$NaPO_3$II, "Madrell salt," is obtained by crystallizing the glass just below 443°. Obtained in this way, it rarely is well crystallized, but when obtained with aid of water, it usually gives well-formed crystals. "Madrell salt" is the stable phase from the incongruent melting of $Na_2H_2P_2O_7$ at 375 to 443°, at which temperature it changes to $NaPO_3$I. The conversion of $NaPO_3$I to $NaPO_3$II in the dry way is difficult and even is slow with the aid of 4% water. It will, however, change to II when heated with water in a sealed tube for a few days within the stability range of $NaPO_3$II. It dissolves very slowly in water.

$NaPO_3$III.—This was obtained by Liddell[7] as an insoluble residue from glassy $NaPO_3$ devitrified at 300°. The optical properties were determined by Earl Ingerson.[8]

$NaPO_3$I′.—This also was prepared by Liddell,[7] and the optical properties were determined by Ingerson.[8] The preparation and the X-ray pattern were confirmed in this Laboratory. A second form, $NaPO_3$I″, was described by Liddell, but we have not been able to prepare it by the method described, and accordingly no more information on it is available than is given in Liddell's paper.

"Kurrol Salt."—Huber and Klumpner[9] have given directions for the preparation of this form of crystalline $NaPO_3$, and Liddell has confirmed the preparation.

There are listed above six forms of crystalline $NaPO_3$, and a seventh form, otherwise unknown, is listed in the A.S.T.M. card index of X-Ray Diffraction Data, First Supplementary Set, II-1725 (1945). The only ones of known stability are those listed above as $NaPO_3$I and $NaPO_3$II. The others may have a region of stability or may be metastable or monotropic, but to establish the facts would be difficult.

---

[7] Robert W. Liddell, THIS JOURNAL, **71**, 207 (1949).

[8] Private communication.

[9] Hans Huber and Karl Klumpner, *Z. anorg. allgem. Chem.*, **251**, 213 (1943).

WASHINGTON, D. C.

[CONTRIBUTION FROM THE WM. H. NICHOLS LABORATORY OF NEW YORK UNIVERSITY]

The Solubilities of the Strontium Halates

BY WILLIAM F. LINKE

RECEIVED MAY 8, 1953

The eutectic of the system $Sr(ClO_3)_2$–H_2O lies at −37.0° and 54.5% $Sr(ClO_3)_2$, with $Sr(ClO_3)_2·3H_2O$ and ice as solids. The transition from trihydrate to anhydrous salt occurs at 10°; a saturated solution boils at 121° and contains 68.7% $(SrClO_3)_2$. The composition of the trihydrate was confirmed by the change in its solubility at −20° when $SrBr_2$ was added to the solution. The eutectic of the system $Sr(BrO_3)_2$–H_2O is at −2.18° and 17.50% $Sr(BrO_3)_2$, with $Sr(BrO_3)_2·H_2O$ and ice as solids. The transition from monohydrate to anhydrous salt occurs at 75.5°, and a saturated solution boils at 104° and contains 41.0% $Sr(BrO_3)_2$. $Sr(IO_3)_2·H_2O$ and $Sr(IO_3)_2·6H_2O$ precipitate from saturated solutions and do not decompose when isolated, but above 6° both are metastable with respect to the anhydrous salt. From the intersections of the solubility curves, the stable transition from hexahydrate to anhydrous salt has been found to occur at 6°, and the metastable transition from hexa- to monohydrate at 20.8°.

Tri-, penta- and octahydrates of strontium chlorate have been reported, and several allotropic modifications of the anhydrous salt are also listed.[1] The solubility of the anhydrous salt has been determined only at 18°. The solubility of monohydrated strontium bromate was determined at 15° by Rammelsberg, and at 18° by Kohlrausch, but little else is known of the hydrates or solubility relations of the salt. The mono- and hexahydrates of strontium iodate are well known, but their relative stabilities, and that of the anhydrous salt have not been investigated. The solubilities reported by earlier investigators do not agree with that found by Colman-Porter and Monk,[2] and various authors[2,3] report anomalies in the preparation of the monohydrate.

