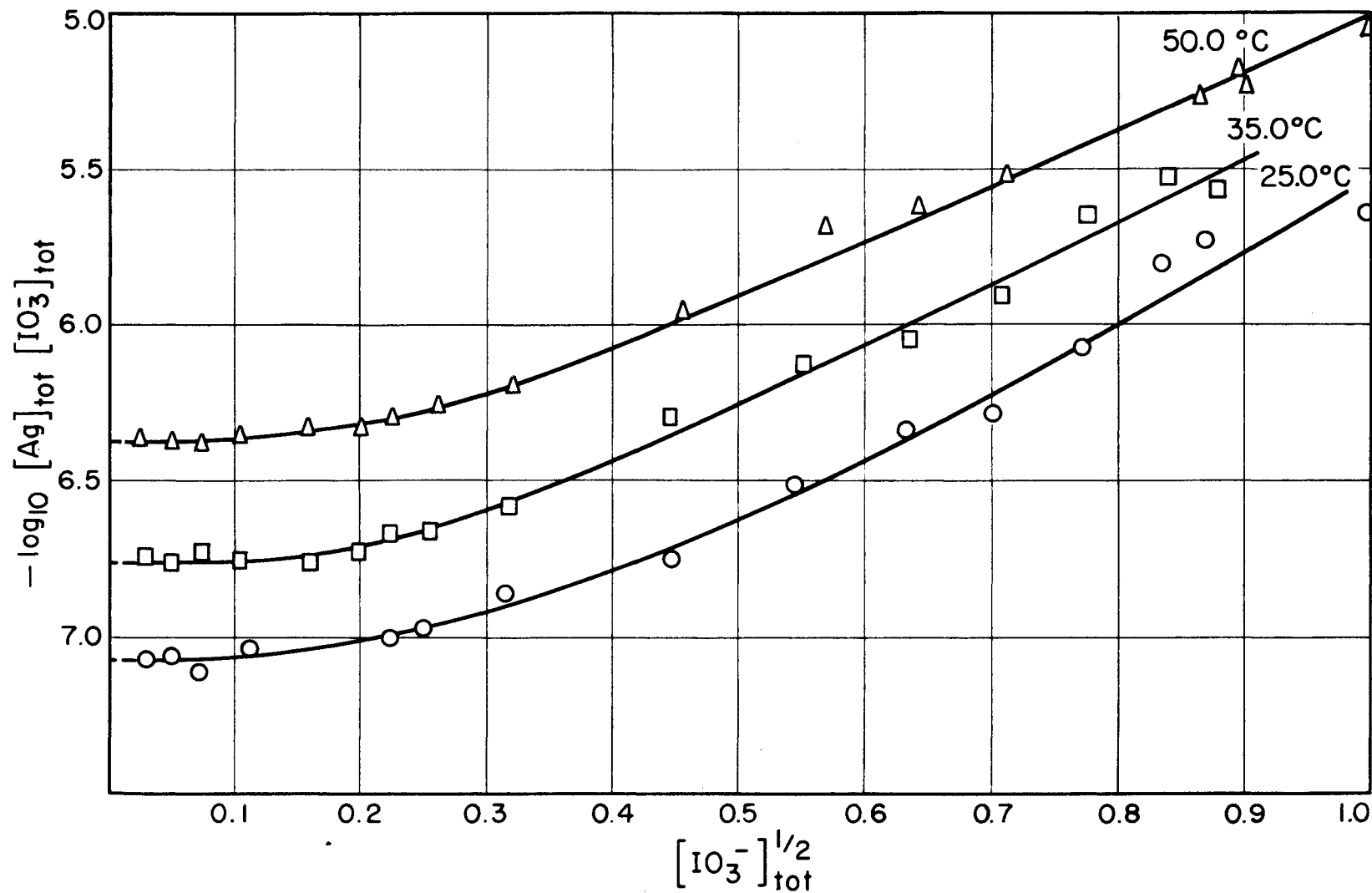


Figure 6. Experimental plots for the evaluation of concentration equilibrium solubility product constants,  $K_A$ , for solutions 1.00 M with respect to  $\text{LiClO}_4$ .



of iodate concentrations and plotting significant differences versus  $[\text{IO}_3^-]_{\text{tot}}$  a straight line function was obtained having an intercept of  $K_B$  and a slope equal to  $K_C$ . The best values for these constants were determined by applying the method of least squares for equally weighted values of the differences and probable errors were computed for the constants of the least squares straight line. The representations of the observed data have been presented in Figure 7.

