

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

The Ternary Systems Silver Sulfate-Alkali Sulfate-WaterBY EDWARD L. SIMONS¹ AND JOHN E. RICCI

Introduction.—The ternary systems of the type silver sulfate-alkali metal sulfate-water have not previously been reported in the literature. The solubility of silver sulfate in aqueous solutions of alkali metal sulfates has been determined, but in many cases it is not possible to determine the exact composition of the equilibrium solid phases from the data given.^{1a-5}

Binary systems containing silver sulfate and another univalent sulfate have been studied,^{6,7} but except in the sulfuric acid system they offer no means of determining the nature of the solid phases stable at temperatures much lower than the melting or transition points of the pure salts.

This investigation was undertaken to determine whether silver sulfate shows any tendency toward formation of compounds or solid solutions with alkali metal salts at ordinary temperatures, similar to the type of behavior observed in systems of the alkali metal salts alone.

Materials.—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. C. p. grade alkali sulfates were used throughout without further purification. The composition of the lithium sulfate monohydrate was verified by determining the loss in weight on heating, first at 250° followed by a short period at 650°. The monohydrate was then used without preliminary drying. The potassium, sodium, and silver sulfates were dried overnight at 110°, and then at 250° for one hour, while the ammonium sulfate was dried only at 110°. All salts after drying, were stored in glass-stoppered weighing bottles in a calcium chloride desiccator.

Solubility Determinations.—The solubility determinations were made according to the usual procedure described in similar investigations in so far 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 water concentration by the loss in weight on evaporation and drying. When the solution contained potassium or sodium

sulfate, the evaporation was carried out at 110°, followed by an hour's drying at 250°. Solutions containing ammonium sulfate were evaporated at 80°, followed by drying at 110°. Solutions containing lithium sulfate were treated like those containing potassium and sodium sulfate. Although constant weight could be obtained by this procedure, the resulting solid lithium sulfate always contained 0.12–0.15% water, which could not be removed except by heating at or above 600°. Consequently this empirical correction was made on all experimental determinations of the solubility of lithium sulfate. The high temperature drying required to remove the last traces of water from the monohydrate has also been described by Akerlof⁸ and by Friend.⁹

The Systems: Silver Sulfate, Water and Potassium, Ammonium or Lithium Sulfate at 25°

The data (in weight per cent.) for the three systems are tabulated in Table I. All three systems are of the simplest type, with two branches for the solubility curve, one for each of the separate component salts, and with no indication of the formation of either solid solutions or double salts. From thermal data Nacken⁷ has inferred that in the binary system silver sulfate-potassium sulfate there is formed a salt having the composition $K_2SO_4 \cdot 3Ag_2SO_4$, with an incongruent melting point at 294°; and that in the binary system silver sulfate-lithium sulfate there is formed a salt $2Li_2SO_4 \cdot 3Ag_2SO_4$, stable only in the range from 420–572°. No evidence for such compounds has been found in the ternary systems with water at 25°. The algebraic extrapolations of the tie-lines were made to a line representing 100% silver sulfate or 100% alkali sulfate (85.92% in the case of $Li_2SO_4 \cdot H_2O$ as solid phase) depending upon the equilibrium solid phase. The extrapolation errors were all a few tenths of a per cent. or less.

System: Silver Sulfate-Sodium Sulfate-Water

Barre^{1,2} has measured the solubility of silver sulfate in aqueous solutions of sodium sulfate at 14.5, 33, 51, 75 and 100°. At 14.5° he found no evidence for either solid solution or double salt formation. At the other temperatures, which are above the transition point for the transformation of sodium sulfate decahydrate to anhydrous sodium sulfate, Barre found that the solid phase in equilibrium with the saturated solutions consisted of "mixed crystals" of the two sulfates. No attempt was made to establish a mathematical relationship between the concentration of sodium sulfate in the solution and in the "mixed crystals" at 75°, the one temperature for which actual analytical data are given for the solid phase. In the present report are included the results of the investigation of the ternary system silver sulfate-sodium sulfate-water at 35, 31.5, 25 and 20°, car-

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(1a) Barre, *Compt. rend.*, **150**, 1321 (1910).

(2) Barre, *Ann. Chim. Phys.*, **24**, 145 (1911).

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

(4) Drucker, *Z. anorg. Chem.*, **23**, 362 (1901).

(5) Harkins, *This Journal*, **33**, 1807 (1911).

(6) Kendall and Davidson, *ibid.*, **43**, 979 (1921).

(7) Nacken, "Neues Jahrbuch für Mineralogie, Geologie und Paläontologie." Beilage Band, **24**, 1 (1907), reported in *C. A.*, **1**, 2345 (1907), in "I. C. T." Vol. **IV**, p. 79, and in Mellor, Vol. **III**, p. 453.

(8) Akerlof, *This Journal*, **48**, 1160 (1926).

(9) Friend, *J. Chem. Soc.*, 2331 (1929).

ried out to determine the distribution existing in the case of the continuous solid solution above the

transition point for the decahydrate of the sodium sulfate, and to determine the change in the nature of the solid phase as the temperature is brought below that point.

