Now rearranging, one obtains

$$Ax_1{}^2 + Bx_1 = \left[\frac{1}{m^2}\left\{\frac{m(\phi_2^0)_m - m_0(\phi_2^0)_{m_0}}{m - m_0}\right\}\right](m - m_0) \quad (13)$$

where $A = -(2.303/2)(\alpha_{12} + \alpha_{21})$ and $B = +2.303\ \alpha_{21}$. If A, B and the quantity in brackets, which may be called C, are weak functions of the total molality m, then x_1 is linear with m. A is zero for the KCl–KBr system and in general is very small, varying but little with m. Hence, it is necessary that α_{12} and C be independent of m for equation 4 to hold. It is readily apparent from Table V and plots of the osmotic coefficients of KCl and KBr against the cube of molality that these conditions are met in the KCl–KBr case, not exactly but sufficiently well that one would not expect the x_1–m plots to be perceptibly non-linear.

[CONTRIBUTION NO. 434 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Solubility of Silver Iodate in Iodate Solutions. Iodato Complexes of Silver*

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Solubilities of silver iodate at 25.0, 35.0 and 50.0° have been measured by means of a radioassay technique in aqueous solutions with various low concentrations of lithium iodate and with solutions having a constant ionic strength of 1.00 *M*. Solubility product constants obtained for these temperatures were $(3.0 \pm 0.15) \times 10^{-8}$, $(6.3 \pm 0.3) \times 10^{-8}$ and $(17.4 \pm 1.0) \times 10^{-8}$, respectively. In addition to the normal equilibrium solubility product relationship, two complexing equilibria were needed to describe the behavior at higher iodate concentrations: $Ag^+ + IO_3^- \leftrightarrows AgIO_3(aq.)$, for which $\Delta F^\circ_{35^\circ} = -1.13 \pm 0.18$ kcal./mole, $\Delta H^\circ_{35^\circ} = 5.1 \pm 4.5$ kcal./mole; $Ag^+ + 2IO_3^- \leftrightarrows Ag(IO_3)_2^-$, for which $\Delta F^\circ_{35^\circ} = -2.53 \pm 0.04$ kcal./mole, $\Delta H^\circ_{35^\circ} = -5.20 + 0.79$ kcal./mole.

Introduction

A radiosilver assay procedure has been utilized to determine the solubility of silver iodate in aqueous solutions of lithium iodate. The method has also been applied to solutions for which ionic strengths were adjusted at 1.00 *M* by means of lithium perchlorate. This work was undertaken when it was noted that significant deviation from the solubility product existed in moderately dilute solutions of lithium iodate. Possibilities for the existence of iodato-silver complexing phenomena were indicated.

Ricci and Amron[1] studied the silver iodate–lithium iodate–water system and concluded that the isotherm for this system was of the simplest type with no evidence of compound formation or solid solution, and qualitative tests for silver in the solutions containing silver iodate and the dissolved salt were negative. Shchigol,[2] employing a conventional iodometric procedure for analyses of equilibrium solution phases, reported the solubility of silver iodate at 20–22° in aqueous solutions for three concentrations of potassium iodate. He considered that silver was present in the equilibrium solution phases only in the form of Ag^+ and $Ag(IO_3)_2^-$ ions and reported an instability constant of 2.22×10^{-6} for the diiodatoargentate species. It was of interest to obtain a more quantitative description by use of an effective radioassay method.

Experimental

Materials.—All water used in this work was prepared by redistilling distilled water from alkali permanganate solutions. Its specific conductance was found to be 2.5×10^{-6} mho cm.$^{-1}$.

Lithium perchlorate was obtained in reagent grade from 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.

Lithium iodate was prepared by adding a stoichiometric amount of iodic acid to an aqueous solution of lithium carbonate. The salt was crystallized after 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° for 24 hours and stored in a desiccator over anhydrous magnesium perchlorate. Analyses of the salt for total iodate content were consistent with the theoretical composition.

