[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Solubilities of Cupric Sulfate and Strontium Chloride in Deuterium Water[1]

BY FRANCIS T. MILES AND ALAN W. C. MENZIES

The solubility of salts in deuterium water has received comparatively little attention. Taylor, Caley and Eyring[2] measured the solubilities of sodium chloride at 25° and of barium chloride at 20°, and found lower solubilities than in ordinary water in both cases. Shearman and Menzies[3] studied the solubility of potassium chloride in deuterium water in the range 0 to 180°. There appears to be no other case in which the change with temperature of the solubility of a salt in deuterium water has been studied.

Method.—The solubilities of cupric sulfate and strontium chloride in deuterium water were measured using the method of Menzies,[4] whose procedure was followed except that a simple low power microscope with ocular micrometer was used to read the volume of water in the graduated tube. At temperatures below 5° a water thermostat cooled with ice was used, and the temperature was measured with a Beckmann thermometer which had been calibrated against a platinum resistance thermometer whose readings were good to 0.01°. In correcting for the weight of the solvent in the vapor phase the pressure was calculated on the assumption that the ratio of the actual pressure of the saturated solution to the pressure calculated using Raoult's law was the same for deuterium as for ordinary water in whose case these pressures are known. This was sufficiently accurate since the largest correction affected the measured solubility by less than 0.5%.

Purity of Materials.—The deuterium water was the same as was used for the measurement of vapor pressure.[5] The concentration of D_2O in this water, as determined from the melting point, was 98.1%.

The cupric sulfate was the same as was used by Collins and Menzies[6] who found it to contain not more than 0.001% of nitrates, chlorides, alkalies or alkaline earths. It was dehydrated in a current of dry air at 90° and then at 250° until the weight was constant. The weight of anhydrous salt, 0.1860 g., and the weight of deuterium water, 1.3308 g., were corrected for the amount of water which, according to Richards,[7] remains in the salt dried at 250°. The dilution of the deuterium water by this water is negligible.

The strontium chloride was the same sample of DeHaën's reagent hexahydrate which was used by Menzies[4] and by Caley.[8] The total impurity was probably less than 0.1%. It was dehydrated first at 55°, then at 120°, and finally at 180° to constant weight. Two sets of measurements were made on strontium chloride. In the first set (A1 to A10 in Table II) 0.5584 g. of anhydrous salt and 1.3314 g. of deuterium water were used. In the second set (obser. B1 to B6) the weights were 1.0593 g. and 1.2148 g., respectively.

Results

For purposes of comparison with the solubilities in ordinary water, which are expressed in "International Critical Tables" in moles of salt per 1000 g. (55.51 moles) of water, the solubilities are here expressed in moles of anhydrous salt per 55.51 moles of deuterium water, extrapolating from 98.1 to 100% as already described.[3] We have made our tables correspond in style and symbology with those in "I. C. T."

The observed solubilities of cupric sulfate are noted in Table I and graphed in Fig. 1. The average divergence of a single observation from the smoothed pentadeuterate solubility curve was 0.3%. In addition to seven points on the pentadeuterate curve and one on the trideuterate curve two points on the metastable portion of the ice curve were observed. This made it possible to locate the eutectic point.

TABLE I

OBSERVED SOLUBILITIES OF CUPRIC SULFATE DEUTERATES IN DEUTERIUM WATER

M = moles $CuSO_4$ (159.61) per 55.51 moles deuterium water

Temp., °C.	M	Temp., °C.	M
Ice (metastable)		S·5 aq.	
2.4	0.97_0	63.2	2.54_8
1.5	1.37_7	79.2	3.39_2
S·5 aq.		90.3	4.19_8
11.6	0.97_0	95.5_5	4.65_7
28.4	1.37_7	S·3 aq.	
47.7_5	1.96_1	104.7	4.80

The observed solubilities of strontium chloride are noted in Table II and graphed in Fig. 1. The average divergence of a single observation from the smoothed hexadeuterate and dideuterate curves was 0.1%. A metastable point on the hexadeuterate curve above the transition point was observed and was useful in locating the transition point. By suitable manipulation of temperature either the metastable point (57.3_7°) or the corresponding stable point on the dideuterate

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(1) The material of this article forms a portion of a thesis submitted by F. T. Miles in partial fulfilment of the requirements for the Ph.D. degree at Princeton University.

(2) Taylor, Caley and Eyring, THIS JOURNAL, **55**, 4334 (1933).

(3) Shearman and Menzies, *ibid.*, **59**, 185 (1937).

(4) Menzies, *ibid.*, **58**, 934 (1936).

(5) Miles and Menzies, *ibid.*, **58**, 1067 (1936).

(6) Collins and Menzies, *J. Phys. Chem.*, **40**, 379 (1936).

