[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Solubility of Silver Chloride in Water at 0°

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Although silver chloride has been used in many precise analytical researches, certain of its properties, upon which the accuracy of the work depends, have remained undesirably obscure. One of these properties, the solubility, has occasioned frequent comment regarding its anomalous character. Incidental to some recent work in this Laboratory, some of the facts underlying the anomalous behavior of silver chloride have been found. It is the purpose of the work described in this paper to supplement these findings.

Reagents.—The reagents used in the experiments described in this report were purified by the methods employed in atomic weight determinations. Silver, ammonia, hydrochloric acid, nitric acid and sodium chloride were prepared by methods previously outlined.[2] The purification of the ammonium, potassium and silver nitrate reagents has also been described.[3] All water, nitric acid, ammonium nitrate and potassium nitrate were tested to ensure the absence of silver and chloride impurities.

Three specimens of silver chloride were used. Specimen No. 1 was prepared by adding a liter of 0.1 *M* silver nitrate solution drop by drop to a liter portion of hydrochloric acid containing a 3% deficiency of HCl. Both solutions were 0.3 *M* in nitric acid. The precipitate was washed sixteen times over a period of a month with 250-cc. portions of water, in a glass-stoppered Pyrex bottle. After further washing with 0.3 *M* nitric acid, the specimen remained in contact with a liter of this acid for about three months. Tests made upon the supernatant liquid showed that it contained substantially equivalent amounts of silver and chloride during this period. The silver chloride was then washed free of acid with a total of six 1600-cc. portions of water, over a period of several months. Immediately before the treatment described below it was again washed with six 250-cc. portions of water. Under the microscope, samples of this specimen appeared as clusters of uniform grains about 0.005 mm. in diameter.

Specimen No. 2, another equal quantity of silver chloride, was prepared and tested in the same manner as Specimen No. 1, with the same result. However, in this case the nitric acid solution left in contact with the material was 0.1 *M* in ammonium nitrate. When the tests were completed, the specimen was washed free of extra electrolytes with six 1600-cc. portions of water, over a period of several months. It was next dissolved in aqua ammonia (prepared by distillation in an all-Pyrex system) and reprecipitated by slow evaporation of the solution. The resulting precipitate was washed with 0.3 *M* nitric acid, then with six 250-cc. portions of water. This preparation consisted of coarse crystals approximately 100 times larger, on the average, than the particles of Specimen No. 1, and much less uniform in size and shape.

Specimen No. 3, a slightly larger quantity of material, was prepared in the same general manner as the other specimens, but with silver and chloride from another source. After a thorough washing with water, the material was used in experiments in which it was dissolved four times in purified aqua ammonia and reprecipitated by evaporation of the solution. After each precipitation it was washed in proper sequence with water and 0.3 to 7 *M* nitric acid. After the final treatment it was thoroughly washed with

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(2) Scott and Johnson, *J. Phys. Chem.*, **33**, 1978 (1929).

(3) Johnson, *ibid.*, **35**, 2238 (1931).

water, dried, and fused in a quartz crucible. The fused salt was poured on a clean unglazed porcelain plate and solidified as a 3-mm. sheet. The solid was cut into pieces with a total surface area of approximately 50 sq. cm. The pieces were thoroughly washed with dilute nitric acid, then with six 150-cc. portions of water. Examination of polished and etched samples under the microscope showed this material to be made up of tightly-packed grains larger even than the crystals composing Specimen No. 2. The average area enclosed by the grain boundaries was about 0.1 sq. mm.

In all of the work with the silver chloride specimens, they were exposed only at a distance to Series OA Wratten Safelights and were usually kept in complete darkness.

Solubility Measurements.—Each specimen of silver chloride was covered with 750 cc. of water in a 2-liter glass-stoppered Pyrex Erlenmeyer flask. After saturation at room temperature the solutions were frozen and melted, then cooled at 0° during the remainder of the experiment, with the flasks three-quarters immersed in shaved ice. The flasks were shaken once only each day during the cooling period. Portions of the supernatant liquids were analyzed by the nephelometric method described by Johnson.[4]

Discussion of Results.—The analytical results are summarized in Table I. The varying excess of chloride in the solutions in contact with the three varieties of silver chloride indicates that we are dealing with an adsorption equilibrium, and places evident limitations on the interpretation of the results as solubility values.