Conversion of  $K_B$  and  $K_C$  to equilibrium formation constants  $K_1$  and  $K_2$  respectively was accomplished through the use of Equations 12, 13 and 14. It was assumed that  $\delta_0$  for the uncharged complex was unity and that ratios of activity coefficients for ions of like charge were also unity. For 25.0°C. and 35.0°C. the equilibrium solubility product constants determined by Li and Lo (38) were employed, for 50.0°C., the experimental value reported in Table 10 was used. The equilibrium constants corresponding to  $K_B$  and  $K_C$ , and related quantities have been included in Table 11.

The constants of Table 11 were used in conjunction with Equation 10 and 11 to calculate solubilities for the various equilibrium solutions and these have been included in Tables 8 and 9 and plotted in Figures 3 and 4 for comparison with the experimental results. The precision of the experimental results was tested by the quantity  $\sqrt{(\sum [1/N] \delta_i^2)}$ , where  $\delta_i$  equals the  $\log[\text{Ag}]_{\text{tot}}$  observed minus  $\log_{10}[\text{Ag}]_{\text{tot}}$  calculated and N is the number of observations involved in an experiment. Results of the tests for all of the experiments are given in Table 12.

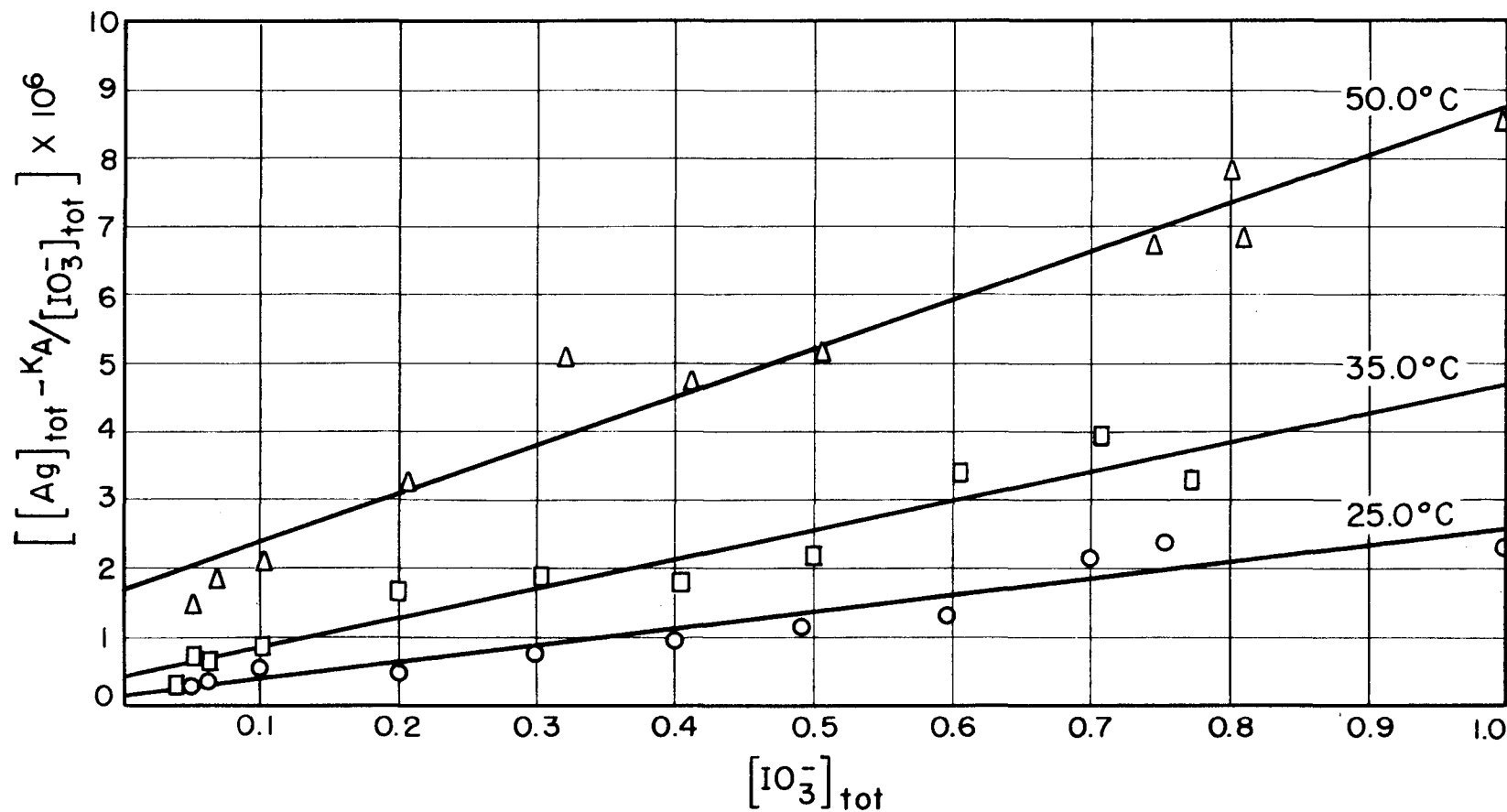


Figure 7. Least-squares representations of experimental data for the determination of the concentration equilibrium formation constants  $K_B$  and  $K_C$ .

Table 11. Formation Equilibrium Constants for  $\text{AgIO}_3$  (aq.)  
and  $\text{Ag}(\text{IO}_3)_2^-$  and Related Quantities

Temperature °C.	moles $2 \frac{K_A}{x} 10^7$	mole $^{-1} \frac{K_B}{x} 10^7$	mole $^{-2} \frac{K_C}{x} 10^6$	$\gamma_{+2}^a$	$\frac{K_1}{\text{mole}^{-1}}$	$\frac{K_2}{\text{mole}^{-2}}$
25.0 $\pm$ 0.1	0.84 $\pm$ .02	1.3 $\pm$ 0.8	2.42 $\pm$ 0.16	0.363 $\pm$ 0.009	4.26 $\pm$ 2.62	79.4 $\pm$ 5.2
35.0 $\pm$ 0.1	1.74 $\pm$ .04	4.1 $\pm$ 1.2	4.29 $\pm$ 0.28	0.371 $\pm$ 0.009	6.34 $\pm$ 1.86	66.4 $\pm$ 4.3
50.0 $\pm$ 0.1	4.26 $\pm$ .10	15.8 $\pm$ 1.8	7.16 $\pm$ 0.33	0.407 $\pm$ .023	9.09 $\pm$ 1.16	41.1 $\pm$ 3.0

<sup>a</sup>  $\gamma_{+2}$  is the mean ionic activity coefficient for  $\text{AgIO}_3$  in 1 M  $\text{LiClO}_4$  solution. Values were obtained by using Equation 12 in conjunction with the values of  $L_1$  and  $L_0$  (38) for the equilibrium solubility product of  $\text{AgIO}_3$  for 25.0°C. and 35.0°C. and the experimental equilibrium solubility product for 50.0°C. reported in Table 10.

