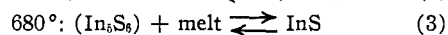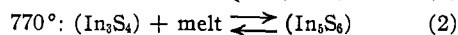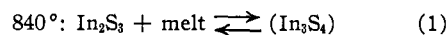melt to consist of two separate phases which exist in the molten state as immiscible liquids probably as high as 1300°.

The melting point of pure In_2S_3 is found to be considerably higher than the 1050° reported by Thiel and Luckmann.[2] A true melting point is difficult to obtain because the compound melts with decomposition. A melting point of between 1090 and 1100° is indicated for the pure compound.

Meritectic temperatures were recorded as

$$840°: \quad In_2S_3 + melt \rightleftarrows (In_3S_4) \qquad (1)$$

$$770°: \quad (In_3S_4) + melt \rightleftarrows (In_5S_6) \qquad (2)$$

$$680°: \quad (In_5S_6) + melt \rightleftarrows InS \qquad (3)$$

The monotectic intersects the miscibility gap at 640°. The reaction line at 370° is believed to be due to the decomposition of the In_3S_4 phase into In_2S_3 and In_5S_6. The In_3S_4 phase apparently exists only above this temperature. No evidence for its existence at room temperature was found in the X-ray studies. The compounds In_3S_4 and In_5S_6 probably are spinel-like compounds and should be written as $InS·In_2S_3$ and $3InS·In_2S_3$, respectively.

The Ternary and Quaternary Aqueous Systems Involving Thallous, Ammonium, Potassium and Cupric Sulfates

BY JOHN E. RICCI AND JACK FISCHER

Some aqueous salt systems involving thallous sulfate have been studied at 25° in order to compare the behavior of the thallous with that of the corresponding silver and alkali metal salts. Continuous solid solution is formed between Tl_2SO_4 and both $(NH_4)_2SO_4$ and K_2SO_4. Both systems apparently belong to Type I of the Roozeboom classification in respect to the distribution between the aqueous solution and the crystalline phase. The Tl_2SO_4–K_2SO_4–H_2O system, studied at 10, 25 and 45°, is unusual in that while the vapor pressure of the saturated aqueous solution has, according to the observed distribution, no minimum for the entire system, the analytical water content has a very distinct minimum. In the system Tl_2SO_4–$CuSO_4$–H_2O the hydrated double salt $Tl_2SO_4·CuSO_4·6H_2O$ was found to be just incongruently soluble at 25°. The equilibrium relations at 25° for the corresponding congruently soluble double salts in the systems $(NH_4)_2SO_4$–$CuSO_4$–H_2O and K_2SO_4–$CuSO_4$–H_2O were reinvestigated, in part, and in both cases the maximum water content of the solubility curve was found not to occur in the pure aqueous solution of the double salt but in a solution containing excess of the univalent sulfate. The 25° isotherms of the two quaternary systems Tl_2SO_4–$(NH_4)_2SO_4$–$CuSO_4$–H_2O and Tl_2SO_4–K_2SO_4–$CuSO_4$–H_2O were determined. In each case there is no isothermally invariant point of threefold saturation, since each involves only the three solid phases $CuSO_4·5H_2O$, a continuous anhydrous solid solution of the univalent sulfates, and a continuous hydrated solid solution of two double salts, one congruently and one incongruently soluble. Jänecke diagrams of the isotherms, with (approximate) contours of water content, are given for both systems.

In order to add to the information on the relations between thallous salts and the salts of other univalent cations, the solubility isotherms at 25° of a number of aqueous systems of thallous sulfate and other sulfates were investigated. The systems chosen involve the salts Tl_2SO_4, $(NH_4)_2SO_4$, K_2SO_4 and $CuSO_4$. Despite certain similarities between argentous and thallous salts, we find continuous solid solution formed between Tl_2SO_4 and both $(NH_4)_2SO_4$ and K_2SO_4 at room temperature, while Ag_2SO_4 forms solid solution with neither of these salts.[1] Moreover, thallous sulfate forms the double salt $Tl_2SO_4·CuSO_4·6H_2O$, a schoenite, isomorphous with the corresponding double salts $(NH_4)_2SO_4·CuSO_4·6H_2O$ and $K_2SO_4·CuSO_4·6H_2O$.

Of the four quaternary aqueous systems involving the four salts under discussion, that consisting of water and the three univalent sulfates, or the system Tl_2SO_4–$(NH_4)_2SO_4$–K_2SO_4–H_2O, has not here been investigated. Every pair of these three salts forms continuous solid solution at room temperature,[2] and it may safely be expected, therefore, that the quaternary isotherm would involve but one solid phase, a ternary anhydrous solid solution of the three simple sulfates. Another of the possible quaternary systems, namely, $(NH_4)_2SO_4$–K_2SO_4–

$CuSO_4$–H_2O, has already been investigated.[3] This involves the two isomorphous double salts $(NH_4)_2SO_4·CuSO_4·6H_2O$ and $K_2SO_4·CuSO_4·6H_2O$, both congruently soluble and forming continuous solid solution with each other. The isotherm (25°) has two curves of twofold saturation, one for quaternary liquid saturated with $CuSO_4·5H_2O$ and the solid solution of the hydrated double salts, and one for saturation with this solid solution and the continuous anhydrous solid solution of $(NH_4)_2SO_4$ and K_2SO_4. Between these curves, or on the solubility surface of the double salt solid solution, there is a ridge of maximum vapor pressure falling from the solubility of the potassium double salt to that of the ammonium double salt. The 25° isotherms of the remaining two quaternary systems are here reported. Their phase relations differ from the preceding in that in each of them one double salt is congruently soluble and the other incongruently soluble.

Materials and General Procedure.—Some of the thallous sulfate used was a pure sample remaining from previous work in this Laboratory,[4] some of it was prepared by purification of commercial C.P. material, and some from Tl_2CO_3 and sulfuric acid. In these preparations the thallous sulfate was heated to dryness and partial melting with excess of H_2SO_4 and then again with ammonium carbonate, finally being recrystallized from water two or three times. The

(1) E. L. Simons and J. E. Ricci, THIS JOURNAL, **68**, 2194 (1946).