TABLE I
SYSTEMS OF Ag_2SO_4 , H_2O , AND $(NH_4)_2SO_4$, K_2SO_4 , OR Li_2SO_4 , AT 25°

Liquid solution			Original complex		Solid ^a phase
Wt. % Ag_2SO_4	Wt. % $(NH_4)_2SO_4$	Density	Wt. % Ag_2SO_4	Wt. % $(NH_4)_2SO_4$	
(1) $(NH_4)_2SO_4$					
0.833		1.004			A
0.90	5.95	1.034	14.97	5.10	A
1.08	11.88	1.074	15.01	10.18	A
1.31 ₁	20.58	1.128	14.93	17.74	A
1.428	28.93	1.176	15.03	24.92	A
1.453	34.48	1.208	14.74	29.83	A
1.441	37.75	1.229	2.44	37.31	A
1.414	40.67	1.243	14.93	35.12	A
1.378	42.92	1.253	9.98	40.06	A + B
1.381	42.87	1.253	4.98	44.98	A + B
1.393	42.91	1.257	3.11	43.92	A + B
1.38 ₁	42.94	1.253	3.05	46.64	A + B
1.383	42.91	1.254	Average		A + B
0.740	43.18	1.246	0.660	49.44	B
	43.45	1.233			B
(2) K_2SO_4					
	K_2SO_4		K_2SO_4		
0.79	3.86	1.033	22.14	2.98	A
.905	7.29	1.067	18.91	5.96	A
.991	9.72	1.084	16.85	8.15	A
1.009	10.25	1.090	4.00	9.93	A
1.03	10.92		10.06	10.01	A + C
1.04	10.92	1.095	14.87	10.28	A + C
1.04	10.94	1.097	3.51	11.46	A + C
1.04	10.95	1.101	2.57	12.43	A + C
1.032	10.93	1.093	5.03	15.03	A + C
1.04	10.91	1.102	1.95	13.37	A + C
1.04	10.93	1.098	4.96	45.46	A + C
1.04	10.93	1.098	Average		A + C
0.885	10.89	1.094	0.755	24.17	C
.568	10.82	1.089	0.480	24.48	C
	10.80	1.084			C
(3) Li_2SO_4					
	Li_2SO_4		Li_2SO_4		
0.786	5.57	1.046	10.04	5.04	A
.89	11.02	1.102	10.03	10.02	A
.95	16.34	1.151	10.02	14.86	A
.963	22.04	1.199	9.80	20.05	A
.951	25.00	1.227	5.00	23.98	A
.954	25.28	1.228	6.02	24.51	A + D
.949	25.35	1.230	4.91	25.08	A + D
.949	25.33	1.230	4.00	24.98	A + D
.949	25.30	1.230	3.99	26.07	A + D
.950	25.34	1.230	3.99	26.10	A + D
.951	25.34	1.233	2.94	27.12	A + D
.952	25.32	1.233	1.48	28.55	A + D
.951	25.32	1.231	Average		A + D
.502	25.40	1.223	0.497	29.48	D
	25.53	1.215			D

* A = Ag_2SO_4 ; B = $(NH_4)_2SO_4$; C = K_2SO_4 ; D = $Li_2SO_4 \cdot H_2O$.

The binary system sodium sulfate-silver sulfate has been investigated by Nacken.⁷ From thermal data he has constructed a temperature-composition diagram which indicates continuous solid solution between the two salts below 177°.

The experimental procedure was the same as previously described. In those cases where the stable saturating solid phase was expected to be sodium sulfate decahydrate, it was necessary to seed the solution with the decahydrate before stable equilibrium could be attained. Where solid solution was observed, the compositions of the solid solutions in equilibrium with the saturated liquid solutions were calculated by the algebraic extrapolation, to the base of the triangular diagram, of appropriate tie-lines through the liquid composition and that of the original complex.

35° Isotherm

The data are tabulated in Table II and plotted in Fig. 1, which shows the disposition of the tie-lines for the distribution of the two isomorphous

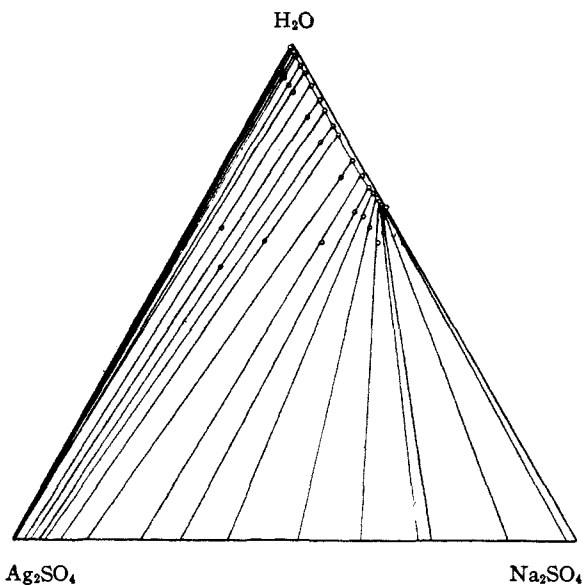


Fig. 1.—System Ag_2SO_4 - Na_2SO_4 - H_2O at 35°.

salts between the two continuous conjugate solutions. The shape of the solubility curve itself cannot be shown on such a scale. It is therefore presented separately in Fig. 2, which brings out the exaggerated inverted S-shape. The marked dip in the curve, accompanied by the convergence of tie-lines in that region, indicates a tendency toward discontinuity of the solid solution and the formation of an isothermally invariant liquid in equilibrium with the two anhydrous salts. The tendency is also seen in the solubility measurements at lower temperatures. The subsequent

mathematical analysis of the distribution of the solute between liquid and solid phases will show that the solid solution displays positive deviations from Raoult's law. This is furthermore in agreement with the behavior reported for the binary

system silver sulfate-sodium sulfate⁷ which shows a minimum (and hence positive deviations, or tendency toward formation of a eutectic) in the melting point curve of the continuous solid solution.

