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Phase Equilibria of the System Sulfur Trioxide–Water[1]

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Although the system sulfur trioxide–water has been extensively studied, there is still much disagreement in the literature. In certain parts of the diagram uncertainty exists even regarding the nature of the solid phase which is in equilibrium with solution.

The melting points and various other properties of hydrates of sulfur trioxide as pure compounds were studied by many authors,[3] as were the behavior of various solutes, including water, in absolute sulfuric acid as a solvent.[4] Four extensive investigations[5] of the phase diagram have used thermal analysis.

In view of the discrepancies in reported results, a different approach, namely, the equilibrium solubility method, was used in this investigation for the determination of all portions of the diagram except those pertaining to pure compounds, eutectics and peritectics. In this method a mixture of solid and liquid phases is agitated at constant temperature until equilibrium is established. The liquid phase is then sampled and analyzed for sulfur trioxide content. By such procedure equilibrium can be ensured, solubilities can be correlated with known and well-defined phases, and the complete solubility curves of stable and metastable solids can be obtained.

Experimental

Three constant temperature baths were used. Between 0 and 40° the bath temperature was controlled within 0.02°, between −50 and 0° within 0.2°, and between −75 and −50° within 0.1°.

Five-junction copper–constantan thermocouples were calibrated at the boiling and freezing points of water, at the sodium sulfate, mercury and carbon dioxide points. The e.m.f. of these thermocouples was measured by a Leeds and Northrup Type K potentiometer, and temperatures were calculated by the method recommended by Scott.[6] All temperature measurements were made with the thermocouple immersed in the actual equilibrium mixture and at an accuracy believed to be better than 0.02°.

All-glass equilibrium vessels were used. These were equipped with liquid-seal stirrers, sulfuric acid being used as sealing liquid.

Sulfuric acid samples were prepared by distillation of reagent grade sulfuric acid in an all-glass still. In all distillations the first and last quarter portions were rejected. The samples in the fuming range were prepared by distilling sulfur trioxide from 60% oleum into sulfuric acid prepared as above. All solutions were colorless, and were discarded if any discoloration appeared.

Samples of a composition between that of the expected solid and liquid phases were placed in the appropriate constant temperature bath and brought to temperature. The composition of the solution was adjusted, when necessary, by adding either stronger or weaker acid until seeding caused the desired phase to crystallize. The mixture was then agitated for sufficient time to establish equilibrium, as determined by observation of temperature and by check samples. After the temperature became constant, check samples were usually taken at three-hour intervals. In the case of some solutions in the fuming range it was found that twelve or more hours were necessary to obtain check analyses.

In the non-fuming range samples were filtered by suction through a Filtros plug directly into a glass stoppered test-tube. A sample for analysis was then weighed in a Lunge–Rey weighing pipet and titrated with sodium hydroxide solution. In the fuming range filtration by suction was considered inadvisable. The solid phase was allowed to settle until the supernatant liquid became perfectly clear. The stem of a previously weighed ampoule was inserted directly into the supernatant liquid and a sample was withdrawn for analysis. The ampoule was then sealed, weighed, and broken with a heavy glass rod under water in a closed cylinder. Escape of any fumes generated in the reaction was thus prevented. Aliquot portions were titrated with sodium hydroxide solution.

Although the equilibrium solubility method is superior to thermal analysis in univariant regions, it is not well adapted to the determination of invariant points. With invariant systems the objections levied against the thermal analytical method do not apply, and it is possible to obtain satisfactory horizontal portions on time–temperature curves even when serious supercooling occurs. Consequently, all eutectic and peritectic temperatures, as well as melting points of congruent compounds, were determined by thermal analysis.

For determining eutectic points, solutions were generally chosen slightly to one side of that anticipated for the eutectic. The solution was cooled until it became supersaturated with respect to one phase and this phase was seeded out. Slow cooling was then continued to 1–2° below the eutectic temperature, and the eutectic was seeded out by adding the other phase. The temperature rose, became constant, and then fell. The constant temperature observed was taken as the eutectic temperature. Transition temperatures were determined in the same way. In some cases samples of the liquid were removed while the temperature was constant, and analyzed to give the eutectic or peritectic composition. In other cases eutectic compositions were determined by extrapolation of the equilibrium curves.

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[6] R. B. Scott, "Temperature, Its Measurement and Control in Industry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 206.