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

Silver^{110m} was the tracer employed. It was obtained from the Oak Ridge National Laboratory in 1.4 ml. of 2 *N* nitric acid and was reported to have a radiochemical purity in excess of 98%. Stock solutions containing radioactive silver were prepared by adding aliquots of this solution to dilute nitric acid solutions containing definite amounts of inactive silver nitrate. These solutions were subsequently scavenged with iron hydroxide and evaporated to dryness with an excess of nitric acid. The radioactive silver was precipitated as the chloride from the dilute nitric acid, filtered from the solution and dissolved with concentrated ammonia. The silver was subsequently electroplated on a platinum gauze cathode according to a method proposed by Slomin.[3] Following this operation, the silver was dissolved from the electrode with 10 *N* nitric acid and the entire purification cycle was repeated. The remainder of the procedure involved a gravimetric determination of the silver on the electrode, dissolution in 10 *N* nitric acid, fuming with perchloric acid and dilution in a volumetric flask.

Tagged silver iodate was prepared by adding solutions of lithium iodate to aliquots of the stock solutions of silver tracer after these had been partially neutralized with lithium hydroxide. The wet masses of crystals which formed were washed repeatedly with many small portions of warm water, and finally they were washed, slurried and transferred to the equilibrium flasks with the aid of many small portions of the solution phase with which they were to be equilibrated.

Primary standards and other chemicals used for this work were all of reagent grade according to ACS specifications.

Apparatus.—Mixtures were equilibrated in thermostated water baths in which temperatures were constant to ±0.1°.

Pyrex erlenmeyer flasks were used to contain the mixtures. Some were of red variety glass and others were wrapped with a black plastic adhesive tape to exclude light. When in use,

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* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(1) J. E. Ricci and I. Amron, THIS JOURNAL, **73**, 3614 (1951).

(2) M. B. Shchigol, *Zhur. Obshchei Khim.*, **22**, 728 (1952).

(3) G. W. Slomin, "Rapid Quantitative Electrolytic Methods of Analysis," 7th ed., E. H. Sargent Co., Chicago, Ill., 1954.

their ground glass caps were sealed with paraffin wax and agitation was provided by Burrell Model CC shakers.

Separations of samples of the equilibrium solution phases were accomplished by filtration with pressure in the thermostated baths. The filtering medium was "fine" fritted glass having a nominal maximum pore size of 5 μ. Before this filtering medium was adopted its effectiveness in removing the solid phase particles was tested. Experiments carried out with equilibrium mixtures and solutions of silver perchlorate in which pore size, pH, iodate and lithium concentrations were varied indicated that "fine" fritted glass discs (nominal pore size, 5 μ) were a suitable medium for use in these experiments if the filter became saturated with silver ion before samples of the equilibrium solution phases were taken for the radioassays. It was observed that <4 ml. of the most dilute silver solutions, drawn through the filters, sufficed to effect their adsorption saturation.

Electrolysis cells were similar to Tracerlab E-16 electroplating cells and were constructed of non-magnetic stainless steel. Electrodes were made from 0.025 mm. platinum stock. Cathodes were cut in the form of discs having a diameter of 2.54 cm. Anodes were 0.5 × 0.7 cm. rectangles and were spot-welded to platinum wires which were sealed into glass tubes 10 cm. in length. The necessary plating voltage was supplied by a Sargent-Slomin Electroanalyzer and stirring was accomplished by means of a motor-driven glass stirrer equipped with a rheostat. When the cell was assembled, a platinum surface of 3.47 cm.^{2} was exposed for silver plating.

A Tracerlab end-window Geiger-Mueller counter Model TCG-1 was used in conjunction with a Nuclear Instrument and Chemical Corporation Model 165 scaling unit for the counting of radioactive samples. The same sample holder, lead housing, commercial plastic counter mount and tantalum backing were used for all samples.

The main stock solution of lithium perchlorate was analyzed by passing aliquots through a column of Dowex-50 cation-exchange resin in the acid form. The equivalent acid liberated was titrated with an aqueous solution of sodium hydroxide which had been standardized against pure potassium acid phthalate.

Total iodate was determined by the conventional iodometric procedure for iodate. Sodium thiosulfate solutions contained a borax preservative and were standardized against doubly recrystallized potassium iodate periodically.