(2) For the system $(NH_4)_2SO_4$–K_2SO_4–H_2O at 25° see A. Weston, J. Chem. Soc., **121**, 1223 (1922), and A. E. Hill and C. M. Loucks, THIS JOURNAL, **59**, 2094 (1937).

(3) R. Hayami, Mem. Col. Sci. Kyoto Imp. Univ., **4**, 359 (1921).

(4) A. E. Hill, N. O. Smith and J E Ricci THIS JOURNAL, **62**, 858 (1940).

product, dried at 110°, gave a pH of ~ 5.3 in 1% solution, indicating very small retention of bisulfate, and it was in each case found to be pure within 0.1% on the basis of determination of thallium. Its solubility at 25°, moreover, was found to be independent of the ratio of solid to liquid used, and the value 5.222 (± 0.005)% agrees well with previous values.[4]

The copper sulfate used was the C.P. pentahydrate, found to be 99.9% pure through both electrolytic and iodometric determination of copper. Other salts were also of dependable C.P. grade.

For the solubility equilibria, complexes of known composition were prepared from the solid salts and water, in Pyrex tubes containing in addition some glass beads and marbles for crushing and internal mixing. The tubes were rotated in large thermostated water-baths. The saturated solutions were then sampled for analysis by means of calibrated delivery pipets fitted with filter paper tips. The composition of the solid phase was calculated through algebraic extrapolation of the tie-lines fixed by the compositions of liquid and total complex.[5]

All data are tabulated in terms of weight percentage.

For brevity of reference the salts and solid phases will be represented by the following symbols:

A = Tl_2SO_4 F = $(NH_4)_2SO_4 \cdot CuSO_4 \cdot 6H_2O$
B = $(NH_4)_2SO_4$ G = $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$
C = $CuSO_4$ AB = Solid soln. of A and B
H = $CuSO_4 \cdot 5H_2O$ AD = Solid soln. of A and D
D = K_2SO_4 EF = Solid soln. of E and F
E = $Tl_2SO_4 \cdot CuSO_4 \cdot 6H_2O$ EG = Solid soln. of E and G

Analysis of Saturated Solutions. Total Solid.—The liquid sample was first evaporated to dryness at 85° (and, with $(NH_4)_2SO_4$ present, further heated at 85° for 24 hours) and then brought to constant weight at 110°.

Copper.—Three methods were used for determination of copper. Electrodeposition, in solution containing H_2SO_4 and HNO_3, could be used only in absence of thallium. Thallium gave a brown deposit (Tl_2O_3?) on the anode in alkaline solution and caused darkening of the anode in acid solution, in either case interfering apparently by polarization of the anode.

Iodometric determination—treatment with KI and titration with standard thiosulfate with starch as indicator—was also used. Nitrobenzene was added near the end-point to prevent adsorption of iodine on the cuprous iodide.[6] Here too, thallium interferes because of the yellow-green color of the mixed precipitates of Cu_2I_2 and TlI.

In presence of thallium, copper was determined, without interference, by potentiometric iodometric titration, with a Beckman research model G pH meter and with platinum and saturated calomel electrodes. Nitrobenzene was not necessary. The titration was carried to a sharp inflection point which corresponded to the visual end-point in absence of thallium.
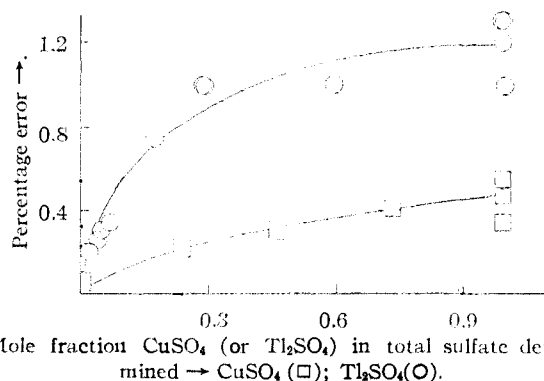
The three methods were tested for concordance and accuracy with Kahlbaum pure copper and with C.P. $CuSO_4 \cdot 5H_2O$.

Thallium.—Unipositive thallium was determined by titration with standard KIO_3 to the iodine monochloride end-point in fairly concentrated HCl.[7] With omission of the addition of ICl, the procedure first used (namely, in seven complexes of the system $Tl_2SO_4-K_2SO_4-H_2O$ at 25°) was essentially that described by Swift and Garner.[8] The concentration of the KIO_3 solution, prepared by dilution of weighed pure KIO_3, was verified by standardization with arsenious oxide. For most of the work, however, the end-point was determined potentiometrically. The determination was made with a Fisher titrimeter and the Beckman pH meter. The use of platinum and tungsten as electrodes gave a drifting potential at the end-point, but platinum and saturated calomel gave excellent results. The final volume was ~200 ml., ~ 3 N in HCl. Both methods (visual and potentiometric end-points) gave errors of less than 0.1% when tested on various amounts of Tl_2SO_4.

Sulfate.—The procedure of Hintz and Weber,[9] in which the hot solution of the sample, containing ~ 2 ml. of concd. HCl in 200 ml., is rapidly mixed with hot dilute $BaCl_2$ solution, gave high results in presence of Na^+, Cu^{++} or Tl^+ ion. Mixing of the solutions cold, followed by digestion, gave better results for Na_2SO_4, while addition of HCl after mixing (hot) gave somewhat better results for Tl_2SO_4. The procedure finally adopted was the rapid mixing of the solution cold, followed by addition of the HCl and then digestion. This gave good results (99.8 to 100.1%) for Na_2SO_4, K_2SO_4 and $(NH_4)_2SO_4$, with high results for $CuSO_4$ (~ 0.5%) and for Tl_2SO_4 (~1%). The correction to be applied was determined by a series of tests on Na_2SO_4 + Tl_2SO_4 and Na_2SO_4 + $CuSO_4$, the results of which are shown in Fig. 1.

