4. Both the beta and the gamma forms can be cooled to below 20°K. the gamma being metastable. The same entropy (33.13 ± 0.05 e. u.) for the room temperature (alpha) form at 298.16°K. is obtained from heat capacities by two paths: (a) starting with the metastable gamma form below 20°K. and heating to the transition point to the alpha form (b) starting with the beta form, heating to and through the transition to the gamma form and then heating the gamma form to its transition to the alpha form. From these results it is considered unlikely that random orientation exists in either the beta or gamma forms at low temperatures.

5. Measurements have been made of the heat of reaction of aqueous methylamine with hydrochloric acid at 298.16°K. as well as of the heats of solution of liquid methylamine and solid methylammonium chloride in water. These results lead to a value of −43,601 ± 100 cal./mole for the heat of reaction of hydrogen chloride and gaseous methylamine.

6. The free energy of dissociation of methylammonium chloride at 298.16°K., calculated from the results, is $\Delta F^0 = 22{,}950 \pm 140$ cal.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary System Silver Sulfate–Sulfuric Acid–Water at 25°

BY EDWARD L. SIMONS[1] AND JOHN E. RICCI

Introduction.—The ternary system silver sulfate–sulfuric acid–water has not previously been reported in the literature, although the solubility of silver sulfate in aqueous solutions of sulfuric acid has been studied over limited ranges of acid concentration by Swann,[1a] Drucker,[2] and Akerlof and Thomas.[3] Kendall and Davidson,[4] however, investigated the binary system silver sulfate–sulfuric acid, and reported the existence of two addition compounds, $Ag_2SO_4 \cdot H_2SO_4$ and $Ag_2SO_4 \cdot 2H_2SO_4$, with the former, the bisulfate, existing in two polymorphic forms. The alpha modification, which crystallizes in thick prisms, is stable below 66°, while the beta modification, which crystallizes in fine needles, is stable above that temperature. By extrapolation, Kendall and Davidson determined the melting point of the bisulfate to be 125°. The transition point between the 1:2 salt and the alpha form of the bisulfate is at 36°. The metastable transition to the beta form occurs at 39°. Kendall and Davidson did not determine the solubility of the bisulfate in water, but the method of preparation of the normal sulfate from the bisulfate, described by Richards and Jones[5] and by Harkins,[6] indicates that the double salt is incongruently soluble. This is clearly shown in the ternary diagram constructed from data obtained in this investigation. Other addition compounds of the type $Ag_2SO_4 \cdot 3H_2SO_4 \cdot 2H_2O$ and $2Ag_2SO_4 \cdot 3H_2SO_4 \cdot 2H_2O$ are mentioned by Mellor[7] as having been reported in the older literature, but no evidence for such compounds has been found in the course of this investigation of the ternary system at 25°.

Materials.—Merck C. P. grade silver sulfate was used without further purification. The purity of the salt, as determined by titration of an aqueous solution of it with potassium thiocyanate, using the Volhard indicator, was 100.0 and 100.1%, respectively, for the two bottles used during the course of the investigation. Two stock solutions (72 and 98% by weight) of C. P. grade sulfuric acid were made up and analyzed by titration with sodium carbonate.

Solubility Determinations.—The solubility determinations were made according to the usual procedure described in similar investigations insofar as method of stirring, sampling, filtering, and temperature control are concerned. Through complexes of known composition, and analysis of the saturated solutions at equilibrium, the solid phases were determined by the usual methods of graphical or algebraic extrapolation, besides occasional analysis of centrifuged wet residues.

The analytical method involved determination of the silver sulfate concentration by titration with potassium thiocyanate using the Volhard indicator, and of the sulfuric acid concentration by titration with standard sodium hydroxide.

In the preparation of complexes care was taken to avoid the absorption of atmospheric moisture by solutions containing more than 70% by weight of sulfuric acid. Sampling of these complexes, high in sulfuric acid content, was done as rapidly as possible to minimize this effect, but nevertheless successive analyses of such solutions showed the composition to be changing slowly in a direction which would indicate that water was being absorbed from the atmosphere. For such concentrated solutions grease could not be used on the glass stoppers, and the use of paper filtering tips on the sampling pipets had to be dispensed with. These liquids were sampled after complete settling of the solid.