(7) Richards, *Z. anorg. Chem.*, **1**, 150 (1892).

(8) Caley, *Ind. Eng. Chem., Anal. Ed.*, **6**, 445 (1934).

curve (60.76°) could be observed at will (obser. A6m and A6s).

TABLE II

OBSERVED SOLUBILITIES OF STRONTIUM CHLORIDE DEUTERATES IN DEUTERIUM WATER

M = moles $SrCl_2$ (158.54) per 55.51 moles deuterium water

Observation no.	Temp., °C.	M	Observation no.	Temp., °C.	M
S·6 aq.			S·2 aq.		
A1	5.83	2.935	A8	79.2	5.737
A2	20.62	3.382	B1	93.5	6.108
A3	31.32	3.795	A9	96.45	6.248
A4	50.75	4.806	A10	116.34	7.017
A5	55.83	5.223	B2	125.2	7.463
S·6 aq. (metastable)			B3	127.8	7.597
A6m	57.37	5.372	S·aq.		
S·2 aq.			B4	133.8	7.78
A6s	60.76	5.372	B5	137.3	7.88
A7	70.6	5.559	B6	141.0	8.01

For purposes of interpolation smooth curves were drawn through the observed points as described by Menzies.[4] These curves are shown in Fig. 1. For lack of other data at a temperature where hydrolysis is beginning to vitiate results, the curve for $CuSO_4 \cdot 3D_2O$ is drawn parallel to that for the trihydrate. Values read from the curves at 5° intervals are noted and compared with the values for ordinary water in Tables III and IV. For this purpose accurate values of solubilities in ordinary water are needed. The solubilities of cupric sulfate given in "International Critical Tables"[9] are evidently not accurate at temperatures above about 70°, since the solubility curves intersect at 101° instead of 95.9°, which has been found by other methods to be the transition point.[7,10] Accordingly, four solubility measurements were made on cupric sulfate in ordinary water using the synthetic method. These yielded solubilities of 1.01, 1.11, 1.27 and 3.33 moles per 1000 g. of water at 7.5, 11.9, 18.4 and 77.2°, respectively. A smooth curve, shown in Fig. 1, was drawn through these values and those taken from "International Critical Tables" giving less weight to the "I. C. T." values above 70° and disregarding entirely the value for 100°. Another curve was drawn through the points above 101°. These curves intersected at 95.9°. Values read from these curves are given in Table III, the last column of which shows the percentage difference between the solubilities in deuterium and ordinary waters, $100 \times (M_{D_2O} - M_{H_2O})/M_{H_2O}$. Extrapolated values are shown in italics.

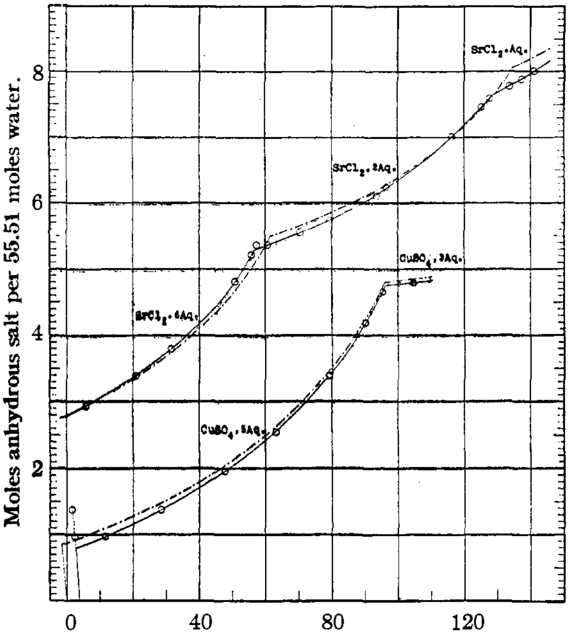

Fig. 1.—Solubilities of hydrates (broken lines) and deuterates (unbroken lines) of cupric sulfate (below) and of strontium chloride (above).

The values of Menzies[4] were used for the solubility of strontium chloride in ordinary water. Since these did not extend below 20°, two measurements were made by the synthetic method, yielding values of 2.94 and 3.18 moles per 1000 g. of water at 5.5 and 15.1°, respectively. The curves through Menzies's values were extended to include these observations. Values for the solubilities of strontium chloride in ordinary and deuterium water and the percentage differences are given in Table IV.

Discussion

The transition points of cupric sulfate penta- to trideuterate and of strontium chloride hexa- to dideuterate and di- to monodeuterate were located by the intersections of the solubility curves, and the eutectic point of cupric sulfate pentadeuterate in deuterium water was found from the intersection of the solubility curve with the curve through the freezing point of deuterium water and the metastable points on the ice curve. The transition point of cupric sulfate penta- to trideuterate was found to be 96.2 ± 0.2°, very close to that of the penta- to trihydrate at 95.9°. In the case of

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(9) "International Critical Tables," Vol. IV, p. 222.