Table 12. Tests for Precision of the Experimental Results

Temperature °C.	Ionic Strength Condition	Number of Observations	$(\sum 1/N \delta_i^2)^{\frac{1}{2}}$
25.00	Constant	15	0.052
	Variable	15	0.052
35.00	Constant	16	0.030
	Variable	16	0.039
50.00	Constant	17	0.028
	Variable	10	0.046

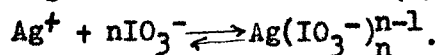
It is important to note that the measured solubilities for experiments performed for variable ionic strength are well represented by the calculated solubilities since the latter were obtained by using the equilibrium constants determined for measurements for constant ionic strength. The basic assumptions regarding activity coefficients in the equilibrium solutions at the constant ionic strength of 1.00 M have therefore yielded an equilibrium description not inconsistent with the solubilities in solutions of low, variable ionic strengths.

#### E. Thermodynamic Properties

Thermodynamic functions for the chemical equilibria represented by Equations 4 and 5 have been estimated from the equilibrium constants  $K_1$  and  $K_2$  and their variations with temperature. These functions have been entered in Table 13. Ionic entropies of 17.5 e.u. for silver ion and 28.0 e.u. for iodate ion recommended by Latimer et. al. (45) and

Latimer (46) respectively were employed to estimate the partial molar entropies of the iodato complexes.

Table 13. Standard Free Energy, Enthalpy and Entropy Changes for the Reactions (35.0°)



The Partial Molar Entropy of  $\text{AgIO}_3$  (aq.) and  $\text{Ag}(\text{IO}_3)_2^-$ .

n	$\Delta F^\circ$ kcal.	$\Delta H^\circ$ kcal.	$\Delta S^\circ$ e.u.	$\bar{S}^\circ$ (complex) e.u.
1	$-1.13 \pm 0.18$	$+5.14 \pm 4.54$	$+20.3 \pm 14.7$	66
2	$-2.53 \pm 0.04$	$-5.20 \pm 0.79$	$-8.50 \pm 2.55$	65

Cobble (47) has proposed a method for estimating the entropy change associated with the complexing of a simple ion by ionic ligands. In his treatment the entropy changes for the reactions to form  $\text{AgIO}_3$  (aq.) and  $\text{Ag}(\text{IO}_3)_2^-$  would be given by Equations 16 and 17.

For  $\text{AgIO}_3$  (aq.):

$$\Delta S = \bar{S}^\circ(\text{AgIO}_3 \text{ (aq.)}) - \bar{S}^\circ(\text{H}_2\text{O}) - \bar{S}^\circ(\text{IO}_3^-) - \bar{S}^\circ(\text{Ag}^-) \quad (16)$$

For  $\text{Ag}(\text{IO}_3)_2^-$ :

$$\Delta S = \bar{S}^\circ(\text{Ag}(\text{IO}_3)_2^-) - 2\bar{S}^\circ(\text{H}_2\text{O}) - 2\bar{S}^\circ(\text{IO}_3^-) - \bar{S}^\circ(\text{Ag}^-) \quad (17)$$

$$\text{where: } \bar{S}^\circ(\text{AgIO}_3 \text{ (aq.)}) = 132 - 354/r_{12} \quad (18)$$

$$\bar{S}^\circ(\text{Ag}(\text{IO}_3)_2^-) = 49 - 99 Z / r_{12} \quad (19)$$

$\bar{S}^\circ$  = Partial molal entropy of the species indicated.

also: Z = absolute integral charge of the complex species.

$r_{12}$  = sum of the appropriate ionic and covalent radii

of the metal atom and ligand respectively. ( $r_{12}$  for the iodato complexes was calculated to be  $3.24 \text{ \AA}$ . from the tabulations of ionic and covalent radii reported in Wells (48).)

By using values of 17.5 e.u. for  $\bar{S}^{\circ}(\text{Ag}^{\dagger})$  (45), 16.7 e.u. for  $\bar{S}^{\circ}(\text{H}_2\text{O})$  (46, p. 39) and 28.0 e.u. for  $\bar{S}^{\circ}(\text{IO}_3^-)$  (46) along with values of the other quantities that were consistent with Cobble's treatment,  $\Delta S$  for the reaction to form  $\text{AgIO}_3$  (aq.) was calculated to be -6 e.u. and  $\Delta S$  for the reaction to form  $\text{Ag}(\text{IO}_3)_2^-$  was estimated to be -21.6 e.u. These values are in fair agreement with the experimental values given in Table 13.

