THE SOLUBILITY OF SILVER CHLORIDE

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The solubility of silver chloride in water, which at 25° is of the order of 2 milligrams per litre, is sufficiently great to cause appreciable errors in accurate analytical work if not allowed for, while in atomic weight determinations involving the precipitation of silver chloride, a knowledge of the solubility is essential. The relation between the solubility determined by the conductivity method and by other means is also of theoretical importance and it is therefore not surprising to find that numerous papers on the subject have been published. Of these the majority refer to the solubility in water, and very little information is available regarding the solubility in nitric acid or salt solutions in which silver chloride is usually precipitated.

The available data for water are shown in Table I, the solubility being expressed in moles. per litre x 10^5. For the purpose of comparison, the values at 25° are given in column 6; these when not recorded directly, have been obtained either by interpolation from the results at other temperatures or, when these are not available, by assuming that the change in solubility in the region under consideration is the same as the one found in our experiments.

The variations in these figures are distinctly larger than might be expected and suggest that factors are present which have not been taken into consideration when presenting the results. One possibility is that some of the methods are inherently wrong or are subject to constant errors. A comparison of results obtained by the same method shows however that this is not a sufficient reason and it is much more probable that the explanation is to be found in the varying solubility of silver chloride according to its method of preparation and subsequent treatment. As long ago as 1871, Stas (*Compt. rend.*, 1871, **73**, 1000) observed that precipitated silver chloride could exist in four different forms which he designated as gelatinous, flocculent, powdery or granular. The solubility of these varied from 19mg./l. for the gelatinous variety to 0.02 mg./l. for the granular. Although the results obtained by Stas cannot be considered very accurate and his observation regarding the low solubility of the granular variety has not been confirmed, his remarks suggest that unless similar specimens are employed for solubility determinations, the values obtained will not be comparable.

Richards and Wells (*J. Amer. Chem. Soc.*, 1905, **27**, 485) observed that if silver chloride was filtered immediately after precipi-

TABLE I.

Solubility of silver chloride in water

No.	Authors	Method employed	Tempe-rature	Solubi-lity	Solubi-lity at 25°	Reference
1	Holleman ...	Conductivity ...	13·8 26·5	0·97 1·82	1·74	*Z. physikal Chem.*, 1893 **12**, 132.
2	Kohlrausch and Rose.	do. ...	2·0 10·0 18·0 26·0 34·0 42·0	0·53 0·68 1·06 1·56 2·11 2·82	1·50	*ibid.*, 1893, **12**, 242.
3	Böttger ...	do. ...	19·95	1·07	1·34	*ibid.*, 1903, **46**, 603.
4	Kohlrausch ...	do. ...	18·0	1·12	1·56	*ibid.*, 1905, **50**, 356.
5	Do. ...	do. ...	1·55 4·68 9·97 17·51 18·0 25·86 34·12	0·39 0·46 0·62 0·91 0·93 1·35 1·91	1·30	*ibid.*, 1908, **64**, 168.
6	Melcher ...	do. ...	18·0	1·05	1·42	*J. Amer. Chem. Soc.*, 1910, **32**, 50.
7a	Van Rossem ...	do. ...	18·0 25·0	1·04 1·43	1·43	*Chem. Weekblad.*, 1912, **9**, 396.
7b	Do. ...	E. M. F. ...	18·0 25·0	1·02 1·43	1·43	*idem.*
8	Goodwin ...	do. ...	25·0	1·25	1·25	*Z. physikal Chem.*, 1894, **13**, 645.
9	Thiel ...	do. ...	25·0	1·41	1·41	*Z. anorg. Chem.*, 1900, **24**, 57.
10	Abegg and Cox...	do. ...	25·0	1·25	1·25	*Z. physikal Chem.*, 1903, **46**, 1.
11	Pinkus and Berkolaiko.	E. M. F. and Nephelometric.	25·0	1·42	1·42	*J. Chim. physique*, 1930, **27**, 364.
12	Scott and Johnson.	Nephelometric ...	0·5	0·50	...	*J. Amer. Chem. Soc.*, 1930, **52**, 3586.
13	Rolla ...	Optical ...	18·0	1·20	1·57	*Atti. R. Acad. Lincei.* 1913, **22**, 2.
14	Hill ...	Volumetric ...	25·0	1·60	1·60	*J. Amer. Chem. Soc.* 1908, **30**, 74.
15	Glowczynski ...	do. ...	25·0	1·20	1·20	*Kolloidchem. Beih.*, 1914 **6**, 147.
16	Whitby ...	Colorimetric ...	21·0	1·07	1·29	*Z. anorg. Chem.*, 1910 **67**, 108.