In the dilute solutions separate samples were taken for the acid and silver determinations, but for the more concentrated solutions both analyses were performed on the same sample. The acid analysis was made with

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[1a] Swann, Chemistry Thesis, Massachusetts Institute of Technology, 1899, as reported in Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 858.

[2] Drucker, *Z. anorg. Chem.*, **28**, 362 (1901).

[3] Akerlof and Thomas, THIS JOURNAL, **56**, 593 (1934).

[4] Kendall and Davidson, *ibid.*, **43**, 979 (1921).

[5] Richards and Jones, *ibid.*, **29**, 826 (1907).

[6] Harkins, *ibid.*, **33**, 1807 (1911).

[7] Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. III, Longmans Green, New York, N. Y., 1927, p. 452.

methyl orange as the indicator, but this was replaced by phenolphthalein when a single sample was used for both silver and acid, to avoid interference by the red color of the methyl orange with the end-point of the thiocyanate titration done in nitric acid solution. In almost all cases a phenolphthalein end-point could be obtained before the formation of any permanent precipitate of silver oxide. In a few cases there was a faint opalescence in the solution, at the end-point, and in one or two cases where the silver concentration was very high, a definite precipitate was obtained. In such a case the precipitate was immediately dissolved by back titration with standard acid, methyl orange added, and the titration finished with that indicator. After the solution had been used for the acid determination, nitric acid was added for the silver determination. To eliminate the red color imparted to the solution by the methyl orange, the solution was heated until the color was destroyed, and the regular silver determination carried out after cooling.

Wet residue analyses were made in many cases to help establish the identity of the solid phase. The wet residue from the solubility tube was filtered through a Gooch crucible, fitted with a glass wool mat which had been washed with sulfuric acid and water. As soon as all supernatant liquid had been sucked through by gentle suction, the crucible was transferred to a centrifuge and centrifuged for fifteen minutes. The dry solid was weighed and then dissolved in water in a 500-ml. or 1-liter Erlenmeyer flask in which the titrations for silver sulfate and sulfuric acid were carried out.

In several tubes made up in regions of high acid content the solubility of the silver salt was observed to drop several per cent. after several days of stirring, prior to which time the silver analysis had been reproducible at a higher value. This was attributed to the formation of a more stable form, the alpha form of silver bisulfate, reported by Kendall and Davidson,[4] since the tie-lines extrapolated to the same point on the base of the triangular diagram from either the high or the low solubility point. The solid residue from one of these tubes was retained, and from that point on all tubes were seeded with a small quantity of it after two analyses on successive days had been performed on them. In most cases the percentage of silver sulfate was observed to drop after seeding. The tubes were allowed to rotate in the bath for two days more after seeding before a sampling was carried out.

The bath used in this work was maintained at 25.04 ± 0.02°.

