$CrO_4^{=}$ to some oxidation state between +6 and +3, but that the limiting current is governed by the formation of a film of chromic hydroxide, or basic chromic chromate, at the electrode surface, which interfered with the further reduction. When the solution was well-buffered at a *p*H between 8 and 10 the diffusion current at −0.3 to −0.4 v. corresponded to the reduction $CrO_4^{=} \longrightarrow Cr(OH)_3$. Apparently the film of basic salt is only stable under the conditions of the present experiments over a *p*H range from about 10.5 to 13.5.

From an analytical viewpoint, 1 *N* sodium hydroxide is the most suitable supporting electrolyte for the polarographic determination of chromate.

BERKELEY, CALIFORNIA
MINNEAPOLIS, MINNESOTA RECEIVED JANUARY 10, 1940

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

Ternary Systems. XXIV. Some Further Solid Solutions of Alums, at 25°[1]

BY ARTHUR E. HILL, NORMAN O. SMITH AND JOHN E. RICCI

This is a report of experiments continuing an investigation, conducted in this Laboratory, of ternary systems involving the formation of solid solutions between isomorphous double salts in equilibrium with aqueous solution. The general purpose of the investigation is the accumulation of reliable data on which to base, ultimately, speculations on the formation of solid solutions between such salts. In this respect it has been of interest especially to study the distribution of the two salts between the conjugate liquid and solid solutions, and to attempt to relate this distribution with the aqueous solubilities of the individual salts. On the basis of results, already published, on the formation of such solid solutions in a series of picromerites, studied as ternary systems of pairs of double salts with water,[2a] and in a number of alum pairs,[2b] an empirical equation has already been suggested[2a] for the relation between the mole fraction of a component in the liquid phase and its mole fraction in the solid phase; the degree of success toward a theoretical interpretation of the observed relation will be presented in a forthcoming publication from this Laboratory, making use of the present and additional data collected on this type of system.

Alums crystallize as regular octahedra and provided the lattice dimensions be not greatly different they would be expected to form solid solutions with one another. Early work with alums had been done by Hollmann[3] with the alum pairs $KFe(SO_4)_2$–$KAl(SO_4)_2$ and $KCr(SO_4)_2$–$KAl(SO_4)_2$, and by Fock[4] with the pair $KAl(SO_4)_2$–$TlAl(SO_4)_2$. In addition Hill and Kaplan[2] have studied the pairs $NH_4Al(SO_4)_2$–$KAl(SO_4)_2$, $NH_4Fe(SO_4)_2$–$NH_4Al(SO_4)_2$ and $NH_4Al(SO_4)_2$–$NaAl(SO_4)_2$. Complete miscibility between the alums was found in all these pairs studied, with the exception of the last mentioned, the sodium alum–ammonium alum pair, which formed no solid solution at all at the temperature of the measurements, 25°. The present paper describes similar measurements for the following pairs of alums in equilibrium with aqueous solutions at 25°: $TlAl(SO_4)_2$–$NH_4Al(SO_4)_2$, $TlAl(SO_4)_2$–$KAl(SO_4)_2$, $NH_4Cr(SO_4)_2$–$KCr(SO_4)_2$ and (partially) the pair $NH_4Fe(SO_4)_2$–$KAl(SO_4)_2$; complete miscibility was found to prevail for all these pairs at the temperature studied. Included also in this report is the ternary system for the formation of thallium alum from its component salts and water at 25°. This was desirable in view of the fact that thallium alum was to be prepared for use in solid solutions with other alums.

As has been emphasized in the preceding papers of this series, the present measurements are distinguished by the fact that special attention has been given to the question of attainment of equilibrium, inasmuch as the uncertainty about equilibrium generally vitiates the older results on the solubilities of such mixed salts. The procedure followed, for this purpose, already has been described,[2] the essential point being that

---

(1) This paper is being published, following the death of Professor Hill, by his collaborators. The material of the article is taken from a thesis presented for the degree of Doctor of Philosophy at New York University, June, 1939, by N. O. Smith, whose present address is the University of Manitoba, St. Vital, Manitoba, Canada.

(2) (a) Hill and Taylor, THIS JOURNAL, **60**, 1099 (1938); (b) Hill and Kaplan, *ibid.*, **60**, 550 (1938).

(3) Hollmann, *Z. physik. Chem.*, **37**, 193 (1901).

(4) Fock, *Z. Krist.*, **28**, 337 (1897).

TABLE I

Tl_2SO_4–$Al_2(SO_4)_3$–H_2O AT 25°

Original complex, wt. %		Liquid solution, wt. %		Solid phase
Tl_2SO_4	$Al_2(SO_4)_3$	Tl_2SO_4	$Al_2(SO_4)_3$	
0.00	....	0.00	27.83 (U)	$Al_2(SO_4)_3 \cdot n\ H_2O^a$
			27.83 (S)	$Al_2(SO_4)_3 \cdot n\ H_2O^a$
2.012	29.93	.118	27.63	$Al_2(SO_4)_3 \cdot n\ H_2O$ + Tl Alum
3.984	29.97	.114	27.64	$Al_2(SO_4)_3 \cdot n\ H_2O$ + Tl Alum
3.987	21.02	.391	20.37	Tl Alum
4.008	11.02	1.341	9.82	Tl Alum
5.996	4.98	3.502	3.343	Tl Alum
6.797	3.91	4.743	2.460	Tl Alum
15.70	6.30	5.774	2.044	Tl Alum + Tl_2SO_4
8.47	2.48	5.764	2.040	Tl Alum + Tl_2SO_4
7.96	1.257	5.590	1.294	Tl_2SO_4
....	0.00	5.208 (U)	0.00	Tl_2SO_4
		5.218 (S)		

