platinized electrodes. The values for the two buffers at 12° are based on hydrogen electrode measurements, but with the type of apparatus illustrated by Fig. 1. At 38° sufficiently accurate measurements on the phthalate buffer cannot be made with the hydrogen electrode so that the comparison of the buffers was made with the precision glass electrode apparatus described elsewhere.[13] In addition many measurements were made with glass electrodes at 25° confirming the values given in Table VII.

TABLE VII

THE *p*H VALUES OF SOME BUFFERS AT DIFFERENT TEMPERATURES

Buffer	12°	25°	38°
CH_3COOH (0.01 *N*) CH_3COONa (0.01 *N*)	4.710 ±0.005	4.700 ±0.005	4.710 ±0.005
CH_3COOH (0.1 *N*) CH_3COONa (0.1 *N*)	4.650 ± .005	4.640 ± .005	4.635 ± .005
Potassium acid phthalate (0.05 *M*)	4.000 ± .005	4.000 ± .005	4.015 ± .005

Summary

Measurement of the potentials, E, of cells of the type (Pt), H_2; buffer solution: KCl (satd.): KCl (0.1 *N*), HgCl; Hg were made at 12, 25 and 38°. The results were interpreted with the purpose of obtaining values of E_0 in the equation $pH = (E - E_0)/(2.3026RT/F)$ which will yield values of *p*H which are as useful as appears to be possible in the determination of ionization and other equilibrium constants. The *p*H values of commonly used acetate and phthalate buffers have been redetermined at the temperatures given and expressed on the basis just described.

NEW YORK, N. Y. RECEIVED JANUARY 6, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Ternary Systems. XXIII. Solid Solution among the Picromerite Double Salts at 25°. The Zinc, Copper and Nickel Ammonium Sulfates

BY ARTHUR E. HILL AND WILLIAM J. TAYLOR, JR.[1]

The picromerite series of double salts, so named from the naturally occurring mineral picromerite,[2] $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ (also known as schönite), includes a large number of compounds formed from sulfates of the divalent metals Mg, Zn, Cu, Ni, Co, Fe (ferrous), Mn or Cd (in general, the vitriol formers) with the alkali metals K, Rb, Cs, NH_4 and Tl. These crystallize from water as hexahydrates, in the monoclinic system, and show close resemblances in many properties; the existence of solid solutions of several pairs of these salts, at temperatures of 12–13°, was demonstrated by Fock,[3] and they have in general been regarded as an isomorphous series. This paper reports a study of three pairs of salts of this series, under conditions of crystallization from aqueous solution so chosen as to ensure attainment of equilibrium. The method used already has been reported on for several of the alums;[4] it consists simply in preparing duplicate samples for each ratio of salts to be studied, with a difference in order of addition. In one sample, one of the two salts is dissolved completely in the water and the second then added in solid form; in the second the order of addition is reversed, with the result that the equilibrium condition in the solid solution will be approached from the two compositions of the two pure salts. Analysis of the liquid solutions gives identical results when the two samples have reached equilibrium, which may be checked by analysis of the solid phases or by the common methods of determining composition indirectly in three-component systems by extrapolation. By following this simple procedure we are relieved from any uncertainty as to attainment of equilibrium—an uncertainty which has been attached to the majority of investigations of this class and because of which the greater part of the data available are not suitable for quantitative use.

The double salts studied are three in number, $(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$, $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$ and $(NH_4)_2SO_4 \cdot CuSO_4 \cdot 6H_2O$, giving three pairs of isomorphous compounds. We have also repeated work on the formation of two of these compounds from their components.

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(1) The material of this paper is an abbreviation of the thesis presented by Mr. Taylor in partial fulfilment of the requirements for the degree of Ph.D. at New York University, June, 1937.

(2) Winchell, "Microscopic Characters of Artificial Minerals," John Wiley and Sons, Inc., New York, N. Y., 1931, p. 240; Dana, "Textbook of Mineralogy," John Wiley and Sons, Inc., 1932, p. 763.