Materials

Strontium Chlorate.—A chloric acid solution was prepared from roughly equivalent quantities of C.P. $Ba(ClO_3)_2$ and H_2SO_4, and small amounts of BaO and H_2SO_4 were then added until no significant tests for Ba^{++} or $SO_4^{=}$ were obtained. C.P. $SrCO_3$ (which was previously leached with a large volume of boiling water) was then added until present in excess. The mixture was filtered, and evaporation by boiling yielded pure white anhydrous $Sr(ClO_3)_2$. The solution did not bump during the evaporation. The solid was recrystallized from water, air-dried, and stored at room temperature. The crystals seemed somewhat moist, and upon standing for several days some of them formed droplets of solution. Potilitzyn[1] has said that $Sr(ClO_3)_2$ is not deliquescent unless it contains $SrCl_2$, but no Cl^- ion was detected when $AgNO_3$ was added to a solution of the salt. A qualitative flame test showed that no sodium, and only traces of calcium were present. Analysis by reduction to chloride and Volhard titration showed 99.6% $Sr(ClO_3)_2$. Loss in weight upon drying at 110° was 0.26%.

$Sr(ClO_3)_2·3H_2O$ was prepared by cooling a concentrated solution of the anhydrous salt in an acetone–Dry Ice-bath. When the solution had become very viscous, vigorous scratching produced the trihydrate. The excess solution was removed by suction, and the moist solid was stored at 7°.

Strontium Bromate.—The monohydrate was prepared from $Ba(BrO_3)_2$, H_2SO_4 and $SrCO_3$ in the same manner as the chlorate. The solution of $Sr(BrO_3)_2$ was evaporated, and in sharp contrast to the behavior of $Sr(ClO_3)_2$, the solid formed a cake on the bottom of the beaker and caused violent bumping. The salt cake was broken up only with difficulty, and the crystals showed strong triboluminescence when scratched. The salt was recrystallized from water and air-dried. Iodometry showed 95.2% $Sr(BrO_3)_2$ (calcd. for $Sr(BrO_3)_2·H_2O$ 95.0%). Loss in weight at 110° was 4.89% (calcd. 4.99%).

Strontium Iodate.—The monohydrate was prepared by mixing equivalent quantities of C.P. $SrCl_2·6H_2O$ and HIO_3

---

[1] For original references to older work, see: J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green & Co., New York, N. Y., 1932, and Gmelin, "Handbuch der anorganischen Chemie," Vol. 29, Strontium, 1931.

[2] C. A. Colman-Porter and C. B. Monk, *J. Chem. Soc.*, 1812 (1952).

[3] S. Peltier and C. Duval, *Anal. chim. acta*, **1**, 355 (1947).

(each in solution) in a large volume of water at 24°. White, finely crystalline $Sr(IO_3)_2 \cdot H_2O$ settled rapidly and was washed by decantation until no test for Cl^- ions was obtained, and until the addition of a small amount of KI produced no immediate brown color, indicating the absence of free acid. The salt air-dried to a fluffy white powder, and analysis by iodometry and loss in weight at 110° showed the theoretical proportions of $Sr(IO_3)_2$ and H_2O to be present (96.0% $Sr(IO_3)_2$ in $Sr(IO_3)_2 \cdot H_2O$).

The hexahydrate was prepared in the same manner as the monohydrate, except that all solutions and wash water were cooled with ice. The solid was indistinguishable from the monohydrate to the naked eye. Drying with acetone produced a fluffy powder which contained 79.85% $Sr(IO_3)_2$ (calcd. for $Sr(IO_3)_2 \cdot 6H_2O$ 80.18%).

Anhydrous $Sr(IO_3)_2$ was obtained by heating either the mono- or hexahydrate to 110° for a few hours, or by boiling them with water.

Methods

Temperatures between 0 and 100° were maintained in water-baths in which the maximum variation never exceeded ±0.1°, and was usually much less. At 110° an acetic acid vapor bath was used.[4] At 0° and below, baths of melting ice and of melting mono-, di- and triethylene glycol were employed. Freezing points were determined from the cooling curves of known mixtures and were reproducible to ±0.05°.