No.	Authors	Method employed	Tempe-rature	Solubi-lity	Solubi-lity at 25°	Reference
17	P o p o ff and Neuman.	Tyndal beam	... 25·0	1·278	1·278	*J. Physical Chem.*, 1930, 1853.
18	Eversole and McLachlan.	do.	... 25·0	1·52	1·52	*J. Amer. Chem. Soc.*, 1932, **54**, 867.
19	Neuman ...	do.	... 25·0	1·273	1·273	*ibid.*, 1932, **54**, 2195.

tation the filtrate contained 1.5 mg./l. of silver chloride, whereas if filtration was deferred for several days, the quantity in solution fell to 1.1 mg./l. The difference is almost certainly due to aggregation of the particles and this aspect of the question has been discussed by Glowczynski (*loc. cit.*) who pointed out that a decrease in the degree of dispersion would lower the solubility.

The first seven determinations given in Table I were all made by the conductivity method, but the first two of them were not carried out under favourable experimental conditions. Determinations Nos. 3 and 5 were conducted with silver chloride precipitated from cold dilute solutions and washed with cold water. The conductivity was determined at closely regulated temperatures and the solution was protected from actinic light during the experiments. Böttger's value was the mean of thirty-two separate and concordant determinations and is in good agreement with the value 1.04 interpolated from Kohlrausch's figures. Melcher and Van Rossem's determinations (Nos. 6 and 7) appear to have been made with as much care as those of Kohlrausch or Böttger, but the silver chloride employed was obtained by precipitation* from boiling solutions, washing with hot water and drying. The results of Melcher are in agreement with those of Van Rossem but not with those of Böttger or Kohlrausch.

Determinations Nos. 7b, 8, 9 and 10 were carried out by the electromotive force method, but except in the case of No. 7b no details are given of the way in which the silver chloride was prepared. Abegg and Cox made a large number of determinations and obtained the value 1.25×10^{-5} *M./L.* (moles. per litre) identical with Goodwin's figure; Van Rossem, however, after a prolonged series of measurements arrived at the figure 1.43×10^{-5} *M./L.* identical with the value he had obtained by the conductivity method and in good agreement with the result obtained by Thiel. It appears highly probable that the discrepancy between the two sets of values is due to differences in the methods of preparing the silver chloride. The wide difference between the results of Glowczynski and of Hill who both made use of the thiocyanate method is probably to be ascribed to the same cause.

Scott and Johnson and also Pinkus and Berkolaiko employed the nephelometric method. The former authors described their silver chloride as 'flocculent' but as they worked only at 0.5° it is not possible to compare the results. Pinkus and Berkolaiko prepared silver chloride by the addition of a slight excess of 0.1N hydrochloric acid to silver nitrate solution and boiling the mixture. The precipitate was washed with cold water and the solubility determined within five hours of precipitation. Their results by the nephelometric and E.M.F. methods were in good agreement.

Popoff and Neuman and subsequently Neuman made several determinations by observing the concentration at which the Tyndal beam due to turbidity just made its appearance. A very high order of accuracy, viz. $1 \times 10^{-8} M./L.$ was claimed for this method, and the two sets of results are in close agreement, but the mean value 1.273×10^{-5} is at great variance with the figure 1.52×10^{-5} obtained by Eversole and McLachlan under similar experimental conditions. It therefore appears probable that the method involves some source of error which has not yet been determined.

The available data for the solubility of silver chloride in nitric acid and sodium nitrate of various concentrations are given in Table II. The concentration of nitric acid and sodium nitrate is expressed in moles. per litre and the solubility of silver chloride in $M./L \times 10^{-5}$

TABLE II.

Solubility of silver chloride in nitric acid and sodium nitrate solutions.