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

(4) Hill and Kaplan, THIS JOURNAL, **60**, 550 (1938).

Zinc Ammonium Sulfate Hexahydrate at 25°.—The formation of the double salt was studied by making up complexes of the constituent salts and water in weighed amounts and rotating the mixtures in glass-stoppered tubes in a water-thermostat at 25 ± 0.03° until equilibrium had been reached. Recrystallized ammonium sulfate served as the one component; for the zinc salt, it was found most convenient to use the monohydrate, prepared by evaporating zinc sulfate solution to dryness in an oven at 100° and drying the solid again for a short time after powdering; the analysis corresponded quite exactly with that required by the formula, since the monohydrate loses water only at an extremely slow rate at 100°. Hexahydrate of constant composition was made only in smaller quantity and with much more difficulty, by allowing crystals obtained between 70 and 35° to come to constant weight in desiccators over the monohydrate as drying agent. In making up the complexes from the monohydrate it was necessary to work in such fashion as to avoid caking of the salt upon addition of the water; to this end, after addition of the salt and water, the system was heated above the transition point of about 70° and then cooled slowly, with shaking, to room temperature, which gave small separate crystals of the heptahydrate. Experience showed that about twenty-four hours of rotation was sufficient for attainment of equilibrium, though longer time was given in all cases. For analysis, a filtered sample was distilled with magnesium oxide and the ammonia caught in standard hydrochloric acid which was titrated back with potassium hydroxide. In a separate sample the zinc was determined by the method given by Kolthoff and Furman,[5] which involves the titration of the zinc in acid solution with ferrocyanide solution, using diphenylbenzidine as internal indicator. The 25° isotherm is given in Table I, and indicated in Fig. 1.

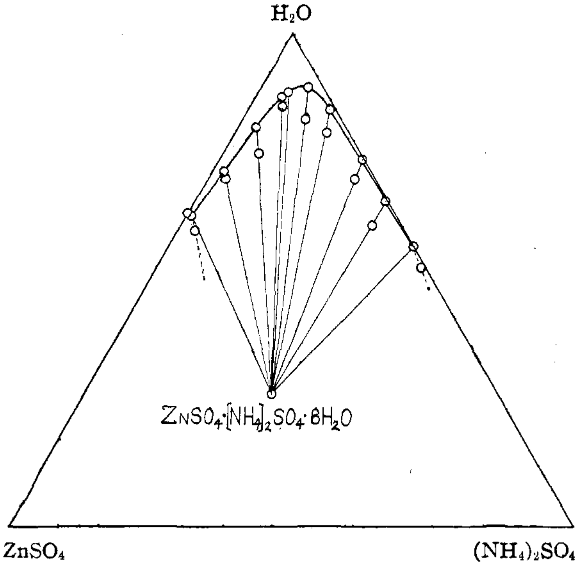

Fig. 1.—The system $ZnSO_4$–$(NH_4)_2SO_4$–H_2O at 25°.

TABLE I

SYSTEM $ZnSO_4$–$(NH_4)_2SO_4$–H_2O at 25°

	Original complex Wt., % $ZnSO_4$	Original complex Wt., % $(NH_4)_2SO_4$	Saturated solution Wt., % $ZnSO_4$	Saturated solution Wt., % $(NH_4)_2SO_4$	Solid phase
1	0.00	...	0.00	43.42	$(NH_4)_2SO_4$
2	1.00	46.83	.09	43.40	$(NH_4)_2SO_4$ + $(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
3	5.08	33.99	.23	34.02	$(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
4	3.98	26.02	.47	25.24	$(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
5	4.14	16.15	1.23	14.65	$(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
6	6.66	11.01	2.96	8.42	$(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
7	...	...	6.73	5.47	$(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
8	...	...	6.73	5.46	$(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
9	9.62	5.86	8.53	4.93	$(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
10	18.41	6.37	16.07	3.29	$(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
11	26.69	3.23	26.21	2.02	$(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
12	37.30	4.62	36.22	0.98	$(NH_4)_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$ + $ZnSO_4 \cdot 7H_2O$
13	...	0.00	36.72	0.00	$ZnSO_4 \cdot 7H_2O$