TABLE II
SYSTEM $\text{Ag}_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$

Temp.	No.	Liquid solution			Original complex		Composition solid solution Wt. % Ag_2SO_4^a	Solid phase
		Wt. % Ag_2SO_4	Wt. % Na_2SO_4	Density	Wt. % Ag_2SO_4	Wt. % Na_2SO_4		
35°	67	0.933		1.002				Ag_2SO_4
	170	.836	0.57	1.007	5.03	0.541	100.1	s.s.
	171	.827	1.04	1.011	4.99	0.990	100.2	s.s.
	172	.824	1.58	1.016	4.99	1.54	99.4	s.s.
	113	.837	2.04	1.019	5.09	1.95	100.1	s.s.
	176	.877	3.62	1.034	5.00	3.50	99.3	s.s.
	112	.924	5.24	1.048	4.98	5.02	100.2	s.s.
	63	1.01	7.54	1.073	31.19	5.87	97.8	s.s.
	111	1.08	10.35	1.099	5.01	10.06	96.7	s.s.
	51	1.122	12.42	1.115	35.33	9.72	95.0	s.s.
	109	1.184	15.32	1.153	4.99	14.94	93.9	s.s.
	62	1.203	17.23	1.165	24.87	14.94	91.5	s.s.
	108	1.207	22.35	1.222	4.98	21.96	86.5	s.s.
	61	1.092	25.53	1.257	14.79	25.10	77.0	s.s.
	136	1.007	27.86	1.275	6.01	28.00	70.2	s.s.
	110	0.931	29.22	1.290	5.02	29.82	61.8	s.s.
	177	.828	30.24	1.305	5.00	31.99	49.4	s.s.
	83	.699	31.03	1.308	1.49	33.27		s.s.
	60	.653	31.42	1.311	5.11	35.05	38.1	s.s.
	138	.597	31.48	1.312	3.00	35.03	28.0	s.s.
	173	.530	31.89	1.315	1.49	33.50	25.8	s.s.
	139	.481	32.13	1.316	1.51	36.97	12.3	s.s.
	50	.316	32.44	1.318	0.48	39.55	1.8	s.s.
	52		32.99	1.319				Na_2SO_4
	31.5°		.899		1.002			
		.814	0.503	1.009	5.05	0.486	99.9	s.s.
		.790	1.066	1.011	5.05	1.03	99.9	s.s.
		.794	1.548	1.019	5.10	1.50	99.8	s.s.
		.813	2.609	1.029	4.96	2.52	99.5	s.s.
		.820	2.74	1.030	5.05	2.66	99.1	s.s.
		.842	3.615	1.035	5.04	3.51	99.0	s.s.
		.887	5.168	1.049	5.02	5.00	98.9	s.s.
		1.062	11.40	1.112	5.05	11.08	96.2	s.s.
		1.154	15.36	1.148	4.98	14.99	93.6	s.s.
		1.181	20.45	1.203	5.05	20.07	88.1	s.s.
		1.118	25.18	1.252	5.01	24.97	79.0	s.s.
		1.034	27.45	1.276	5.04	27.58	70.3	s.s.
		0.919	29.46	1.297	5.01	30.01	62.3	s.s.
		.858	30.15		4.00	31.01	55.0	s.s.
		.772	30.92	1.304	3.01	32.01	46.7	s.s.
		.731	31.23	1.308	1.99	31.99	43.2	s.s.
126		.705	31.35	1.309	5.00	34.95	37.7	s.s.
		.656	31.53	1.313	4.75	35.26	36.1	s.s.
		.654	31.58	1.311	4.26	35.84	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ + s.s.	
		.660	31.57	1.317	1.51	32.53	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ + s.s.	
		.659	31.58	1.315	1.010	33.01	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ + s.s.	
		.653	31.62	1.314	0.759	33.25	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ + s.s.	
		.656	31.57	1.314	Average		$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ + s.s.	
		.588	31.58	1.310	0.498	33.50	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	
	.310	31.58		0.255	33.75	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$		
		31.57	1.302			$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$		

TABLE II (Concluded)

Temp.	No.	Liquid solution			Original complex		Composition	Solid phase
		Wt. % Ag ₂ SO ₄	Wt. % Na ₂ SO ₄	Density	Wt. % Ag ₂ SO ₄	Wt. % Na ₂ SO ₄	Wt. % Ag ₂ SO ₄ ^a	
25°		.833		1.004				Ag ₂ SO ₄
		.744	0.507	1.009	5.03	0.49	100.2	s.s.
		.722	1.016	1.013	4.98	0.99	99.7	s.s.
		.733	2.07	1.020	4.97	2.00	99.6	s.s.
		.756	3.09	1.031	5.00	2.99	99.2	s.s.
		.786	4.14	1.040	5.04	4.02	98.6	s.s.
		.831	5.42	1.054	9.91	4.94	99.8	s.s.
		.844	5.88	1.053	14.86	5.22	98.7	s.s.
		.893	7.80	1.073	5.01	7.53	98.6	s.s.
		.983	10.63	1.106	10.08	10.03	95.6	s.s.
		1.02	12.89	1.126	5.02	12.53	95.6	s.s.
		1.079	15.88	1.159	9.94	14.99	93.4	s.s.
		1.101	17.40	1.170	15.12	15.93	92.2	s.s.
		1.115	18.62	1.185	7.00	18.01	90.7	s.s.
		1.121	20.44	1.202	4.93	19.98	90.3	s.s.
		1.118	20.83	1.206	4.50	20.43	89.7	s.s.
		1.120	21.37		14.94	19.82	88.4	s.s.
		1.113	21.78	1.218	9.01	20.99	86.8	s.s.
		1.111	21.76	1.217	8.49	21.49	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.115	21.78	1.214	3.05	21.98	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.113	21.83	1.218	5.61	22.83	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.113	21.84	1.218	4.95	25.00	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.119	21.80	1.217	2.05	23.32	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.114	21.80	1.217	Average		Na ₂ SO ₄ ·10H ₂ O +	s.s.
		0.836	21.80	1.214	0.746	24.23		Na ₂ SO ₄ ·10H ₂ O
	.316	21.75	1.206	0.272	24.73		Na ₂ SO ₄ ·10H ₂ O	
		21.64	1.202				Na ₂ SO ₄ ·10H ₂ O	
20°		.783		1.004				Ag ₂ SO ₄
		.691	0.500	1.010	5.01	0.484	100.2	s.s.
		.673	1.044	1.013	5.01	1.01	99.9	s.s.
		.682	2.07	1.022	5.02	1.99	99.8	s.s.
		.704	3.15	1.032	5.01	3.02	99.8	s.s.
		.731	4.19	1.040	5.02	4.05	99.0	s.s.
		.771	5.33	1.051	10.07	5.02	97.9	s.s.
		.836	7.77	1.075	5.03	7.53	97.8	s.s.
		.919	10.72	1.105	10.04	10.03	96.5	s.s.
		.971	12.92	1.127	5.04	12.56	95.4	s.s.
		1.015	15.51	1.154	5.03	15.05	95.3	s.s.
		1.026	15.92	1.156	4.51	15.52	94.9	s.s.
		1.02	16.11	1.163	4.03	16.07	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.025	16.14	1.159	3.03	17.08	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.031	16.16	1.161	2.00	18.06	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.030	16.12	1.161	1.49	18.51	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.03	16.03	1.157	1.50	18.58	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.041	16.11	1.161	0.969	19.01	Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.030	16.11	1.160	Average		Na ₂ SO ₄ ·10H ₂ O +	s.s.
		1.066 ^b	16.11	1.161	0.964	19.08		Na ₂ SO ₄ ·10H ₂ O
	0.570	16.09	1.157	0.50	19.60		Na ₂ SO ₄ ·10H ₂ O	
		15.89	1.147				Na ₂ SO ₄ ·10H ₂ O	