Equilibrium in saturated solutions was established by repeated analysis after several hours of internal stirring. Representative points were checked by approach from supersaturation, and the results agreed well in each case. Each reported value is the average of at least two closely agreeing determinations. Filtered samples of the solution were withdrawn with preheated calibrated pipets, and approximate densities were calculated.

Analysis for chlorate was made by reduction to chloride with nitrite and subsequent Volhard titration.[5] Bromate and iodate were determined iodometrically.

Results and Discussion

System $Sr(ClO_3)_2$–H_2O.—The system was studied from the eutectic (−37.0°) to the boiling point (121°). Below 10° the stable phase is the trihydrate ($Sr(ClO_3)_2 \cdot 3H_2O$), and above 10° is the anhydrous salt. The anhydrous salt forms supersaturated solutions readily, and a solution which is saturated at room temperature can be cooled to a glass (at −80°) without crystallization. The trihydrate precipitates from the cooled solutions when the walls of the container are scratched vigorously.

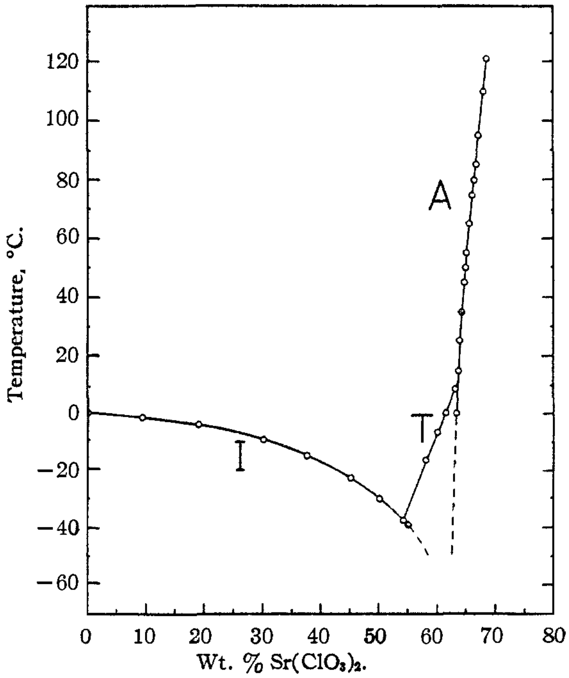

Fig. 1.—System $Sr(ClO_3)_2$–H_2O: I, ice; T, trihydrate; A, anhydrous.

The solubilities are listed in Table I, and plotted in Fig. 1. Their precision is about one part per thousand. The densities were less reproducible, and so the experimental data were plotted and a smooth curve drawn through the points. The values reported in Table I were read from the curve and their estimated accuracy is two to three parts per thousand.

TABLE I

EQUILIBRIUM IN THE SYSTEM $Sr(ClO_3)_2$–H_2O

Temp., °C.	G. $Sr(ClO_3)_2$ per 100 g. satd. soln.	Temp., °C.	G. $Sr(ClO_3)_2$ per 100 g. satd. soln.	Density[b]
		$Sr(ClO_3)_2 \cdot 3H_2O + Sr(ClO_3)_2$		
− 1.8	9.29	10 ± 1g	63.4g	1.829
− 4.0	17.92			
− 9.4	29.94		$Sr(ClO_3)_2$	
−14.2	37.46			
−22.2	45.11	0m	63.23m	1.828m
−29.4	49.87	15	63.55	1.830
−38.1m[a]	55.0m	25	63.78	1.831
		35	64.17	1.833
Ice + $Sr(ClO_3)_2 \cdot 3H_2O$		45	64.55	1.835
		50	64.65	1.837
−37.0 ± 0.5	54.5g[b]	55	64.95	1.838
		65	65.32	1.842
$Sr(ClO_3)_2 \cdot 3H_2O$		75	66.0	1.845
		80	66.07	1.847
−28	57.1	85	66.41	1.849
−16.7	57.9	95	67.08	1.853
− 7	59.9	110	67.8	1.861
0	61.4	121 ± 1	68.7g	1.867
9	63.47			

[a] m = metastable. [b] g = determined graphically.