Glowczynski...	...	25°	HNO_3	0·0005	0·001	0·01	0·3
			AgCl	1·15	1·19	1·24	1·54
Eversole and McLachlan.		25°	HNO_3	0·0238	0·119	0·238	0·52
			AgCl	1·54	1·62	1·70	2·35
Scott and Johnson	...	0·5°	HNO_3	0·11	0·24	0·49	0·99
			AgCl	0·628	0·698	0·711	0·732
Mulder	...	... 15–20°	$NaNO_3$	0·047	0·093	0·355	...
			AgCl	6·7	9·3	17·6	...

The results of Mulder (*Die Silberprobirmethoden, Leipzig*, 1859) are very old and the exact temperature is not specified. They serve to indicate, however, that the solubility of silver chloride is largely increased by the addition of sodium nitrate, and the values are of the same order as those we have obtained.

The solubility of silver chloride in aqueous solutions of nitrates has also been studied by Popoff and Neuman (*loc. cit.*) but their work, was confined to solutions of very low concentrations of the order

0.00001-0.01 M. as the object in view was the study of the applicability of modern theories of strong electrolytes to such solutions.

To supplement these results we have determined the solubility of silver chloride in water and in solutions of nitric acid and sodium, potassium and ammonium nitrates over a range of temperature from 0 to 50°.

EXPERIMENTAL.

Preparation and purification of materials.—The pure water used in all the experiments was obtained by redistillation of the laboratory distilled water from a dilute, slightly alkaline solution of potassium permanganate. The distillation was carried out in an all-glass apparatus, with a ground-in condenser of fused transparent silica. The water was prepared immediately before use and stored in bottles of resistance glass. It was found to be halogen free when tested in a nephelometer and had a specific conductivity of about 1×10^{-6} mhos.

The silver employed for the preparation of silver chloride was of a high degree of purity (99.996 per cent.) and when dissolved in pure nitric acid the solution was always clear and halogen-free.

The alkali nitrates were purified by repeated evaporation to dryness with concentrated nitric acid to remove traces of chloride which were found to be present in some of them. Three or four digestions with nitric acid always yielded halogen-free material which was then recrystallised and employed for preparing solutions of the required concentrations.

The silver chloride required for the solubility determinations was prepared as follows :—An accurately weighed quantity of silver (1.0788 g.) was placed in a conical flask which was provided with a funnel to collect the spray. Dilute nitric acid (20 c.c. of 1 : 3) was introduced into the flask which was then gently warmed. After the silver had dissolved, the liquid in the flask was diluted by the addition of 100 c.c. of water through the funnel, and boiled for about 10 minutes. The liquid was then cooled, transferred to a litre measuring flask and made up to the correct volume. A solution of sodium chloride of exactly equivalent concentration to the silver solution, i.e. containing 0.5846 g. of NaCl per litre was next prepared. Equal volumes (200 c.c.) of the solutions of silver and sodium chloride were mixed in a stoppered conical flask and shaken vigorously for about 10 minutes.

Shaking was continued for 5 minutes at intervals of $\frac{1}{2}$ hour for a period of about 10 hours and the flask then set aside. At the end of about 24 hours it was found that the silver chloride had settled completely leaving the supernatant liquid quite clear and it was possible to pour off all but 20 c.c. 500 c.c. of water was then poured into the flask, shaken with the precipitate periodically, allowed to settle and poured off. The silver chloride remaining after four such washings was considered to be sufficiently pure. When the solubility was to be measured in nitric acid or a salt solution, a portion of the solution was used for the last two washings instead of water. The precipitation as well as the washing of the silver chloride was carried out at room temperature in a room illuminated by ruby light and the precipitated silver chloride always remained moist.

In order to determine the solubility, the moist silver chloride (0.1-0.2 g.) and the solvent (100 c.c.) were kept in separate vessels in a thermostat at the required temperature for about $\frac{1}{2}$ hour, after which the silver chloride was added to the solvent and agitated frequently with a glass stirrer during 4 hours. After standing for periods which varied from 24 to 48 hours a portion of the clear supernatant liquid was decanted into another vessel kept in the thermostat and used for determining the solubility. It was found that the solubility did not vary with the period of standing. For temperatures from 25 to 30° the thermostat employed was capable of being regulated to within 0.02°, but for higher temperatures the variation reached 0.5°. For temperatures below that of the room, a large Dewar vessel containing cold water was employed and the temperature regulated by slowly adding iced water. In this case also the variation was 0.5°.