* By extrapolation. ^b Metastable.

According to a relation already shown to hold with at least approximate correctness in a number of cases of pairs of isomorphous salts,¹⁰ the distribution of the salts of the present investigation, at equilibrium between their solid and liquid

solutions, is given by the expression

$$\log R_1 = \log K + m \log R_2 \quad (1)$$

in which R_1 is the mole ratio of sodium to silver in the liquid solutions, R_2 is the same ratio in the solid solution, K represents the square root of the

(10) Hill, Durham and Ricci, THIS JOURNAL, 62, 2723 (1940).

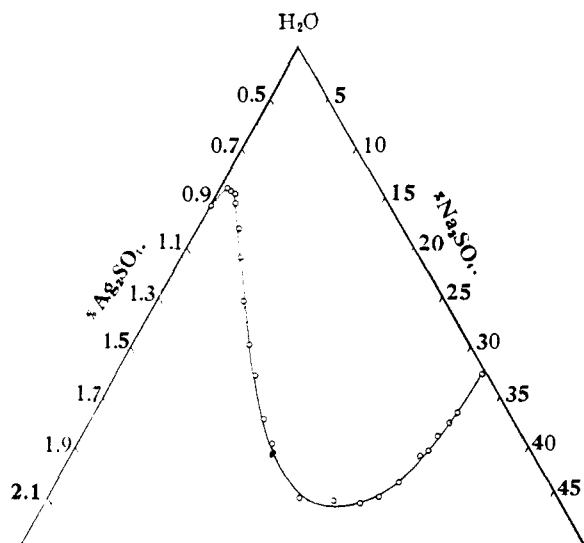


Fig. 2.—Solubility curve: $\text{Ag}_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ at 35° .

ratio of the thermodynamic solubility product of sodium sulfate to that of silver sulfate, and m is an empirical constant characteristic of the particular pair of salts and representing some measure of the degree of non-ideality of the solid solution formed by them. With ideal relations, $m = 1$. The equation, although essentially empirical, has been found to apply fairly well to a number of systems both of alums and of picromerites.¹⁰

The quantities required for testing this distribution equation in the present system are listed in Table III. Here R_1 and R_s are the ratios already explained, and x and y are the mole fractions of sodium sulfate in the solid and in the liquid phases, respectively, excluding water.

TABLE III
DISTRIBUTION BETWEEN LIQUID AND SOLID SOLUTIONS OF SILVER SULFATE AND SODIUM SULFATE AT 35°

No.	Log R_1	Log R_s	Log R_1/R_s	y	x
67				0	0
63	1.2146	-1.3104	2.5250	0.94	0.047
111	1.3235	-1.1267	2.4502	.96	.070
51	1.3865	-0.9363	2.3228	.96	.104
109	1.4552	-.8480	2.3032	.97	.124
62	1.4985	-.6912	2.1897	.97	.169
108	1.6079	-.4641	2.0720	.98	.26
61	1.7068	-.1844	1.8912	.98	.40
136	1.7819	-.0306	1.8125	.98	.48
110	1.8390	.1319	1.7071	.99	.58
177	1.9033	.3522	1.5511	.99	.69
60	2.0183	.5528	1.4655	.99	.78
138	2.0622	.7517	1.3106	.99	.85
173	2.1209	.7910	1.3299	.99	.86
139	2.1670	1.1945	0.9725	.99	.94
50	2.3458	2.0781	0.2677	.99	.99
52				1	1

The data were first plotted to see whether the solid solutions of these salts constituted a "regu-