System $Tl_2SO_4-(NH_4)_2SO_4-H_2O$ at 25°.—Attainment of equilibrium in this system, involving continuous solid solution, was slow. Complexes totaling 20 g. were rotated for a minimum of 60 days before analysis, and the composition of the saturated solution was found to be constant on reanalysis after 30 more days of stirring. The solution was analyzed for total solid and for Tl. The data,[10] in weight percentage, are plotted in the usual triangular diagram in Fig. 2. Solution u, for saturation with Tl_2SO_4 in pure
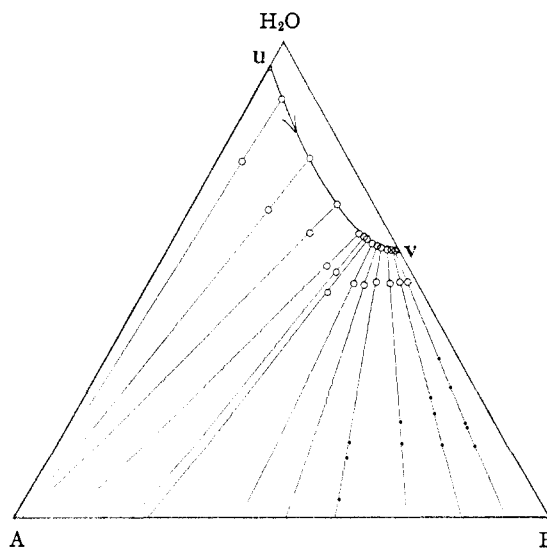
Fig. 2.—System $Tl_2SO_4(A)-(NH_4)_2SO_4(B)-H_2O$ at 25°.

Mole fraction $CuSO_4$ (or Tl_2SO_4) in total sulfate determined → $CuSO_4$ (□); Tl_2SO_4(O).

Fig. 1.—Determination of sulfate in mixtures of Na_2SO_4 with $CuSO_4$(□) and with Tl_2SO_4(O).

(5) A. E. Hill and J. E. Ricci, *ibid.*, **53**, 4305 (1931).

(6) W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 248.

(7) This application of the general Andrews method was apparently first suggested by A. G. Berry, *Analyst*, **51**, 137 (1926), and **59**, 736 (1934); G. F. Smith and C. S. Wilcox, in *Anal. Chem.*, **14**, 49 (1942), describe the use of amaranth as indicator.

(8) E. H. Swift and G. S. Garner, THIS JOURNAL, **58**, 113 (1936).

(9) E. Hintz and H. Weber, *Z. anal. Chem.*, **45**, 31 (1906).

(10) The complete table of numerical data for this isotherm is available on microfilm. Order Document 3369 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

water, contains 5.222% Tl_2SO_4, with density, 1.046; for $(NH_4)_2SO_4$ the solubility in pure water, point v, is 43.40%, density 1.239.

With all the tie-lines passing, when extended, to the right of the H_2O corner of the triangle, the solid solution relations are seen to be those of Type I in Roozeboom's classification,[11] with the mole fraction of $(NH_4)_2SO_4$ in the dissolved salts always greater than its mole fraction in the solid phase. These fractions are plotted in a Roozeboom distribution diagram in Fig. 3. The plot of log R_1 (R_1 = mole ratio of dissolved salts) against R_s (R_s = mole ratio in solid phase) is not linear, so that the distribution coefficient[12] is not constant. The plot of log (R_1/R_s) against the mole fraction in the solid is also not linear, except for a small region in the middle range, so that the solid solution is not "regular" (in Hildebrand's sense[13]).

The Type I distribution means that in isothermal evaporation of the saturated aqueous solution the composition of the solution moves in the direction u → v, toward the solution saturated with pure $(NH_4)_2SO_4$. The vapor pressure of the saturated solution therefore decreases steadily, without passing through a minimum, in the direction of the arrow in Fig. 2. At the same time it is seen in Fig. 2 that the analytical water content also decreases steadily from u to v, although the variation of the density, which passes through a maximum, shows that there must be some considerable complexity in the solution.

System $Tl_2SO_4-K_2SO_4-H_2O$.—The complexes (~20 g.) in this system at 10 and 25° had to be rotated for at least two months and for as long as 10 weeks for those with low proportions of Tl_2SO_4. Establishment of equilibrium at 25° was proved for two of the points of the solubility curve by a special procedure (using 40-g. complexes). The complexes labeled 1 and 2 were rotated directly at 25°. These labeled 1′ and 2′, with identical respective compositions, were first rotated for 37 days at 45° and then at 25°. Complex 1″, with the same final total composition as 1 and 1′ but first lacking 0.5 g. Tl_2SO_4, was stirred for 37 days at 25° before the rest of the Tl_2SO_4 was added. All five tubes were sampled after a total time of 141 days, and the solution compositions were found to be essentially the same for each total composition. The complexes at 45° (~ 20 g.) were stirred for 38–85 days. All solutions at 25° were reanalyzed to verify equilibrium; at 10° and at 45° only a few complexes were reanalyzed and the others were allowed to run a longer time before sampling and analysis.

The solutions were analyzed for total solid and for Tl. The results are listed in Table I; the complete data for the temperatures 10 and 45° are available on microfilm.[10] The 25° isotherm is plotted in Fig. 4, the isotherms at 10 and at 45° being very similar to this. The shape of the solubility curve, with its very sharp minimum of water content, is suggestive of a break in the curve and hence of a discontinuity in the solid solution of the two salts. The solubility curve is nevertheless apparently smooth and continuous; despite the nearness of many of the points determined on the curve, no point of invariance can be detected in the liquid composition at any of the three temperatures investigated. The solid solution is therefore continuous at each of these temperatures.

The distribution of the salts between the aqueous solution and the saturating-solid solution is plotted for the three temperatures in Fig. 3. As in the preceding system $Tl_2SO_4-(NH_4)_2SO_4-H_2O$, the rela-

(11) H. W. B. Roozeboom, Z. physik. Chem., **8**, 521 (1891).

(12) A. E. Hill, G. S. Durham and J. E. Ricci, THIS JOURNAL, **62**, 2723 (1940).

(13) J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1950, p. 46.