## IV. DISCUSSION

The extent to which the objectives set forth in the beginning of this work have been achieved may now be considered. It is believed that the radiochemical procedure devised for the mounting and counting of equilibrium samples was definitely superior to the radioassay methods applied to other silver salts. Its applicability and ease of operation were independent of the composition or density of the equilibrium solution samples and the securing of reproducible samples for counting was only a function of the effectiveness of a plating procedure. The shortcomings of procedures that were used by Jonte and Martin (20) and Leden et. al. (21, 22, 23) have been thoroughly discussed in Part B of II, consequently they will not be restated here. In retrospect, the geometry of counting could have been rendered slightly more reproducible by employing a more precise mount for the sample holder than the commercial plastic one that was used.

From the results of the experiments that were performed to test the effectiveness of the fritted glass filters it is evident that an evaluation of the method used to obtain equilibrium solution samples should form an integral part of investigations such as this one. It is quite possible that the disagreement between the results of various investigators (19, 20, 21) for the silver chloride-chloride ion-water system is partially attributable to the inclusion of particles of colloidal dimensions into the equilibrium solution samples or the adsorption or reduction of silver on the filtering media used. A thorough study of these factors for the chloride system may prove

useful in eliminating existing discrepancies.

The equilibrium solubility product constants that were obtained in this investigation for 25.0°C. and 35.0°C. are in good agreement with the values of Li and Lo (38). This fact and the additional fact that measurements performed with silver of different specific activities were compatible with one another is strong evidence for the consistency of the data and indicates that procedures employed for the removal of radiotracer impurities from the radiosilver and for the preparation of the radioactive stock solutions of silver-110m were adequate. It must be stated, however, that for salts as soluble as silver iodate, equilibrium solubility product constants cannot be determined by use of a radioassay method with the degree of accuracy attainable by the usual methods since even under ideal conditions the accuracy of the radiochemical procedure is limited by the counting statistics and the reproducibility of sample mounting techniques.

The magnitude of the equilibrium formation constants  $K_1$  and  $K_2$  for  $\text{AgIO}_3$  (aq.) and  $\text{Ag}(\text{IO}_3)_2^-$  respectively were not great and in the case of the measurements at 50.0°C. were separated by only a factor of five. These facts are strongly reflected in the precision indexes reported for these quantities in Table 11, nevertheless, values for  $K_2$  may be considered to be quite well established. Formation constants determined for the analogous chloro-complexes of silver were much greater and the magnitudes of successive constants were separated by a factor of one hundred, consequently the concentration range in which each were operative was well defined. In the plots of Figures 3 and 4 the slopes of the solubility curves are in no case greater than 1.0



for the concentration range studied. In the work of Leden and Berne (21) on the silver chloride-chloride ion-water system slopes of comparable curves became greater than 1.0 at concentrations of chloride in the range  $0.1 \text{ M} \leq [\text{Cl}^-] \leq 1 \text{ M}$ . To account for the increase in slope it was necessary for these investigators to describe the  $\text{AgCl}_3^-$  and the  $\text{AgCl}_4^{2-}$  species. Certainly it has been demonstrated that the degree of complexing of silver by chloride ligands is much greater than for iodate ligands. This fact is further substantiated by the observation that the minimum solubility of silver iodate in solutions containing iodate ion is only a factor of approximately two greater than the minimum solubility of silver chloride in solutions containing chloride ion, whereas their solubilities in pure water are separated by a factor of approximately eight. It has also been noted that the tendency for iodate ion to complex with manganese (II) in iodate solutions was slight, however, the opposite tendency was observed in the case of manganese (III) and manganese (IV) (49). Data for iodato complexes in the literature are not extensive. This fact is probably a consequence of the tendency for iodate ion to form insoluble salts with many metal ions in aqueous solution. It is possible that a radiochemical method similar to that described in this work is one manner in which further useful information for aqueous iodate systems may be obtained.