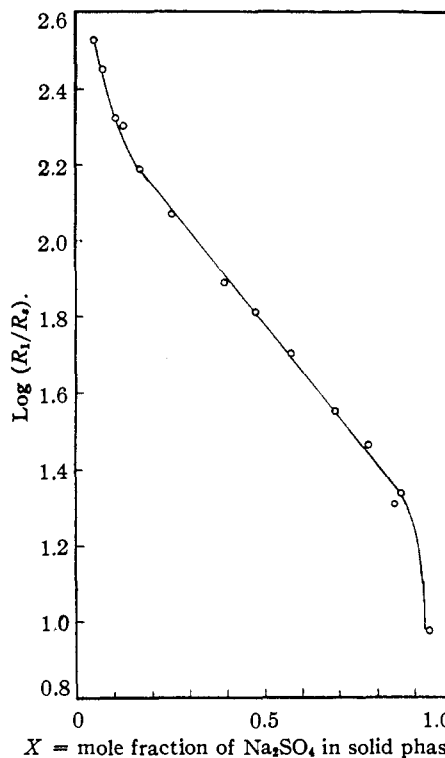


Fig. 3.—Test of "regularity" of the solid solution (at 35°).

lar" solution in the Hildebrand sense.¹¹ This would require a linear relation between $\log (R_1/R_s)$ and x , the mole fraction of one of the salts in the solid. Figure 3 shows the relation to be sensibly linear only for values of x for sodium sulfate between 0.15 and 0.85; the last point ($x = 0.99$) of Table III cannot even be shown in the figure. The data also have been plotted to test equation (1), and Fig. 4, which includes all the points of the Table, shows an over-all linearity in the relation between $\log R_1$ and $\log R_s$, especially with respect

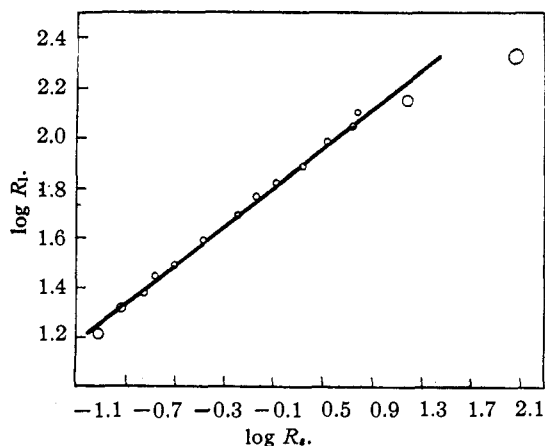


Fig. 4.—Distribution curve according to equation (1), at 35° .

(11) Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1936, p. 65.

to intermediate values of the ratios, where the experimental data are most reliable. The slope of the line gives a value of $m = 0.41$. At $\log R_s = 0$, $\log R_l = \log K = 1.78$.

This "observed" value of $\log K$ is to be compared with that calculated from the activity products of the separate salts in their respective saturated solutions. This was done, using isopiestic vapor pressure data of Robinson, Wilson and Stokes¹² for the activity coefficient of sodium sulfate, and data of Chloupek and Danes¹³ for the activity coefficient of silver sulfate, obtained from solubility measurements in the presence of other salts. The values of the thermodynamic solubility products were calculated from the relation

$$K_a = K_m (\gamma_{\pm})^3 \quad (2)$$

in which K_m is the ordinary molal solubility product and γ_{\pm} is the mean molal activity coefficient for the salt in its saturated solution in pure water. The distribution constant, K , in equation (1), is then calculated (as explained in ref. 10) as $(K_a/K_m)^{1/3}$, which gives a value for $\log K$ of 2.17, compared with the "observed" value of 1.78.

This may be considered as fair agreement, but it is not as good as that generally found for the alum and picromerite systems studied. Ricci and Smiley,¹⁴ in applying the distribution equation to the solid solutions of barium bromate and barium chlorate, found approximately the same disagreement between "observed" and "calculated" values of $\log K$. This discrepancy was attributed principally to the uncertainty in the value of the activity coefficient of the soluble salt, barium chlorate monohydrate, which had to be estimated by analogy with barium nitrate. Assuming the distribution equation to be correct, it was suggested that the "observed" value of $\log K$ might be used to calculate the activity coefficient of barium chlorate monohydrate in its pure saturated solution. A similar calculation has been made in the present case, and the value for the activity coefficient of sodium sulfate so obtained is 0.075, compared to the experimental value of 0.136.¹² In this case, however, it is very doubtful that there could be such error in the measured value of the activity coefficient of the sodium sulfate, and it seems that the agreement found between $\log K$ "calculated" and "observed" only serves to reflect the approximate nature of the assumptions underlying the application of the semi-empirical distribution relation.

The principal assumption in "deriving" this empirical equation from the thermodynamic definition

$$\log R_l(f_1/f_2)_1 = \log K + \log R_s + \log (f_1/f_2)_s \quad (3)$$

is that the effect of the last term, involving the unknown ratio of activity coefficients of the interchanging ions in the solid solution, may be represented, in the non-ideal case, by a constant ex-

ponential effect upon R_s and hence as the constant coefficient m in equation (1). The linearity of the plot of $\log R_l$ against $\log R_s$ in most of the systems studied is unquestionable. But the value of $\log K$ thus obtained seems to diverge more and more from the "theoretical" or calculated value, as m diverges from 1. Taking the value of m as an indication of the degree of non-ideality of the solid solution, this means that despite the continued linearity of the relation, or the approximate constancy of m in any particular system, the effect of the last term of the exact equation (3) is not adequately represented by the coefficient m when the solution is far from ideal. Further modification of the equation does not seem possible, however, without actual determination of the activity coefficients involved, or at least of their ratio.

Finally, as has already been shown,¹⁰ a value of m smaller than 1 indicates positive deviation from ideality. This would mean that the system belongs to Type II in Roozeboom's classification of such solid solutions,¹⁵ and consequently that a plot of x (the mole fraction of sodium sulfate with respect to the dissolved salts in the liquid phase) against y (the corresponding mole fraction in the solid) should cross the 45° diagonal. The experimental data are not sufficient to show such a crossing of this curve (which is therefore not shown), but it may be calculated from the relation

$$y/(1-y) = K[x/(1-x)]^m \quad (4)$$

which is derivable from equation (1), that with $m = 0.4$ and $K = 60.3$ (from $\log K = 1.78$), $x = y$, or the curve crosses the diagonal, at $x = 0.9989$, a value beyond accurate experimental handling.