[a] n is probably 17.

equilibrium is approached, for every solubility determination, from opposite sides as follows. Complexes are made up in duplicate from weighed amounts of the two alums and water in 50-ml. glass-stoppered solubility tubes and brought to equilibrium by rotation in a thermostat at 25 ± 0.02°; each solubility tube also contained two glass marbles which by their rolling motion kept the solid phases well ground. Following the usual procedure the duplicates differed only in the order of addition of the components, so that in one tube one of the two alums was dissolved completely and the second then added in solid form; in the duplicate tube the order of addition of the salts was reversed. Agreement between the duplicates upon analysis of the liquid and solid phases after rotation is proof that the measurements represent equilibrium, a factor of prime importance for our ultimate purpose.

Thallium Alum at 25°.—Complexes were made up from weighed amounts of recrystallized Eimer and Amend thallous sulfate, Merck hydrated aluminum sulfate and water. The thallous sulfate was found to be 99.61% pure by precipitation as the chromate. The composition of the aluminum salt, as a result of efflorescence, did not correspond exactly to that of a single hydrate, being always somewhat less hydrated than the usually accepted formula $Al_2(SO_4)_3 \cdot 18H_2O$; the analytically determined composition was therefore always used in calculating the compositions of the complexes. We may point out that similar observations on the low hydration of aluminum sulfate (low compared to the formula $Al_2(SO_4)_3 \cdot 18H_2O$) were being made at the same time by Horan and Skarulis,[5] who in fact offer serious evidence for doubting the usually accepted value for the hydration, and suggest the possibility of the formula $Al_2(SO_4)_3 \cdot 17H_2O$ for the hydrate in equilibrium with solution at 0°. Although it seems likely, on the basis of the work of Horan and Skarulis and of further investigations now being conducted by one of us (Dr. N. O. Smith), that the formula may be $Al_2(SO_4)_3 \cdot 17H_2O$, we are temporarily not assigning any definite formula to this hydrate in the present paper. Similar uncertainty exists for the degree of hydration of the corresponding chromic sulfate, for which the hepta-decahydrate formula also has been suggested.[6]

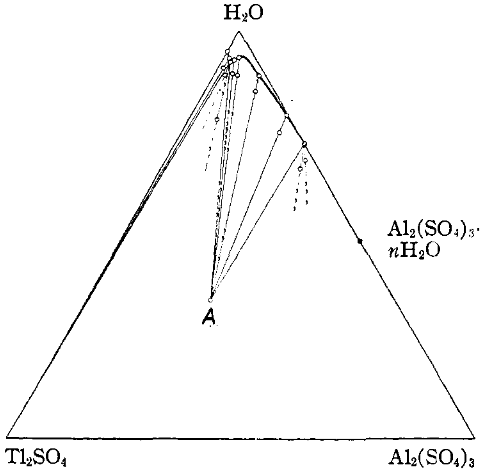

Fig. 1.—The system Tl_2SO_4–$Al_2(SO_4)_3$–H_2O at 25°; A = $TlAl(SO_4)_2 \cdot 12H_2O$.

Solubility equilibrium was found to be reached in this simple system within twenty-four hours, provided that the thallous sulfate was dissolved in the water before the addition of the aluminum sulfate. Only the liquid phases were analyzed. Thallium was determined volumetrically by the method of Zintl and Rienäcker[7] in which thallous ion is oxidized to thallic ion by standard bromate in 5% hydrochloric acid solution at 80° using methyl orange as indicator. In order to determine aluminum it was necessary first to remove thallium by precipitation as the sulfide in hot solution made alkaline with sodium hydroxide to retain the aluminum. After removal of sulfur the fil-

---

[5] Horan and Skarulis, THIS JOURNAL, **61**, 2689 (1939).

[6] Mellor, "Treatise on Inorganic Chemistry," Vol. **11**, 1922, p. 436; in particular, Weinland and Krebs, *Z. anorg. Chem.*, **49**, 157 (1906).

[7] Zintl and Rienäcker, *Z. anorg. allgem. Chem.*, **153**, 276 (1926).

TABLE II

$TlAl(SO_4)_2$–$NH_4Al(SO_4)_2$–H_2O AT 25°

No.	Original complex, wt. % $TlAl(SO_4)_2$	Original complex, wt. % $NH_4Al(SO_4)_2$	Liquid solution, wt. % $TlAl(SO_4)_2$	Liquid solution, wt. % $NH_4Al(SO_4)_2$	Solid phase, wt. % $TlAl(SO_4)_2$	Solid phase, wt. % $NH_4Al(SO_4)_2$
1 U	....	0.000	6.986	0.000	66.20	0.000
S			6.991			
2 A	12.00	1.000	6.045	.723	62.53	2.992
B	12.00	1.000	6.082	.780	62.62	2.995
3 A	10.00	2.700	4.558	2.039	55.71	8.42
B	10.00	2.700	4.640	1.968	55.03	8.96
4 A	6.455	4.000	3.387	3.107	45.62	16.31
B	6.455	4.000	3.417	3.063	45.72	16.47
5 A	5.300	5.667	2.387	4.004	36.27	23.24
B	5.300	5.667	2.425	3.964	35.86	24.06
6 A	2.500	5.928	1.536	4.780	24.74	32.72
B	2.500	5.928	1.544	4.780	24.80	32.80
7 A	2.000	9.000	0.689	5.563	14.17	41.34
B	2.000	9.000	.764	5.498	13.45	41.86
8 U	0.000	...	.000	6.16	0.00	52.31
S				6.14		

trate was analyzed for aluminum by precipitation with 8-hydroxyquinoline according to the gravimetric method of Kolthoff and Sandell.[8]