TABLE I

SUMMARY OF ANALYSES

No.	Days cooled	Mg. Ag per liter as Chloride[a]	Silver	No.	Days cooled	Mg. Ag per liter as Chloride[a]	Silver
1	3	0.47	0.32	2	7	0.51	0.34
	3	.48	.34		7	.50	.34
	5	.47	.32	3	3	.62	.35
	5	.49	.33		3	.62	.36
2	3	.53	.33		9	.64	.37
	3	.51	.33		9	.62	.36
	7	.53	.35		9	.63	.35

[a] The numbers in this column are chloride concentrations, in milligrams per liter, multiplied by the factor Ag/Cl.

In another connection the information furnished by the results is of more interest. The usual directions[5] for preparing pure silver chloride involve the assumption that on repeated washing of the compound with pure water, equivalent amounts of silver and chloride are dissolved. The present experiments show that when silver chloride is repeatedly washed with pure water the washings carry away an excess of chloride over silver. There are also reasons[6] for believing that some compound containing more silver than chloride, or silver itself, is retained by the precipitate. This material dissolves when the precipitate is treated with dilute or concentrated nitric acid. If this behavior shown by the silver chloride under the specified conditions is characteristic, there are a considerable number of

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(4) Johnson, *J. Phys. Chem.*, **36**, 1942 (1932).

(5) Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, 1932, p. 68.

(6) Johnson, *J. Phys. Chem.*, **35**, 2241 (1931); **36**, 1945 (1932).

misleading statements in the literature regarding the purification and properties of the compound, and the results of many researches involving its use acquire a new significance.

Conductance Measurements.—To obtain further evidence upon this subject, conductance measurements with silver chloride have been made by a new method which greatly reduces uncertainties due to carbon dioxide and air in the conductivity water. The method is a general one, and may be applied to advantage in many conductance measurements with difficultly soluble salts. The technique used in the experiments may be inferred from the diagram of the conductance cell and auxiliary parts, shown in Fig. 1. This apparatus consists of a 40-cc. conductance cell C of known resistance capacity, connected to a reservoir A for the conductivity water, and a storage bulb B into which discarded solutions and washings may be decanted. The system is made of Pyrex glass. The polished platinum electrodes are introduced by a special platinum-tungsten connection, in which the tungsten is covered by glass. The arrangement provides a means of bringing highly purified water into contact with a substance whose conductance is to be measured, in an evacuated system. It also permits the determination of the conductance of the solutions made with successively distilled fractions of the water and successive "layers" of the material.

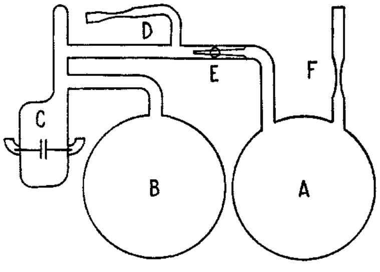

Fig. 1.—Vacuum conductance apparatus.

For the first set of tests a liter of triply-distilled water having a specific conductance of 2 × 10^{-6} at 25° was placed in the 1500-cc. bulb G (not shown in Fig. 1) which was connected to a pump through a series of suitable traps and also to bulb A, through F. After the water had been boiled under reduced pressure to remove air and carbon dioxide, the connection to the pump was sealed and 400 cc. of the water was distilled into the 500-cc. bulb A. The capillary at F was then sealed. The other side of the system was next evacuated to a pressure equivalent to 0.5 × 10^{-5} mm. of mercury and sealed off at D. The special joint[7] at E was then opened, and the conductance of various fractions of the water was determined at 0°. Standard methods were used in the conductance measurements. The next two sets of experiments were carried out in the same manner, except that 10 cc. of saturated barium hydroxide solution was added to the liter of water placed in bulb G.

In the third set of tests, several pieces of fused silver chloride (Specimen 3) were placed in the bottom of the conductance cell. The cell was designed so that the volume change due to the addition of the solid was not significant. Fractions 1, 3 and 4 of the water were left in contact with the silver chloride at room temperature for about sixteen hours, with occasional gentle shaking. At the end of this time, the conductance of the solution was measured and the cooling was started. With Fraction 2, the time of contact with the water at room temperature before cooling was reduced to one hour, in an attempt to approach the equilibrium point from the unsaturated side. The low conductance values obtained in this case are undoubtedly due to the extremely slow rate of solution of the fused silver chloride.

Discussion of Results.—The conductance determinations are summarized in Table II. The last column of the table gives the time after packing the cell in ice at which the final observations were begun, and the

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(7) For a more complete description see Briscoe and Little, *J. Chem. Soc.*, **105**, 1323 (1914).

interval over which the maximum, minimum and average conductance was recorded.