31.5° Isotherm

The data are tabulated in Table II and plotted in Fig. 5. The observed solid solution is not con-

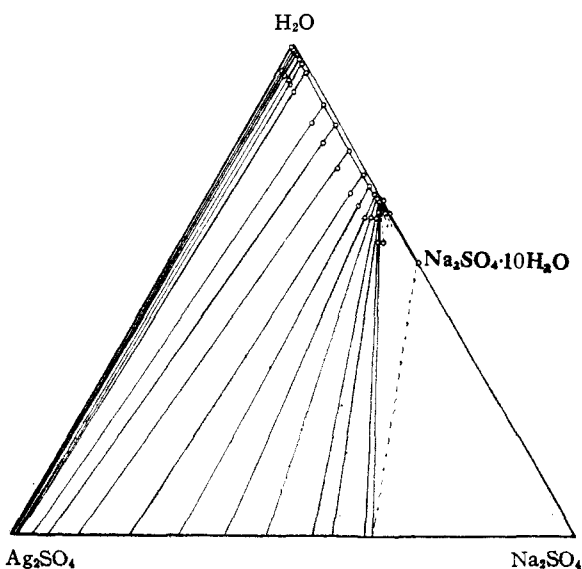


Fig. 5.—System Ag_2SO_4 - Na_2SO_4 - H_2O at 31.5°.

(12) Robinson, Wilson and Stokes, *THIS JOURNAL*, **63**, 1011 (1941).

(13) Chloupek and Danes, *Coll. Czech. Chem. Comm.*, **4**, 8 (1932).

(14) Ricci and Smiley, *THIS JOURNAL*, **66**, 1011 (1944).

(15) Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891).

tinuous, but has an upper limit at 64% sodium sulfate. Beyond this there is an isothermally invariant region in which the saturating solid phases are the solid solution and sodium sulfate decahydrate. This is followed by a small area representing solutions of silver sulfate and sodium sulfate in water, in which sodium sulfate decahydrate is the saturating solid phase.

Since it is quite obvious that the solid solution at 35°, where the separate salts are themselves anhydrous, must be anhydrous, the tie-lines were used to obtain the composition of the solid phase by extrapolation to the base of the triangular diagram. At 31.5°, however, sodium sulfate is decahydrated, and there is at least the formal, though highly unlikely, possibility that the solid solution may be hydrated, with compositions falling on a straight line connecting the corner Ag_2SO_4 with the point representing $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. If such were the case, the solubility tube containing complex number 126, which is almost the last tie-line in the solid solution region, would have held about half solid and half liquid phase, by weight, at equilibrium. Even considering the difference in density between the solid and liquid phases, the amount of solid actually observed was much less than that to be expected if the solid had been decahydrated.

If the base line were from silver sulfate to the decahydrate, the intercept of the tie-line for complex number 126 with this base line would indicate a solid phase containing almost 50% by weight of water. The solid phase present in this tube at equilibrium was, in fact, removed, centrifuged, weighed, and dried at 110° overnight. The loss in weight indicated only 12.5% water, which was probably water from the mother liquor which had not been completely removed by centrifuging.

For this reason, and on the basis of the expected continuity of the phase at the two temperatures, 35 and 31.5°, the solid solution at 31.5° is assumed to be anhydrous, and its composition is again calculated by extrapolation of the tie-lines to the base of the triangle.

Although solid solution is not continuous in this isotherm, nevertheless it covers a wide enough range so that the data obtained at 31.5° may be used to test the distribution equation. The solid has been found to be "regular" in the Hildebrand sense only for values of x between 0.20 and 0.75. The plot of $\log R_1$ against $\log R_2$ has been found to be linear, with a slope of 0.39 and a value of $\log K = 1.79$ when $\log R_2 = 0$.

Since the solid solution is not hydrated, the metastable solubility of sodium sulfate at 31.5° (with anhydrous sodium sulfate as the saturating phase¹⁶) had, of course, to be used in determining the calculated value of $\log K$. This value of $\log K$ is found to be 2.20, compared with the "observed" value of 1.79, roughly the same agreement

(or disagreement) as noted at 35°. With $m = 0.39$, the system is again Type II of Roozeboom's classification.

25 and 20° Isotherms

The data are tabulated in Table II, and the ternary diagrams, though not shown, would be similar to Fig. 5. As at 31.5°, the solid solution observable is not continuous, but has an upper limit of about 13% sodium sulfate at 25°, and 5% at 20°. The range of solid solution is not wide enough at these temperatures for the data to be used significantly in testing the distribution equation.

General Discussion.—In all four isotherms a large-scale plot of the solubility curve shows a definite initial drop in the solubility of silver sulfate with the addition of small amounts of sodium sulfate, followed by a rapid increase in the solubility as the concentration of sodium sulfate is further increased. Although a solid solution, the solid phase remains practically pure silver sulfate up to considerable concentrations of sodium sulfate in the liquid phase. Hence this shape of the solubility curve is essentially that expected for a moderately insoluble salt in the presence of increasing concentrations of a salt with a common ion: an initial drop in solubility caused by the "common ion effect," and then a rise resulting from the increase in ionic strength. In every case the solubility curve ultimately turns again toward zero per cent. of silver sulfate, both because the solid phase becomes poorer and poorer in silver sulfate and because of the "salting-out effect" in very high ionic strength.

The rapid decrease in the limiting composition of the observed solid solution as the temperature is lowered no doubt accounts for Barre's inability (on the basis of his measurements at 14.5°^{1a,2} to find "mixed crystals" in equilibrium with the liquid solutions at temperatures below the transition temperature for sodium sulfate decahydrate. At 14.5° it is doubtful whether the extent of solid solution in equilibrium with the liquid would be sufficient to be detected, even by plotting the data on a ternary diagram.

