

Studies on Ionic Solutions in Diethyl Ether

III. Studies on the Soluble Silver-Iodide Complex formed in LiClO₄-Ether Solution

BERNER ALIN, LARS EVERS, and LARS GUNNAR SILLÉN

*Department of Inorganic Chemistry, Royal Institute of Technology, and
Institute of Inorganic and Physical Chemistry, University, Stockholm, Sweden*

As described in Part II in this series^{1,2}, Althin, Wählin, and Sillén² made potentiometric titrations of Ag⁺ with Cl⁻, Br⁻ and I⁻ in LiClO₄-ether medium. Using silver electrodes, they obtained curves of the same type as for the corresponding titrations in aqueous medium, and could calculate the solubility products for AgCl and AgBr in LiClO₄-ether, just as it is usually done in H₂O. For AgI, however, an unexpected complication arose. The precipitate of AgI first formed was found to dissolve in excess of I⁻; even for I⁻ concentrations as low as 50 mC, the solubility of AgI proved to be considerable (more than 1 mC, as found from the figures below).

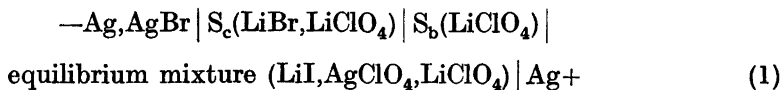
It is true that a similar phenomenon is observed in aqueous solutions^{3,4}; the I⁻ excess needed there is, however, larger. For instance, Erber⁴ found that 0.82 C HI dissolves 4.3 mC AgI, 1.02 C HI dissolves 9.7 mC AgI, and 8.09 C HI dissolves 5.22 C AgI. There is some uncertainty about the composition of the soluble complex in aqueous solutions. From the predominance of bivalent silver complexes such Ag(CN)₂⁻, and Ag(NH₃)₂⁺, one might expect the formula to be AgI₂⁻. However, Bodländer and Eberlein³, and Erber⁴ considered their data to be more consistent with formulas such as Ag₂I₇⁵⁻ and Ag₂I₆⁴⁻.

Althin, Wählin, and Sillén assumed the simplest formula, AgI₂⁻, and from this and their data calculated the complex formation constant for AgI₂⁻, and the solubility product for AgI. However, as stated by these authors, the results were only preliminary. With the apparatus and chemicals then used, a slow oxidation of the dissolved iodide ions took place so that the solutions, which were at first almost colorless, were colored light brown at the end of a titration.

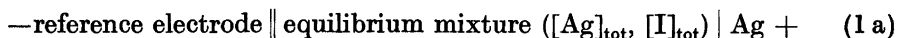
It seemed desirable to study these equilibria with an improved apparatus where this source of error was eliminated. This has now been done. Our results corroborate the work of Althin, Wåhlin, and Sillén, as regards the composition of the complex, and the magnitude of the complex constant and the solubility product.

PRINCIPLES

The cells used may be written schematically:



or



As a reference electrode, the Ag, AgBr electrode was chosen since it proved to keep a stable potential for a longer time than the corresponding electrode with Ag, AgI, and LiI.

In all solutions, diethyl ether was the solvent. In the solution to the right, the amount of LiClO₄ added was such as to keep $[\text{ClO}_4^-] + X_e = 1 \text{ C}$, where X_e is the halogenide excess defined by equation (14). The solution to the right was prepared by adding known amounts of one or two solutions (T, or T₁ and T₂) from burettes to an initial amount, usually 50 ml, of a solution S.