Since the solubility of silver chloride in the solvents employed increases appreciably with temperature it was necessary to dilute all solutions prepared at temperatures higher than that of the room to prevent separation of silver chloride when they were cooled for examination. This was done as follows :—The saturated solution of silver chloride was added to a known volume of water contained in a calibrated 125 c.c. measuring flask with 0.1 c.c. graduations on the neck until the level was near the top of the graduations, and the flask was stoppered, shaken and allowed to attain the temperature of the laboratory. The level of the liquid was then read, giving the quantity of saturated solution added, volume changes on mixing being negligible even with the most concentrated solutions employed. The quantity of water in the flask was sufficient to prevent precipitation on cooling and was calculated from the results of preliminary solubility determinations.

TABLE III.

Solubility of silver chloride, M./L. × 10^{-5}.

Solvent	Molarity	0°	8°	18°	25°	30°	40°	50°
[1] Water	... ...	0·49	...	1·01	1·39	1·69	2·63	3·82
HNO$_3$ ...	0·11	0·60	...	...	1·51	...	...	...
	0·48	0·71	0·89	1·38	1·64	1·84	3·98	7·69
	0·81	0·77	...	...	1·68	...	...	...
	1·00	0·79	...	...	1·74	...	...	...
[2] NaNO$_3$ ...	0·0001	...	...	...	...	1·69	...	...
	0·001	...	...	...	...	1·91	...	...
	0·01	...	...	...	...	2·80	...	...
	0·05	...	...	...	7·35	...	...	...
	0·10	1·35	3·00	4·94	10·1	10·1	10·2	10·8
	0·50	...	...	...	13·5	...	...	...
	0·75	...	...	...	15·5	...	...	...
	1·00	...	...	...	17·1	...	...	...
	3·00	...	...	...	17·5	...	...	...
	Sat. soln.	...	...	...	18·4	...	...	...
KNO$_3$ ...	0·10	0·79	0·84	1·42	2·71	2·93	4·30	6·05
	0·50	...	...	...	...	5·15	...	...
	0·75	...	...	...	...	5·92	...	...
	1·00	...	...	...	...	6·93	...	...
NH$_4$NO$_3$ ...	0·10	0·68	0·82	1·44	3·27	3·28	4·84	6·75
	0·50	...	...	...	5·23	...	...	...
	0·75	...	...	...	6·33	...	...	...
	1·00	...	...	...	7·40	...	...	...

TABLE IV.

Solubility of silver chloride in mixed solvents at 30°.

KNO$_3$+HNO$_3$		S.	NH$_4$NO$_3$ + HNO$_3$		S.	NaNO$_3$ + HNO$_3$		S.
0·10	0·25	2·94	0·10	0·25	3·29	0·10	0·25	10·1
0·10	0·50	2·98	0·10	0·50	3·32	0·10	0·50	10·2
0·50	0·25	5·19	0·50	0·25	5·25	0·50	0·25	13·5
0·50	0·50	5·21	0·50	0·50	5·26	0·50	0·50	13·8

The solubility of silver chloride in water in the range studied increases with rise in temperature but it was found that the results could not be expressed by a parabolic equation of the usual type. The expression

$$\log S = 0.01816\, t - 0.318$$

calculated by the method of least squares, S being the solubility, fits the experimental results within the limit of error as shown in Table V.

[1] The solubility of silver chloride in water at 10° was found to be 0·72.

