exciting lines and has not been included in Table I.

The effect of electrolytes on the bands of water was noticeable. The band at 700 cm.$^{-1}$ tends to decrease in intensity, that at 1650 cm.$^{-1}$ remains practically constant in intensity, while that at 3433 cm.$^{-1}$ increases. Finally the manganese sulfate solution brought out another band at 7500 cm.$^{-1}$.

Summary

A Raman investigation of the possible existence of certain complexes in aqueous solutions of ammonium sulfate and manganese sulfate has been made with negative results. Several new lines were found for manganese sulfate and ammonium sulfate solutions.

SEATTLE, WASHINGTON RECEIVED DECEMBER 1, 1937

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

Ternary Systems. XXII. Formation of Solid Solutions from Alums

BY ARTHUR E. HILL AND NATHAN KAPLAN[1]

Since the introduction of the idea of isomorphism into chemical thought by Mitscherlich,[2] the clarification of that concept has not proceeded as rapidly as might have been wished. Originally conceived somewhat vaguely perhaps as a condition of simultaneous crystallization of crystallographically similar bodies, isomorphism was recognized much later by van't Hoff[3] as a condition of solid solution, though the allocution "mixed crystals" still remains in general usage to confuse thought. Experimental work has differentiated cases of unlimited mutual solubility from cases of limited mutual solubility, and Roozeboom[4] has discussed the five classes which are commonly met with, based upon the ratio of components in the liquid and in the solid phases; to these Ricci[5] recently has suggested that a sixth class might well be added. Since the time of the application of X-ray methods to the determination of structure of solids, much has been learned with regard to the structure of solid solutions.

With respect to the relations of solid solutions to liquid solutions, although there has been a considerable amount of painstaking work, nevertheless, the total is not impressive as representing a century of effort. Not only is the quantity of this work not very large, but some fractions of it are not suitable for quantitative use because no criteria have been applied as to the existence of a true state of equilibrium in the solid phase. The present paper and others which are to follow are intended to present results in which there may be confidence as to the attainment of equilibrium with the hope that they may contribute reliable data toward the eventual moulding of a theory of solid solutions.

The alums constitute a class in which isomorphism was recognized by Mitscherlich; as far as they have been investigated, it appears that they are in most cases mutually soluble in all proportions. Of the four alums used in this investigation, three have been studied previously as to their formation from their component salts. We have included a study of the formation of the fourth of these, the ammonium aluminum alum, together with the mutual relations of three pairs of alums. Brief statements will be made as to the analytical methods used in each case; the following general statements apply to all the experiments. The work was conducted at 25 ± 0.03°, in small glass-stoppered tubes, containing about 50 g. of material. The original complexes were weighed into the tube, using materials chosen so that their composition could be relied upon to give a fixed point upon the tie-lines to be used in determining composition of solid phases by extrapolation. In order to establish that the solid solutions had reached equilibrium, duplicate complexes were made up for each experiment, but in different order of addition; in one tube the first solid component was dissolved in the water completely and the second solid then added, while in the second tube the order was reversed, thus ensuring that the final solid had been formed from the two different pure components in the two

---

(1) This paper is an abbreviation of the thesis presented by Mr. Kaplan in partial fulfilment of requirements for the Ph.D. degree at New York University, June, 1936.

(2) Mitscherlich, *Berl. Akad. Abhand.*, 426 (1818–1819); *Ann. chim. phys.*, **14**, 72 (1820); **19**, 350 (1821).

(3) Van't Hoff, *Z. physik. Chem.*, **5**, 323 (1891).

(4) Roozeboom, *ibid.*, **8**, 504 (1891).

(5) Ricci, THIS JOURNAL, **57**, 805 (1935).