We shall now assume — as has been confirmed both by our data and the measurements in parts I and II^{1,2} — that because of the large excess of LiClO₄ we can neglect the diffusion potential and consider the activity factors of the various ions as constant. The emf of the cell, E , is then the difference between the electrode potential of the right electrode, e , and that of the reference electrode, e_{ref} .

$$E = e - e_{\text{ref}} \quad (2)$$

Moreover, if our assumptions hold true e varies with the concentration of the silver ions according to Nernst's equation (for 18° C)

$$e = e_{0\text{Ag}} + 57.77 \log [\text{Ag}^+] \quad (3)$$

By combining (2) and (3) we find

$$E - 57.77 \log [\text{Ag}^+] = e_{0\text{Ag}} - e_{\text{ref}} \quad (4)$$

In those parts of our titrations where we have an excess of Ag⁺ ions, both quantities to the left in equation (4) are known, and so the difference $e_{0\text{Ag}} - e_{\text{ref}}$ can be calculated. Our data like those in Part II² have shown that this expression keeps reasonably constant, as it should according to our assumptions.

When this constant is known, one may calculate also the low $[\text{Ag}^+]$ for solutions with excess of I^- . Of course, one must not postulate *a priori* that these very low concentrations are correct. However, just as for aqueous solutions they are supported by the fact that they fit in with a simple and plausible scheme for the equilibria in the solutions.

Let us denote the total analytical concentrations of silver and iodide ions added to the solution by $[\text{Ag}]_{\text{tot}}$ and $[\text{I}]_{\text{tot}}$ C (mole l^{-1}). From both these figures should be subtracted $[\text{AgI}]_{\text{prec}}$, the amount of AgI precipitated, expressed in mole l^{-1} . We shall assume that the solution contains, in addition to Ag^+ and I^- , only one soluble complex, $\text{Ag}_x\text{I}_y^{(y-x)-}$. (In the following we shall often leave out its charge for the sake of brevity.)

Denoting the equilibrium constant for the complex formation by κ we have

$$[\text{Ag}_x\text{I}_y] = \kappa [\text{Ag}^+]^x [\text{I}^-]^y \quad (5)$$

The content conditions are

$$[\text{I}]_{\text{tot}} = [\text{I}^-] + [\text{AgI}]_{\text{prec}} + y [\text{Ag}_x\text{I}_y] \quad (6)$$

$$[\text{Ag}]_{\text{tot}} = [\text{Ag}^+] + [\text{AgI}]_{\text{prec}} + x [\text{Ag}_x\text{I}_y] \quad (7)$$

The equations hitherto given should hold true for all points in any of our titrations. We shall now consider the special case of solutions with iodide excess, thus $[\text{I}]_{\text{tot}} > [\text{Ag}]_{\text{tot}}$. In such solutions, $[\text{Ag}^+]$ may be neglected in comparison with the other quantities in (7).

In a *clear solution*,

$$[\text{AgI}]_{\text{prec}} = 0$$

$$[\text{Ag}_x\text{I}_y] = x^{-1} [\text{Ag}]_{\text{tot}} \quad (8)$$

and

$$[\text{I}^-] = [\text{I}]_{\text{tot}} - yx^{-1} [\text{Ag}]_{\text{tot}} \quad (9)$$

as is easily seen from (6) and (7). By taking logarithms in (5) and rearranging we find, using (8) and (9)

$$\log \kappa = \log [\text{Ag}]_{\text{tot}} - \log x - x \log [\text{Ag}^+] - y \log ([\text{I}]_{\text{tot}} - yx^{-1} [\text{Ag}]_{\text{tot}}) \quad (10)$$

With the special assumption that the complex is AgI_2^- , (10) takes the form

$$\log \kappa = \log [\text{Ag}]_{\text{tot}} - \log [\text{Ag}^+] - 2 \log ([\text{I}]_{\text{tot}} - 2 [\text{Ag}]_{\text{tot}}) \quad (11)$$

In equation (10), $[\text{I}]_{\text{tot}}$ and $[\text{Ag}]_{\text{tot}}$ are known from the analyses and the volumes added, and $[\text{Ag}^+]$ is known from the emf measurements. One may thus, for a titration, try various values for x and y , calculate κ by means of (10)

and test which set of x and y gives the best constancy in κ . As will be seen below our data point to the composition AgI_2^- .