Mole fraction in solid solution.
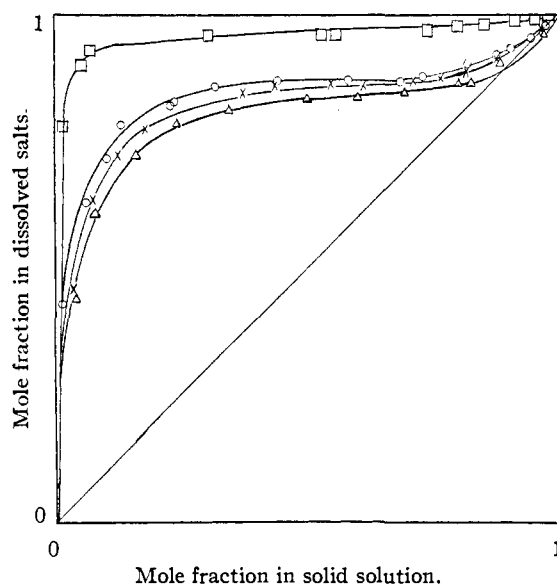
Fig. 3.—Distribution between liquid and solid phases: □, $Tl_2SO_4-(NH_4)_2SO_4-H_2O$ at 25°; ○, $Tl_2SO_4-K_2SO_4-H_2O$ at 10°, X at 25°, △ at 45°.

tions are apparently those of the Roozeboom Type I, although it is possible, according to Fig. 3, that the curves may cross the diagonal as in Type II. The last points at both 10 and 25° are practically on the diagonal, while the last point at 45° is actu-

TABLE I

SYSTEM $Tl_2SO_4(A)-K_2SO_4(D)-H_2O$

	Complex A, %	D, %	Solution A, %	D, %	Density	D in solid, %
		m: region of minimum water content.				
			Temperature: 10°			
...		0.00	3.568	0.00	1.031	0
	6.50	8.68	(2.94	7.29	1.087)m	32.5
	0.00	...	0.00	8.42	1.066	100
			Temperature: 25°			
point u			5.222	0.00	1.046	0
	14.95	1.49	5.04	1.51	1.056	1.2
	16.94	3.02	4.98	3.04		2.9
	14.98	4.43	4.91	4.38	1.080	4.8
	14.81	5.82	4.84	5.67	1.091	6.9
	12.99	8.45	4.50	8.40	1.113	8.9
	12.30	9.49	4.46	8.64	1.113	17.2
	11.49	10.50	4.26	9.37	1.118	21.0
	10.63	11.38	4.25	9.31	1.118	29.7
	10.03	11.96	(4.21	9.43)m		35.4
	9.00	12.98	4.13	9.42	1.118	45.9
	8.29	14.01	3.79	9.46	1.113	53.1
	7.52	14.93	3.61	9.53	1.113	59.9
	5.98	17.08	2.80	9.88		60.4
(1″)	3.20	17.19	1.79	10.24	1.100	83.3
(1′)	3.20	17.19	1.79	10.31	1.101	
(1)	3.20	17.19	1.79	10.26	1.099	
(2′)	1.80	18.20	1.02	10.46	1.093	91.0
(2)	1.80	18.20	1.03	10.44	1.093	
point y			0.00	10.76	1.085	100
			Temperature: 45°			
...		0.00	7.72	0.00	1.064	0
	15.95	15.07	(6.40	11.30	1.146)m	34.6
	0.00	...	0.00	13.58	1.098	100

Fig. 4.—System Tl₂SO₄(A)-K₂SO₄(D)-H₂O at 25°.

ally across it, with 0.963 as the mole fraction of K₂SO₄ in the dissolved salts and 0.966 in the solid solution. Again as in the preceding system, neither the plot of $\log R_1$ against $\log R_s$ nor that of $\log (R_1/R_s)$ against mole fraction in the solid is linear.

With Type I the vapor pressure of the saturated solution would diminish steadily in the direction u → y shown in Fig. 4, toward the solution saturated with pure K₂SO₄, while with Type II the point of minimum vapor pressure for the solubility curve would be at the crossing of the diagonal in Fig. 3 or at that point on the solubility curve for which the tie-line passes, when extended, through the H₂O corner in Fig. 4. In either case, however, it is clear that the vapor pressure minimum does not at all coincide with the point of minimum water content of the solubility curve, which is simply the minimum of the curve as plotted in Fig. 4. Such relations are probably not infrequent, but the present system is unusual in degree. If a saturated solution with composition at the H₂O minimum of the solubility curve is evaporated isothermally, its composition must move in the direction of the arrow while a solid of higher proportion of Tl₂SO₄ is being precipitated. Such evaporation must therefore lead to a solution of higher water content, although always, of course, to one of lower vapor pressure. The extent of divergence, in the present case, between the water content minimum and the vapor pressure minimum, is indicative of a great degree of non-ideality, probably complex ion formation, in the liquid solution. The shape of the curve may be interpreted, in fact, as an abnormal increase of the solubility of Tl₂SO₄ by the K₂SO₄; a similar effect of Na₂SO₄ has been noted in the system Tl₂SO₄-Na₂SO₄-H₂O,[14] which is simpler in not involving solid solution.

Finally, the maximum density at each temperature seems to correspond with the minimum of water content.

System Tl₂SO₄-CuSO₄-H₂O at 25°.—The double salt Tl₂SO₄·CuSO₄·6H₂O was reported by Locke[15] to have a

(14) J. E. Ricci and J. Fischer, THIS JOURNAL, 74, 1607 (1952).