TABLE I

$(NH_4)_2SO_4$-$Al_2(SO_4)_3$-H_2O AT 25°

No.	Original complex Wt. % $Al_2(SO_4)_3$	Original complex Wt. % $(NH_4)_2SO_4$	Liquid solution Wt. % $Al_2(SO_4)_3$	Liquid solution Wt. % $(NH_4)_2SO_4$	Solid phase
1	0.00	....	0.00	43.32	$(NH_4)_2SO_4$
2	5.026	50.147	.332	42.78	$(NH_4)_2SO_4 + NH_4Al(SO_4)_2 \cdot 12H_2O$
3	6.033	30.047	.463	32.69	$NH_4Al(SO_4)_2 \cdot 12H_2O$
4	7.012	20.077	.726	21.13	$NH_4Al(SO_4)_2 \cdot 12H_2O$
5	9.991	15.022	.845	14.72	$NH_4Al(SO_4)_2 \cdot 12H_2O$
6	9.865	10.039	1.190	8.753	$NH_4Al(SO_4)_2 \cdot 12H_2O$
7	9.622	4.028	3.875	2.014	$NH_4Al(SO_4)_2 \cdot 12H_2O$
8	16.987	6.004	4.630	1.439	$NH_4Al(SO_4)_2 \cdot 12H_2O$
9	12.020	3.000	7.497	0.973	$NH_4Al(SO_4)_2 \cdot 12H_2O$
10	19.616	4.973	14.45	.550	$NH_4Al(SO_4)_2 \cdot 12H_2O$
11	20.053	4.012	14.81	.352	$NH_4Al(SO_4)_2 \cdot 12H_2O$
12	24.205	3.016	21.18	.125	$NH_4Al(SO_4)_2 \cdot 12H_2O$
13	30.303	2.014	27.29	.02	$NH_4Al(SO_4)_2 \cdot 12H_2O + Al_2(SO_4)_3 \cdot 18H_2O$
14	....	0.00	27.39	.00	$Al_2(SO_4)_3 \cdot 18H_2O$

cases. When analysis of the two solutions showed the same composition, or analysis of the centrifuged residues agreed, there could be certainty that equilibrium had been reached, or at least the small displacement from equilibrium became known. No confidence is felt in the rather common practice of assuming that equilibrium is quickly reached if the amount of solid phase is small, inasmuch as evidence given later shows that the change occurs at least in considerable extent by diffusion in the solid phase, and is therefore dependent for its rate upon the size of the crystals rather than upon their amount.

The Ammonium Aluminum Alum.—The materials used were analyzed grades of ammonium sulfate and aluminum sulfate, which were purified further by recrystallization. The ammonium sulfate was dried at 100°; to obtain an aluminum sulfate of constant composition, the recrystallized $Al_2(SO_4)_3 \cdot 18H_2O$ was allowed to come to constant weight in desiccators over partially dehydrated salt of the same origin. These salts with water were used in weighed amounts in making up the complexes. The systems were found to have reached equilibrium in all cases in less than three or four days, after which pipetted samples were analyzed for ammonia by treatment with alkali and distillation into standard acid, and for aluminum by precipitation with *o*-hydroxyquinoline (oxine), following the directions of Kolthoff and Sandell.[6] The results are shown in Table and in Fig. 1.

The tie-lines intersect at approximately the composition of the alum, $NH_4Al(SO_4)_2 \cdot 12H_2O$, over a very wide range of compositions. Algebraic extrapolations[7] of the tie-lines leave no doubt as to the solid phase, but are not as accurate as have been found in other instances, probably owing to small errors in the oxine method or possibly to small variations in composition of the aluminum sulfate octadecahydrate; the average deviation of the tie-lines extrapolated to the water content of the alum is +1.31%. The solubility curves for the two simple salts are too short to be seen in Fig. 1, the one isothermally invariant solution containing only 0.332% of aluminum sulfate and the other a mere trace of ammonium sulfate, estimated as 0.02%. The alum is of course congruently soluble, but the value for its solubility is widely different from the only figures previously existing. Working with a recrystallized sample of the alum, and approaching equilibrium from undersaturation and supersaturation, we obtained a value 6.19 ± 0.01%. This is slightly different from the curve of Fig. 1, but is widely divergent from the value of 8.42% obtained by Locke[8] and the early value of 8.50% obtained by Poggiale,[9] taking into consideration that Poggiale's values for the potassium and ammonium alum were inverted in printing, as shown by Berkeley.[10]