For a solution with *precipitated AgI present*, we have the additional equilibrium condition

$$[\text{Ag}^+][\text{I}^-] = k_s \quad (12)$$

From (5) and (12) we find

$$[\text{Ag}_x\text{I}_y] = \kappa k_s^x [\text{I}^-]^{(y-x)} \quad (13)$$

The excess of iodide ions, X_e is defined by

$$X_e = [\text{I}]_{\text{tot}} - [\text{Ag}]_{\text{tot}} \quad (14)$$

We find from (6), (7), (14), and (13)

$$X_e = [\text{I}^-] + (y-x) [\text{Ag}_x\text{I}_y] = [\text{I}^-] + (y-x) \kappa k_s^x [\text{I}^-]^{(y-x)} \quad (15)$$

If we had neglected the formation of the soluble complex, set $[\text{I}^-] = X_e$, and tried to calculate the solubility product, we would have got an apparent solubility product k'_s ,

$$k'_s = [\text{Ag}^+]X_e = k_s (1 + (y-x) \kappa k_s^x [\text{I}^-]^{(y-x-1)}) \quad (16)$$

The apparent solubility product will thus in general vary with $[\text{I}^-]$. However, in the special case where the complex is AgI_2^- we have

$$k'_s = k_s (1 + \kappa k_s) \quad (17)$$

which should be independent of $[\text{I}^-]$. In this case the simplest way of treating the data is by first calculating the quantity

$$e'_{0\text{AgI}} - e_{\text{ref}} = E + 57.77 \log X_e \quad (18)$$

which should be a constant. By combining (4) and (18) we obtain

$$(e'_{0\text{AgI}} - e_{\text{ref}}) - (e_{0\text{Ag}} - e_{\text{ref}}) = 57.77 \log k'_s \quad (19)$$

One thus first computes with (18) an average value for $(e'_{0\text{AgI}} - e_{\text{ref}})$, then the average k'_s with (19) and finally by means of (17) and the κ value determined before, one finds the real k_s .

In this connection we should like to point out two printing errors in Part II. Equation (II, 8) should be $X_e = [\text{I}]_{\text{tot}} - [\text{Ag}]_{\text{tot}}$ like (14) here, and (II, 12) should be $\log k'_s = 58.86^{-1} (e'_{0\text{AgI}} - e_{0\text{Ag}})$, in analogy to (19) in this paper.

REAGENTS

Purest available anhydrous *diethyl ether* was refluxed over sodium for 2–4 hours in a nitrogen atmosphere. After discarding the first portion, the ether was distilled directly into a vessel where the solid salt to be dissolved was stored under nitrogen. This was the same vessel where the salt had previously been dried (except for LiI, see below).

In order to exclude daylight, the whole room was blacked out, and only subdued artificial light was used. Moreover the whole apparatus was always wrapped in black paper when ether and LiI were present.

Lithium perchlorate and *lithium bromide* were obtained as described in Part I, *silver perchlorate* as described in Part II.

Lithium iodide (anhydrous) was purchased in Baker's BPC quality. A 25 g package was opened, and the whole contents transferred without delay to a vessel previously filled with nitrogen and connected to a distillation apparatus. By this procedure, the LiI solution was shielded from oxygen and light, so that it remained colorless for several weeks.

The solutions were analysed in the ways described in Parts I–II.

The *nitrogen* used in all preparations and experiments was previously purified and dried by Meyer and Ronge's method ⁶.

APPARATUS

The apparatus was so constructed that all operations could be carried out in a nitrogen atmosphere, without the admission of even traces of air. The solutions were stored in flasks like that in Fig. 1; a ground stopper with one plain hole and one hole connected to a long glass tube. By turning the stopper, these holes may either be shut, or connected in two different ways to two tubes sealed to the outer side of the neck. Nitrogen may be flushed over the solution in the flask, and the solution may be pressed out by tilting the flask and applying nitrogen pressure; the idea is the same as in an apparatus used in previous work on aqueous solutions (Sillén ⁵, Fig. 2).