(15) J. Locke, Am. Chem. J., 27, 455 (1902).

solubility of 8.1 g. of anhydrous salt per 100 ml. of water, or ~ 7.5% by weight. It was studied further by Benrath,[16] who, reporting graphically (without numerical data) the 30° isotherm of the system Tl₂SO₄-CuSO₄-H₂O, pointed out the incongruent solubility of the salt at that temperature. In the 25° isotherm here reported the double salt is still incongruently soluble, in respect to Tl₂SO₄. Its saturated solution is possible only in the presence of excess of CuSO₄, so that Locke's "solubility" may represent the concentration of the solution saturated with both double salt and Tl₂SO₄. By comparison with Benrath's very small diagram it is not possible to state whether the double salt approaches congruence of saturation with rising or with falling temperature.[17]

The complexes (totaling 30-40 g.) were stirred for 13-17 days before sampling, and the saturated solution was analyzed for copper and for thallium in separate samples; equilibrium was verified by reanalysis in every case. The important points of the isotherm are listed in Table II and all the experimental points are plotted in Fig. 5; the complete data are available on microfilm.[10] Algebraic extrapo-

TABLE II

SYSTEM Tl₂SO₄(A)-CuSO₄(C)-H₂O AT 25°

Point	A, %	C, %	Density	Solids
u	5.22	0.00	1.046	A
a	5.65	1.86	1.070	A + E
b	2.81	18.70	1.237	E + H
w	0.00	18.50	1.206	H

lation of the tie-lines for saturation with the double salt E to the line of 13.99% H₂O (theoretical for E) gives 65.60 (average deviation 0.40) % Tl₂SO₄, as compared to the theoretical 65.34. The invariant point a, for saturation with Tl₂SO₄ and double salt, is seen to lie just to the right of the line joining E and the H₂O corner; the weight percentage of CuSO₄ in the salts at point a is 24.77 as compared to 24.02% in E, and the weight percentage of total salt at a is 7.51, which seems therefore to be the value reported by Locke.
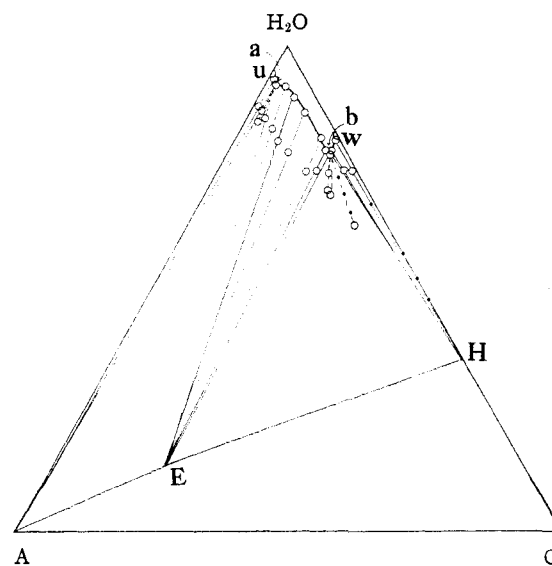
Fig. 5.—System Tl₂SO₄(A)-CuSO₄(C)-H₂O at 25°.

System (NH₄)₂SO₄-CuSO₄-H₂O at 25°.—This isotherm had already been studied by Caven and Mitchell,[18] who analyzed the solutions for copper iodometrically and for total sulfate as BaSO₄, without mentioning, however, any correction necessitated by the copper in the sulfate determination. Some new measurements, listed in Table III, were therefore made, as described for the preceding system,

(16) A. Benrath, Z. anorg. Chem., 151, 21 (1926).

(17) According to Benrath the double salt has a "decomposition point" (a term not further explained) at 25.6-25.8°.

(18) R. M. Caven and T. C. Mitchell, J. Chem. Soc., 125, 1428 (1924)

TABLE III

SYSTEM $(NH_4)_2SO_4(B)$–$CuSO_4(C)$–H_2O AT 25°

Point	B, %	C, %	Density	Solids
d	43.31	0.36	1.246	B + F
m_7	11.24	6.20	1.129	F
	10.12	7.42	1.134	F
	8.37	10.15	1.157	F
c	5.38	19.47	1.247	F + H
w	0.00	18.50	1.206	H

the solution being analyzed for copper and for total sulfate on separate samples, with reanalysis to prove equilibrium. Some of these percentages differ from those in ref. 18 by as much as 0.3. The isotherm is plotted in Fig. 6 where it is seen that the maximum, point m_6, of the solubility curve of the double salt F, or the point of maximum water percentage ($\sim$82.6), does not coincide with the aqueous solubility ($\sim$18.52% salt) of the compound, fixed by the line F–H_2O. The divergence is probably connected with equilibria of complex species in the solution. The maximum vapor pressure for solutions saturated with F must be at the actual aqueous solubility, however, since isothermal evaporation must cause the composition of the solution to move away from this point on either side of it, with simultaneous loss of water and of F from the solution. Isothermal evaporation of a saturated solution just on the left of the pure aqueous solubility, or one with a slight excess of $(NH_4)_2SO_4$, therefore causes the water content of the solution to pass through a maximum as the composition of the solution travels to the invariant point d, a behavior similar to that discussed under the system Tl_2SO_4–K_2SO_4–H_2O.

Fig. 6.—System $(NH_4)_2SO_4(B)$–$CuSO_4(C)$–H_2O at 25°.

System K_2SO_4–$CuSO_4$–H_2O at 25°.—Here again only a few points (Table IV) were redetermined (through analysis and reanalysis for copper and for total sulfate) in order to verify and to supplement the data for the isotherm reported by Caven and Mitchell.[18] Similar differences of up to 0.3 were noted in the salt percentages. The solubility of the double salt G in pure water is $\sim$10.32%, but again, as seen in Fig. 7, the point m_7 of maximum water percentage ($\sim$90.2) is in a saturated solution containing excess of K_2SO_4, so that the relations are similar to those in the preceding system.

TABLE IV

SYSTEM $K_2SO_4(D)$–$CuSO_4(C)$–H_2O AT 25°

Point	D, %	C, %	Density	Solids
f	11.03	1.29	1.097	D + G
m_7	6.35	3.42	1.085	G
	5.70	4.30	1.089	G
	5.38	4.94	1.093	G
e	3.09	19.16	1.246	G + H

Fig. 7.—System $K_2SO_4(D)$–$CuSO_4(C)$–H_2O at 25°.