Table I shows the results, which are plotted in Fig. 1. The solubilities listed for the pure salts, thallous sulfate and hydrated aluminum sulfate, are averages from closely agreeing measurements from both under- and super-saturation (these approaches to equilibrium are marked U and S, respectively, in this and subsequent similar tables). That for thallous sulfate, 5.213%, is in good agreement with the figures of Berkeley[9] (5.21% by interpolation), and of Noyes and Stewart[10] (5.22%); the figure for the aluminum salt, 27.86%, is in fair agreement with the determinations of Poggiale[11] (27.6%), Wirth[12] (27.82%), Britton[13] (27.70%) and Hill and Kaplan[2] (27.39%). The solid phase over the greater part of the diagram is shown by algebraic extrapolation[14] to be the hydrated double sulfate, thallium alum, and the small average absolute deviation (= 0.24%) between the extrapolated and the theoretical percentage of thallous sulfate in the solid phase is indicative of the experimental accuracy. The solubility curve of the hydrated aluminum sulfate as solid phase is of course too short to be represented on the diagram. Inspection of the figure shows that at 25° the alum is congruently soluble to an extent of about 7% of anhydrous salt (see also Table II).

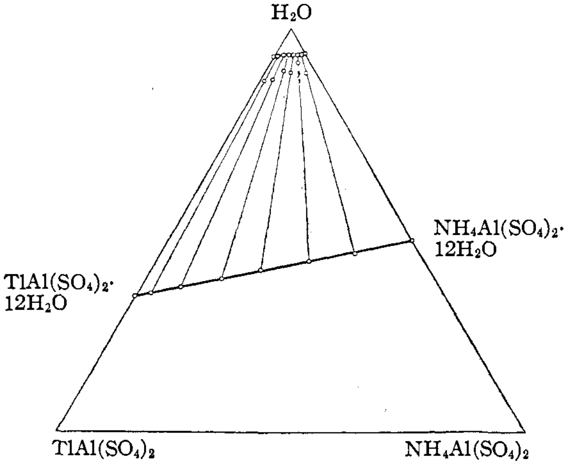

Fig. 2.—The system $TlAl(SO_4)_2$–$NH_4Al(SO_4)_2$–H_2O at 25°.

Thallium Alum, Ammonium Alum, Water at 25°.—Inasmuch as an attempt will be made to relate the distribution of the isomorphous salts between aqueous and crystalline phases, to the molar solubilities, this particular alum pair is of special interest because of the considerable difference in the molecular weights of the pair. Both alums were prepared by mixing solutions of equimolecular quantities of the component salts (analyzed grades) at about 60° and allowing the solution to cool with prolonged stirring. In the case of the ammonium alum this procedure gave a product of composition corresponding to the theoretical value. The thallium alum so prepared, however, as if, apparently, incongruently soluble at higher temperatures, was contaminated with excess thallous sulfate; this difficulty was therefore overcome by returning the crystals to the mother liquor, adding a considerable excess of aluminum sulfate, heating to dissolve the solid, and cooling with stirring for twenty hours. The solubilities of the individual alums were determined from under- and super-saturation

---

[8] Kolthoff and Sandell, THIS JOURNAL, **50**, 1900 (1928).

[9] Berkeley, *Trans. Roy. Soc. London*, **A203**, 189 (1904).

[10] Noyes and Stewart, THIS JOURNAL, **33**, 1658 (1911).

[11] Poggiale, *Ann. chim. phys.*, (3) **8**, 467 (1843).

[12] Wirth, *Z. anorg. Chem.*, **79**, 360 (1913).

[13] Britton, *J. Chem. Soc.*, **121**, 982 (1922).

[14] Hill and Ricci, THIS JOURNAL, **53**, 4306 (1931).

TABLE III

$TlAl(SO_4)_2$–$KAl(SO_4)_2$–H_2O AT 25°

No.	Original complex, wt. %		Liquid solution, wt. %		Solid phase, wt. %	
	$TlAl(SO_4)_2$	$KAl(SO_4)_2$	$TlAl(SO_4)_2$	$KAl(SO_4)_2$	$TlAl(SO_4)_2$	$KAl(SO_4)_2$
1	...	0.000	6.989	0.000		0.00
2 A	6.604	3.000	4.202	2.519	51.43	11.97
B	6.604	3.000	4.200	2.506	51.42	11.89
3 A	6.000	5.956	2.606	4.020	37.28	23.56
4 A	2.000	6.352	1.321	5.280	21.42	36.73
B	2.000	6.352	1.323	5.308	21.45	36.63
5 A	1.000	10.000	0.403	6.17	7.035	48.28
B	1.000	10.000	0.402	6.18	7.042	48.20
6 U	0.000	....	0.000	6.59	0.000	
S				6.58		

and the complexes were made from the two alums and water in duplicate as described above. In Table II the complexes marked A were made with thallium alum and those marked B with ammonium alum as the original solid phase. After two or three weeks in the thermostat both liquid and solid phases were analyzed for thallium (volumetrically as described above) and for ammonium by distilling the ammonium liberated by potassium hydroxide into standard acid and titrating the excess acid with standard base. The solid phases were centrifuged and air-dried before being analyzed. The results of analysis are shown in Table II and plotted in Fig. 2.