In determining the melting points of pure compounds, solutions of composition as near as possible to that of the pure compound were prepared, and the freezing points were determined by a method similar to that used for eutectics.

Results and Discussion

The results obtained in this investigation for sulfur trioxide contents of 0–93.7% by weight are summarized in Table I. This table gives the temperatures and compositions of liquid phases which are in equilibrium with the various solid phases. The data are presented graphically in Figs. 1, 2 and 3. Eight solid phases were encountered, all of which exhibit congruent melting points except $H_2SO_4\cdot 6H_2O$ and $H_2SO_4\cdot 3H_2O$. The melting points of all compounds, and the temperatures and compositions of all invariant points are given in Table II.

The composition of a compound which has a congruent melting point corresponds to the maximum of its solubility curve. The composition of the trihydrate, which does not have a congruent melting point, was obtained as follows. A solution close to the composition of this compound gave at the peritectic reaction a liquid phase containing 52.81% SO_3, or $H_2SO_4\cdot 2.95\ H_2O$. The remainder of the sample, on cooling slightly below the peritectic temperature, was found to be completely solid, and to contain 52.05% SO_3, which corresponds to $H_2SO_4\cdot 3.09\ H_2O$. The fact that the residue was solid immediately below the peritectic temperature indicates that it consisted of a mixture of $H_2SO_4\cdot 4H_2O$ and the unknown phase. Consequently the composition of the unknown solid must lie between 2.95 and 3.09 H_2O, and hence the most likely formula is $H_2SO_4\cdot 3H_2O$. This hydrate apparently has not been reported previously.

The compound which undergoes a peritectic reaction at −53.73° was reported by Hulzmann and Biltz[5c] to be $H_2SO_4\cdot 6H_2O$. Since nothing has arisen in this study to make us question this conclusion, the composition of this compound was not redetermined.