[2] The solubility of silver chloride in 0·1 M. solutions of sodium nitrate at 22 and 23·5° was found to be 5·86 and 6·56 respectively.
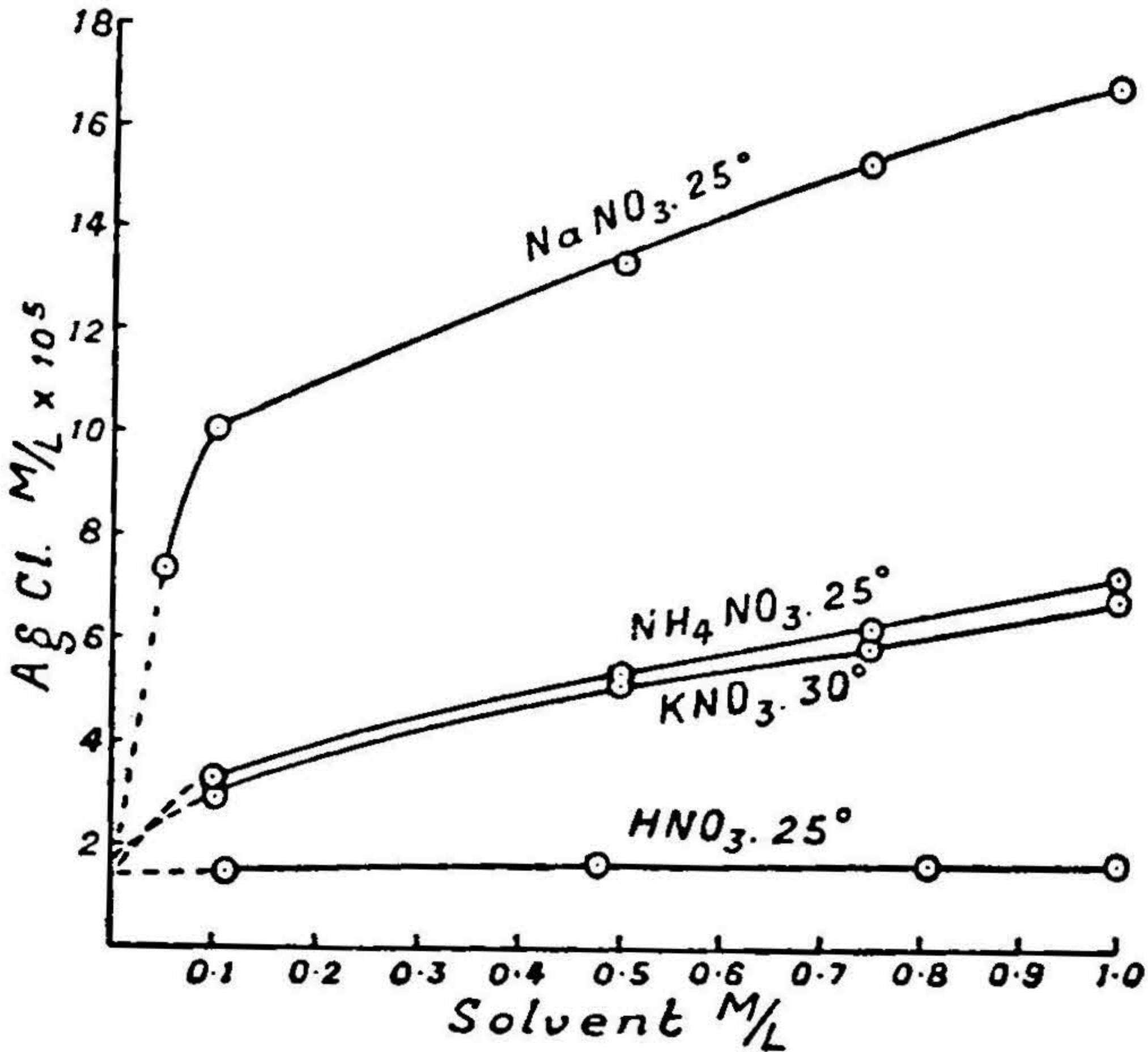
Fig. 1.

TABLE V.

| Temp.	...	...	...	0	10	18	25	30	40	50
S calc.	...	...	...	0·48	0·73	1·02	1·37	1·69	2·56	3·89
S found.	...	...	...	0·49	0·72	1·01	1·39	1·68	2·63	3·82

The addition of nitric acid or nitrates in small quantities up to a concentration of 0.1 M. results in a marked increase in solubility as may be seen from fig. 1 which shows the results at 25°. On increasing the concentration, the solubility continues to rise but not nearly as rapidly as with more dilute solutions. The effect with nitric acid is the least and with sodium nitrate the greatest. Potassium and ammonium nitrates behave in a similar manner to each other.

The temperature-solubility curves are somewhat remarkable owing to their irregular nature as may be seen from fig. 2. It will be observed that in two cases an abrupt rise is found very near to 25°. As this is the lowest temperature at which an automatically controlled

Fig. 2.