For comparison with the solubility here reported for thallium alum at 25°, 6.989%, we note that Fock[4] gives 7.07%, Locke[15] 6.97% and Berkeley,[9] by interpolation, 7.19%. The solubility of ammonium alum, 6.15%, which is an average (from both under- and super-saturation) of both ammonium and aluminum analyses, is in satisfactory agreement with the recent determination of Hill and Kaplan,[2] 6.19%. The fact that the ternary results from the duplicate tubes (A and B) are in agreement is proof that they are results at equilibrium. Figure 2 shows that the two alums form a complete series of solid solutions, and the directions of the tie-lines indicate that the concentration of ammonium alum in the liquids (neglecting water content) is always greater than that in the conjugate solids. The over-all accuracy of the analytical procedure was again checked by extrapolating algebraically the tie-lines joining the compositions of the original complexes and the liquid solutions, to the straight line on the diagram joining the points representing the single alums; the average absolute deviation between the observed and the extrapolated compositions of the solid phases was only 0.19%.

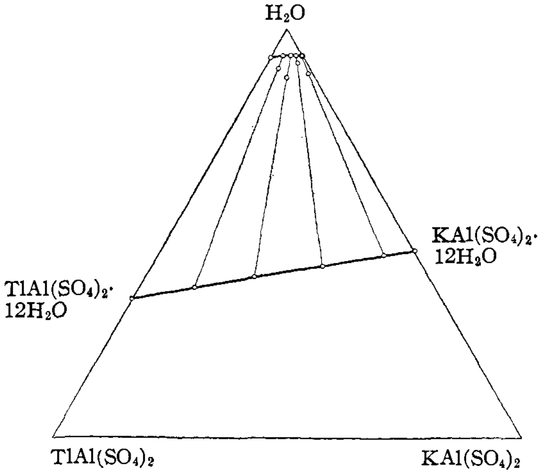

Fig. 3.—The system $TlAl(SO_4)_2$–$KAl(SO_4)_2$–H_2O at 25°.

Thallium Alum, Potassium Alum, Water at 25°.—This system is one already studied by Fock[4] but as his analyses appear to be of doubtful accuracy it was thought desirable to repeat the work. It may be observed that thallium alum and potassium alum have very similar solubilities by weight but quite different solubilities in molar units, a fact of some interest in connection with interpreting their behavior ultimately.

The complexes were made up in duplicate according to the procedure for the preceding system, the A tubes (Table III) having thallium alum and the B tubes potassium alum present as the initial solid phase. The potassium alum used was recrystallized Baker Analyzed material. After four weeks rotation in the thermostat the equilibrium liquids and solids were analyzed for both thallium and aluminum as described above, the solids being first centrifuged and air-dried. Table III gives the resulting data, which are shown graphically in Fig. 3.

The solubility of potassium alum here reported (6.58%) is again in close agreement with the determination of Hill and Kaplan[2] (6.60%). As shown in Fig. 3, the two alums are completely mutually soluble, the proportion of potassium alum being greater in the liquids than in the conjugate solids, concentrations being on the dry basis. When Fock's figures for this isotherm are plotted on such a triangular diagram, the liquid curve shows considerable irregularity.

---

(15) Locke, *Am. Chem. J.*, **26**, 166 (1901).

TABLE IV

$NH_4Cr(SO_4)_2$–$KCr(SO_4)_2$–H_2O AT 25°

No.	Original complex, wt. % $NH_4Cr(SO_4)_2$	Original complex, wt. % $KCr(SO_4)_2$	Liquid solution, wt. % $NH_4Cr(SO_4)_2$	Liquid solution, wt. % $KCr(SO_4)_2$	Solid phase, wt. % $NH_4Cr(SO_4)_2$	Solid phase, wt. % $KCr(SO_4)_2$
1 U	....	0.000	13.65	0.000		0.00
S			13.68			
2 A	12.46	5.015	9.99	4.504	43.18	12.05
B	12.46	5.015	10.28	4.612	43.12	12.08
3 A	10.79	12.01	6.86	9.44	30.21	25.45
B	10.79	12.01	6.85	9.40	30.26	25.26
4 A	8.00	16.08	4.882	12.18	21.88	34.09
B	8.00	16.08	4.852	12.14	21.91	34.15
5 A	3.997	17.46	2.958	14.74	13.50	42.69
B	3.997	17.46	2.986	14.75	13.52	42.76
6 A	1.500	20.49	1.162	17.30	5.226	51.32
7 U	0.000	....	0.000	18.79	0.00	56.71
S				18.79		

The internal agreement in the present data can again be judged by the small average absolute deviation (of only 0.09%) between the extrapolated and the observed compositions of the solid phases.

Ammonium Chrome Alum, Potassium Chrome Alum, Water at 25°.—Hydrated chromic salts in general are known to exist in both violet and green forms, but in the case of the (solid) chrome alums only the violet forms appear to have been prepared. A solution of the violet form becomes green on heating, and there is evidence[16,17] that an equilibrium exists in the liquid between the dissolved violet and green forms. In the determinations of the solubility of a chrome alum an abnormally long time is required for complete equilibrium to be reached, the reason for this undoubtedly being related to the additional equilibria involved.