TABLE I

FREEZING POINTS

(m) = metastable equilibrium

Solid phase	SO_3, %	Temp., °C.	Solid phase	SO_3, %	Temp., °C.	Solid phase	SO_3, %	Temp., °C.	Solid phase	SO_3, %	Temp., °C.
H_2O	1.48	− 0.59	$H_2SO_4\cdot 4H_2O$	41.48	−34.20	$H_2SO_4\cdot H_2O$	65.07	− 1.40	H_2SO_4	82.04	+ 8.36
H_2O	1.97	− 1.06	$H_2SO_4\cdot 4H_2O$	43.33	−30.97	$H_2SO_4\cdot H_2O$	65.58	+ 1.24	H_2SO_4	82.67	5.51
H_2O	4.38	− 2.27	$H_2SO_4\cdot 4H_2O$	44.21	−29.89	$H_2SO_4\cdot H_2O$	66.45	4.41	H_2SO_4	82.86	3.56
H_2O	6.87	− 3.84	$H_2SO_4\cdot 4H_2O$	45.20	−29.10	$H_2SO_4\cdot H_2O$	66.69	4.44	H_2SO_4	83.00	1.87
H_2O	8.74	− 5.14	$H_2SO_4\cdot 4H_2O$	46.01	−28.62	$H_2SO_4\cdot H_2O$	67.53	7.13	H_2SO_4	83.36	+ 0.78
H_2O	10.86	− 7.01	$H_2SO_4\cdot 4H_2O$	47.05	−28.36	$H_2SO_4\cdot H_2O$	68.25	8.21	H_2SO_4	83.53	− 1.97
H_2O	13.84	−10.29	$H_2SO_4\cdot 4H_2O$	47.42	−28.41	$H_2SO_4\cdot H_2O$	68.49	8.40	H_2SO_4	84.16	− 6.06
H_2O	16.72	−14.48	$H_2SO_4\cdot 4H_2O$	49.01	−29.37	$H_2SO_4\cdot H_2O$	68.79	8.16	H_2SO_4	84.44	− 6.53
H_2O	19.52	−19.95	$H_2SO_4\cdot 4H_2O$	49.60	−29.86	$H_2SO_4\cdot H_2O$	68.83	8.57	H_2SO_4	84.45	− 9.96
H_2O	21.41	−24.66	$H_2SO_4\cdot 4H_2O$	51.25	−32.66	$H_2SO_4\cdot H_2O$	68.87	8.38	$H_2SO_4 + H_2S_2O_7$	84.50	−10.15
H_2O	22.77	−28.81	$H_2SO_4\cdot 4H_2O$	52.62	−36.60	$H_2SO_4\cdot H_2O$	69.31	8.28	$H_2S_2O_7$	84.58	− 9.15
H_2O	24.32	−34.34	$H_2SO_4\cdot 4H_2O$(m)	54.10	−41.66	$H_2SO_4\cdot H_2O$	69.65	8.10	$H_2S_2O_7$	84.66	− 8.77
H_2O	25.98	−41.18	$H_2SO_4\cdot 4H_2O$(m)	55.06	−46.14	$H_2SO_4\cdot H_2O$	70.77	5.24	$H_2S_2O_7$	84.81	− 4.48
H_2O	26.63	−44.98	$H_2SO_4\cdot 4H_2O$(m)	55.97	−51.80	$H_2SO_4\cdot H_2O$	70.90	5.27	$H_2S_2O_7$	84.87	− 4.12
H_2O	27.37	−49.44	$4H_2O + 3H_2O$	52.81	−36.56	$H_2SO_4\cdot H_2O$	71.79	+ 2.40	$H_2S_2O_7$	84.83	− 3.44
H_2O	28.13	−54.62	$4H_2O + 2H_2O$			$H_2SO_4\cdot H_2O$	72.35	0.00	$H_2S_2O_7$	85.53	− 1.20
H_2O	28.80	−59.23	(m)	55.35	−47.46	$H_2SO_4\cdot H_2O$	72.65	− 1.36	$H_2S_2O_7$	85.33	+ 1.37
H_2O	29.14	−61.91	$H_2SO_4\cdot 3H_2O$	53.62	−36.98	$H_2SO_4\cdot H_2O$	73.33	− 4.64	$H_2S_2O_7$	85.47	+ 3.23
H_2O(m)	29.64	−65.31	$H_2SO_4\cdot 3H_2O$	55.08	−38.38	$H_2SO_4\cdot H_2O$	73.98	− 9.18	$H_2S_2O_7$	85.92	9.07
H_2O(m)	30.09	−69.22	$H_2SO_4\cdot 3H_2O$	56.31	−41.22	$H_2SO_4\cdot H_2O$	74.81	−15.32	$H_2S_2O_7$	86.07	12.16
H_2O(m)	30.30	−71.21	$H_2SO_4\cdot 3H_2O$(m)	57.15	−43.50	$H_2SO_4\cdot H_2O$	75.41	−20.72	$H_2S_2O_7$	86.09	9.68
$H_2O + 6H_2O$	29.20	−61.98	$H_2SO_4\cdot 3H_2O$(m)	57.87	−46.29	$H_2SO_4\cdot H_2O$	75.57	−23.17	$H_2S_2O_7$	86.28	14.27
$H_2O + 4H_2O$(m)	30.65	−73.10	$H_2SO_4\cdot 3H_2O$(m)	58.53	−49.35	$H_2SO_4\cdot H_2O$	76.02	−28.24	$H_2S_2O_7$	86.81	19.44
$H_2SO_4\cdot 6H_2O$	29.55	−61.33	$3H_2O + 2H_2O$	56.90	−42.70	$H_2SO_4\cdot H_2O$	76.43	−33.84	$H_2S_2O_7$	86.85	19.23
$H_2SO_4\cdot 6H_2O$	30.85	−58.67	$3H_2O + 1H_2O$			$H_2SO_4\cdot H_2O$ +			$H_2S_2O_7$	87.46	24.50
$H_2SO_4\cdot 6H_2O$	31.62	−57.12	(m)	59.10	−52.85	H_2SO_4	76.55	−34.86	$H_2S_2O_7$	87.46	24.31
$H_2SO_4\cdot 6H_2O$	33.06	−55.74	$H_2SO_4\cdot 2H_2O$(m)	55.44	−47.01	H_2SO_4	76.58	−34.61	$H_2S_2O_7$	88.80	33.51
$6H_2O + 4H_2O$	34.62	−53.73	$H_2SO_4\cdot 2H_2O$(m)	56.09	−44.18	H_2SO_4	76.91	−28.94	$H_2S_2O_7$	89.08	34.42
$H_2SO_4\cdot 4H_2O$(m)	31.27	−71.39	$H_2SO_4\cdot 2H_2O$	56.93	−42.76	H_2SO_4	77.36	−24.46	$H_2S_2O_7$	89.60	34.66
$H_2SO_4\cdot 4H_2O$(m)	31.49	−69.91	$H_2SO_4\cdot 2H_2O$	58.11	−40.45	H_2SO_4	77.75	−19.63	$H_2S_2O_7$	89.65	34.90
$H_2SO_4\cdot 4H_2O$(m)	31.74	−68.41	$H_2SO_4\cdot 2H_2O$	59.04	−39.72	H_2SO_4	78.39	−14.91	$H_2S_2O_7$	89.81	34.85
$H_2SO_4\cdot 4H_2O$(m)	32.72	−63.27	$H_2SO_4\cdot 2H_2O$	59.70	−39.51	H_2SO_4	78.74	− 9.95	$H_2S_2O_7$	89.86	35.15
$H_2SO_4\cdot 4H_2O$(m)	32.29	−65.29	$2H_2O + 1H_2O$	60.15	−39.87	H_2SO_4	79.37	− 5.43	$H_2S_2O_7$	90.58	34.07
$H_2SO_4\cdot 4H_2O$(m)	33.62	−58.59	$H_2SO_4\cdot H_2O$(m)	59.12	−52.15	H_2SO_4	79.83	− 1.98	$H_2S_2O_7$	90.85	33.12
$H_2SO_4\cdot 4H_2O$(m)	34.03	−56.72	$H_2SO_4\cdot H_2O$(m)	59.41	−49.08	H_2SO_4	80.33	+ 0.46	$H_2S_2O_7$	91.11	30.09
$H_2SO_4\cdot 4H_2O$	34.81	−53.48	$H_2SO_4\cdot H_2O$(m)	59.89	−44.15	H_2SO_4	80.56	2.80	$H_2S_2O_7$	91.61	26.37
$H_2SO_4\cdot 4H_2O$	35.50	−50.95	$H_2SO_4\cdot H_2O$	60.68	−34.57	H_2SO_4	80.87	4.97	$H_2S_2O_7$	92.74	16.11
$H_2SO_4\cdot 4H_2O$	36.25	−48.47	$H_2SO_4\cdot H_2O$	61.29	−28.89	H_2SO_4	81.51	9.17	$H_2S_2O_7$	93.27	10.04
$H_2SO_4\cdot 4H_2O$	37.71	−43.65	$H_2SO_4\cdot H_2O$	61.97	−22.81	H_2SO_4	81.62	10.372	$H_2S_2O_7$	93.11	5.32
$H_2SO_4\cdot 4H_2O$	38.54	−41.49	$H_2SO_4\cdot H_2O$	62.52	−18.21	H_2SO_4	81.65	10.32	$H_2S_2O_7$	93.33	3.31
$H_2SO_4\cdot 4H_2O$	38.98	−39.86	$H_2SO_4\cdot H_2O$	62.89	−15.12	H_2SO_4	81.69	10.22	$H_2S_2O_7$	93.69	2.24
$H_2SO_4\cdot 4H_2O$	40.38	−36.63	$H_2SO_4\cdot H_2O$	63.63	− 9.82	H_2SO_4	81.77	9.66			
			$H_2SO_4\cdot H_2O$	64.76	− 3.21	H_2SO_4	81.80	8.36			