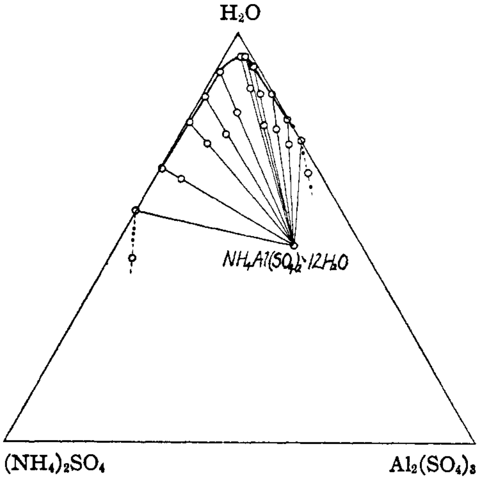

Fig. 1.—The system $(NH_4)_2SO_4$-$Al_2(SO_4)_3$-H_2O at 25°.

Ammonium Aluminum Alum, Potassium Aluminum Alum and their Solid Solutions.—This pair of alums is among the pairs studied by Krickmeyer,[11] who showed that

---

(6) Kolthoff and Sandell, THIS JOURNAL, **50**, 1900 (1928).

(7) Hill and Ricci, *ibid.*, **53**, 4305 (1931).

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

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

(10) Berkeley, *Phil. Trans.*, **203A**, 214 (1904).

(11) Krickmeyer, *Z. physik. Chem.*, **21**, 53 (1896).

a continuous series of solid solutions is found; the proof was found to lie in the existence of a series of crystals varying in density continuously from that of the one alum to that of the other. Krickmeyer made no analysis of conjugate liquid and solid solutions. For our work, analyzed alums were recrystallized, washed successively with water, alcohol and ether and allowed to dry in the air before storage; it was demonstrated that the alums are neither deliquescent nor efflorescent under usual laboratory conditions. Analyses, by the methods given below, were in good agreement with the calculated composition. As outlined earlier in this paper, duplicate complexes were weighed out in such fashion that the final equilibrium solid solution is formed in one case from the ammonium alum and in the duplicate case from the potash alum. The tubes were rotated from seven to fourteen days; in all cases equilibrium had been reached in the solid phase, as will appear in the table. The liquid solutions and the solid phases were analyzed, the latter after being centrifuged and washed; determination of ammonia and of total aluminum gave data for calculating the composition in terms of the two alums with errors which appear to be small despite the indirect method. The results follow in Table II and are shown in Fig. 2. In experiments 2, 3 and 4, the upper line represents experiment with potash alum as the original solid phase, the lower line that with ammonium alum as original solid.

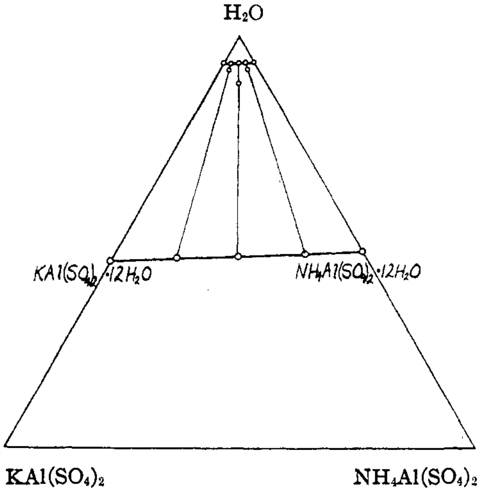

Fig. 2.—The system $KAl(SO_4)_2$–$NH_4Al(SO_4)_2$–H_2O at 25°.

In line 3, although the two original complexes failed somewhat of being exact duplicates, the agreement in the liquid phases and in the solid phases is as good as in the other instances. It will be observed in Fig. 2 that the tie-lines connecting the conjugate solid and liquid solutions pass quite exactly through the water axis; the significance of this relation will be discussed toward the end of this paper.

TABLE II

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

	Orig. complex Wt. %		Liquid solution Wt. %		Solid phase Wt. %	
No.	KAl-$(SO_4)_2$	NH_4Al-$(SO_4)_2$	KAl-$(SO_4)_2$	NH_4Al-$(SO_4)_2$	KAl-$(SO_4)_2$	NH_4Al-$(SO_4)_2$
1	0.000	...	0.000	6.19	0.000	52.32
2	2.003	5.945	1.755	4.589	12.38	40.31
	2.005	5.944	1.654	4.675	12.26	40.71
		Average	1.706	4.632	12.32	40.51
3	5.799	5.505	3.282	3.142	27.11	26.50
	5.601	5.599	3.258	3.146	27.30	26.13
		Average	3.270	3.144	27.20	26.32
4	6.035	2.000	4.855	1.633	40.96	12.93
	6.036	2.001	4.898	1.585	39.34	14.55
		Average	4.876	1.609	40.15	13.74
5	...	0.000	6.60	...	54.47	...