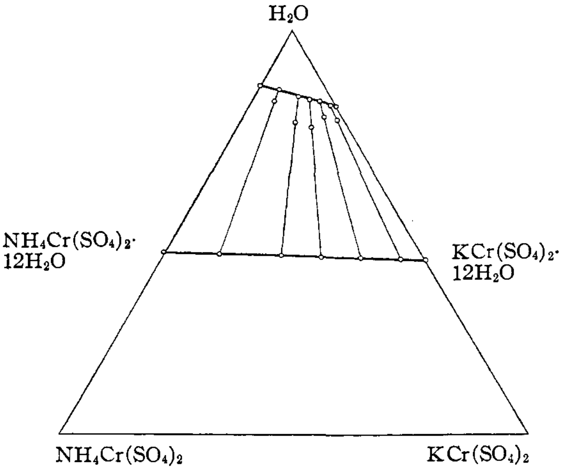

Fig. 4.—The system $NH_4Cr(SO_4)_2$–$KCr(SO_4)_2$–H_2O at 25°.

Baker and Adamson chemicals were used in the present work. After recrystallization from water (maximum temperature 60°) the alums were dried in a desiccator over the corresponding partly dehydrated salts. Analysis of the ammonium chrome alum for both ammonium and chromium content showed agreement with theory. The potassium chrome alum, as a result of efflorescence, changed slightly in composition during the preparation of the complexes; this change was taken into consideration in the calculation of the composition of the original complexes listed in Table IV. The complexes were made up in duplicate as already described, the A tubes with potassium chrome alum and the B tubes with ammonium chrome alum as the original solid. Three months of rotation in the thermostat was necessary for equilibrium to be reached as shown by successive analyses of tubes containing the separate alums and water when their single solubilities were being determined from under- and from super-saturation. At the end of such a period of rotating, both the liquid and the solid phases were analyzed for ammonium and chromium content, the former by the ammonia distillation method and the latter by oxidation to chromate with sodium peroxide followed by reduction with iodide and titration with thiosulfate.[18] The solids were centrifuged and air-dried for a short time before analysis. The results are given in Table IV and shown graphically in Fig. 4.

Our figure for the solubility of ammonium chrome alum (13.66%) is in agreement with the value of 13.2% interpolated from Koppel's data[17] but very far from that of Locke[15] (9.63%), whose measurements were made after only a few hours. Locke's figure for potassium chrome alum (11.01%) is subject to the same error, and is consequently very different from the solubility here reported, of 18.78%. As the diagram shows, the alums of this system are completely miscible in the solid state, and again the proportion of the potassium alum in the liquids is seen always to exceed that in the conjugate solids, provided concentrations are taken on the dry basis. The

---

[16] Montemartini and Vernazza, *L'Ind. Chimica*, **7**, 857 (1932); **8**, 445 (1933); *cf. Brit. Chem. Abstracts*, **A**, 912 (1932); 562 (1933).

[17] Koppel, *Ber.*, **39**, 3738 (1906).

[18] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1922, pp. 158, 161.

TABLE V

$NH_4Fe(SO_4)_2$–$KAl(SO_4)_2$–H_2O AT 25°

	Original complex, wt. %		Liquid solution, wt. %			Solid phase, wt. %			
Point	$NH_4Fe(SO_4)_2$	$KAl(SO_4)_2$	$NH_4Fe(SO_4)_2$	$KAl(SO_4)_2$	$KFe(SO_4)_2$	$NH_4Fe(SO_4)_2$	$KAl(SO_4)_2$	$NH_4Al(SO_4)_2$	Moles of water per mole of total double sulfate in solid
1 U	0.00	...	0.00	6.59	0.00	0.000	54.43	0.00	12.00
S				6.58					
2 A[a]	12.21	8.20	...	...	...	7.033	18.47	26.27	12.82
B[a]	12.21	8.20	...	...	...	6.932	19.41	26.61	12.25
3 A	24.34	4.040	21.24	1.100	3.066	26.81	3.22	21.72	13.07
B	24.34	4.040	21.23	1.260	3.054	26.46	5.33	20.99	12.57
4 A	30.18	4.025	24.51	0.637	3.979	37.92	3.82	11.16	12.79
B	30.18	4.025	24.51	.574	4.111	38.61	4.16	11.32	12.19
5 A	32.09	2.016	27.57	.432	2.107	45.94	1.967	7.085	11.88
B	32.09	2.016	27.55	.515	2.124	45.62	1.880	6.910	12.17
6 A	33.05	0.983	29.16	.336	1.223	49.10	0.919	3.514	12.71
B	33.05	.983	29.23	.348	1.252	49.98	.780	3.965	12.10
7 U	...	.000	31.17	.000	0.00	55.17	.000	0.000	12.00
S			31.23						

[a] Liquid solutions 2A, 2.327% $(NH_4)_2SO_4$, 8.251% $Fe_2(SO_4)_3$, 2.191% $Al_2(SO_4)_3$; 2B, 2.324% $(NH_4)_2SO_4$, 8.281% $Fe_2(SO_4)_3$, 2.167% $Al_2(SO_4)_3$.

average absolute deviation between the analytical and the extrapolated compositions of the solid phases in this system was 0.37%.