The most suitable stopcock grease in both this and other parts of the apparatus proved to be a mixture of glycerol and starch, heated to 140° C; this grease is insoluble in ether and in the ether solutions used.

The solutions S and T to be used in the titrations were prepared by mixing measured amounts of stock solutions and pure ether in measuring flasks on the top of which was sealed a joint like that in Fig. 1. The stock solutions were added through the apparatus shown in Fig. 2. The central bulb, the "mixer", of volume about 500 ml, was provided with holes for four burettes, with one hole for evacuating and admitting nitrogen, and with a stopcock. The inner part of the stopcock was provided with a little funnel through which the solutions could be directed to either of four different outlets, each of which could be connected to a measuring flask.

First the calculated volume of LiI, AgClO₄, or LiBr solution was added to a certain measuring flask. Then

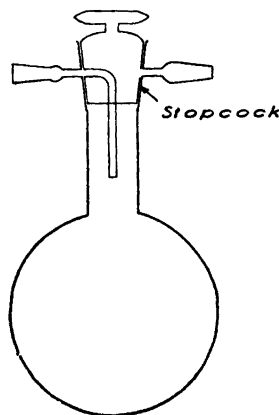


Fig. 1. Flask for storing solutions under nitrogen.

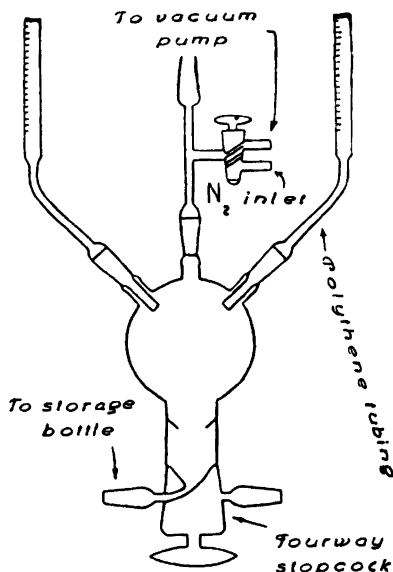


Fig. 2. "Mixer" for preparing solutions of known composition. The central tube goes to the pressure levelling system.

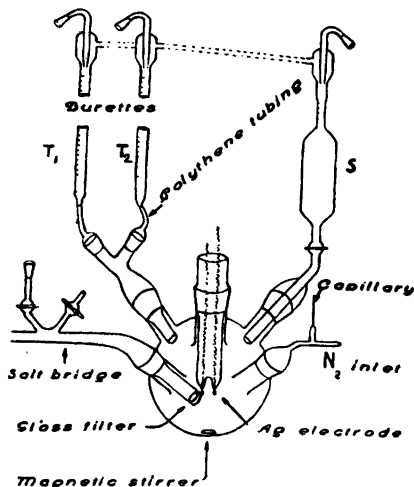


Fig. 3. Main parts of titration apparatus.

we added the calculated volume of LiClO₄ solution and finally pure ether until the mark was reached in the measuring bulb. In this way the inorganic salts were washed out of the mixer before the next measuring flask was to be filled.

Instead of with stopcocks the burettes were closed with a short polythene tubing containing a small "glass-bead valve". In this way the apparatus became more flexible and less liable to break than if it had been made entirely of glass: moreover stopcocks were undesirable since ether under pressure has a strong tendency to creep out even through closed and greased stopcocks. In order to level out the pressure the nitrogen in the upper part of the burettes (cf. Fig. 3) was connected to the mixing bulb by the central tube in Fig. 2.

By means of this apparatus a number of solutions could be mixed in one procedure, without admitting air.

The titrations were carried out in a complicated apparatus, the principal parts of which are drawn schematically in Fig. 3.