A radioassay technique was developed to determine the concentration of silver in a given equilibrium sample. 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. The technique 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 predetermined amounts of silver carrier (usually 10 mg.). To ensure 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 to convert the solutions into suitable silver plating baths: 0.3 g. of KCN, 9 g. of KNO_3, 1 g. of KOH, $^3/_4$ ml. of 37% formaldehyde solution, 5 ml. of H_2O. 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. The plating baths were heated and finally separated from undissolved solids by decantation. They were transferred into electrolysis cells, heated nearly to their boiling temperatures, and the current was passed through them for a period of 35 minutes. Best results were obtained by operating at cathode current densities in the range 0.05–0.10 amp./cm.^{2} under an applied voltage in the range 2.5–5.0 volts. In all the electrolyses the baths were stirred constantly. The anodes served as baffles; and if they were carefully positioned, the plates appeared completely uniform without light spots which otherwise resulted from the vortex action of the stirring. 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 ammoniacal cyanide baths. The baths were subsequently removed from the carbon tetrachloride by means of a pipet equipped with a syringe.

The plates obtained were thoroughly washed with many small portions of water and acetone and dried in an oven for ten minutes at 120°. The silver deposited was determined gravimetrically and was counted to determine its activity. From these data the activities corresponding to 100% recovery of the carriers were computed. The application of corrections for self-absorption and radioactive decay converted the observed activities to values 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.

Two-ml. aliquots of the stock solutions of radioactive silver were treated in the same manner as outlined above to determine the specific activity of the silver in the tagged silver iodate. The variation of the measured activity, corrected for the fraction of recovery of the silver carrier, with plate thickness, was also determined in order that all counting data could be normalized to a standard thickness (1.4 mg./cm.^{2}). Agreement between successive analyses of a solution was normally within 2.5%.

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 sealed with paraffin wax, inserted into a constant temperature bath, and clamped in the shaking mechanism which operated continuously. For measurements performed at constant ionic strength slurries were made with solutions which 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 from which the ionic strength of 1.00 was attained 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. No systematic difference in the observed solubilities for seven representative samples was obtained between the two procedures.

To sample an equilibrium solution phase, a filter tube was brought to the equilibrium temperature, inserted into the mixture and pressure was applied until a suitable amount of clear filtrate passed through the filter into the tube. The level of the solution in the tube was never allowed to reach the neck of the flask. Pipets 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 ensure that all filters were completely saturated with silver ion before samples were taken for radioassays, the first portions of the equilibrium solution phases were always taken for iodate analysis.

Results and Discussion

Results from the Solubility Determinations.—Results of the analyses of the equilibrium solutions have been listed in Table I. Instances in which radioactive silver of different specific activities was employed have been indicated. The plots of the total silver concentrations against iodate with a log-log scale in Figs. 1 and 2 show very clearly the minimum which occurred in the solubility function. They also indicate the limiting slope of -1.0 in the region of low iodate activity in which the solubility approached the solubility product function. It can also be seen that even at the highest iodate concentration utilized, the slope of the solubility function was less than $+1.0$. Consequently, it can be concluded that complex species with more than two iodate ligands per central silver atom never became a major constituent in the region studied.

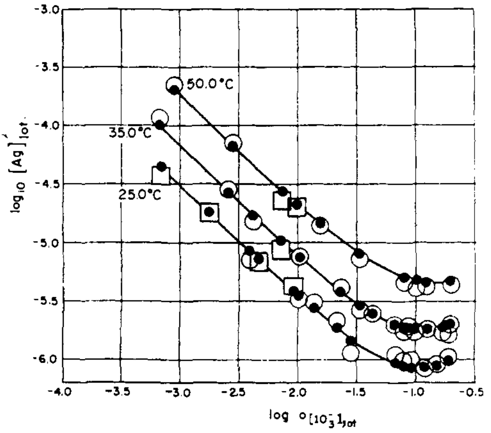

Fig. 1.—Solubility of $AgIO_3$ in solutions of $LiIO_3$: ●, points calculated by equation 8 with the parameters in Table II; O, observed values for specific activities of 2.89 × 10^6 cts./min. mg. (Table I); □, observed values for specific activities of 1.98 × 10^6 cts./min. mg. (Table I).

