The Solubility of Cobaltous Iodate in the Presence of Sodium Chloride, Sodium Iodate and Cobaltous Sulfate

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The solubilities of the various hydrates of cobaltous iodate have been investigated carefully by Meusser.[1] The dihydrate is the stable form at and near room temperature; hence it was used in this study.

Preparation of Materials

Cobaltous iodate dihydrate is readily prepared by the reaction of any soluble cobaltous salt with any soluble iodate in aqueous solution. If the reagents are mixed in the cold this salt separates slowly, forming a close knit and hard mass of tiny crystals which can be removed from the precipitation vessel and purified only with difficulty. When the hot solutions are mixed with rapid stirring a more highly hydrated form, probably the tetrahydrate, separates along with the dihydrate, both forming larger crystals. Upon agitating the mixture with the mother liquor for some days, however, conversion to the dihydrate is complete, and good crystals are formed. Cementing together of the crystals is thus avoidable. This method was employed in preparing cobaltous iodate, using the best obtainable cobaltous nitrate and sodium iodate. The product was washed thoroughly and dried to constant weight at 50°. Repeated analyses established its exact composition and its purity.

The sodium chloride was a special product marked "for analysis" and was not further purified. Sodium iodate was prepared in this Laboratory, and several times recrystallized. Cobaltous sulfate was also recrystallized for use, starting with a commercial C. P. product. Redistilled water was used in the preparation of the salts and in preparing the solutions for saturation.

Experimental Methods and Results

Cobaltous iodate dihydrate dissolves very slowly; consequently saturated solutions are produced only after extended agitation. Contrary to the usual behavior of salts, too, saturation is approached from a condition of supersaturation much more slowly than from undersaturation. In three experiments in which solutions previously saturated at 60° were agitated with crystals of the dihydrate at 30° saturation had not yet been reached after a week. This persistence of metastable equilibrium was so great that solutions showed no separation of solute, even when allowed to stand for weeks at temperatures somewhat below that at which they had been saturated. Equilibrium was therefore always approached from below in these experiments, and times of

(1) Meusser, *Ber.*, **34**, 2440 (1901).

seventy-five and one hundred and twenty hours were allowed in every case. A number of experiments with pure water and with solutions of various added salts showed that saturation was reached in the shorter time in every case.

All solutions were saturated at 30°. Their preparation and analysis were carried out in duplicate—many of them in triplicate. Solutions of sodium chloride, sodium iodate and cobaltous sulfate, respectively, were made up in suitable concentrations and analyzed and their densities were determined. Chloride concentrations were determined by the Volhard method. Sulfate was determined in the cobaltous sulfate solutions by the usual gravimetric method. Iodate was determined in all cases by iodometric titration. Potassium iodate was used in standardizing the thiosulfate solutions. After saturation, excess cobaltous iodate was filtered off, using a quantitative filter paper designed for the filtration of very fine precipitates. Then followed the iodometric titration of the iodate present in the saturated solutions. Carefully calibrated apparatus was used in all the determinations. The densities of the saturated solutions were determined in every case.

In the solutions in which sodium iodate was the added salt titration gave total iodate. Other samples of these solutions were treated with an excess of hydrochloric acid and boiled to destroy the iodate present and to remove the chlorine liberated by the reaction. Cobalt was then precipitated from the solutions as hydroxide by rendering them slightly alkaline with sodium hydroxide. After filtering and washing this precipitate, it was dissolved in hydrochloric acid and the cobalt was determined by the perborate method. From this determination the concentration of cobaltous iodate in each of the saturated solutions was calculated. The concentration of sodium iodate was found by difference. It was possible, also, to calculate the concentrations of these salts by the method, given below, which was used in those cases where sodium chloride and cobaltous sulfate were the added salts. This method of calculation gave results which agreed well with those from the direct analyses.

For the solutions with sodium chloride and cobaltous sulfate as added salts, titration gave

TABLE I

SOLUBILITIES OF $Co(IO_3)_2 \cdot 2H_2O$ AT $30°$

In NaCl Solutions

Molalities

NaCl	$Co(IO_3)_2$	Densities
0.0	0.01165	1.0006
.0029	.0119	1.0007
.0052	.0120	1.0008
.0069	.0121	1.0009
.0111	.0124	1.0010
.0140	.0125	1.0011
.0267	.0131	1.0016
.0355	.0134	1.0020
.0532	.0139	1.0029
.0941	.0149	1.0054
.1449	.0158	1.0085

In $NaIO_3$ Solutions

$NaIO_3$		
0.0	0.01165	1.0006
.0044	.0102	1.0006
.0076	.0093	1.0007
.0087	.0090	1.0008
.0127	.0080	1.0011
.0174	.0069	1.0014
.0202	.0063	1.0017
.0280	.0050	1.0026
.0360	.0040	1.0037
.0483	.0030	1.0056
.0999	.0010	1.0135

In $CoSO_4$ Solutions

$CoSO_4$		
0.0	0.01165	1.0006
.0026	.0113	1.0008
.0052	.0111	1.0011
.0061	.0111	1.0012
.0123	.0107	1.0019
.0129	.0106	1.0020
.0235	.0102	1.0034
.0258	.0101	1.0037
.0516	.0095	1.0076
.0774	.0094	1.0117
.1032	.0093	1.0155

directly the concentration of cobaltous iodate. Subtracting the weight of this salt present in each liter of solution from the weight of that volume of solution gave the weight of the solution of the added salt which entered into it. It was then a simple matter to calculate the weight of added salt and of water per liter. Calculation of the molalities of the salts present gave the data of Table I.

Summary

The solubility of cobaltous iodate dihydrate in solutions of sodium chloride, sodium iodate and cobaltous sulfate has been studied in the region of concentration 0 to approximately 0.1 molal for the added salt.

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The Allotropic Forms of Diphenylsulfone and the Determination of their Transition Point

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In the course of an examination of certain still residues remaining from the preparation of phenol by the fusion of sodium benzene sulfonate with sodium hydroxide, we separated a crystalline solid, in a yield of over 30%, whose chemical properties and analysis coincided with those of diphenylsulfone. The formation of this compound as a by-product in the manufacture of phenol by the process stated has been known for years. The only puzzling thing about our product was its melting point. The literature on this subject is confusing, some investigators giving the figure as 124°, others as 128°.

It seemed of interest, therefore, to ascertain if possible the reason for this discrepancy, and our study of the problem disclosed the following facts.

(1) Diphenylsulfone exists in two reciprocally convertible allotropic forms, one melting at 124° and the other at 128°. (2) The transition temperature for the two is in the neighborhood of 75°. When crystallization is induced (no matter how) above this temperature, the product always melts (if pure) at 128°; if induced below this, it melts at 124°.

Otto[1] obtained both forms, but concluded that the 124° form, because of its lower m. p., was probably impure.

Remsen and Saunders[2] gave 124° as the correct m. p. for the sulfone. Because they were unable by recrystallization to raise this m. p. to the

(1) Otto, Ann., 136, 160 (1865).
(2) Remsen and Saunders, Am. Chem. J., 17, 364 (1895).