After assembling the cell with its electrodes and burettes, the air was expelled from it by alternately evacuating and letting in nitrogen. In order to keep out oxygen and moisture, even in the case of small leakages, a certain overpressure of nitrogen was maintained in it. The nitrogen inlet was provided with a T-tube with a small capillary tube through which a stream of nitrogen continuously poured out.

The initial solution S was measured in the vessel to the right of the figure, and added by turning the stopcock. (The pressure was levelled out here as in the burettes.) The solutions T₁ and T₂ to be added in the titration were kept in burettes, closed by polythene tubings with glass-bead valves.

The reference electrode vessel was similar to the titration vessel and always contained 100 mC LiBr, 900 mC LiClO₄ (= S_c). The silver and Ag, AgBr electrodes were prepared as described in Part II. The salt bridge was partly made of polythene tubing; it was provided at both ends with sintered glass filters Jena G4, which easily let through gases on evacuation or flushing with nitrogen, but which were rather efficient barriers to the diffusion of the viscous LiClO₄-ether solutions. The salt bridge was wide enough to be filled directly without applying a suction, which would have caused the loss of an unknown amount of solution from the titration vessel. With our apparatus the whole cell could be filled with nitrogen and the air expelled by means of a single gas inlet.

The solution in the titration vessel was agitated by means of a magnetic stirrer.

Since it would have been exceedingly difficult to keep this complicated apparatus immersed in a liquid bath, the whole apparatus was kept in a thermostat room, the air temperature of which varied within the limits $18.0 \pm 0.2^\circ \text{C}$. The variations of the temperature in the solutions was probably still less.

The emf measurements were carried out with a valve potentiometer (Radiometer PHM 3 g).

RESULTS

Table 1 gives a survey of the 5 titrations performed. In titrations 1 and 2 there was Ag⁺ in S and I⁻ in T, in titrations 3–5 S contained I⁻ and T Ag⁺. In the latter case two different T solutions were used, one with about 5 mC Ag⁺ (T₁), and one with about 50 mC (T₂). At the beginning of such a titration, the solution T₁ with the lower Ag⁺ content was added. After a precipitate of AgI had formed, the Ag⁺ content was raised more sharply by adding T₂. A constant *E* value was usually found within 15 minutes after each addition of T.

Table 2 gives the results of a titration (nr 4) with I⁻ in S and Ag⁺ in T. The table is almost self-explanatory. When 18 ml T₁ had been added, a precipitate of AgI was visible. Altogether 25 ml T₁ was added, and then T₂ was added from the other burette.

Table 1. Survey of the titrations.

Titr. nr.	Ion	S (50 ml) mC	Ion	T ₁ mC	Total volume added	T ₂ mC	Total volume added
1	Ag ⁺	15.0	I ⁻	225.0	75		
2	Ag ⁺	15.0	I ⁻	225.0	31		
3	I ⁻	54.6	Ag ⁺	15.0	8	50.0	40
4	I ⁻	50.4	Ag ⁺	5.0	25	75.6	45
5	I ⁻	53.5	Ag ⁺	5.0	20	68.0	75

All solutions in addition contained Li⁺ and ClO₄⁻ so as to make $[\text{ClO}_4^-] + X_e = 1\text{C}$.

Table 2. Details of titration nr. 4.