The mechanism by which a solid phase changes its composition until it attains equilibrium with the liquid phase is a matter of interest. Two processes at once suggest themselves. The one process involves the repeated dissolution and reprecipitation of solid, until the final precipitation attains the equilibrium composition; the other would consist of a diffusion in the solid phase, whereby the ion in excess over equilibrium composition would pass outward into the liquid, while the other ion migrates inward to replace it. A simple experiment to test the occurrence of the first process has not suggested itself, but a test of the diffusion process was carried out successfully. A single large crystal of potassium alum was grown by slow evaporation of a saturated solution; this was dried, sketched as to form and weighed (0.3037 g.). It was several mm. in diameter, and had comparatively few and large facets. This was now suspended in a saturated solution of ammonium alum at 25° and slowly rotated, at the end of a glass rod passed through a mercury seal, for three weeks. The crystal now had the same apparent shape as before, its weight was not substantially changed (0.3048 g.) and no small pieces had fallen into the liquid: to the eye, the only change was that the crystal had become milky or frosted in appearance, whereas originally it was almost wholly transparent. Analysis of both liquid and solid phases showed that the solid had lost potassium and gained ammonium while the liquid had undergone the reverse change.

	Wt. % $KAl(SO_4)_2$	Wt. % $NH_4Al(SO_4)_2$
Liquid solution	0.495	5.714
Solid solution	30.20	23.62

The solid had not yet reached equilibrium, as was known from the general diagram of the system (Fig. 2); but it is significant that in a crystal of this magnitude nearly half of the potassium had been replaced by ammonium in as short a time as three weeks, and that the actual penetration of the ammonium ion was to a distance measurable in millimeters. It is of course impossible to draw any conclusion as to how much of the change, during the usual rotation of a mass of crystals, occurs in the solid phase and how much in the liquid phase, but in this system it is clear that a considerable amount of diffusion in the solid phase occurs. That ordinary recrytallization also plays a part is indicated by our observation that the crystals increased in size during the rotation from an average of 60 μ × 80 μ to an average of 120 μ × 200 μ.

Ammonium Aluminum Alum and Sodium Aluminum Alum.—Contrary to early expectations founded upon the

TABLE III

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

No.	Original complex Wt. %		Liquid solution Wt. %		Wet residue Wt. %		Solid phase
	$NaAl(SO_4)_2$	$NH_4Al(SO_4)_2$	$NaAl(SO_4)_2$	$NH_4Al(SO_4)_2$	$NaAl(SO_4)_2$	$NH_4Al(SO_4)_2$	
1	0.000	....	0.000	6.19	...	...	$NH_4Al(SO_4)_2 \cdot 12H_2O$
2	5.012	14.980	6.823	3.459	2.010	37.09	$NH_4Al(SO_4)_2 \cdot 12H_2O$
3	9.011	12.011	11.69	2.339	4.911	29.80	$NH_4Al(SO_4)_2 \cdot 12H_2O$
4	12.513	12.513	16.47	1.600	2.35	44.38	$NH_4Al(SO_4)_2 \cdot 12H_2O$
5	20.084	9.967	25.42	0.499	7.019	37.11	$NH_4Al(SO_4)_2 \cdot 12H_2O$
6	....	5.39	30.54	.099	...	...	$NH_4Al(SO_4)_2 \cdot 12H_2O + NaAl(SO_4)_2 \cdot 12H_2O$
7	....	0.000	30.65	.00	...	...	$NaAl(SO_4)_2 \cdot 12H_2O$

