

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 elsewhere² 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 sample of clear supernatant liquid was withdrawn with a pipet, passed rapidly through a rinsed

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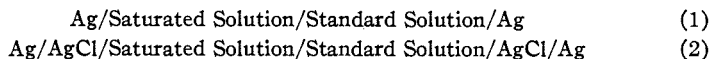
(2) Johnson, *J. Phys. Chem.*, **35**, 2241, 2581 (1931); **36**, 1945 (1932).

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

sintered-glass filter, and collected in a rinsed receiver. Under the conditions of cooling, when the flasks were uncovered sufficiently to permit temperature observations, the values recorded were generally about $+0.05^\circ$, and never more than $+0.10^\circ$. Since the flasks remained packed in ice during removal of the samples, it is safe to say that most withdrawals were made at temperatures close to 0.00° .

Portions of the 110 to 150 cc. samples were analyzed nephelometrically and potentiometrically by comparison with standard solutions containing equivalent amounts of silver nitrate and potassium chloride, each measured accurately to the equivalent of 0.002 mg. of silver per liter. The standards were made up in liter quantities with nitric acid taken from the same large quantity which furnished acid for preparing the silver chloride solutions. The nephelometric analyses were made by the method described by Johnson,⁴ with one improvement. In each analysis the test portions of the silver chloride solution were compared with two standard solutions, one more and one less concentrated than the test solution. The corresponding interpolation from the observed nephelometric ratios was found to give a much more precise result than a comparison with a single standard.

The potentiometric measurements were made at 0° by the method described by Johnson and Low,⁵ with the cells:



It was considered good policy in these analyses to use standard solutions which would remain unsaturated when cooled to 0° . It was found that the correction due to essential differences in the electrode pairs could be made precisely either by "reversing" the electrodes for half of the readings, or by making final readings with the electrodes in the same solution. Some idea of the sensitivity and precision of the potentiometric analytical method may be obtained from the fact that these undoubtedly significant corrections rarely exceeded 0.01 mg. of silver or its chloride equivalent per liter.

The expressions used in calculating the silver and chloride concentrations from the e. m. f. values for Cells 1 and 2 were, respectively: $\log [\text{Ag}] = \pm E_1/0.0542 + \log S$, and $\log [\text{Cl}] = \pm E_2/0.0542 + \log [\text{Ag}]$. E_1 and E_2 are in volts, S is the silver concentration of the standard solution, and all concentrations are expressed in milligrams of silver per liter, for convenience. The signs are governed by the observation that in Cell 1 the electrode *in the solution* containing excess silver was positive, and in Cell 2 the electrode *in a test solution* with excess chloride was negative. It became evident during the experiments that the e. m. f. of Cell 2 should be interpreted as a measure of the difference between the silver and chloride

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

(5) Johnson and Low, *ibid.*, **36**, 2390 (1932).

concentrations of the test solution, and not as a measure of the difference between the original chloride concentrations of the standard and test solutions. In short, the potentiometric chloride analyses, although precise, are dependent upon the silver analyses.

Solubility determinations were made in 0.252, 1.020, 0.0010 and 15.2 molar nitric acids, which replaced the 0.103 *M* acid in the order indicated. In these determinations the general methods described above were used, with a few modifications. The flasks containing the systems 0.252 molar in nitric acid were packed in ice immediately after addition of the cooled acid, so that equilibrium would be approached from the unsaturated side. In the other cases the solutions were wholly or partly saturated at room temperature before cooling. In the potentiometric analyses with 0.0010 *M* acid, it was necessary to add 2.00-g. quantities of pure potassium nitrate to the 50.0-cc. portions of standard and test solution from which the samples used in making the cells were drawn.

TABLE I
SUMMARY OF ANALYSES

Mol. HNO ₃	No.	Time cooled, days ^a	Nephelometric analyses		Potentiometric analyses	
			Mg. Ag per liter as Chloride ^b	Silver	Mg. Ag per liter as Chloride ^b	Silver
0.0010	1	10	0.404	0.418	0.411	0.406
	1	10	.406	.406	.406	.406
	2	11	.412	.403	.401	.402
	2	12	.410	.404	.406	.409
	3	4	.407	.402	.405	.404
	3	6	.409	.408	.405	.407
				Median: .407		.406
0.103	1	8	0.539	0.526	0.524	0.524
	1	10	.523	.518	.525	.522
	2	11	.533	.536	.523	.525
	2	13	.525	.524	.526	.525
	3	4	.63	.62	.60	.60
	3	9	.546	.522	.533	.535
	3	11	.532	.533	.531	.528
			Median: .529		.525	
0.252	1	2	0.32	0.31	0.52	0.52
	1	7	.598	.593	.594	.594
	1	11	.597	.591	.595	.594
	2	3	.59	.57	.57	.57
	2	4	.615	.597	.600	.597
	2	7	.594	.597	.602	.599
	3	113-1.00	.272	.215	.320	.315
	3	233-0.89	.428	.407	.436	.431
	3	329-.78	.507	.498	.498	.495
	3	476-.67	.553	.557	.568	.563
	3	598-.45	.593	.588	.598	.598
	3	618-.34	.589	.590	.596	.595
			Median: .594		.597	

TABLE I (Concluded)

Mol. HNO ₃	No.	Time cooled, days ^a	Nephelometric analyses		Potentiometric analyses	
			Mg. Ag per liter as Chloride ^b	Silver	Mg. Ag per liter as Chloride ^b	Silver
1.020	1	4	0.642	0.641	0.660	0.651
	1	12	.648	.661	.663	.655
	1	12	.660	.649	.646	.650
	2	4	.654	.653	.650	.650
	2	6	.654	.655	.651	.650
	2	7	.652	.655	.654	.653
	3	6	.651	.652	.652	.654
	3	8	.650	.657	.649	.652
	3	9	.665	.655	.657	.657
				Median: .653		.652
15.2	1	7	0.13	0.11		
	1	8	.11	.13		
	1	8	.11	.12		

^a For Specimen 3, in 0.252 *M* acid, the time is given in hours, and is followed by the volume of the solution in liters. ^b The values in this column are chloride concentrations in milligrams per liter, multiplied by the factor Ag/Cl.

Sensitive quantitative control experiments showed that detectable effects due to solution of the silver electrodes under the specified analytical conditions were confined to the measurements with 1.02 molar nitric acid.

Discussion of Results.—The 142 values given in Table I are taken from a total of 202 analyses. Eighteen equally good triplicate values are omitted, as well as seven results showing errors greater than 0.04 mg. of silver per liter. The results of thirty-five "range-finding" analyses are also omitted. A few values of this latter type, included in the table to give some idea of the rate at which equilibrium is attained, should be distinguished from the solubility data.

The belief that the two methods of analysis give correct estimates of the normal solubility seems to be amply justified. The measured solubilities are independent of the particle size of the specimens over a wide range. The values also lie on a smooth curve when plotted against the acid concentration of the solutions, whether the equilibrium was approached from the saturated or unsaturated side. The agreement of the independent and basically different nephelometric and potentiometric analyses offers even more conclusive evidence on this point.

Summary

Measurements of the normal solubility of silver chloride in 0.0010 *M* to 15.2 *M* nitric acid at 0° have been made by two independent methods.

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