The solubility of silver chloride at various temperatures in water and in 0.1 M. solutions of the nitrates of sodium, ammonium and potassium
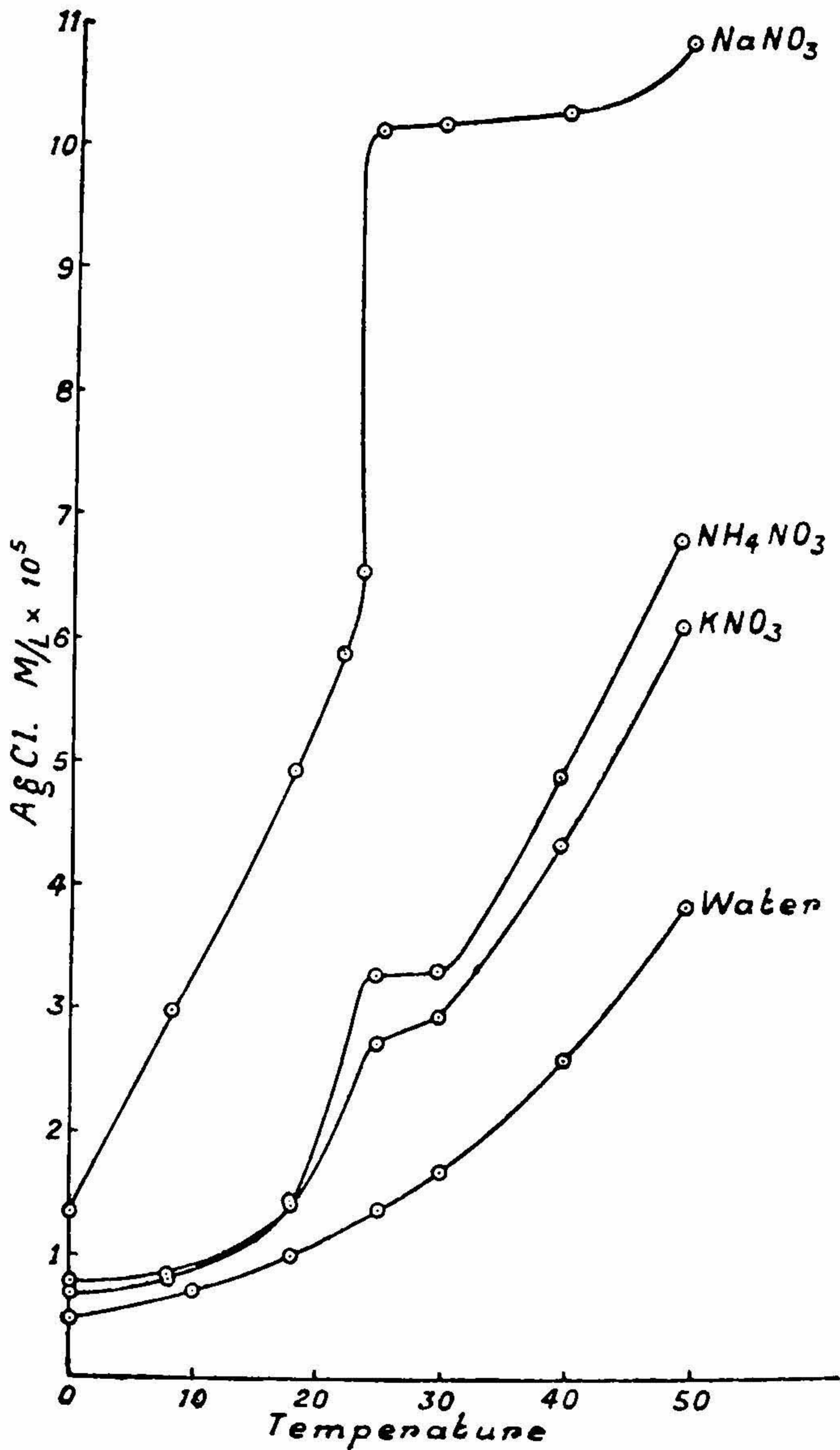
thermostat was used it was suspected that the discontinuity might be due in part to change in the method of temperature control, but several additional determinations made just below and just above 25° in the hand-controlled bath confirmed the previous results.