TABLE II

MELTING (M), EUTECTIC (E) AND TRANSITION (T) POINTS

First composition and temperature given for each point is result of this paper; m denotes metastable equilibrium

Solid phases	Composition % SO_3				Temp., °C.		
$H_2SO_4·6H_2O$, H_2O(E)	29.20				−61.98	−62.0[3c]	
H_2O, $H_2SO_4·4H_2O$(E)(m)	30.65	30[5c]	31[3k]	31[5a]	−73.10	−72.4[5c] −75[5a]	−72[3k]
$H_2SO_4·6H_2O$, $H_2SO_4·4H_2O$(T)	34.62	38[5c]			−53.73	−54.0[5c]	
$H_2SO_4·4H_2O$(M)					−28.36	−28.7[5c] −25.0[5a]	−29[3i]
$H_2SO_4·4H_2O$, $H_2SO_4·3H_2O$(T)	52.81				−36.56		
$H_2SO_4·4H_2O$, $H_2SO_4·2H_2O$(E)(m)	55.35	55.5[5c]	55.1[3k]		−47.46	−47.2[5c]	−46[3k]
$H_2SO_4·3H_2O$, $H_2SO_4·2H_2O$(E)	56.90				−42.70		
$H_2SO_4·2H_2O$(M)					−39.51	−39[5c]	−38.9[3i] −36.7[3k]
$H_2SO_4·3H_2O$, $H_2SO_4·H_2O$(E)(m)	59.10				−52.85		
$H_2SO_4·2H_2O$, $H_2SO_4·H_2O$(E)	60.15	60.0[5c]	61.1[3k]		−39.87	−39.5[5c]	−41[3k]
$H_2SO_4·H_2O$(M)					8.56	8.50[3a,5c,d]	8.53[5a]
$H_2SO_4·H_2O$, H_2SO_4(E)	76.55	76.3[5c] 76[5a]	75[5b]		−34.86	−35.4[5c] −38.0[5a]	−34.0[5b]
H_2SO_4(M)					10.371 10.45[4a] 10.35[3c]	10.1[5c] 10.0[5b] 10.5[3a]	10.43[4c] 10.35[5a]
H_2SO_4, $H_2S_2O_7$(E)	84.50	85.1[5d] 85.2[3k]	85[5b]		−10.15 −12[5b]	−10.5[5d] − 9.5[3k]	
$H_2S_2O_7$(M)					35.15	35.07[5d]	36[3b]