ml T ₁	ml T ₂	Total volume T ₁ + T ₂	[I ⁻] _{tot} mC	[Ag ⁺] _{tot} mC	X _e mC	E mV	e' _{oAgI} - e _{ref} mV	log κ
2			48.5	0.192	48.3	-285		21.92
3			47.5	0.283	47.2	-274		21.92
4			46.7	0.370	46.3	-266		21.92
5			45.8	0.454	45.3	-259		21.91
6			45.0	0.536	44.5	-253		21.89
7			44.2	0.614	43.6	-248		21.89
8			43.5	0.690	42.8	-241		21.83
9			42.7	0.763	41.9	-237		21.83
10			42.0	0.833	41.2	-235		21.85
11			41.3	0.902	40.4	-234		21.88
12			40.7	0.968	39.7	-232		21.90
13			40.0	1.04	39.0	-230	-311	21.91
14			39.4	1.09	38.3	-229	-311	21.93
15			38.8	1.15	37.6	-228	-310	21.96
16			38.2	1.21	37.0	-224	-307	21.92
17			37.6	1.27	36.3	-222	-305	21.93
18			37.1	1.32	35.8	-221	-305	21.94
19			36.5	1.38	35.1	-227	-311	
25		25	33.6	1.67	31.9	-225	-311	
	5	30	31.5	6.29	25.2	-217	-309	
	10	35	29.7	10.4	19.3	-208	-307	
	15	40	28.0	14.0	14.0	-197	-304	
	20	45	26.5	17.2	9.3	-175	-292	
	25	50	25.2	20.2	5.0	-144	-277	
	30	55	24.0	22.8	1.2	-74	-243	
					[Ag ⁺]		e' _{oAg} - e _{ref}	
		57	23.6	23.8	0.2	+865	[+1079]	
		60	22.9	25.2	2.3	+892	+1044	
		62	22.5	26.1	3.6	+904	+1045	
		64	22.1	27.0	4.9	+911	+1044	
		66	21.7	27.8	6.1	+917	+1045	
		68	21.4	28.6	7.2	+920	+1044	
		70	21.0	29.4	8.4	+924	+1044	

Average e_{oAg} - e_{ref} = + 1044 ± 1 mV

Average log κ' = 21.90

Average e'_{oAgI} - e_{ref} = - 308 ± 4 mV

log κ = 21.89

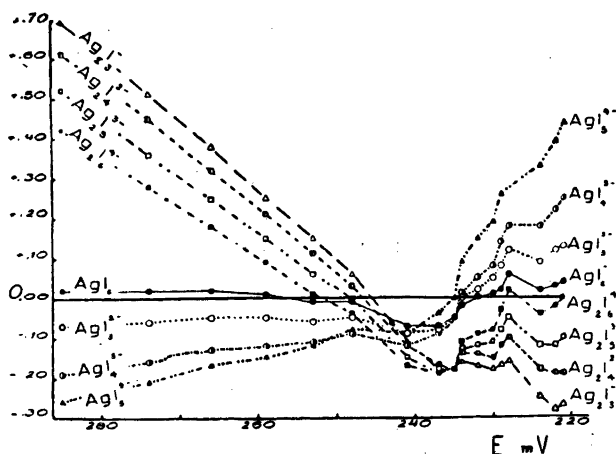


Fig. 4. Testing the constancy of κ for various possible formulas of the soluble complex, using the data of titration 4.

In order to find out the formula of the complex, we tried a number of possible compositions Ag_xI_y of the complex, and calculated $\log \kappa$ by means of equation (10) from the points obtained before a visible precipitate had formed. The results are shown graphically in Fig. 4, where the deviations of $\log \kappa$ from an arbitrary intermediate value are plotted for each set of x and y against E . It is seen immediately that all complexes containing 2 Ag are ruled out since they give a very strong trend in the "constant". A still greater slope would have been obtained by assuming complexes with more than 2 Ag. We thus conclude that the predominant complex formed is mononuclear. Of the mononuclear complexes tried, AgI_4^{3-} and AgI_5^{4-} are completely ruled out, and the constancy is decidedly better for AgI_2^- than for AgI_3^{2-} .

We thus feel justified in assuming that the predominant soluble complex is AgI_2^- , which is made still more plausible by the analogy with other bivalent silver complexes.