Ferric Ammonium Alum, Potassium Alum, Water at 25°.—This pair of alums, not containing a common cation, constitutes with water a quaternary system, but only that portion of the system was examined where the total compositions can be expressed in terms of the two alums and water. The complexes were again made up in duplicate from weighed amounts of potassium alum (recrystallized Baker Analyzed), ferric ammonium alum (recrystallized Baker and Adamson) and water, as in the preceding systems. As in the case of potassium chrome alum mentioned above, the composition of the ferric ammonium alum changed during manipulation as a result of efflorescence, and a correction for the change was applied in calculating the compositions of the complexes, by means of a time extrapolation. After one month of rotation in the thermostat, both liquid and solid phases were analyzed, as follows, for ammonium, iron and total iron and aluminum: for ammonium by the ammonia distillation method, for iron by the Zimmermann–Reinhardt reduction followed by titration with standard ceric sulfate, for combined iron and aluminum by the simultaneous precipitation of both cations by 8-hydroxyquinoline.[8,19] The accuracy of the latter procedure was found to be satisfactory by preliminary tests.

These determinations are sufficient for the determination of the complete composition of the phases, provided it can be assumed that in any phase the number of moles of trivalent sulfates equals the number of moles of univalent sulfates, whereupon the remaining constituents can be calculated. This assumption is justified so long as the system remains quaternary, or so long as no hydrolytic products are formed. Actually a very small amount of a finely-divided insoluble solid was formed in all the tubes. This was probably a basic iron complex, but being present in such small quantity it was not analyzed. The liquids were analyzed without interference by waiting long enough for the settling of all solids, before sampling. The main solid phase itself was also easily obtained free of this hydrolytic precipitate because the latter passed through the finest filter paper, so that the main solid was washed free of it by the supernatant liquid. The main solid phases were sucked dry on filters and analyzed while moist.

The results are presented in Table V, in which the A complexes began with ferric ammonium alum and the B complexes with potassium alum as the only solid. The figure for the solubility of ferric ammonium alum (31.20%), which is the average of both iron and ammonium analyses, is slightly higher than the reports of Locke[15] (30.7%) and of Hill and Kaplan[2] (30.85%).

The analytical results are shown calculated in terms of the three alums ammonium–iron, potassium–aluminum, and potassium–iron; the difference, water, is shown, for the solid phases, in the last column, as moles of water per mole of total double sulfate in the solid. The agreement of these figures with the theoretical number 12 required for alums supports the assumption that the solids are all quaternary solid solutions or mixed alums. The internal consistency of the results was further checked by methods of algebraic extrapolation,[14] in which by assuming the theoretical alum hydration for the solids, any one of the three percentages listed under "the solid phase" could be calculated by extrapolation, for comparison with the observed value. The average error found, testing all three columns, was only 0.37%. In these averages, however

---

(19) Berg, *Z. anal. Chem.*, **76**, 193 (1929).

TABLE VI

$NH_4Fe(SO_4)_2$–$KAl(SO_4)_2$–H_2O AT 25°

Units: moles per 100 grams of mixture or phase (average of duplicates)

Point	Original complex $NH_4Fe(SO_4)_2$	Original complex $KAl(SO_4)_2$	Liquid solution $NH_4Fe(SO_4)_2$	Liquid solution $NH_4Al(SO_4)_2$	Liquid solution $KFe(SO_4)_2$	Liquid solution $KAl(SO_4)_2$	Solid phase $NH_4Fe(SO_4)_2$	Solid phase $NH_4Al(SO_4)_2$	Solid phase $KFe(SO_4)_2$	Solid phase $KAl(SO_4)_2$
1	0	...	0	0	0	0.0255	0	0	0	0.2108
2	0.04590	0.03176	0.03520	0.01274	0.00614	.01274	0.02625	0.1378	0.02625	.04710
			.02246		.01888			.1115		.07335
3	.0914	.01566	.07985		.01066	.00457	.10013	.09006		.01657
			.07526	.00457	.01523		.08356	.10663	.01657	
4	.1136	.01558	.09215		.01409	.00235	.1439	.04741		.01545
			.08980	.00235	.01644		.1284	.06286	.01545	
5	.1206	.00781	.10361		.00737	.00183	.1721	.02951		.00745
			.10178	.00183	.00920		.1646	.03696	.00745	
6	.1243	.00381	.10975		.00431	.00133	.1863	.01577		.00329
			.10843	.00133	.00563		.1830	.01906	.00329	
7	...	0	.1173	0	0	0	.2074	0	0	0

tubes 2A and 2B were not included; these two tubes were found to contain considerably more of the above-mentioned hydrolytic precipitate than any of the other complexes. The very same method of algebraic extrapolation, however, showed that even in this case the main solid phase was evidently quaternary, although the basic solid and consequently also the liquid solution must be of higher order. Extrapolation further indicated that the basic solid contained neither ammonium nor aluminum.

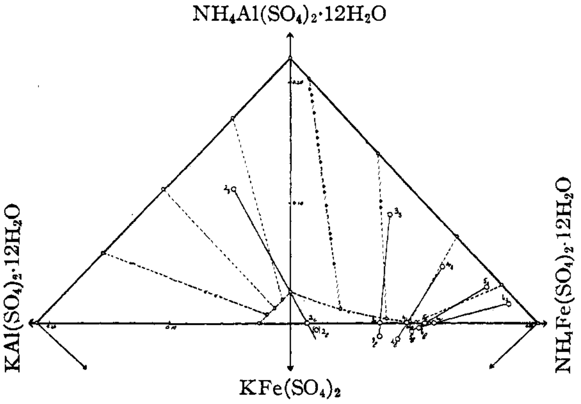

Fig. 5.—Part of the system $KAl(SO_4)_2$–$NH_4Fe(SO_4)_2$–H_2O at 25°. Units: moles of salt per 100 g. of mixture or phase. Subscripts l, c, s denote liquids, complexes and solids, respectively.