The composition of the trihydrate could not be determined by direct analysis. Several attempts were made to dry the solid by suction, with filter paper, and by repeated washing with acetone. In each case the salt was kept at about −15°, but the results were not reproducible. Analysis of the "dried" solid indicated 4.8–6.6 moles of water per mole of salt when suction was used, and 3.5–4.3 moles of water after washing with acetone. The composition was finally established by determining the solubility of the trihydrate in strontium bromide solutions from −18 to −23°.

Known complexes were prepared by weighing together anhydrous $Sr(ClO_3)_2$, analyzed $SrBr_2 \cdot 6H_2O$, and water. Sufficient water was always present to dissolve the salts completely at about room temperature, and when they had dissolved the solutions were cooled with Dry Ice and seeded with the trihydrate. The trihydrate precipitated rapidly upon seeding, and the mixtures were then placed in a bath of melting ethylene glycol (about −20°, but constant for each sample) and stirred for 1–2.5 hr. Separate samples of each solution were analyzed for (1) bromide, by Volhard titration, and (2) total halide, after reduction of ClO_3^- to Cl^- with NO_2^-. The analyses were tested on

---

[4] W. F. Linke, *J. Chem. Ed.*, **29**, 492 (1952).

[5] J. E. Ricci and A. J. Freedman, THIS JOURNAL, **74**, 1765 (1952).

known mixtures of KBr and $NaClO_3$, and showed an accuracy of 1 or 2 parts per thousand. The results are listed in Table II. Algebraic extrapolation gave an average of 17.30% H_2O, as compared with 17.51% H_2O for the formula $Sr(ClO_3)_2 \cdot 3H_2O$, confirming Potilitzyn's statement that the solid is a trihydrate.

TABLE II

EQUILIBRIUM IN THE SYSTEM $Sr(ClO_3)_2$–$SrBr_2$–H_2O

Temp., °C.	Wt., % Original complex $Sr(ClO_3)_2$	Wt., % Original complex $SrBr_2$	Wt., % Saturated soln. $Sr(ClO_3)_2$	Wt., % Saturated soln. $SrBr_2$	Wt., % H_2O in solid (by extrap.)
−18	58.91	4.07	52.66	5.16	17.75
−20	58.41	4.98	50.86	6.54	17.48
−20	58.91	5.11	50.14	7.01	17.51
−20	58.38	4.47	51.33	5.78	17.54
−23	57.84	5.17	49.97	6.81	17.35
−23.5	58.14	4.48	51.08	5.71	16.14

When a hot saturated solution is allowed to cool, anhydrous $Sr(ClO_3)_2$ crystallizes as distinct octahedra. If the solution is exposed to the air, however, a solid crust forms on the surface, and when this crust is broken apart the fragments appear as plates and needles. These crystal forms have been reported previously,[1] but have not been isolated because they seem to disintegrate upon drying. In order to determine the conditions under which the various crystals are formed, saturated solutions were prepared at a number of temperatures (up to 100°), and then allowed to cool. The resulting crystals were examined microscopically. When a solution was cooled in such a way that evaporation was impossible (as under a cover glass or in a pipet), only rhombic octahedra were produced. If the solution was exposed to the air a crust formed on the surface, but the octahedra were produced in the body of the liquid. Microscopic examination of the crusts did not reveal any distinct crystals, but showed striations and clear patches which apparently broke into needles and plates when agitated. Similar plate-like aggregates were formed in solutions which were held at high temperatures and allowed to evaporate, and the tendency to crystallize at the surface is especially noticeable when a saturated solution is boiled. When the solubility measurements were made the solutions were usually open to the air and free to evaporate. There is no suggestion of polymorphism in the smooth solubility curve, and it seems that the plate and needle forms may simply be the result of evaporation and rapid crystallization.