The lowest stable eutectic in the system occurs at −62.0° and involves ice and $H_2SO_4·6H_2O$ (Fig. 1). The hydrate $H_2SO_4·6H_2O$ undergoes a peritectic reaction at −53.73° to form $H_2SO_4·4H_2O$. However, it was found that the tetrahydrate and ice will both supercool below the temperatures where they are stable, and that they form a eutectic at −73.10° and 30.65% SO_3. That this eutectic is metastable is proved by the fact that the eutectic will change into a mixture containing

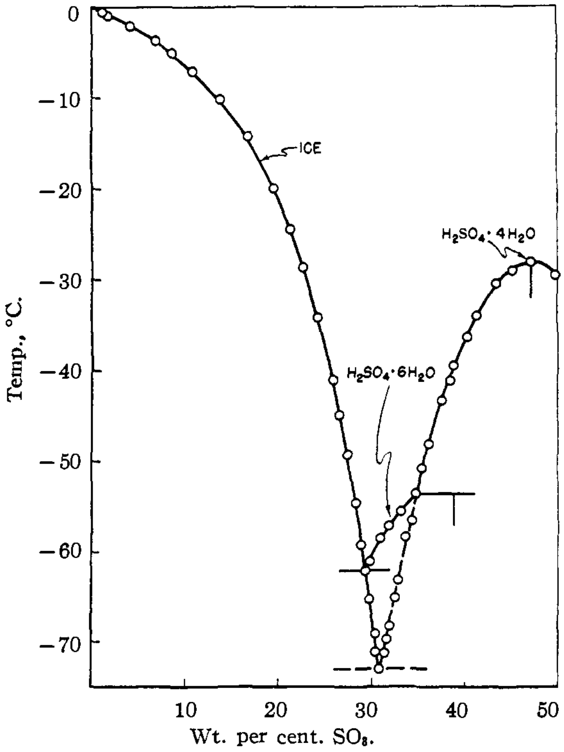

Fig. 1.—Freezing points.

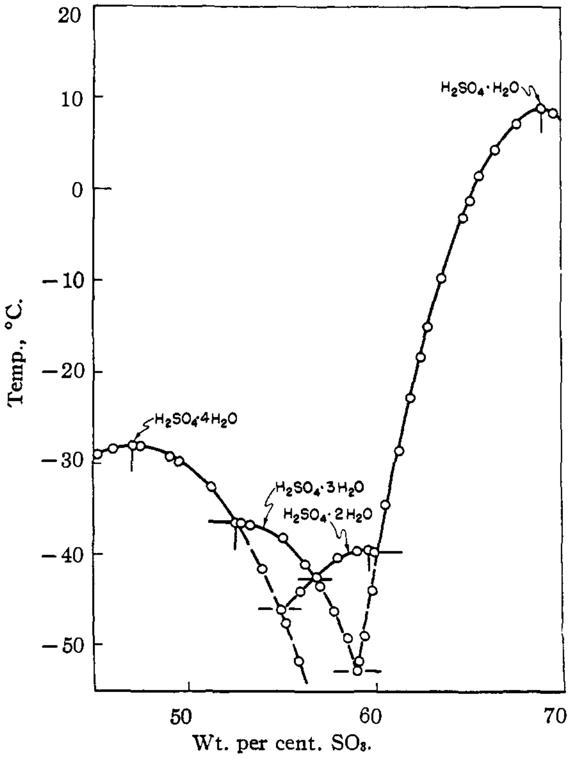

Fig. 2.—Freezing points.