The data of Table V were recalculated, using the averages for the duplicate tubes, to moles per 100 g. of mixture, and listed as such in Table VI. Using the graphical method of extrapolation for such reciprocal quaternary systems of Ricci and Loucks[20] the results, in these units, are plotted in Fig. 5, which is a projection on the base of the isothermal tetrahedral pyramid model for the quaternary system. The points are numbered in accordance with the table. It may be pointed out, in elucidation of the figure, that inasmuch as the original complexes were made up from water and the two alums $KAl(SO_4)_2$ and $NH_4Fe(SO_4)_2$, the compositions of the complexes all fall, in this projection, on the horizontal axis connecting these alums. The units of the diagram are moles of the respective salts per 100 g. of mixture (including water), the water being plotted, in the solid model, on a vertical axis perpendicular to the base pictured, at the intersection of the axes joining the reciprocal alums. The ends (not shown) of the four horizontal axes would represent the number of moles of the respective (anhydrous) alums in 100 g. of the pure salt. The dashed curves and tie-lines show the results of Hill and Kaplan on two of the ternary systems making up the main quaternary system. If the complete quaternary system were to be studied, the isothermal model, except for regions of quinary behavior, would probably consist of two surfaces bounded by four edges, the one a curved surface representing liquid and the other also a curved surface representing the saturating solid solutions. The data of Hill and Kaplan, in Fig. 5, therefore give two edges of each surface, and our data some points on these surfaces. Point 2 is in doubt for reasons stated above. Further information concerning the trend in direction of the tie-lines, and general relations between the liquids and the solids in the quaternary system, was obtained by projecting the points and lines of the solid model onto the two diagonal planes of the pyramid passing through

---

(20) Ricci and Loucks, *J. Chem. Education*, **15**, 329 (1938).

TABLE VII

DISTRIBUTION OF ALUMS BETWEEN LIQUID PHASE AND SOLID PHASE

Point	$NH_4Al(SO_4)_2$ with $TlAl(SO_4)_2$ Mole fraction of $NH_4Al(SO_4)_2$ In dissolved salts Y	In solid solution X	$KAl(SO_4)_2$ with $TlAl(SO_4)_2$ Mole fraction of $KAl(SO_4)_2$ In dissolved salts Y	In solid solution X	$NH_4Cr(SO_4)_2$ with $KCr(SO_4)_2$ Mole fraction of $NH_4Cr(SO_4)_2$ In dissolved salts Y	In solid solution X
1	0.000	0.000	0.000	0.000	0.000	0.000
2	.181	.079	.495	.276	.294	.206
3	.438	.219	.717	.509	.560	.437
4	.618	.391	.868	.737	.698	.591
5	.747	.539	.962	.918	.821	.745
6	.847	.703	1.000	1.000	.932	.901
7	.932	.843			1.000	1.000
8	1.000	1.000				

the vertical water axis; these projections however are not shown, for reasons of space-saving. Some of the significant aspects of the distribution of the salts between the liquid and solid phases, however, are shown below, together with similar information on the simpler systems studied.

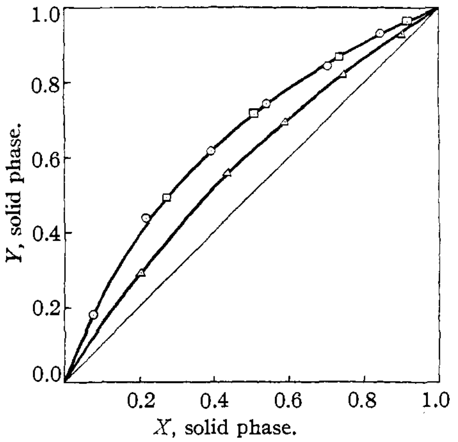

Fig. 6.—Distribution of alums between liquid solution and solid solution at 25°: circles, ○, $TlAl(SO_4)_2$–$NH_4Al(SO_4)_2$; squares, □, $TlAl(SO_4)_2$–$KAl(SO_4)_2$; triangles △, $NH_4Cr(SO_4)_2$–$KCr(SO_4)_2$.

Distribution between Liquid Solution and Solid Solution.—In order to interpret some of the above data in terms of the Roozeboom[21] classification of solid solutions, the concentrations have been recalculated into mole fractions of the two alums, disregarding water, in the two phases. The results, showing for each system the mole fraction of the more soluble alum, are listed in Table VII, and are plotted in Fig. 6, where the Y values represent the mole fraction of the more soluble alum in the liquid phase and X its mole fraction in the solid phase.

All three ternary systems studied apparently belong to Class I of Roozeboom's classification, in which there is complete miscibility in the solid phase and in which one of the components is present in higher proportion in the liquid than in the conjugate solid phase throughout the series of solid solutions. It is conceivable of course that this relation may not hold true at the extreme edges of the diagram, for which there are no data, but in the light of further theoretical work not yet published such a possibility appears unlikely These curves, it may be noted, all follow the equation previously suggested, $y = x^m$, with m a constant for each system. For the present we observe merely that the component present in greater concentration in the liquid than in the solid is that component with the greater aqueous molar solubility; for example, though ammonium and potassium alums both have smaller weight solubilities than thallium alum, their molar solubilities are much greater, a fact to be taken into account in considering the observed distribution.