No evidence of a penta- or octahydrate was found. As was mentioned by Potilitzyn,[1] the "glass" obtained by cooling a saturated solution from room temperature to −80° has approximately the composition $Sr(ClO_3)_2 \cdot 8H_2O$, and this "hydrate" has been listed because of this reference.

System $Sr(BrO_3)_2$–H_2O.—The monohydrate is the stable phase from the eutectic (−2.18°) to 75.5°. From 75.5° to the boiling point (104°) saturated solutions are in equilibrium with the anhydrous salt. Both solid phases attain equilibrium rapidly, but the precision of the data involving the anhydrous salt is somewhat less than those of the monohydrate. Duplicate solubility determinations at temperatures just above the transition point differed from each other by as much as 0.5 wt %, although no such deviations occurred at higher or lower temperatures. Graphical determination of the transition temperature was consequently unreliable, and so the solids were analyzed directly. Samples of the anhydrous and monohydrated salts and their saturated solutions were stirred for several hours at temperatures near the transition point, and the solids were then analyzed. At 73, 74 and 75° (all ±0.05°), the monohydrate remained unchanged, while the anhydrous material became hydrated. At 76° the anhydrous salt was unaffected, and the hydrate lost water. The transition temperature was thus found to lie between 75° and 76°.

Contrary to the observation of Potilitzyn,[1] strontium bromate forms supersaturated solutions, but only at low temperatures. When a solution containing 18.48% $Sr(BrO_3)_2$ was cooled, ice crystals were formed instead of the expected monohydrate. In addition, cooling curves which were used to fix the position of the ice curve showed an apparently reproducible eutectic halt at about −3.0°, but the intersection of the saturation curves lies at −2.18°. Direct determinations of the eutectic temperature were then made by cooling mixtures which contained an excess of the solid monohydrate. In each case the temperature −2.18° (± 0.02°) was observed. The lower temperature which was observed on the cooling curves of unsaturated solutions must thus have been due to supersaturation.

The data are reported in Table III. The estimated accuracy of the solubilities is 1 to 2 parts per thousand, and of the densities is 2 to 3 parts per thousand.

TABLE III

EQUILIBRIUM IN THE SYSTEM $Sr(BrO_3)_2$–H_2O

Temp., °C.	G. $Sr(BrO_3)_2$ per 100 g. satd. soln.	Density
	Ice	
−1.14	9.38	.....
−1.84	14.94	.....
−2.03	16.15	.....
−2.10	16.85	.....
−2.28m[a]	18.48m	.....
	Ice + $Sr(BrO_3)_2 \cdot H_2O$	
−2.18	17.50g	1.165g[b]
	$Sr(BrO_3)_2 \cdot H_2O$	
0	18.32	1.177
4.4	20.11	1.199
15	23.97	1.241
25	27.25	1.285
35	30.03	1.320
45	32.69	1.356
55	35.15	1.384
65	37.57	1.422
72	39.15	.....
75	39.75	1.458
	$Sr(BrO_3)_2 \cdot H_2O$ + $Sr(BrO_3)_2$	
75.5 ± 0.5	39.9g	1.458g
	$Sr(BrO_3)_2$	
76	39.9	.....
77	39.9	1.457
79	40.1	.....
80	40.1	1.461
82	40.37	.....
85	40.60	1.462
90	40.75	1.465
95	40.89	1.465
104 ± 1	41.0g[b]	1.470g

[a] m = metastable. [b] g = determined graphically.

System $Sr(IO_3)_2$–H_2O.—The system was studied from 0 to 95°. Below 6° the stable phase is the hexahydrate, and above 6° is the anhydrous salt. The monohydrate is metastable with respect to the anhydrous salt at all temperatures, and with respect to the hexahydrate below 20.8°.

Equilibrium was attained after an hour or two of stirring when either of the hydrates was the saturating phase. The anhydrous salt reached equilibrium much more slowly (especially from supersaturation), and in one case at a low temperature had not reached equilibrium after 6 hr. of stirring.