(10) "International Critical Tables," Vol. III, p. 367.

TABLE III

SOLUBILITIES OF CUPRIC SULFATE IN DEUTERIUM WATER AND IN ORDINARY WATER

M = moles $CuSO_4$ (159.61) per 55.51 moles water

Temp., °C.	M_{H_2O}	M_{D_2O}	% diff.
	Ice + S·5aq.		
−1.5 E_{H_2O}	0.85		
	S·5aq.		
0	0.88		
		Ice + S·5aq.	
2.7 E_{D_2O}	0.92	*0.79*	*−14*
		S·5aq.	
5	0.96	*0.83*	*−13*
10	1.06	*0.93*	*−12*
15	1.17	1.05	−10
20	1.27	1.16	−9
25	1.39	1.29	−7
30	1.51	1.42	−6
35	1.65	1.56	−5.5
40	1.80	1.71	−5.0
45	1.95	1.86	−4.6
50	2.12	2.04	−3.8
55	2.30	2.22	−3.5
	S·5aq.	S·5aq.	
60	2.49	2.42	−2.8
65	2.71	2.64	−2.6
70	2.95	2.88	−2.4
75	3.21	3.14	−2.2
80	3.51	3.44	−2.0
85	3.84	3.77	−1.8
90	4.23	4.16	−1.7
95	4.70	4.62	−1.7
	S·5aq. + S·3aq.		
95.9 U_{H_2O}	4.80	4.72	−1.7
	S·3aq.	S·5aq. + S·3aq.	
96.2 U_{D_2O}	4.80	4.75	−1.0
		S·3aq.	
100	4.82	4.77	−1.0
105	4.85	*4.80*	*−1.0*
110	4.88	*4.83*	*−1.0*

TABLE IV

SOLUBILITIES OF STRONTIUM CHLORIDE IN DEUTERIUM WATER AND IN ORDINARY WATER

M = moles $SrCl_2$ (158.54) per 55.51 moles water

Temp., °C.	M_{H_2O}	M_{D_2O}	% diff.
	S·6aq.	S·6aq.	
0	2.79	*2.78*	*−0.4*
5	2.92	*2.91*	*−0.3*
10	3.05	3.05	0.0
15	3.19	3.20	0.3
20	3.33	3.36	0.9
25	3.50	3.54	1.1
30	3.69	3.73	1.1
35	3.89	3.94	1.3
40	4.10	4.17	1.7
45	4.34	4.44	2.3
50	4.62	4.76	3.0
55	4.95	5.14	3.8
		S·6aq. + S·2aq.	
56.4 U_{D_2O}	5.06	5.28	4.4
		S·2aq.	
60	5.35	5.35	(0.0)
	S·6aq. − S·2aq.		
61.4 U_{H_2O}	5.50	5.38	−2.2
	S·2aq.		
65	5.56	5.45	−2.0
70	5.65	5.54	−1.9
	S·2aq.	S·2aq.	
75	5.76	5.65	−1.9
80	5.86	5.76	−1.7
85	5.98	5.88	−1.7
90	6.10	6.02	−1.3
95	6.24	6.17	−1.2
100	6.39	6.34	−0.8
105	6.56	6.52	−0.6
110	6.74	6.72	−0.3
115	6.95	6.94	−0.2
120	7.17	7.18	+0.1
125	7.43	7.45	0.3
		S·2aq. + S·aq.	
128.5 U_{D_2O}	7.61	7.64	0.3
		S·aq.	
130	7.74	7.68	(−0.8)
	S·2aq. + S·aq.		
134.4 U_{H_2O}	8.06	7.80	−3.2
	S·aq.		
135	8.08	7.82	−3.2
140	8.20	7.97	−2.8
145	8.33	*8.14*	*−2.3*

strontium, however, the transition point of the hexa- to dideuterate was 56.4 ± 0.2°, and that of the di- to monodeuterate, 128.5 ± 0.5°. These points are, respectively, 4.9 and 5.9° lower than the corresponding transition points[4] of the hydrates. In both cases the increase of solubility with temperature was more rapid in deuterium water than in ordinary water, which is consonant with the behavior of deuterium water in other respects. Solubility differences will be discussed further when additional data are presented.

Summary

The solubilities of cupric sulfate and of strontium chloride deuterates in deuterium water are reported in the ranges from 2.7 to 110° and from 0 to 145°, respectively.

Transition temperatures are determined of

cupric sulfate pentadeuterate to trideuterate, of strontium chloride hexadeuterate to dideuterate and dideuterate to monodeuterate. These values are compared with the corresponding values in ordinary water.