Table 3 gives the mean values of the following quantities from five different titrations: $e_{0\text{Ag}} - e_{\text{ref}}$ from (4), $e'_{0\text{AgI}} - e_{\text{ref}}$ from (18), $e_{0\text{Ag}} - e'_{0\text{AgI}}$, pk'_s from (19), and $\log \kappa$ from (11). For titration 5, two sets of values are listed. The values in parentheses were obtained by using all measured points with Ag^+ excess. However, a comparison with the other titrations made it exceedingly probable that the first few points after the equivalence point had been measured without waiting sufficiently long for the equilibrium. On excluding these values, we obtained the set of figures actually used.

Table 3. Average values for constants from the titrations.

Titr.	$e_{\text{oAg}} - e_{\text{ref}}$	$e'_{\text{oAgI}} - e_{\text{ref}}$	$e_{\text{oAg}} - e'_{\text{oAgI}}$	pk'	$\log \kappa'$	$\log \kappa$
1	+1042	-315	+1357	23.49		
2	1041	-315	1356	23.47		
3	1040	-314	1354	23.44	21.86	21.85
4	1044	-308	1352	23.40	21.90	21.89
5	1055	-298	1353	23.42	21.78	21.76
	(1048)		(1346)	(23.30)	(21.66)	(21.64)
	Mean values		1355 ± 3	23.45 ± 0.05	21.85 ± 0.07	21.83 ± 0.07

For titrations 1 and 2 no $\log \kappa$ values are given for the simple reason that a perfectly clear solution was never obtained in these titrations. There was always AgI present, as was easily understood when the equilibrium constants later on became known. (Cf. ref. 24 and Table 1.)

When approximative values for κ and k_s are found, one may calculate at what point AgI would have precipitated in the solutions if equilibrium had always been achieved. For a solution at equilibrium with solid AgI, (13) gives inserting $x = 1$ and $y = 2$

$$[\text{AgI}_2^-] = \kappa k_s [\text{I}^-] \quad (20)$$

One may prove from (20), (8), and (9) that in a clear solution where AgI is just about to precipitate

$$\frac{[\text{Ag}]_{\text{tot}}}{[\text{I}]_{\text{tot}}} = \frac{\kappa k_s}{1 + 2\kappa k_s} \quad (21)$$

Fig. 5 gives corresponding values of $[\text{I}]_{\text{tot}}$ and $[\text{Ag}]_{\text{tot}}$ for the points of three titrations, starting with I^- in S. (Titrations nr 3, 4, and 5.) The thick line crossing the titration lines corresponds to equation (21), and thus gives the points where AgI would have precipitated at equilibrium. The points, where a precipitate was actually first observed, are marked by arrows. To be strict, one should perhaps exclude all points corresponding to supersaturated solutions (points between the thick line and the arrow) in taking the average value of κ . This has been done in the last column, $\log \kappa$, in Table 3; in the column next to the last, $\log \kappa'$ was obtained using all values where a precipitate was not observed. For instance in titration 4, all values in the "log κ " column of Table 2 were used for calculating $\log \kappa'$, but those within brackets were excluded in calculating $\log \kappa$.

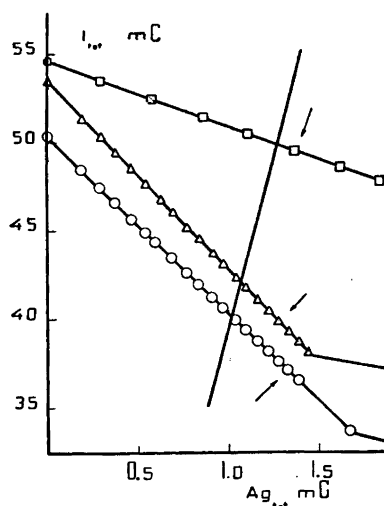
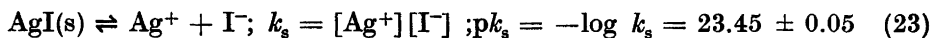
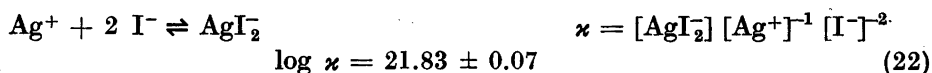
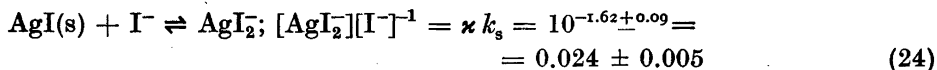