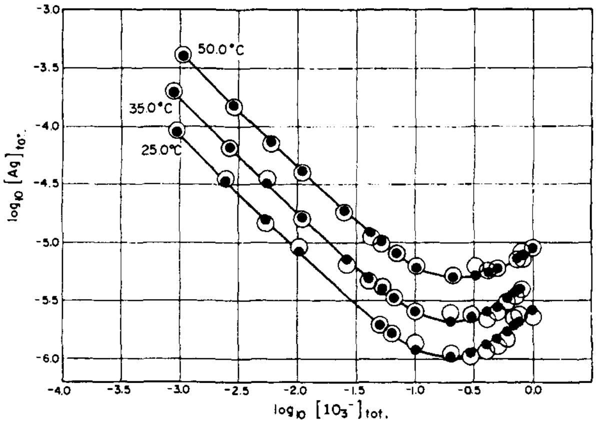

Fig. 2.—Solubility of $AgIO_3$ in solutions of $LiIO_3$ and $LiClO_4$ with ionic strengths of 1.00: ●, points calculated by equation 9 with the parameters in Table II; O, observed values (Table I).

For Fig. 1 iodate ion activities were computed from the concentrations by employing activity coefficients, $\gamma_{\pm}$, for a singly charged ion. These were interpolated from the tabulation of γ_1, presented by Crouthamel and Martin.[4] Activity coefficients applied to iodate concentrations in the range $0.1 < [IO_3^-]_{tot} < 0.27$ mole/liter were used with the reservation that they represented only a fair approximation to the true values for silver iodate in aqueous solutions of lithium iodate. In all calculations it could be assumed that only a negligible fraction of the total iodate was supplied by dissolution of silver iodate or utilized in the formation of iodate complexes.

Description of the Complexing Equilibria.—Since there was no evidence for higher complexes than $Ag(IO_3)_2^-$ the equilibrium state of the system

TABLE I

DATA FROM SOLUBILITY EXPERIMENTS WITH $AgIO_3$

System: $AgIO_3$–$LiIO_3$–H_2O			$AgIO_3$–($LiIO_3$ + $LiClO_4$ = 1.00 *M*)–H_2O		
$[Ag]^a_{tot}$ Obsd.	$[IO_3^-]^a_{tot}$ Obsd.	$[Ag]_{tot}$ Calcd.	$[Ag]_{tot}$ Obsd.	$[IO_3^-]_{tot}$ Obsd.	$[Ag]_{tot}$ Calcd.
For 25°					
37.0[b]	0.000722	45.2	90.2	0.000940	89.5
18.1[b]	.00187	18.2	35.4	.00248	34.0
7.03	.00421	8.46	14.5	.00540	15.6
6.85[b]	.00493	7.34	9.05	.0103	8.30
4.29[b]	.0101	3.86	1.96	.0501	1.93
3.30	.0110	3.59	1.68	.0634	1.60
3.05	.0151	2.73	1.38	.1001	1.21
2.12	.249	1.84	0.885	.2000	1.04
1.13	.0353	1.43	1.04	.298	1.13
1.11	.848	1.00	1.14	.400	1.31
0.978	.1023	0.865	1.33	.492	1.49
.993	.1180	.845	1.44	.596	1.71
.835	1.540	.849	2.27	.699	1.94
.915	.2042	.892	2.48	.754	2.06
1.04	.2580	.975	2.30	.998	2.63
For 35.0°					
87.5	0.000693	99.7	198	0.000900	193
28.0	.00272	27.2	64.3	.00265	66.1
15.1	.00435	17.5	34.4	.00544	32.4
8.66[b]	.00780	10.4	15.9	.0110	16.3
7.68	.0114	7.58	6.52	.0263	7.13
4.09	.0266	3.80	4.65	.0400	4.93
2.71	.0398	2.90	4.15	.0505	4.06
2.46	.0520	2.48	3.30	.0659	3.33
1.99	.0836	1.99	2.58	.101	2.56
1.73	.1023	1.88	2.52	.200	2.14
1.89	.1068	1.86	2.43	.305	2.28
1.69	.1279	1.81	2.21	.404	2.57
1.80	.1682	1.80	2.50	.501	2.81
1.74	.2292	1.91	3.67	.605	3.29
1.66	.2523	1.96	4.19	.707	3.78
1.97	.2700	2.01	3.48	.772	3.95
For 50°					
217	0.00914	206	409	0.00107	400
65.6	.00283	70.9	146	.00285	151
23.0[b]	.00800	27.8	71.5	.00583	74.7
19.9[b]	.0109	21.5	40.1	.0110	40.4
13.7	.0177	14.4	18.3	.0253	18.6
7.26	.0395	8.15	11.3	0.0414	12.1
3.64	.1008	5.12	9.72	.0515	10.2
4.05	.1317	4.75	7.95	.0694	8.22
4.24	.1580	4.62	6.21	.1030	6.22
4.34	.2660	4.70	5.31	.207	5.12
			6.35	.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	.810	7.91
			8.96	.998	9.16