law of isomorphism, sodium alum has never been shown, by any convincing experiments, to form solid solutions with other alums; Krickmeyer[11] found no solid solution of the sodium alum with either the potassium alum or the ammonium alum. However, as no complete isotherm of the system containing the sodium and ammonium alums has been made previously, we have included that system in our study. Sodium alum was prepared by the method of Dobbins and Byrd,[12] but, as has been previously noted, the salt is so highly efflorescent that it is not easy to prepare specimens of constant composition; our complexes accordingly were made up of ammonium alum and of such quantities of anhydrous sodium sulfate and aluminum sulfate octadecahydrate as corresponded to the composition of sodium alum. As appears in Fig. 3, based upon Table III, the extrapolations through the composition of the complex were not good, for which reason wet residues were analyzed and used in drawing the tie-lines. It developed, as expected, that no solid solution or double salt is formed and that the more insoluble ammonium alum dominates the diagram. Three or four days of rotation in the thermostat gave equilibrium results; determination of ammonia and of total aluminum gave data for the total composition. It appears conclusively that, if formation of solid solution be the criterion of isomorphism, then sodium alum is not isomorphous with ammonium alum at 25°.

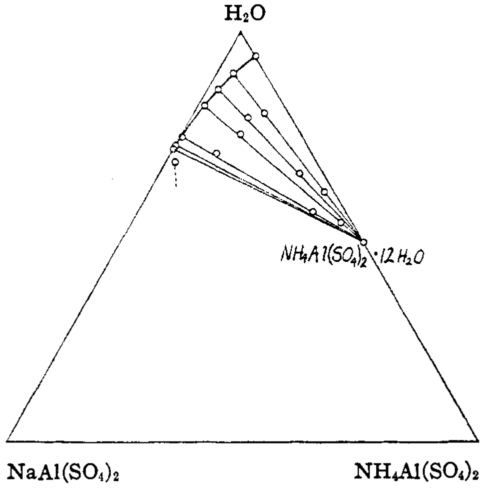

Fig. 3.—The system $NaAl(SO_4)_2$–$NH_4Al(SO_4)_2$–H_2O at 25°.

Ammonium Aluminum Alum, Ammonium Ferric Alum and Water.—In these two alums, the variation is in the trivalent metal; there is also a wide difference in the aqueous solubility of the two. The ferric alum used was purified by crystallization and brought to constant composition in desiccators over partially dehydrated alum. The solutions appeared to come to equilibrium in four or five days when the concentration of aluminum alum was high in both liquid and solid phases, but required several weeks with grinding *in situ* where the aluminum alum concentrations were low (on the left side of Fig. 4). The aqueous solutions were analyzed for total ammonia as in the other cases and for iron by titration with permanganate. The results are given in Fig. 4 and Table IV;

TABLE IV

$(NH_4)Fe(SO_4)_2$–$NH_4Al(SO_4)_2$–H_2O AT 25°

No.	Original complex Wt. %		Liquid solution Wt. %		Solid phase Wt. %	
	$NH_4Fe(SO_4)_2$	$NH_4Al(SO_4)_2$	$NH_4Fe(SO_4)_2$	$NH_4Al(SO_4)_2$	$NH_4Fe(SO_4)_2$	$NH_4Al(SO_4)_2$
1	0.00	...	0.00	6.19	0.00	52.32
2	5.064	12.96	6.12	4.15	.40	52.00
3	10.007	10.005	11.00	2.98		
	9.998	10.003	11.12	2.76	4.28	48.22
4	15.040	10.032	16.03	1.93		
	15.042	10.034	16.37	1.92	10.38	42.62
5	17.997	7.006	18.82	1.59		
	17.989	7.005	18.94	...	12.50	40.50
6	21.223	6.499	21.49	1.04		
	21.200	6.499	21.54	1.08	19.66	33.74
7	23.600	4.55	23.13	0.556		
	23.605	4.55	23.31	.620	25.85	27.85
8	25.056	3.015	24.74	.301		
	25.051	3.015	24.97	...	26.84	26.96
9	27.033	5.023	26.17	.230		
	27.040	5.008	26.31	.295	30.18	23.72
10	28.083	4.014	26.47	...		
	28.055	4.015	26.79	.172	34.08	19.92
11	29.894	5.036	26.90	.283		
	29.926	5.040	27.06	.219	37.11	17.19
12	30.024	3.006	28.02	...		
	30.005	3.003	28.29	...	38.50	16.00
13	29.990	1.500	28.50	...		
	30.033	1.502	28.55	...	41.88	12.72
14	33.015	2.002	28.17	...		
	33.031	2.001	28.49	...	47.10	7.70
15	......	0.00	30.85	.00	55.16	0.00

[12] Dobbins, *et. al.*, *J. Phys. Chem.*, **35**, 3673 (1931); **35**, 3086 (1931); **39**, 637 (1935).

the duplicate results represent attainment of equilibrium from the two directions. The composition of the solid phases is calculated by extrapolation of tie-lines through the average values for the complex and the liquid solution.