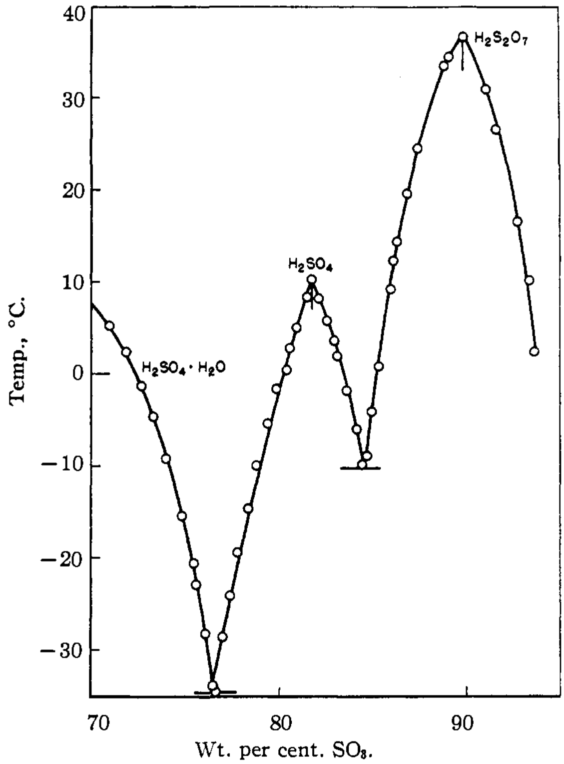

Fig. 3.—Freezing points.

$H_2SO_4 \cdot 6H_2O$ with an abrupt rise in temperature if seeded with this phase.

No evidence was found for the existence of the compound $H_2SO_4 \cdot 8H_2O$. Hulzmann and Biltz[5c] report that this hydrate has an incongruent melting point at −62°. This invariant point, however, is in reality the eutectic formed by the hexahydrate and ice at −62.0°. That this point is a eutectic is demonstrated by the fact that solutions on both sides of the eutectic composition became completely solid at −62°.

The tetrahydrate also undergoes a peritectic reaction to form the trihydrate at −36.56° and 52.81% SO_3. However it may be supercooled below this temperature until at −47.46° it forms a metastable eutectic with the dihydrate. A stable eutectic is formed by the trihydrate and dihydrate at −42.70°, and a metastable eutectic is formed by the monohydrate and trihydrate at −52.85°. Finally the curves of the monohydrate and dihydrate meet at −39.87° and 60.15% SO_3 to form a stable eutectic. An inspection of the graph shown in Fig. 2 leaves little doubt as to the solid phases which are involved in the formation of any of these invariant points.

The extreme tendency of this system to supercool, and to form metastable phases, causes great difficulties in thermal analysis. Thus, for a solution containing 56% SO_3, the trihydrate is the stable phase, and should crystallize at −40.5°. However, usually this solid phase will not appear unless seeded. Instead, at −45° the dihydrate may precipitate, or the tetrahydrate at −51°. Actually this solution can be supercooled to −75° without crystallizing, to yield a liquid supersaturated with respect to three possible solid phases. It is not surprising, therefore, that Pickering[5a] reported for this region the tetrahydrate as a solid phase, Hulzmann and Biltz[5c] the dihydrate, while Knietsch[5b] found no solid phase at all. It is evident that any result obtained in this range by thermal analysis will be one of pure accident, and will depend on rate of cooling or heating, stirring, or the nature of the solid phase used for seed.

Summary

The solid–liquid phase diagram for the system sulfur trioxide–water from 0 to 93.7% SO_3 has been determined by use of the equilibrium solubility method in combination with thermal analysis for the invariant points. Eight solid phases have been found in the range investigated; namely: ice, $H_2SO_4 \cdot 6H_2O$, $H_2SO_4 \cdot 4H_2O$, $H_2SO_4 \cdot 3H_2O$, $H_2SO_4 \cdot 2H_2O$, $H_2SO_4 \cdot H_2O$, H_2SO_4 and $H_2S_2O_7$. All of these compounds except $H_2SO_4 \cdot 6H_2O$ and $H_2SO_4 \cdot 3H_2O$ exhibit congruent melting points. The compound $H_2SO_4 \cdot 3H_2O$ has not been reported previously.

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