[a] All silver concentrations are in units of moles/liter × 10^6 and all iodate concentrations are in units of moles/liter.
[b] These values were obtained with silver of specific activity 1.98 × 10^6 counts/minute mg. All other values were obtained with silver of specific activity 2.89 × 10^5 counts/minute mg.

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(4) C. E. Crouthamel and D. S. Martin, Jr., THIS JOURNAL, **73**, 569 (1951).

is satisfactorily described by the three equilibria

$$AgIO_3(s) \rightleftarrows Ag^+ + IO_3^-;\ K_{sp} \qquad (1)$$

$$Ag^+ + IO_3^- \rightleftarrows AgIO_3(aq);\ K_1 \qquad (2)$$

$$Ag^+ + 2IO_3^- \rightleftarrows Ag(IO_3)_2^-;\ K_2 \qquad (3)$$

Formation equilibrium constants for the two iodato complexes and the equilibrium solubility product constant are represented by the scheme

$$K_{sp} = [Ag^+][IO_3^-]\gamma_\pm^2 \qquad (4)$$

$$K_1 = [AgIO_3(aq)]\gamma_0/[Ag^+][IO_3^-]\gamma_\pm^2 \qquad (5)$$

$$K_2 = [Ag(IO_3)_2^-]\gamma_2/[Ag^+][IO_3^-]^2\gamma_\pm^2\gamma_- \qquad (6)$$

where γ_- is the activity coefficient for IO_3^-, γ_0 is the activity coefficient for $AgIO_{3(aq)}$, γ_2 is the activity coefficient for $Ag(IO_3)_2^-$, $\gamma_\pm$ is the mean ionic activity coefficient for $AgIO_2$ in the equilibrium solutions, and brackets denote concentrations in moles/liter.

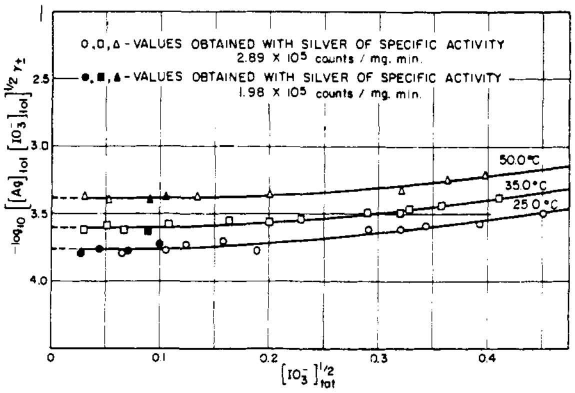

Fig. 3.—Experimental plots for the evaluation of solubility product constant, K_{sp}.