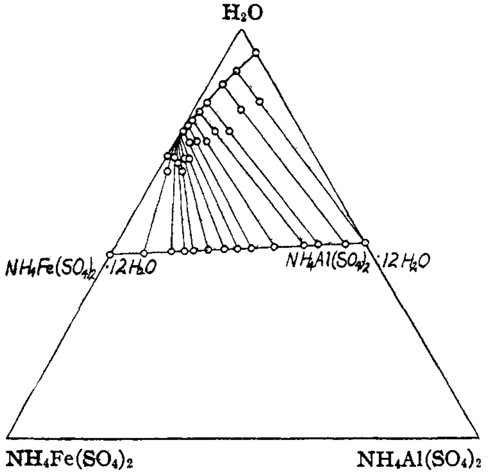

Fig. 4.—The system $NH_4Fe(SO_4)_2$-$NH_4Al(SO_4)_2$-H_2O at 25°.

Classification of the Solid Solutions.—The results of Tables II and IV have been plotted to determine which of Roozeboom's classes are represented. In the case of the ammonium–potassium pair, it was noted that the tie-lines (Fig. 2) pass through the water apex, which means that the ratio of the two alums is the same in the aqueous phase as in the solid phase; when plotted (Fig. 5) with respect to these two ratios, the points fall nearly upon the true diagonal, this giving what may be regarded as a special or ideal example of Roozeboom's class 1. It does not appear that other examples of this type have been noted; the case may be described as one in which, whatever are the departures of the two phases from the properties of ideal solutions, the deviations are quantitatively similar. Whatever also may be the underlying determinants in the properties of the solid solutions, it can hardly be a coincidence that the case in which this simple distribution ratio is found is the one in which the aqueous solubilities are practically identical. The second pair, in which the variant is the trivalent metal (Al–Fe), is one in which the iron alum predominates in the liquid phase through all concentrations, and gives the usual type of diagram of Roozeboom's class 1. The iron alum has much the greater aqueous solubility.

Other pairs of alums also are being studied with respect to their mutual solubility.

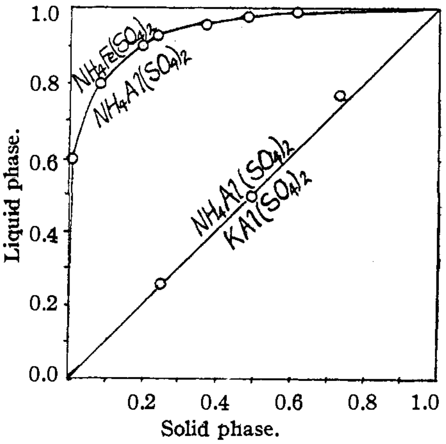

Fig. 5.—Distribution of alums between liquid solution and solid solution at 25°.

Summary

The system $(NH_4)_2SO_4$–$Al_2(SO_4)_3$–H_2O has been studied at 25°, and the concentration range of stability for the alum determined. The system consisting of the ammonium alum and the potassium alum was studied at 25° and found to give a continuous series of solid solutions, in which the distribution ratio of the two salts between the liquid phase and the solid phase is a constant; this case does not appear to have been noted before. The sodium alum and the ammonium alum have been found to form no solid solutions at this temperature. The ammonium–aluminum alum and the ammonium–ferric alum form a continuous series of solid solutions, with the ferric alum present in the aqueous phase in larger ratio throughout. It also has been shown that diffusion in the solid phase is rapid enough in the alums to play a measurable part in the attainment of equilibrium.

NEW YORK, N. Y. RECEIVED NOVEMBER 24, 1937