The maximum percentage of sodium sulfate in the observed solid solution is plotted as a function of the temperature in Fig. 6. The intercept of the curve with the temperature axis at 100% sodium sulfate has been taken as 32.4°, the transition temperature, instead of 35°, the temperature at which continuous solid solution was observed, because the relationships of the isotherms would indicate that continuous solid solution would be observed in the ternary system at all temperatures above the transition temperature for sodium sulfate decahydrate.

The continuous solid solution obtained between silver sulfate and sodium sulfate is not surprising in view of the similarity of their crystalline structures. Both are orthorhombic, and the axial ra-

(16) Estimated from plot of data obtained from "International Critical Tables," Vol. III, p. 371.

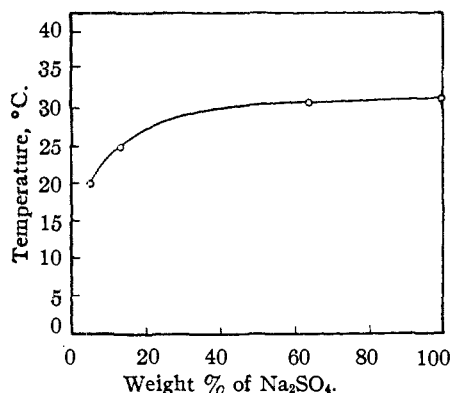


Fig. 6.—Limiting compositions of solid solutions.

tios, $a:b:c$, given by Wyckoff¹⁷ for silver sulfate are 0.570:1:1.235, while for sodium sulfate the ratios are 0.600:1:1.261. Winchell¹⁸ gives for sodium sulfate the values 0.598:1:1.252.

The complete relations for the condensed system at temperatures below the transition point, 32.4°, are shown schematically in Fig. 7. Although the point B represents the limit of the solid solutions observable through the study of the equilibrium involving liquid phases, it must be assumed that the anhydrous solid solution of silver sulfate and sodium sulfate is continuous up to pure sodium sulfate. This seems at least very reasonable, and there is no evidence to the contrary, on the basis of Nacken's phase diagram of the anhydrous binary system,⁷ and the continuity of the solid solution at 35° as observed through the ternary system at that temperature. The line AC, then, as a binary condensed system, represents a continuous solid solution of the two salts. Addition of water insufficient for the formation of a condensed phase containing water, simply adds a vapor phase. But if a new condensed phase, containing water, is formed, the diagram shows that for compositions on the left of B, and including B, a liquid solution on curve $a-b$ will appear, in equilibrium with the solid solution, according to the tie-lines shown (and experimentally observed). For compositions on the right of B, the new phase is simply sodium sulfate decahydrate (point D) and the schematic tie-lines indicate that the region BDC is a two-phase (condensed) equilibrium of this decahydrate and anhydrous solid solution. The triangle BbD is isothermally invariant.

Ternary solubility methods are often of great value for the investigation of a binary system of two salts, because of the great rapidity and ease of attaining the binary equilibrium at ordinary temperatures. But the anhydrous binary system is thereby actually studied only so long as the liquid solution is in equilibrium with anhydrous phases. It is simply the variation of point B with temperature that is plotted in Fig. 6. It indicates

(17) Wyckoff, "The Structure of Crystals," Supplement to 2d. Edition, Reinhold Publishing Corp., New York, N. Y., 1935, p. 64.

(18) Winchell, "Microscopic Characters of Artificial Minerals," John Wiley and Sons, Inc., New York, N. Y., 1931, p. 216.

not a limit to the solid solution of sodium sulfate in silver sulfate, but merely the interruption of the liquid phase by the decahydrate of sodium sulfate as the condensed phase in equilibrium with the anhydrous solid solution.

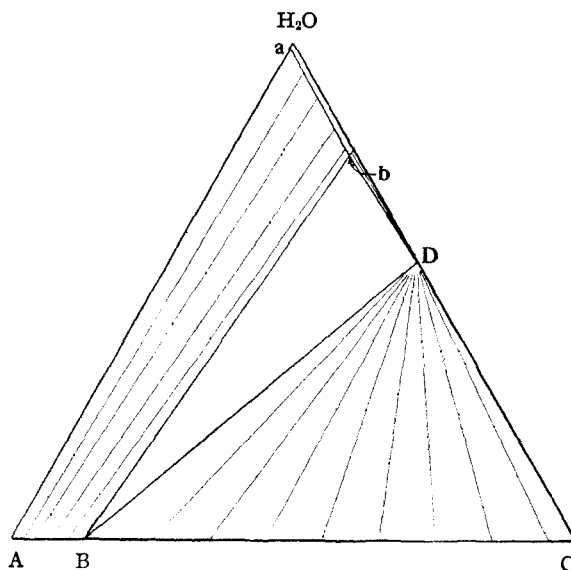


Fig. 7.—Condensed system below 32.4° (schematic): A = Ag₂SO₄; C = Na₂SO₄; D = Na₂SO₄ · 10H₂O.

Summary

1. The ternary systems silver sulfate-potassium sulfate-water, silver sulfate-ammonium sulfate-water, silver sulfate-lithium sulfate-water, have been studied at 25°. The only solid phases observed were the pure salt components (the monohydrate in the case of lithium sulfate), with no evidence for the formation of double salts or solid solutions at this temperature.

2. The ternary system silver sulfate-sodium sulfate-water has been studied at 35, 31.5, 25 and 20°. At 35° continuous solid solution has been observed between the two anhydrous salts, and at the other temperatures the solid solution observed is not continuous but has an upper limit, in equilibrium with aqueous solutions, at 64, 31 and 5% sodium sulfate, respectively. The other solid phase observed in these isotherms is sodium sulfate decahydrate.