Quaternary System Tl_2SO_4–$(NH_4)_2SO_4$–$CuSO_4$–H_2O at 25°.—The quaternary curves of twofold saturation start from the ternary isothermally invariant points a, b, c, d of tables II, III and Figs. 5, 6. These curves were investigated by addition of progressive amounts of the third salt component to each of these ternary solutions, with analysis of the saturated solution at equilibrium. Since both of the solid solutions, one anhydrous, of Tl_2SO_4 and $(NH_4)_2SO_4$, and the other hydrated, of the two double salts, are continuous, the quaternary isotherm is found not to contain any point saturated with three solids. The curve originating at b with addition of $(NH_4)_2SO_4$ is continuous with that starting from c with addition of Tl_2SO_4, and a similar continuous quaternary curve of twofold saturation joins the points a and d. The first curve represents solution saturated with pure $CuSO_4 \cdot 5H_2O$ and the solid solution of the double salts with compositions on the straight line joining point E and point F. The second curve represents solution saturated with this EF solid solution and the solid solution of the anhydrous univalent sulfates running from A to B. There are thus three parts of the solubility surface: the section bwc for saturation with pure $CuSO_4 \cdot 5H_2O$ (phase H), abcd for saturation with the solid solution EF, and uadv for saturation with solid solution AB.

Large complexes ($\sim$200 g.) were made up in 240-ml. glass stoppered bottles, so that sufficient liquid would be available for obtaining several points on a given curve by successive addition of one of the salts. The solutions were sampled after 2 to 4 weeks of stirring, known to be sufficient for equilibrium on the basis of reanalysis of seven complexes after further stirring (a general procedure used in all the quaternary work reported). The analysis involved determination of Tl, Cu and total sulfate in separate samples, with $(NH_4)_2SO_4$ calculated by difference.

The compositions of the saturated solutions are listed in Table V, in terms of weight percentage. The two curves, with the experimental points obtained, are plotted in Fig. 8. This is a Jänecke or radial projection from the H_2O apex to the salt base of the quaternary isothermal tetrahedral diagram, and shows only the salt proportions (relative proportions by weight) in the liquid and solid phases involved. In this projection the curve ad crosses the line EF (at the point x) because the double salt E is incongruently soluble while F is congruently soluble.

The continuous nature of the two curves indicates that the solid solution of the double salts, like that of the simple univalent sulfates, is continuous. Further proof of this was obtained by a study of the section H_2O–E–F of the quaternary system. The portion of this section limited by the point x near the Tl_2SO_4–$CuSO_4$ side may be treated as a quasi-ternary section of the quaternary isotherm, as brought out by data presented in Table VI. These measurements were made on complexes with compositions falling on the plane H_2O–E–F, equivalent to mixtures of water and the two double salts. The saturated solutions at equilibrium, how-

TABLE V

SYSTEM Tl₂SO₄-(NH₄)₂SO₄-CuSO₄-H₂O AT 25°

Curve	A, %	B, %	C, %	Density	Solids
b→c	2.43	0.86	18.90	1.246	H + EF
b→c	2.49	0.87	18.86	1.248	H + EF
b→c	2.34	1.29	18.91	1.251	H + EF
b→c	1.62	2.73	19.12	1.256	H + EF
b→c	0.67	4.44	19.34	1.261	H + EF
b→c	0.32	5.01	19.44	1.256	H + EF
b→c	0.25	5.02	19.46	1.256	H + EF
EF	1.71	3.24	16.78	1.225	EF
surface	1.07	4.63	16.22	1.223	EF
	1.01	4.11	18.57	1.247	EF
a→d	5.76	1.23	1.76	1.076	AB + EF
a→d	5.97	2.76	1.69	1.090	AB + EF
a→d	6.20	4.30	1.63	1.101	AB + EF
a→d	6.26	4.68	1.63	1.104	AB + EF
a→d	6.49	6.55	1.54	1.119	AB + EF
a→d	7.10	13.23	1.32	1.166	AB + EF
a→d	6.20	30.79	0.60	1.256	AB + EF
a→d	6.18	30.88	0.60	1.255	AB + EF
a→d	6.15	30.92	0.59	1.255	AB + EF
a→d	5.39	34.56	0.49	1.256	AB + EF
a→d	5.31	34.95	0.46	1.267	AB + EF
a→d	3.14	39.53	0.38	1.265	AB + EF
a→d	2.52	40.54	0.38	1.261	AB + EF

ever, were analyzed as quaternary solutions, for Cu, Tl and total sulfate, and their compositions, all falling on the line xF, are therefore equivalent to solutions of the two double salts in water. The solid phase is then one on the line EF.
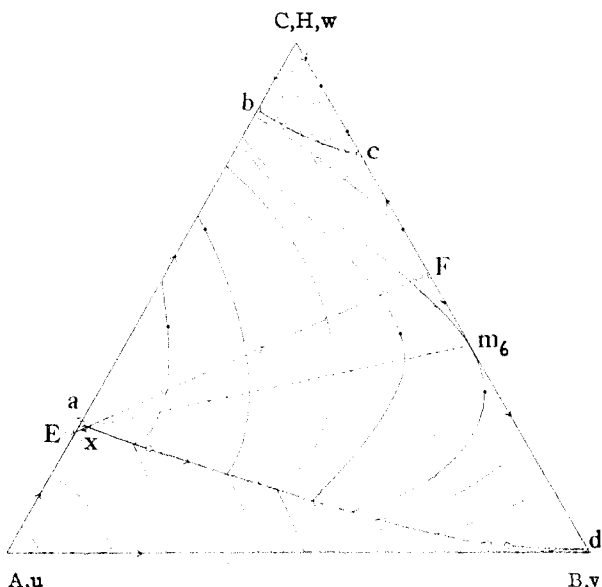

Fig. 8.—System Tl₂SO₄-(NH₄)₂SO₄-CuSO₄H₂O at 25° (Jänecke diagram).

The usual triangular plot of the section, or of the data of Table VI, given in Fig. 9, shows, with its continuous solubility curve, that the solid solution of the double salts is continuous. The distribution relations are seen to be those of Roozeboom's Type I, as in the related ternary system Tl₂SO₄-K₂SO₄-H₂O, with x → F' as the direction of isothermal evaporation, or with the vapor pressure always falling from x to F in Fig. 8. The distribution curve, relating the mole fraction of the double salt F in dissolved salts to its fraction in the solid solution, resembles that of the system Tl₂SO₄-K₂SO₄-H₂O shown in Fig. 3. It may safely be concluded, therefore, that the direction of isothermal evaporation on the quaternary curves of twofold saturation is b → c and a → d.