Assumptions about activity coefficients in solutions of constant ionic strength may have introduced some uncertainty into the formation constants for the iodato complexes, however, the manner in which representations of the experimental data obtained for variable ionic strength were reproduced by means of suitable equations and equilibrium

formation constants obtained for constant ionic strength seemed to indicate that possible errors from this source were contained within the limits of accuracy of the experiment.

The thermodynamic description of the silver iodate-iodate ion-water system that was obtained in this work was not definitive in an absolute sense in that iodate appeared to be a very weak complexing agent for silver and the moniodatosilver species possessed a low stability which was difficult to evaluate quantitatively.

## V. SUMMARY

Solubilities of silver iodate in aqueous solutions containing various concentrations of lithium iodate have been measured for 25.0°C., 35.0°C. and 50.0°C. by means of an improved radioassay technique for silver activity. They have also been measured for the same temperatures in aqueous solutions containing various proportions of lithium iodate and lithium perchlorate. In the latter experiments, the ionic strengths of all equilibrium solutions were fixed at a value of 1.00 M.

The refined radiotracer method has been described in detail and the advantages which it possesses over existing techniques for radiosilver assay have been discussed. A series of experiments performed to test the procedure for sampling of the equilibrated mixtures have also been presented.

The data have been interpreted in terms of equilibria which involve the species  $\text{Ag}^+$ ,  $\text{AgIO}_3(\text{s})$ ,  $\text{AgIO}_3(\text{aq.})$ , and  $\text{Ag}(\text{IO}_3)_2^-$  and equilibrium constants for reactions involving these species have been calculated. From the solubilities and their temperature coefficients thermodynamic quantities for the iodato complexes have also been computed. The entropy changes observed for the reactions to form  $\text{AgIO}_3(\text{aq.})$  and  $\text{Ag}(\text{IO}_3)_2^-$  have been compared with those calculated from a semi-empirical formulation proposed by Cobble (47).

## VI. LITERATURE CITED

1. Zimmerman, H. K., Chem. Rev., 51, 59(1952).
2. Paneth, F. and G. von Hevesey, Z. anorg. Chem., 82, 323(1913).
3. Hevesey, G. von and E. Róna, Z. physik. Chem., 89, 294(1915).
4. Ishibashi, M. and O. Funahashi, J. Chem. Soc. Japan, 57, 1028(1936).
5. Ferla, F., Ann. Chim. appl., 28, 331(1938).
6. Ferla, F. and B. N. Cacciapuoti, Ann. Chim. appl., 29, 166(1939).
7. Ruka, R. and J. E. Willard, J. Phys. & Colloid Chem., 53, 351(1949).
8. Moeller, T. and G. H. Quinty, J. Am. Chem. Soc., 74, 6123(1952).
9. Joris, G. G. and H. S. Taylor., J. Chem. Phys., 16, 45(1948).
10. Haïssinsky, M. and R. Bovy, Bull. soc. chim. France, 1950, 827.
11. Süe, P., Bull. soc. chim. France, 1947, 405.
12. Cunningham, B. B. and L. B. Werner, J. Am. Chem. Soc., 71, 1521(1949).
13. Moeller, T. and G. Schweitzer, Anal. Chem., 20, 1201(1948).
14. Neiman, M. B., V. B. Miller and A. I. Fedoseeva, Doklady Akad. Nauk S.S.S.R., 75, 719(1950).
15. Jordan, P., Helv. Phys. Acta, 26, 378(1953).
16. Crouthamel, C. E. and D. S. Martin, Jr., J. Am. Chem. Soc., 72, 1382(1950).
17. Crouthamel, C. E. and D. S. Martin, Jr., J. Am. Chem. Soc., 73, 569(1951).
18. Fry, A. J., J. E. Barney II, and R. W. Stoughton, U.S. Atomic Energy Commission Report AECD - 249, 1948.
19. Barney, J. E., II, W. J. Argersinger, Jr., and C. A. Reynolds, J. Am. Chem. Soc., 73, 3785(1951).
20. Jonte, J. H. and Don S. Martin, Jr., J. Am. Chem. Soc., 74, 2052(1952).
21. Leden, I. and E. Berne, Svensk. Kem. Tidskr., 64, 88(1953).
22. Leden, I. and E. Berne, Z. Naturforsch., 8a, 719(1953).