The molar concentration of each silver bearing species is formulated as a function of the total iodate concentration and the activity coefficients. A summation of these molarities represents the total silver concentration in an equilibrium solution, $[Ag]_{tot}$, the quantity determined by the radioassay. In equation form

$$[Ag]_{tot} = [Ag^+] + [AgIO_3(aq)] + [Ag(IO_3)_2^-] \qquad (7)$$

$$[Ag]_{tot} = K_{sp}/\gamma_\pm^2[IO_3^-]_{tot} + K_1K_{sp}/\gamma_0 + K_2K_{sp}[IO_3^-]_{tot}\,\gamma_-/\gamma_2 \qquad (8)$$

Unfortunately the degree of iodato complexing in the concentration region for which it was valid to use the interpolated activity coefficients was not extensive. This fact required the evaluation of K_1 and K_2 from experiments in which the ionic strength was constant. Equilibrium solubility product constants were conveniently secured from the data obtained for solutions in which the ionic strength varied. Equation 8 was simplified for application to data taken for constant ionic strength by the approximation that activity coefficients were effectively constant and could be included in the equilibrium constants to form a set of three concentration constants. The total silver was then given by

$$[Ag]_{tot} = K_A/[IO_3^-]_{tot} + K_B + K_C\,[IO_3^-]_{tot} \qquad (9)$$

Determination of the Equilibrium Solubility Product Constants. A form of equation 8 that is convenient for determining equilibrium solubility product constants is given by equation 10

$$\log_{10}([Ag]_{tot}[IO_3^-]_{tot})^{1/2}\gamma_\pm = \log_{10}(K_{sp} + K_1K_{sp}[IO_3^-]_{tot}/\gamma_0 + K_2K_{sp}\gamma_-[IO_3^-]_{tot}^2/\gamma_2)^{1/2} \qquad (10)$$

It predicts that a plot of $\log_{10}([Ag]_{tot}[IO_3^-]_{tot})^{1/2}$ $\gamma_\pm$ must approach $^1/_2\log_{10}K_{sp}$ with a small slope as $[IO_3]_{tot}^{1/2}$ approaches zero. Plots of equation 10 for the data at the three temperatures studied are given in Fig. 3. The dashed sections indicate the extrapolations to zero ionic strength. Values of the equilibrium solubility product constants are contained in Table II.

TABLE II

EQUILIBRIUM SOLUBILITY PRODUCTS FOR $AgIO_3$ AND FORMATION CONSTANTS FOR IODATO COMPLEXES OF SILVER

Temp., °C.	$K_{sp} \times 10^8$	$K_A \times 10^7$	$K_B \times 10^7$	$K_C \times 10^6$
25.0	3.0 ± 0.15	0.84 ± 0.02	1.3 ± 0.8	2.42 ± 0.16
35.0	6.3 ± .3	1.74 ± .04	4.1 ± 1.2	4.29 ± .28
50.0	17.4 ± 1.0	4.26 ± .10	15.8 ± 1.8	7.16 ± .33

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 $\log[Ag]_{tot}[IO_3^-]_{tot}$ *vs.* $[IO_3^-]_{tot}^{1/2}$ and extrapolating to an iodate concentration of zero. These functions have been graphed in Fig. 4. Good extrapolations were possible since the experimental curves approached the vertical axis at an extremely small angle from the horizontal.

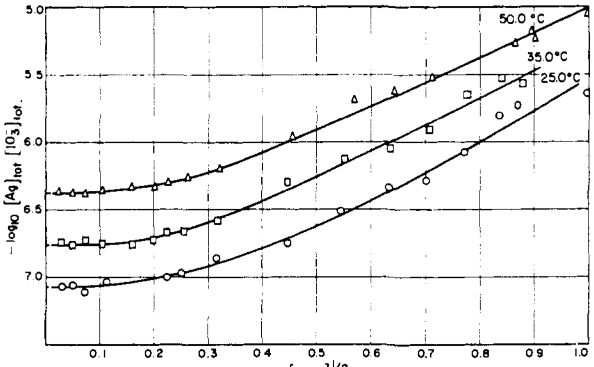

Fig. 4.—Experimental plots for the evaluation of the concentration solubility product, K_A, for solutions with ionic strengths of 1.00.

Equation 9 was also employed for the evaluation of K_B and K_C. By subtracting the term containing K_A from the experimental values of $[Ag]_{tot}$ and plotting differences *vs.* $[IO_3^-]_{tot}$ a straight line function was obtained having an intercept of K_B and a slope equal to K_C. The 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 Fig. 5, and the concentration equilibrium constants have been presented in Table II.