Determinations of solubility by the conductivity method.—Several determinations of the conductivity of silver chloride solutions have been carried out from time to time as will be seen from Table I, but the results obtained do not exhibit satisfactory agreement for the reasons already explained. We have therefore carried out measurements of the conductivity of saturated solutions of silver chloride prepared under the definite conditions described earlier with a view to compare the values obtained by this method with those determined nephelometrically.

The apparatus employed for the conductivity measurements was of the usual type, comprising a Leeds and Northrup bridge. The electrolytic cell was made of pyrex and the electrodes were platinum discs of about 18 mm. in diameter and 3 mm. apart. The determination of the cell constant and the calculation of the molar concentration of silver chloride in the solvent employed were all performed in the usual manner, assuming that silver chloride was completely dissociated in solution, and adopting Johnston's values (*J. Amer. Chem. Soc.*, 1909, **31**, 1015) for the equivalent conductances of ions.

The mean value at 25° obtained from three separate experiments involving about 20 determinations was 1.373×10^{-5} *M./L.* which is in fair agreement with the value 1.388×10^{-5} *M./L.* obtained nephelometrically.

COMPLEX FORMATION

The large increase in solubility produced by the addition of salts points to complex formation, the extent of which can be calculated by means of the equation given by Pinkus and Berkolaiko (*loc. cit.*) who have calculated the degree of complexity of solutions of silver chloride in potassium chloride.

According to these authors if α_{Ag}, V_{Ag} and $[Ag^+]$ are the activity, the coefficient of activity and the concentration respectively of Ag^+ ion, S the solubility and x the degree of complexity.

$$S = [Ag^+] + Sx \text{ or } x = 1 - \frac{\alpha_{Ag}}{V_{Ag} \times S} \text{ since } [Ag] = \frac{\alpha_{Ag}}{V_{Ag}}$$

Since S is known and the values of α_{Ag} and V_{Ag} may be obtained

from tables of activity coefficients (Lewis and Randall, *Thermodynamics*, p. 382) x may be calculated for the various solutions examined. The results so obtained are given in Table VI.

TABLE VI.

Complexity of silver chloride solutions.

Solvent	Conc.	Temp.	$S \times 10^5$	γ_{Ag}	$\alpha_{Ag} \times 10^6$	x
NaNO₃	0·1	0	1·35	0·77	2·27	0·78
	,,	18	4·94	,,	2·65	0·93
	0·05	25	7·35	0·80	3·27	0·94
	0·1	,,	10·07	0·77	2·48	0·97
	0·001	30	1 91	0·97	14·25	0·23
	0·01	,,	2·81	0·90	10·47	0·59
	0·1	,,	10·09	0·77	3·41	0·96
	0·1	40	10·23	,,	8·79	0·89
	,,	50	10·78	,,	17·60	0·79
NH₄NO₃ ·	0·1	0	0·69	0·77	4·43	0·17
	,,	18	1·44	,,	9·11	0·18
	,,	25	3·27	,,	7·65	0·70
	,,	30	3·29	,,	10·44	0·59
	,,	40	4·84	,,	18·6	0·50
	,,	50	6·75	,,	28·12	0·46
KNO₃	0·1	0	0·79	0·77	3·88	0·36
	,,	18	1·42	,,	9·22	0·16
	,,	25	2·71	,,	9·21	0·56
	,,	30	2·93	,,	11·71	0·48
	,,	40	4·30	,,	20·91	0·37
	,,	50	6·18	,,	30·68	0·36

These figures indicate that (1) the degree of complexity is a maximum at 25°, (2) it is much greater for solutions of sodium nitrate than for ammonium and potassium nitrates and (3) in the case of sodium nitrate it increases with the concentration of the solution at constant temperature.

SUMMARY

1. The solubility of silver chloride in water and in aqueous solutions of nitric acid and the nitrates of sodium, potassium and ammonium has been determined by a nephelometric method over a temperature range 0-50° under conditions approximating to those prevailing during analytical work.

2. The solubility in water at 25° has been deduced from conductivity measurements giving the value 1.373×10^{-5} M/L as compared with $1.388 \times 10^{-5} M/L$ by the nephelometric method.

3. The solubility of silver chloride in solutions of sodium nitrate has been found to be much higher than in the other solutions studied and this is due to the existence as complex ions of a large proportion of the silver ions.

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