TABLE VI

THE SECTION Tl₂SO₄·CuSO₄·6H₂O(E)-(NH₄)₂SO₄·CuSO₄· 6H₂O(F)-H₂O

A, %	Complex B, %	C, %	A, %	Solution B, %	C, %	Density	Solid phase
7.56	0.90	3.52	4.75	0.87	2.69	1.077	EF
7.58	4.52	7.85	2.89	4.27	6.02	1.116	EF
3.81	7.26	9.98	1.58	6.52	8.28	1.140	EF
1.52	9.07	11.43	0.60	7.81	9.53	1.154	EF
0.38	9.75	11.90	0.16	8.28	9.95	1.155	EF

The data show, moreover, that there is also no minimum of the analytical water content on the curves xF, bc, and ad, the water content falling steadily from the Tl₂SO₄ to the (NH₄)₂SO₄ side of Fig. 8.

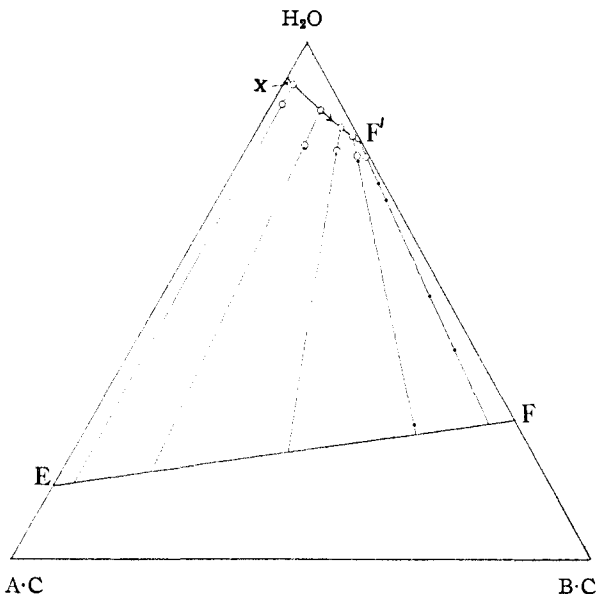Fig. 9.—The section Tl₂SO₄·CuSO₄·6H₂O(E)-(NH₄)₂SO₄· CuSO₄.6H₂O(F)-H₂O.

The solubility surface of the double salt solid solution, represented in projection as the region abcFdx of Fig. 8, is thus a rounded surface with a ridge of maximum vapor pressure running (with decreasing vapor pressure) from x to F, and with the vapor pressure falling away from this ridge both toward the curve bc and toward the curve ad. The maximum of the analytical water content on the side cFd, however, is not at point F but at m₆, or in the presence of excess of (NH₄)₂SO₄. In the quaternary composition tetrahedron, therefore, the surface has a ridge of maximum water percentage running from a point at or near x to point m₆.

The arrows on Fig. 8 represent the direction of decreasing vapor pressure or of the course of saturated solutions during isothermal evaporation under equilibrium conditions. These arrows coincide with the direction of decreasing analytical water content everywhere except in the region xFm₆. The light curves on the figure represent, in approximate fashion, contours of equal water content.

Quaternary System Tl₂SO₄-K₂SO₄-CuSO₄-H₂O at 25°.— The experimental procedure was entirely similar to that used for the preceding system. The compositions of solutions saturated with two solids are listed in Table VII and plotted in the Jänecke diagram of Fig. 10 which, as a projection, is quite similar to Fig. 8. Although again the vapor pressure of the saturated quaternary solutions falls steadily from the Tl₂SO₄ to the K₂SO₄ side of the system, there is now a trough of minimum water percentage running from m₄ on AB (Fig. 4) to a similar distinct minimum, m, on the curve af. Point m then marks the start of a minimum trough on the solubility surface abef of the solid solution EG, but the data are not conclusive on whether or not this minimum trough extends across the ridge of maximum water content, running from x' to m₇, and up to the quaternary curve be. A shallow minimum, m″, is at least faintly evident for curve be in the data of Table VII. The same is true for the
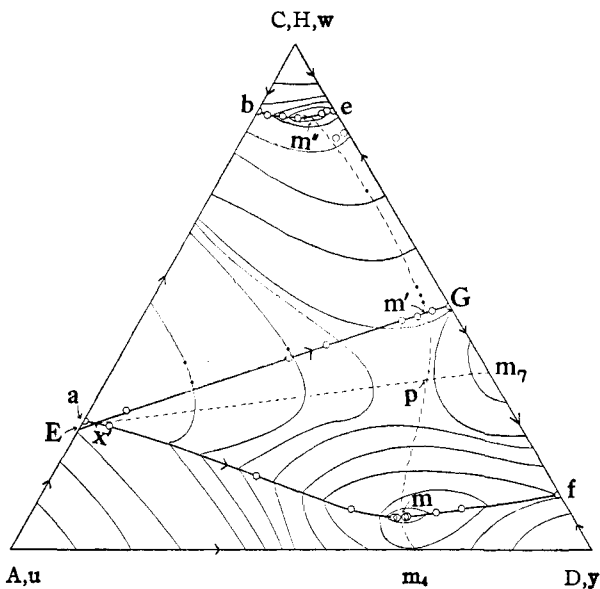
Fig. 10.—System Tl₂SO₄-K₂SO₄-CuSO₄-H₂O at 25° (Jänecke diagram).

"quasi-ternary" section x'G. The data for this section, corresponding to xF of Fig. 8, are given in Table VIII. Graphically, except for the suggestion of a shallow minimum (m') in the curve, this quasi-ternary section is similar to Fig. 9. Despite a possible minimum in percentage of water, the distribution relations are apparently still those of Type I, with the proportion of the potassium salt in the dissolved salts always greater than the proportion in the solid solution.