Similar (partial) calculations are shown in Table VIII, for part of the quaternary system $NH_4Fe(SO_4)_2$–$KAl(SO_4)_2$–H_2O. The table lists the number of moles of $^1/_2K_2SO_4$ and $^1/_2Fe_2(SO_4)_3$ per mole of total double sulfate in both liquid solutions (Y) and solid solutions (X). Although these figures may be interpreted as indicating that the proportion of potassium alum (ferric

TABLE VIII

DISTRIBUTION BETWEEN LIQUID AND SOLID PHASES FOR PART OF THE SYSTEM $NH_4Fe(SO_4)_2$–$KAl(SO_4)_2$–H_2O

Point	Mole fraction of $^1/_2K_2SO_4$ In dissolved salts Y	In solid solution X	Mole fraction of $^1/_2Fe_2(SO_4)_3$ In dissolved salts Y	In solid solution X
1	1.000	1.000	0.000	0.000
2	(.349)	(.347)	(.651)	(.653)
3	.160	.080	.952	.484
4	.151	.075	.978	.696
5	.082	.036	.984	.823
6	.049	.016	.989	.907
7	.000	.000	1.000	1.000

---

[21] Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891); **30**, 385 (1899).

or aluminum) is greater in the liquid than in the solid solutions, and the same for (potassium or ammonium) ferric alum, the results do not of course have the significance of those shown above in Table VII and Fig. 6, since Roozeboom's classification applies only to ternary systems.

Summary

1. The system Tl_2SO_4–$Al_2(SO_4)_3$–H_2O has been studied at 25° and the isotherm found to consist of the three solubility curves of Tl_2SO_4, $TlAl(SO_4)_2 \cdot 12H_2O$, and $Al_2(SO_4)_3 \cdot nH_2O$, respectively (n being probably 17).

2. The 25° isotherms for the ternary systems consisting of water and the three alum pairs thallium alum–ammonium alum, thallium alum–potassium alum and ammonium chrome alum–potassium chrome alum have been studied. In all three a complete series of solid solutions has been found, and their assignment to Roozeboom's Class I demonstrated.

3. That part of the quaternary system ferric ammonium alum–potassium alum–water, where the total compositions can be expressed in terms of $NH_4Fe(SO_4)_2$, $KAl(SO_4)_2$ and H_2O, has been studied at 25°. Where the concentration of $KAl(SO_4)_2$ relative to that of $NH_4Fe(SO_4)_2$ in the total composition is large, the behavior becomes that of a system of more than four components, apparently because of slight hydrolysis; all the quaternary solids, however, are solid solutions of alums.

NEW YORK, N. Y. RECEIVED JANUARY 23, 1940

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

Some Properties of Sodium Palmitate Curd as Studied in the Centrifuge

BY JAMES W. MCBAIN AND T. FOSTER FORD

Soap curd[1] is a felt of hydrated crystalline fibers enmeshing a mother liquor that is slightly alkaline water with almost no soap. The fibers, although exceedingly fine,[2] yield good X-ray patterns as has been shown by Thiessen and others, and they are strikingly visible in the ultramicroscope. Ordinary solutes diffuse and sediment freely through their interstices.[3] The mechanical structure of the felt is sufficiently firm that sodium palmitate curd more concentrated than 0.2 M does not sediment or crush in a centrifugal field of 250,000 times gravity. Incidentally, this is likewise true of household soap, liquid crystalline sulfonic acid solution of 2 M, and of a potassium coconut oil liquid crystalline neat soap.

The densities of sodium palmitate curds at 20° with and without added salt, referred to water at 20° as 0.99820, are given in Table I. Compositions are given in true weight %.

The density of the hydrated curd fibers themselves was found by adding sodium palmitate solution to saturated sodium chloride solution until the curd fibers just began to sediment, instead of having a tendency to float. The result, 1.15, agrees fairly well with that calculable from Table I.

TABLE I

Wt. % NaP	Wt. % NaCl	Wt. % H_2O	Density of curd
1.39	0	98.61	1.0000
2.105	0	97.895	1.0014
2.78	0	97.22	1.0014
2.065	1.92	96.0	1.0136
2.025	3.77	94.2	1.0269
2.725	1.91	95.3	1.0130
2.67	3.74	93.5	1.0194

Observations in the Air-Driven Spinning Top.—For observation of sedimentation in the one-piece rotor the effective arrangement shown in Fig. 1 was devised. By looking obliquely down into the top, as shown by the arrow, it is possible to see directly the separation of water from curd. Calibration was by observation when known weights of water were added to the empty top, the internal radius of which was 0.80 cm., with opening of radius 0.5 cm., height of annular space 0.26 cm., and volume of annular space 0.32 cc. Forty seconds are required for the 20 mm. rotor to attain its full speed of 2650 r. p. s. at 80 lb. (5 atm.) pressure of air.

Separation of curd from water occurred so rapidly, in about one minute, that sedimentation velocity of curd fibers has not yet been accurately

---

[1] Jerome Alexander, "Colloid Chemistry, Theoretical and Applied," Vol. I, Chemical Catalog Co., Inc., New York, N. Y., 1926, p. 138.

[2] J. W. McBain, J. M. McDowell and M. E. Worden, THIS JOURNAL, **61**, 2540 (1939).

[3] J. W. McBain and C. Alvarez-Tostado *ibid.*, **59**, 2489 (1937).