PRINCETON, N. J. RECEIVED SEPTEMBER 22, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Stability of Solutions of Trivalent Columbium in Sulfuric Acid

BY SAMUEL J. KIEHL, ROBERT L. FOX AND HENRY B. HARDT

The reduction of pentavalent columbium to trivalent columbium furnishes the basis for a number of analytical methods[1] for the determination of columbium. In these methods complete reductions were accomplished in various ways and the amounts of columbium determined by an oxidimetric titration. A complete reduction was secured electrolytically at a mercury cathode[2] and the oxidation–reduction potentials of the oxidant-reductant system determined.[2] In the course of these reductions, moreover, depending upon the concentration of sulfuric acid, the color of the solutions varied from a light blue to a reddish-brown, to a brown. From such solutions many attempts have been made to separate compounds, among the most successful of which were those of Ott,[3] who prepared a red crystalline substance to which the possible formula, $Cb_2(SO_4)_3\cdot(NH_4)_2SO_4\cdot H_2SO_4\cdot 6H_2O$, was given. It, moreover, was shown that the color disappeared upon dilution and that in the colored solutions the columbium was upon an oxidation level of three.[2] During attempts to separate compounds, it was discovered that the colored solutions became clear upon standing in an atmosphere of hydrogen sometimes with and sometimes without a deposit of the white hydrated columbic oxide. All the reduced solutions are unstable. Hydrogen is evolved during the change.

An account of a study of the conditions which affect the stability of the solutions and of pressure developed during the change, at constant volume and constant temperature of the gas hydrogen, which was confirmed by test and analysis, is given below.

Preparation of Materials

Columbic Oxide Solutions.—Columbic oxide of a very high degree of purity was dissolved in hot concentrated sulfuric acid. This solution, upon cooling, was diluted to 1 *M* with respect to sulfuric acid and heated at 100° for twelve hours. During this treatment, a white flocculent precipitate of hydrated columbic oxide formed, which was separated and washed by centrifuging. The purified oxide was then dissolved in concentrated sulfuric acid and diluted to the desired acid and columbium concentrations. During the dilution, the temperature was not allowed to rise above 20°.

Mercury.—The mercury was distilled as recommended by Hulett,[4] washed in a tower containing dilute nitric acid according to the method of Hildebrand[5] and finally in a tower of distilled water.

Hydrogen.—Commercial electrolytic hydrogen was used. Whatever impurities it contained were removed so far as possible by passing it successively over heated copper gauze, through soda lime, cotton, and finally through 9 *M* sulfuric acid. To avoid contamination with oxygen, all joints were glass seals except the rubber tubing connecting the bottles containing the solutions, the piece in the pressure apparatus and two pieces near the reduction apparatus, where flexibility was required. Pressure rubber tubing treated with castor oil, and covered with either "Picëin" a commercial wax, or shellac was used.

Nitrogen.—The purification of the nitrogen was accomplished by two Van Brunt[6] towers, modified as described by Cowperthwaite and La Mer,[7] in one the nitrogen was passed over closely packed spirals made of copper wire, wet with an ammoniacal solution of ammonium carbonate; in the other, over pieces of glass wet with sulfuric acid. Finally the gas was passed through a tube loosely packed with cotton.

The other chemicals used—the sulfuric acid, potassium permanganate, ferrous ammonium sulfate, the potassium bisulfate, ammonium hydroxide, acetone, and ether—were of the highest purity obtainable.

Apparatus

Baths.—To maintain constant temperatures of 30, 45 and 60°, three thermo-regulated[8] baths were employed, the one at 30° within ± 0.01°, the next at 45° within ±0.05°, and the last, which was filled with oil, at 60° well within ±0.5°.

Reduction Apparatus.—Figure 1, A, B, C, shows a modification of the apparatus used by Kiehl and Hart.[2] There are three parts, A, B, C, all united by means of

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[1] Osborne, *Am. J. Sci.*, [3] **30**, 328 (1885); Levy, *Analyst*, **40**, 204 (1905); Giles, *Chem. News*, **95**, 1 (1907); **99**, 1 (1909); Metzger and Taylor, *J. Soc. Chem. Ind.*, **28**, 818 (1909); Schwartz, *Z. angew. Chem.*, **46**, 552 (1933).

[2] (a) Kiehl and Hart, THIS JOURNAL, **50**, 1608 (1928); (b) Kiehl and Hart, *ibid.*, **50**, 2337 (1928).

[3] Ott, *Z. Elektrochem.*, **18**, 349 (1912).

[4] Hulett, *Z. physik. Chem.*, **33**, 611 (1900).

[5] Hildebrand, THIS JOURNAL, **30**, 1672 (1908).

[6] Van Brunt, *ibid.*, **36**, 1448 (1914).

[7] Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

[8] D. J. and J. J. Beaver, *Ind. Eng. Chem.*, **115**, 359 (1923).