TABLE II

SUMMARY OF CONDUCTANCE MEASUREMENTS

Solution or water tested[a]	Temp., °C.	Specific cond. $\times 10^6$			Interval, minutes
		Max.	Min.	Av.	
G 1	24			1.8	
A 1	0.00	0.36	0.33	0.35	40–85
A 2	.00	.47	.45	.46	80–140
A 3	.00	.52	.51	.52	60–70
G 2	25			2.0	
A 1	0.00	.226	.224	0.225	100–130
A 2 a	.00	.207	.197	.203	75–125
A 2 b	.00	.182	.168	.175	95–135
A 3 a	.00	.202	.192	.195	75–125
A 3 b	.00	.177	.172	.175	135–155
Residue	.00			.173	110–120
G 3	24			1.8	
A 1 + AgCl	25			3.0	
A 1 + AgCl	0.00	1.13	1.09	1.12	195–1335
A 2 + AgCl	24			1.9	
A 2 + AgCl	0.00	0.70	0.62	0.66	645–1580
A 3 + AgCl	25			3.2	
A 3 + AgCl	0.00	1.22	1.18	1.20	165–1665
A 4 + AgCl	25			3.1	
A 4 + AgCl	0.00	1.15	1.14	1.15	420–1530

[a] Notation: G 1, original water added to bulb G in first tests; A 1, first fraction distilled from bulb A.

Comparison of the first two sets of tests shows the effectiveness of adding barium hydroxide to supplement the procedure of boiling the water under reduced pressure. It is also noteworthy that the observed specific conductance at 0° agrees quantitatively with the value calculated on the assumption that hydrolysis occurs to the extent indicated by the nephelometric analyses reported above. However, there are difficulties which prevent us from maintaining the view that silver chloride hydrolyzes. On the other hand, the conductance data justify the rejection of the hypothesis that the observed effects are due to reduction of the silver chloride by light or impurities. This view cannot be reconciled with the fact that the solutions prepared with successive fractions of the water in the darkened evacuated system persistently returned to a (constant) specific conductance of 1.2×10^{-6} at 0°. In any case, it may be concluded that there are difficulties in the way of making direct measurements of the solubility of silver chloride in pure water.

No.	Specific conductance of solution $\times 10^6$				
	Due to: HCl	AgCl	H_2O (obs.)	Calcd.	Obs.
3	0.68	0.25	0.18	1.11	1.15

Summary

Experiments bearing on the preparation of pure silver chloride and silver chloride solutions have been recorded.

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Solubility of Silver Chloride in Nitric Acid at 0°

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In the preceding paper, and elsewhere[2] are described experiments which show that: (1) pure silver chloride cannot be obtained by washing the compound repeatedly with pure water, (2) equilibrium is attained only slowly when nitric acid solutions in contact with silver chloride are cooled at 0°, and (3) colloidal material formed in solutions shaken in contact with silver chloride coagulates very slowly. These observations were applied in the present experiments to prepare solutions of silver chloride containing equivalent amounts of silver and chloride, normally saturated at 0°.

New nephelometric and potentiometric methods of analysis developed in the course of this work were used in measuring the chloride and silver content of these saturated solutions. The present measurements should be distinguished from certain incidental ones,[3] made previously, which are valid only as estimates of the amounts of silver and chloride in solutions shaken occasionally in contact with the precipitated material.

Solubility Measurements.—The three specimens of silver chloride prepared and used as described in the preceding paper were next allowed to stand for ten days in contact with 3 *M* nitric acid. Each specimen was washed free of this liquid with four 100-cc. portions of 0.103 *M* nitric acid, then covered with 1000 cc. of the acid. The solutions were saturated at room temperature by allowing the systems to stand for a sufficient time with the minimum shaking required to ensure effective mixing. The 2-liter Pyrex flasks containing the systems were then three-quarters immersed in shaved ice, until equilibrium had been reached and a sufficient number of satisfactory analyses of the solutions had been completed. The ice was kept well packed and drained. During the cooling period each flask was shaken once only each day, always just after the removal of test portions.

For each set of analyses, a 110 to 150 cc. sample of clear supernatant liquid was withdrawn with a pipet, passed rapidly through a rinsed

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[2] Johnson, *J. Phys. Chem.*, **35**, 2241, 2581 (1931); **36**, 1945 (1932).

[3] Johnson, *ibid.*, **35**, 830, 2581 (1931).