Thermodynamic Properties.—Thermodynamic functions for the chemical equilibria represented by equations 2 and 3 have been estimated from the equilibrium constants K_1 and K_2 and their variations with temperature. These functions are given in Table III.

TABLE III

STANDARD FREE ENERGY, ENTHALPY AND ENTROPY CHANGES FOR THE REACTIONS (35.0°)

$$Ag^+ + nIO_3^- \rightleftarrows Ag(IO_3)_n^{n-1}$$

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

To convert K_B and K_C to equilibrium formation constants K_1 and K_2, the accurate values of the equilibrium solubility product constants for 25.0 and 35.0° of 3.06×10^{-8} and 6.46×10^{-8} reported by Li and Lo[5] were employed with the approximations that $\gamma_0 = 1$ and $\gamma_-/\gamma_2 = 1$. For 50.0° the experimental value given in Table II was used since none had been reported previously for this temperature.

Ionic entropies of 17.5 e.u. for silver ion and 28.0 e.u. for iodate ion given by Latimer, Pitzer and Smith[6] and Latimer,[7] respectively, were employed to estimate partial molar entropies of the iodato complexes. According to the method of Cobble[8] for estimating entropy changes associated with the complexing of a simple ion by ionic ligands, ΔS for reaction 2 was calculated to be -6 e.u. and ΔS for reaction 3 was estimated to be -21.6 e.u. These values are in fair agreement with the experimental values given in Table III, considering the experimental uncertainties.

The constants of Tables II and III were used in conjunction with equations 8 and 9 to calculate solubilities for the various equilibrium solutions, and these have been included in Table I and plotted in Figs. 1 and 2 for comparison with the experimental results. As a test for the fit of equations 8 and 9 with the equilibrium constants of Table II to the experimental data, the quantity, $\sqrt{\Sigma\delta_i^2/N}$, was computed in which δ_i was $(\log[Ag]_{tot\text{-}obsd.} - \log[Ag]_{tot\text{-}calcd.})$, and the summation was over the N determinations in each set. The values obtained for each set fell in the range 0.028–0.052. The measured solubilities for experiments performed for variable ionic strength were therefore well represented by the calculated solubilities. Consequently, the basic approximations regarding activity coefficients in the equilibrium solutions at the constant ionic strength of 1.00 M have yielded an equilibrium description which was consistent with the solubilities in solutions of low, variable ionic strengths.

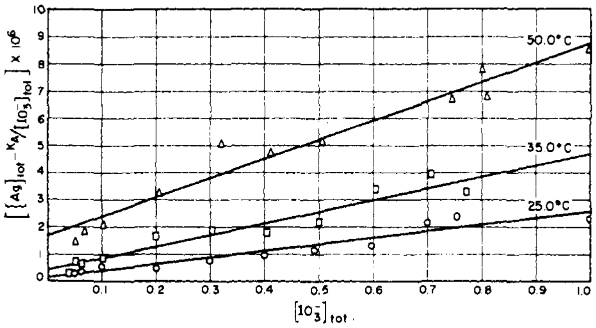

Fig. 5.—Plots for the evaluation of concentration equilibrium constants, K_B and K_C, for solutions with ionic strengths of 1.00. Straight lines given by least-squares treatment.

The equilibrium solubility product constants which were obtained in this investigation for 25.0 and 35.0° were in good agreement with the values of Li and Lo.[5] This fact and the additional fact that measurements performed with silver of different specific activities were compatible with one another were strong evidence for the consistency of the data and indicated that procedures employed for the removal of radiotracer impurities from the radiosilver and for the preparation of the radioactive stock solutions of Ag^{111m} were adequate.

When the results of this investigation are compared with those for the analogous chloro complexes of silver,[9,10] it is seen that the degree of complexing of silver ion 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 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 is slight; however, the opposite tendency was observed in the case of manganese(III) and manganese(IV).[11]

The magnitudes of the equilibrium formation constants K_1 and K_2 were not great and in the case of the measurements at 50.0° were separated by only a factor of five. These facts are strongly reflected in the precision indexes reported for these quantities in Table II; nevertheless, values for K_2 may be considered to be rather well established.

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