23. Leden, I. and N. H. Schön, Trans. Chalmers Univ. Technol. Gothenburg, 144, 3(1954).
24. Shchigol, M. B., Zhur. Obshchey Khim., 22, 728(1952).
25. Longi, A., Gazz. chim. ital., 13, 87(1883).
26. Noyes, A. A. and D. A. Kohr, J. Am. Chem. Soc., 24, 1144(1902).
27. Bottger, W., Z. Physik. Chem., 46, 521(1903).
28. Kohlrausch, F., Z. Physik. Chem., 44, 225(1903).
29. Sammet, V., Z. physik. Chem., 53, 644(1905).
30. Kohlrausch, F., Z. physik. Chem. 64, 168(1908).
31. Hill, A. E. and J. P. Simmons, J. Am. Chem. Soc., 31, 821(1909).
32. Whitby, G. S., Z. anorg. Chem., 67, 107(1910).
33. Roth, Walther Adolf "Physikalisch-Chemische Übungen", 3rd ed. Leipzig, Leopold Voss 1921.
34. Landolt-Bornstein, "Physikalisch-Chemische Tabellen", 5th ed. Vol. II. Berlin, Julius Springer 1923.
35. Baxter, W. P., J. Am. Chem. Soc., 48, 619(1926).
36. Roth, Walter Adolf "Physikalisch-Chemische Übungen" 4th ed. Leipzig, Leopold Voss 1928.
37. Kolthoff, I. M. and J. J. Lingane, J. Phys. Chem. 42, 133(1938).
38. Li, N. C. C. and Y. Lo, J. Am. Chem. Soc., 63, 394(1941).
39. Keefer, R. M. and H. G. Reiber, J. Am. Chem. Soc., 63, 689(1941).
40. Derr, F. P., R. M. Stockdale and W. C. Vosburgh, J. Am. Chem. Soc., 63, 2670(1941).
41. Ricci, J. E. and I. Amron, J. Am. Chem. Soc., 73, 3614(1951).
42. Gum, J. R. and M. L. Pool, Phys. Rev., 80, 315(1950).
43. Cork, J. M., W. C. Rutledge, C. E. Branyan, A. E. Stoddard, W. J. Childs and J. M. Le Blanc, Phys. Rev., 80, 286(1950).
44. Slomin, G. W., "Rapid Quantitative Electrolytic Methods of Analysis", 7th ed. Chicago, Ill., E. H. Sargent Co. 1954.

45. Latimer, W. M., K. S. Pitzer and W. V. Smith, J. Am. Chem. Soc., 60, 1829(1938).
46. Latimer, Wendell M. "Oxidation Potentials" 2nd ed. N.Y., Prentice-Hall, Inc. 1952.
47. Cobble, J. W., J. Chem. Phys., 21, 1446(1953).
48. Wells, A. F. "Structural Inorganic Chemistry" 2nd ed. London, Oxford University Press 1950.
49. Waterbury, G. R. and D. S. Martin, Jr., J. Am. Chem. Soc., 75, 4162(1953).

## VII. ACKNOWLEDGMENTS

The author wishes to express a sincere feeling of gratefulness to Mr. Alfred F. Marks and Mr. Richard F. Reade for their invaluable assistance in accomplishing the large amount of routine work that was involved in this investigation. Special grateful acknowledgment must be extended to Dr. Don S. Martin, Jr. whose interest, encouragement and sound guidance were unfailing.