TABLE I

SYSTEM Ag_2SO_4–H_2SO_4–H_2O AT 25°

Liquid, solution		C, original complex R, wet residue		
wt. % Ag_2SO_4	wt. % H_2SO_4	wt. % Ag_2SO_4	wt. % H_2SO_4	Solid phase[c]
0.833				A
.990	4.75	C 10.00	4.29	A
.946	11.34	C 9.92	10.28	A
.618	21.13	C 9.98	24.50	A
.411	38.12	C 9.98	34.41	A
.400	54.30	C 10.00	49.03	A
.632	62.15	C 8.34	57.23	A
.831	64.97	C 10.01	58.80	A
1.897	70.86	C 9.96	64.90	A
2.273	71.87	C 20.94	58.24	A
2.84	72.60	R 95.2	3.03	A
		R 94.9	3.26	A
2.94	72.68	C 14.98	63.83	A
3.89	73.66	R 44.2	42.35	A
4.06	73.78	R 62.6	28.96	A
		R 62.0	29.06	A
4.50	74.03	C 22.04	60.23	A
4.74	74.26	C 10.19	70.04	A
5.50*	74.26	R 93.9	3.34	A
5.63	74.19	C 10.01	70.98	A
6.57	74.21	C 10.06	71.90	A + B_β
6.55	74.47	C 21.34	63.56	A + B_β
6.61	74.25	C 35.08	62.50	A + B_β
6.59	74.31	C 9.98	71.92	A + B_β
6.52	74.5	C 19.68	65.37	A + B_β
6.57	74.35	Average		A + B_β
6.18	74.30			A + B_α
6.23[a]	74.08			A + B_α
6.32	74.31			A + B_α
6.32	73.95			A + B_α
6.27[a]	74.07	R 85.29	12.21	A + B_α
6.26	74.14	Average		A + B_α
6.58	74.95			B_β
6.54	75.13	R 55.63	38.68	B_β
6.57	75.93	C 10.00	73.49	B_β
7.14	77.9	C 21.03	67.59	B_β
7.97	79.73	C 21.23	69.16	B_β
9.13	80.78	C 9.93	80.3	B_β
9.42	80.92	C 19.21	72.81	B_β
10.85[a]	81.27	R 33.1	60.69	B_β
11.39[a]	81.21			B_β
12.70[a]	80.89			B_β
13.58	80.57	C 19.92	75.10	B_β
5.58[a]	75.43			B_α
4.94	76.78			B_α
4.34	80.27	R 59.2	36.8	B_α
4.51	81.59	R 55.3	40.03	B_α
4.79	82.22	R 28.29	63.64	B_α
6.13[a]	82.68			B_α
7.94	83.01			B_α
12.81	81.62	R 59.7	38.93	B_α
19.45	77.86	C 43.58	55.26	$B\alpha$ or B_β
19.82[a]	77.64	R 51.78	47.21	$B\alpha$ or B_β
20.81	76.98	C 25.41	73.09	$B\alpha$ or B_β
21.01	76.41	R 74.35	24.80	$B\alpha$ or B_β
21.45	76.32	C 30.06	68.50	$B\alpha$ or B_β[b]
21.50	76.55	C 25.43	73.0	$B\alpha$ or B_β[b]
21.82	76.17	C 25.25	73.27	$B\alpha$ or B_β[b]

[a] Analyzed following seeding with α·$AgHSO_4$. [b] May be invariant region for $AgHSO_4$ and $Ag_2SO_4 \cdot 2H_2SO_4$. [c] "A" = Hg_2SO_4, "$B\beta$" = β-$AgHSO_4$, "$B\alpha$" = α-$AgHSO_4$.

Results.—The results are collected in Table I and plotted in Fig. 1. The algebraic extrapolations of the tie-lines were made to a line representing the theoretical percentage of silver sulfate in the expected solid phase, and the deviations of the tie-lines from these points, expressed in percentage of sulfuric acid, were in most cases small, but cover a range of several per cent. for the complexes high in acid concentration. In cases where an analysis lies on the curve, it is retained in the table despite a poor extrapolation, since the latter simply indicates a degree of uncertainty in the exact composition of the complex as it was originally made up, or indicates absorption of water by the solution. In cases of doubt as to the solid phase, analysis of it directly cleared up that point.

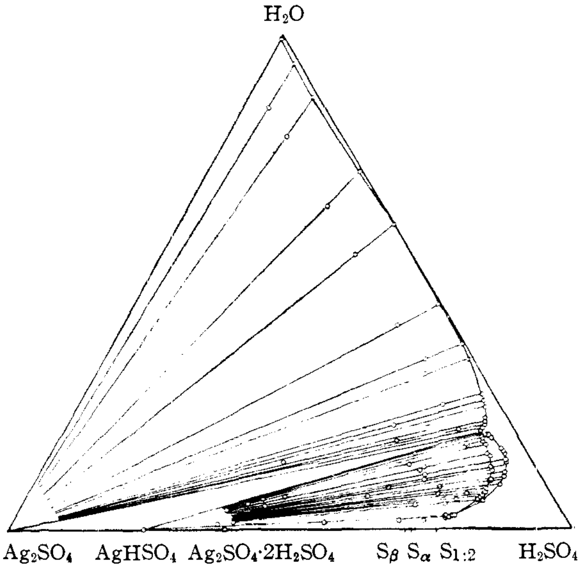

Fig. 1.—System Ag_2SO_4–H_2SO_4–H_2O at 25°: S_β, S_α, solubilities (metastable) of the β and α forms of the bisulfate in H_2SO_4; and $S_{1:2}$, stable solubility of $Ag_2SO_4 \cdot 2H_2SO_4$, in H_2SO_4, as estimated from ref. 4.