TABLE VII

SYSTEM Tl₂SO₄-K₂SO₄-CuSO₄-H₂O AT 25°

Curve	A, %	D, %	C, %	H₂O, %	Density	Solids
b→e	2.62	0.42	18.77	78.20	1.244	H + EG
b→e	2.13	1.07	18.90	77.90	1.249	H + EG
b→e	1.56	1.70	19.02	77.72	1.251	H + EG
b→e	0.56	2.53	19.17	77.74	1.249	H + EG
b→e	0.25	2.67	19.22	77.85	1.245	H + EG
b→e	0.23	2.72	19.23	77.82	1.247	H + EG
EG {	0.51	3.11	15.57	80.81	1.204	EG
surface {	0.17	3.31	15.90	80.62	1.207	EG
a→f	5.58	0.38	1.91	92.14	1.073	AD + EG
a→f	5.04	3.51	1.42	90.04	1.093	AD + EG
a→f	4.93	7.27	1.04	86.76	1.119	AD + EG
a→f	4.57	9.41	0.927	85.09	1.131	AD + EG
a→f	4.50	9.56	0.912	85.12	1.134	AD + EG
a→f	4.31	9.68	0.911	85.10	1.133	AD + EG
a→f	4.23	9.71	0.926	85.14	1.132	AD + EG
a→f	4.21	9.69	0.933	85.17	1.132	AD + EG
a→f	3.29	9.99	1.005	85.71	1.125	AD + EG
a→f	2.51	10.26	1.078	86.14	1.119	AD + EG

TABLE VIII

THE SECTION Tl₂SO₄·CuSO₄·6H₂O(E)-K₂SO₄·CuSO₄·6H₂O (G)-H₂O

Complex			Solution					
A, %	D, %	C, %	A, %	D, %	C, %	H₂O, %	Density	Solid phase
7.57	0.52	2.87	5.15	0.47	2.12	92.26	1.073	EG
7.57	3.65	5.74	3.12	2.77	3.55	90.56	1.088	EG
7.29	5.64	7.47	2.48	3.42	3.95	90.15	1.092	EG
2.29	7.33	7.44	0.98	4.71	4.66	89.65	1.095	EG
1.52	7.85	7.67	0.68	4.93	4.76	89.63	1.094	EG
0.76	8.36	7.90	0.37	5.14	4.87	89.62	1.093	EG

The vapor pressure on the saturation surface of the solid solution EG, or abeGfx', is a maximum along the ridge x'G, falling from x' to G and falling away on both sides to be and to x'f. With respect to the analytical water content, how-

ever, there is a ridge of maximum water percentage, falling from x' to point m₇, and a trough of minimum water content joining the minima m, m', m″ on af, x'G, and be, respectively. The result is a "saddle point" p on the saturation surface at the intersection of ridge and trough, as brought out by the (approximate) contours of water percentage on Fig. 10.

Since the course of isothermal evaporation, however, is related to the actual vapor pressure of the solutions, the relations, indicated again by the arrows of the figure, are the same as those in Fig. 8. Both systems, therefore, behave, in equilibrium isothermal evaporation, according to the schematic diagram of Fig. 11. All quaternary solutions with original salt proportions in the triangle ECF dry up to a mixture of pure solid H and a hydrated solid solution (s) on the line EF, the final liquid disappearing as it travels on the curve bc toward c. The actual relation between the composition of the liquid on bc and that of the saturating solid solution on EF has not been determined, but it must be of the nature represented in the 3-phase triangle Hls, for the schematic relation of the three condensed phases at equilibrium as the liquid on the curve bc travels toward c.
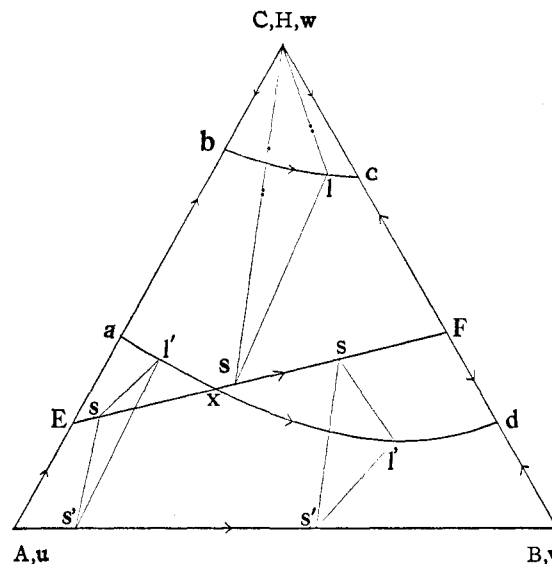

Fig. 11.—System Tl₂SO₄-(NH₄)₂SO₄ (or K₂SO₄)-CuSO₄-H₂O at 25° (schematic).

Similarly, quaternary solutions with original salt proportions in the rhombus AEFB dry up to a mixture of hydrated solid solution of double salts on EF and anhydrous solid solution (s') of the simple salts on AB, the final liquid disappearing on the curve ad. The schematic relations of the compositions of the three condensed phases for liquid traveling on the curve ad toward d is that of the two triangles sl's'.

The nature of the solid first appearing on evaporation of an unsaturated solution is fixed by the salt proportions in relation to the three surfaces, projected as bwc, abcd, uadv, while the solids remaining when the solution finally dries up (with complete equilibrium) depend on the regions EHF and AEFB. With complete equilibrium, then, solutions with salt proportions in the limited region Eax first precipitate solid solution on AB when they become saturated, and then the double salt solid solution EF when they reach the curve ax. But as they travel on the curve in the direction a → x, the first solid solution (primary crystallization) comes to be consumed at the expense of the second. The phase reaction on this section of the curve is therefore of the transition type: liquid + AB → EF + H₂O↗. When all of the first solid solution is consumed, the remaining liquid, now saturated with only one solid phase, leaves the curve and enters upon the solubility surface of solid solution EF, to dry up on curve bc to a mixture of H and EF. The rest of the curve ad (or the section xd) and the curve bc, are never left by solutions which once reach them; but the section ax is crossed, therefore, in isothermal evaporation with complete equilibrium by solutions reaching it with original salt proportions in the region Eax.

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