3. The systems at 35 and 31.5° have been found to belong to Type II of Roozeboom's classification of solid solutions, involving positive deviations from ideality.

4. The distribution constant for the two isomorphous salts between their aqueous solutions and the saturating solid solutions was determined on the basis of a semi-empirical equation previously suggested,¹⁰ from a plot of the data for the 35 and 31.5° isotherms. $\log K$ so found at 35° is 1.78, as compared with the value 2.17 calculated from the separate aqueous solubilities of the two salts. At 31.5° $\log K$ "observed" was 1.79, $\log K$ "calculated" was 2.20.

5. The disagreement in this case can hardly be attributed to any uncertainty in the experimental data or in the measured activity coefficients for the pure salts in their saturated aqueous solutions, but probably reflects the limitations of the assumptions embodied in the empirical equation itself.

6. The ternary isotherms obtained for this system have been compared with the binary diagram⁷ for the system silver sulfate-sodium sulfate, and a schematic diagram has been drawn for the isotherm of the condensed system.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Behavior of Uranyl Solutions in a Mercury Reductor

BY EARLE R. CALEY¹ AND L. B. ROGERS²

McCay and Anderson,³ McCay,⁴ and Furman and Murray⁵ have shown that the mercury reductor may be used with advantage in the volumetric determination of antimony, iron, molybdenum or vanadium. These authors say very little about the behavior and possible interference of uranium in such determinations. McCay and Anderson³ simply state that uranyl ion is not reduced, but one of us (E.R.C.) noticed that this is not true if the solution contains hydrochloric acid in sufficient concentration. Moreover, in contrast to the action of amalgamated zinc the reduction appeared to stop after reaching the quadrivalent stage. Consequently the development of a very convenient method for the determination of uranium seemed possible. Subsequent investigation has now shown that this reduction is never entirely quantitative, though it is so nearly so that accurate results may be obtained by the use of a small correction factor.

Experimental

Apparatus and Solutions.—The reducers were of the type described by McCay.⁴ These were charged with distilled mercury. The weights and volumetric ware were carefully calibrated before use.

Potassium dichromate solution, exactly 0.1000 *N*, prepared from carefully dried salt of high purity, was used as the standard oxidizing reagent. Ferrous sulfate solution, approximately tenth normal, was the reducing reagent. This was always standardized immediately before use, the end-point of this titration, and of the back titrations in experimental runs, being detected by means of a platinum-tungsten pair of electrodes in connection with a vacuum tube voltmeter, as designed by Garman and Droz.⁶

The standard uranium solution, approximately tenth normal, was a uranyl acetate solution acidified with just sufficient acetic acid to prevent spontaneous hydrolysis. This was standardized by precipitating the uranium in measured volumes with carbonate-free ammonium hydroxide reagent, igniting the precipitates to uranium oxide in a muffle furnace at 800°, and weighing. The results of this gravimetric standardization were checked by reducing other measured portions in a Jones reductor according to the procedure of Lundell and Knowles,⁷ and

then titrating the resulting uranous solution with standard dichromate solution according to the method of Kolthoff and Lingane.⁸ The volumetric results checked those obtained gravimetrically within one part per thousand.

General Procedure.—A 25.00-ml. portion of the standard uranium solution was pipetted into a reductor containing 250 g. of mercury. A measured volume of a given acid, usually hydrochloric, was added together with sufficient distilled water to bring the final volume of the water phase to 100 ml. In some experiments certain amounts of sodium chloride were introduced into the system along with the uranium solution. After the air above the liquid had been displaced with carbon dioxide or nitrogen, the reductor was placed in a shaking machine for shaking at a given rate for a given time period. The reduced solution was then transferred to a folded filter with the aid of boiled and cooled distilled water, and the solution thus freed from suspended mercury and mercurous chloride was collected in a measured volume of the standard dichromate solution. The excess of dichromate solution was then determined by back titration with the standardized ferrous sulfate solution, and the degree of reduction calculated.

Results

Effect of Hydrochloric Acid Concentration.—

The importance of the concentration of hydrochloric acid is clearly shown by the results in the first two columns of Table I. These

TABLE I
EFFECT OF HYDROCHLORIC ACID CONCENTRATION AND TIME ON COMPLETENESS OF REDUCTION

Effect of acid		Effect of time ^a	
Normality of acid	Per cent. reduced	Reaction time, min.	Per cent. reduced
0.96	1.0	5	11.3
2.16	5.2	10	14.9
2.64	10.8	20	31.6
3.00	28.9	45	34.7
3.60	51.0	70	75.5
4.32	98.6	105	94.3
5.28	98.9	305	96.9
6.00	99.1		
7.00	99.3		
8.00	99.4		
9.00	99.3		

^a In 3.36 *N* hydrochloric acid.

results were obtained at room temperature with a fifteen-minute reduction period and a fixed vigorous rate of shaking of the reductor. It will be seen that under these conditions the degree of reduction does not reach a maximum until the concentration of the hydrochloric acid is around 7 *N*,

(8) Kolthoff and Lingane, *THIS JOURNAL*, **55**, 1871 (1933).

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(3) McCay and Anderson, *THIS JOURNAL*, **43**, 2372 (1921); **44**, 1018 (1922).

(4) McCay, *Ind. Eng. Chem., Anal. Ed.*, **5**, 1 (1933).

(5) Furman and Murray, *THIS JOURNAL*, **55**, 1689 (1936).

(6) Garman and Droz, *Ind. Eng. Chem., Anal. Ed.*, **11**, 398 (1939).

(7) Lundell and Knowles, *Ind. Eng. Chem.*, **16**, 723 (1924).