Discussion.—In the region from 0% sulfuric acid to about 6% silver sulfate and 74% sulfuric acid the solid phase in equilibrium with the saturated solutions is the normal sulfate. After an initial increase in the solubility of silver sulfate upon the addition of sulfuric acid, its value decreases with increasing sulfuric acid concentration until the curve approaches the region of the bisulfate, where the solubility of the silver sulfate rises markedly. The solubility measurements of Akerlof and Thomas[3] in very dilute sulfuric acid solutions indicate an initial decrease in the solubility of silver sulfate upon the addition of sulfuric acid. This is followed, in the presence of somewhat higher acid concentrations, by the "initial" solubility increase noted in the present investigation, in which the lowest concentration of sulfuric acid used (4.75%) is high enough so that the increase in solubility caused by the high ionic strength overcomes the expected decrease from the common ion effect.

Two solubility curves are seen to represent solutions in equilibrium with a solid having the stoichiometric composition of one mole of silver sulfate to one mole of sulfuric acid. Since the concentration of a saturated solution in this region was often observed to change spontaneously from a point on the inner curve to one on the outer curve, the latter represents the stable solubility curve of silver bisulfate at 25°, while the former is a metastable solubility curve. Since the alpha form of the bisulfate has been shown by Kendall and Davidson[4] to be the stable modification below 66°, this must be the solid phase in equilibrium with the solutions represented on this outer curve. Presumably Kendall and Davidson's beta form, stable above this temperature, is the solid phase in equilibrium with the solutions represented on the inner curve.

These two solubility curves must intersect the solubility curve for the normal sulfate at two different points, giving rise to a stable and a metastable isothermally invariant point. It proved difficult, as verified by actual analysis, to prepare complexes such that their compositions could be depended upon to fall in the invariant region, and so that the resulting liquids might be accepted as the invariant solution in question. The invariant region is so narrow that the taking up of small amounts of water during sampling would be sufficient to move the complex composition up into the normal sulfate region. The values for the stable and metastable invariant points were therefore estimated in two ways. One estimation was made by taking the arithmetic average of the analyses for a number of points which seemed grouped together in what appeared to be the region of crossing. The other method involved plotting the solubility curves on a graph drawn ten times normal scale (Fig. 2) and finding the crossing by extrapolation of the three curves to their intersections. Below is a comparison of the values obtained by the two methods:

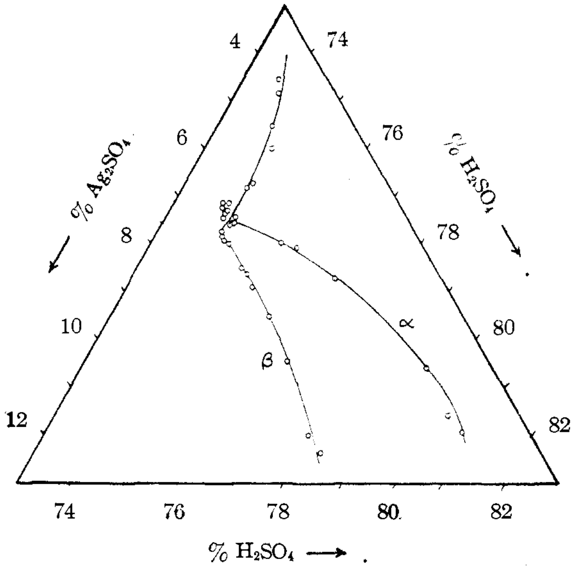

Fig. 2.—Part of system Ag_2SO_4–H_2SO_4–H_2O at 25° (10×).

Stable invariant Extrap.	Stable invariant Average		Metastable invariant Extrap.	Metastable invariant Average
6.33	6.26	% Ag_2SO_4	6.57	6.57
74.19	74.14	% H_2SO_4	74.21	74.35

In the region of still higher acid concentration the solubility increases sharply and the metastable and stable curves are seen to approach each other rapidly until in the most highly concentrated solutions there appears to be another grouping of points in one spot, and it is not possible to say, in that region, whether a point lies on the metastable or on the stable curve. These points, which are grouped around 21% silver sulfate and 76.5% sulfuric acid, may indicate one or both of the invariant points between the two forms of the bisulfate and the 1:2 addition compound. Kendall and Davidson's measurements on the binary system sulfuric acid–silver sulfate,[4] show that this 1:2 salt is the stable solid phase at 25°. Its solubility, calculated from their data to be 24% silver sulfate by weight, should be represented by a point on the silver sulfate–sulfuric acid base of the ternary diagram at 25°, and from that point there should be a short but definite solubility curve for this salt. This curve, however, was not experimentally realizable in this study, which was limited to the use of 98% sulfuric acid, making it impossible to prepare complexes with compositions close enough to the base of the triangle to give rise to the 1:2 salt. Solid residue analyses always showed the solid phase to be the 1:1 salt.