Fig. 5. Plot of $[I]_{\text{tot}}$ versus $[Ag]_{\text{tot}}$. Lines with marks, points of titrations 3, 4 and 5. To the right of the thick line, solid Ag I should be present at equilibrium. At the arrows, precipitate was actually observed.

Using equation (17) and the mean values in Table 3, we find as our final values:



which gives



These values should be valid under our experimental conditions, in ether solutions containing 1 C LiClO_4 , at 18°C . They may be compared with the preliminary values in Part II: $\text{p}k_s = 22.8$ and $\kappa = (2 \pm 1) \cdot 10^{22}$ for 23.5°C ; the earlier measurements thus gave the right order of magnitude, in spite of the sources of error mentioned above.

SUMMARY

An improved equipment is described for electrometric titrations of ionic solutions in LiClO_4 -ether medium. The following operations can be carried out in a nitrogen atmosphere, with the exclusion of oxygen and moisture; stock solutions of LiClO_4 and various other salts in ether are prepared; ether and stock solutions are mixed in definite proportions to give the concentrations

and ionic strength desired; titrations are carried out, adding one solution from a burette to a measured amount of another; and the emf is measured between an electrode in the titrated solution and a reference electrode also in LiClO₄-ether medium.

In LiClO₄-ether medium, AgI is soluble in excess of I⁻; this occurs at lower I⁻ than in aqueous solutions. By titrations in 1 C LiClO₄-ether, the soluble complex was shown to be very probably AgI₂⁻. The equilibrium constants at 18° C in this medium were found to be; $k_s = [Ag^+][I^-] = 10^{-23.45 \pm 0.05} C^2$. $\kappa = [AgI_2^-][Ag^+]^{-1}[I^-]^{-2} = 10^{-21.83 \pm 0.07} C^{-1}$ and $[AgI_2^-][I^-]^{-1} = 0.024 \pm 0.005$.

This work has been supported by a grant from *Statens Naturvetenskapliga Forskningsråd* (Research Council for Scientific Research) which is gratefully acknowledged.

We wish to thank Professor Karl Myrbäck for the kind interest he has shown in this work and Professor Arne Ölander for allowing us to work in his institution. We have had valuable discussions with Mrs. Ulla Larsson-Berglund, Mrs. Karin Ekelin, Mr. Bengt Althin, and Mr. Erik Wählin.

ERRATA

In Part II, Table 1, a few errors have unfortunately slipped in. The v values from 27.1 on are too high by 0.5, and the chloride concentration in S is 0.0160 C instead of 0.0161. In the calculations, more digits were sometimes used than are given in the Tables. — With the correct values, the value for $e_{0Ag} - e_{0AgCl}$ from this experiment comes out as 846.0 instead of 845.6. This does not change the average mean value for pk_s for AgCl in the solvent.

REFERENCES

1. Berglund, U., and Sillén, L. G. *Acta Chem. Scand.* **2** (1948) 116 (Part I).
2. Althin, B., Wählin, E., and Sillén, L. G. *Acta Chem. Scand.* **3** (1949) 321 (Part II).
3. Bodländer, G., and Eberlein, W. *Z. anorg. Chem.* **39** (1904) 197.
4. Erber, W. *Z. anorg. u. allgem. Chem.* **248** (1941) 36.
5. Sillén, L. G. *Svensk Kem. Tid.* **58** (1946) 56.
6. Meyer, F. R., and Ronge, G. *Angew. Chem.* **52** (1939) 637.

Received June 29, 1951.