TABLE IV

EQUILIBRIUM IN THE SYSTEM $Sr(IO_3)_2$–H_2O

		Wt., % $Sr(IO_3)_2$		
	Temp., °C.	Anhydrous	Monohydrate	Hexahydrate
	0	0.098m[a]	0.1453m	0.0861
T	6 ± 1g[b,c]	.117g	......	.117g
	7	.120	.1763m	.1230m
	11	.130	......	.1505m
	15	.138	.2115m	.1822m
	18	......	......	.2135m
	20	.161	.2369m	.2302m
T	20.8 ± 0.5g	......	.241mg	.241mg
	25	.165	.2606m	.2914m
	35	......	.3116m	
	40	.203	.3399m	
	45	......	.3657m	
	55	.242	.4216m	
	65	.267	.4769m	
	75	.296	.5344m	
	85	.315	......	
	95	.340	......	
	100	.350g	.68mg	

[a] m = metastable. [b] g = determined graphically. [c] T = transition temperature.

The data are listed in Table IV and plotted in Fig. 2. The estimated accuracy is ±0.005 wt. % for solutions saturated with the anhydrous salt, and ±0.0005 wt. % when the hydrates were present.

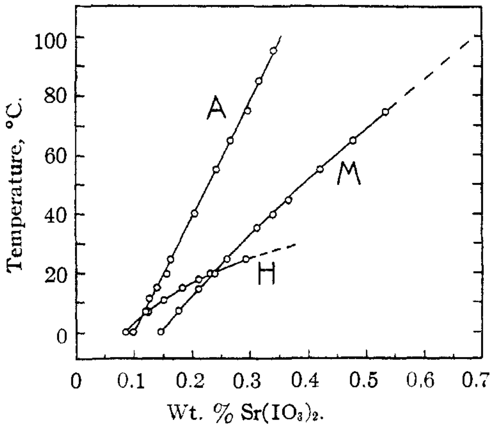

Fig. 2.—System $Sr(IO_3)_2$–H_2O: A, anhydrous; M, monohydrate; H, hexahydrate.

The transition temperatures were determined graphically. Although they are metastable, the hydrates do not change to the anhydrous salt at low temperatures. The solubility of the monohydrate did not change after 6.5 hours stirring at 35°, nor after 4.5 hours at 65°. At 75° no change occurred after one hour stirring, but after two hours the much more voluminous anhydrous salt was formed, and the solubility decreased sharply. The behavior of the hexahydrate was similar to that of the monohydrate. There was apparently no tendency to change to the anhydrous salt at low temperatures. At 25°, where the hexahydrate is metastable with respect to both anhydrous and monohydrate forms, no change in its solubility was detected after two days stirring. At 40°, however, the hexahydrate was converted to the monohydrate within an hour. Several of the various metastable solutions were seeded with the more stable phases, but without effect.

The behavior of the hydrates at various temperatures in open air was investigated by repeated weighings of samples after varying periods of time. Samples of the monohydrate stood at room temperature (about 25°) for several months without change. At about 16° there was no change in weight after two months. At 50 and 55° the monohydrate lost only negligible amounts of water after one month. At 62° a slow loss in weight occurred, and at 72° it became more rapid, but the water of hydration was not lost completely after 6 days at this temperature. At 110° the salt becomes anhydrous in 2–3 hr. The hexahydrate lost weight slowly at 25°, and in two days had lost about 20% of its water of crystallization. At 16°, however, there was no significant loss in weight after two months. At high temperatures (110°) it rapidly becomes anhydrous.

The interesting metastable relationships of the various solids explain the anomalies reported by previous investigators. For example, Peltier and Duval[3] report that mixing $SrCl_2$ and HIO_3 solutions produces "a mixture of the anhydrous and monohydrated products." Colman-Porter and Monk[2] found that "(monohydrated)...crystals formed by mixing solutions at 80° showed lower solubility which showed considerable variation." In both cases the metastable monohydrate had partially decomposed to the anhydrous salt.

Experiments showed that if a solution is cooled below 20.8° (the hexahydrate–monohydrate transition temperature), the hexahydrate will precipitate. Above 20.8°, and up to about 65°, the monohydrate is formed, and at higher temperatures (boiling solution) the anhydrous salt is obtained.

NEW YORK 53, N. Y.