From a plot of Kendall and Davidson's data it was possible to estimate by extrapolation the metastable solubilities, at 25°, in pure sulfuric acid, of the alpha and beta forms of the bisulfate. The value for the alpha was estimated to be equivalent to 28.5% silver sulfate by weight, and that for the beta 29.5% silver sulfate. If these points are marked off on the silver sulfate–sulfuric acid side of the ternary diagram, it can be seen that they represent the points to which the bisulfate solubility curves would most likely have extended had they not been interrupted by the formation of the 1:2 compound in the highest concentrations of sulfuric acid.

Summary

1. The ternary system Ag_2SO_4–H_2SO_4–H_2O has been studied at 25° to the limit of 98% sulfuric acid by weight.

2. The solid phases observed were the normal sulfate, Ag_2SO_4, and the bisulfate, $AgHSO_4$.

3. Two solubility curves have been obtained for the 1:1 addition compound, the stable solubility curve being that for the alpha form of the bisulfate, the metastable curve being that for the beta form, both forms already having been reported by Kendall and Davidson.[4]

4. A stable and metastable invariant point have been determined for the crossing of the bisulfate solubility curves with that for the normal sulfate.

5. An indication of an invariant point between the bisulfate curves and the solubility curve for the salt $Ag_2SO_4 \cdot 2H_2SO_4$ has been obtained, but the 1:2 addition compound itself was not observed in this investigation, because of the limitation in the concentration of the sulfuric acid used.

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CONTRIBUTION FROM THE SOCONY-VACUUM LABORATORIES (A DIVISION OF SOCONY-VACUUM OIL CO., INC.), RESEARCH AND DEVELOPMENT DEPARTMENT]

Inter-polymerization of Isobutene and 2-Methyl-2-butene Using an Alumina–Silica Catalyst. Composition of the Hydrogenated Nonenes

BY GEORGE C. JOHNSON AND FRANK S. FAWCETT

When isobutene and 2-methyl-2-butene react in the presence of a solid catalyst composed of alumina and silica at temperatures of the order of 110°, the main product is a mixture of nonenes. Other products are octenes, decenes and trimers. A similar nonene product is formed in the reaction of *t*-butyl alcohol with *t*-amyl alcohol in the presence of sulfuric acid. The *t*-butyl alcohol is equivalent to isobutene and the *t*-amyl alcohol is equivalent to 2-methyl-2-butene or to 2-methyl-1-butene in those cases where the reactants are first dissolved in the acid.

The nonanes formed by hydrogenating the nonenes have special properties as a fuel for internal combustion engines. The power output of the engine under rich-mixture conditions—*i.e.*, high fuel–air ratios—is remarkably high. Too, the power delivered by the engine is unusually sensitive to the inlet air temperature when the nonanes are used as the fuel. These special properties depend upon the composition of the nonanes, especially upon the total content of tetramethylpentanes, and the composition depends in turn upon the method of carrying out the reaction.

The composition of the nonane mixture has been determined by distilling the mixture into fractions with an efficient column, by measuring the physical properties of these fractions and then comparing these properties with those of the 35 isomeric nonanes.

Alumina–silica catalysts have been used before to polymerize olefins[1–6] and some studies of the

(1) Gurvich, *Kolloid-Z.*, **11**, 17 (1912); *J. Russ. Phys.-Chem. Soc.*, **47**, 827 (1915); *Z. physik. Chem.*, **A107**, 235 (1923).

(2) Lebedev and Filonenko, *Ber.*, **58**, 163 (1925).

(3) Van Winkle, *J. Am. Pharm. Assoc.*, **17**, 544 (1928).

(4) Gayer, *Ind. Eng. Chem.*, **25**, 1122 (1933).

(5) Lebedev and Borgman, *J. Gen. Chem.* (U. S. S. R.), **5**, 1595 (1935).

(6) Houdry, Burt, Pew and Peters, *Natl. Petroleum News*, **30**, R570 (1938).