Lines 7 and 8 were obtained using the pure double salt as solid phase; calculation from the zinc sulfate found gives a solubility of 12.24%, which is slightly lower than the value found by Locke[6] (12.34%), and distinctly lower than that found by Tobler[7] (12.88% by interpolation), and by Caven and Gardner[8] (12.91% by interpolation). The stable form of zinc sulfate at this temperature is the rhombic heptahydrate as shown by Bury;[9] our solubility figure of 36.72% is very slightly higher than was found by Cohen[10] (36.67%), by Callender and Barnes[11] (36.69%) and by Caven and Gardner[8] (36.57%). Caven and Gardner's[8] isotherm at 25° and our own are in fair agreement, the difference being that the ammonium sulfate content of our saturated solutions is consistently lower by a few tenths of one per cent. The algebraic extrapolation of the tie-lines in Fig. 1 to the water content of the double salt gives the assumed 1:1 ratio of the two salts within an average deviation of 0.74%;

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(5) Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, Inc., New York, 1929, p. 254.

(6) Locke, *Am. Chem. J.*, **27**, 455 (1902).

(7) Tobler, *Ann.*, **95**, 193 (1855).

(8) Caven and Gardner, *J. Chem. Soc.*, 943 (1933).

(9) Bury, *J. Chem. Soc.*, **125**, 2538 (1924).

(10) Cohen, *Z. physik. Chem.*, **34**, 179 (1900).

(11) Callender and Barnes, *Proc. Roy. Soc.* (London), **62**, 149 (1897).

as analytical errors are multiplied largely in this calculation, it follows that they must be of a small order of magnitude.

Nickel Ammonium Sulfate Hexahydrate at 25°.—In making up the complexes for this system, a saturated solution of recrystallized nickel sulfate was used, after analysis, because of the difficulty in preparing a solid salt of constant composition. Nickel was determined in the equilibrium mixtures by precipitation with dimethylglyoxime, and dried to constant weight at 105° as outlined in Treadwell and Hall.[12] The results are given in Table II and in Fig. 2.

TABLE II

SYSTEM $NiSO_4$–$(NH_4)_2SO_4$–H_2O at 25°

	Original complex		Saturated solution		
	Wt., % $NiSO_4$	Wt., % $(NH_4)_2SO_4$	Wt., % $NiSO_4$	Wt., % $(NH_4)_2SO_4$	Solid phase
1	0.00	...	0.00	43.42	$(NH_4)_2SO_4$
2	2.51	46.00	.023	43.36	$(NH_4)_2SO_4$ + $(NH_4)_2SO_4{\cdot}NiSO_4.6H_2O$
3	5.03	34.98	.048	35.20	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
4	5.06	29.94	.079	29.44	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
5	4.97	25.00	.125	23.91	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
6	5.13	19.92	.209	17.87	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
7	4.95	15.04	.352	12.57	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
8	...	...	3.82	3.27	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
9	14.89	5.03	12.32	1.94	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
10	19.86	4.04	18.23	1.49	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
11	24.16	4.04	22.75	1.23	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
12	27.64	4.48	26.20	1.01	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
13	28.08	2.96	27.25	0.95	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$
14	32.13	5.17	28.92	0.83	$(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$ + $NiSO_4{\cdot}7H_2O$
15	...	0.00	28.97	0.00	$NiSO_4{\cdot}7H_2O$

This system was studied previously by Caven and Gardner,[8] whose results are not in good agreement with ours. Their figure of 6.16% for the double salt is much below ours of 7.09% given in line 8 of Table II as arrived at both from supersaturation and from undersaturation; other figures close to this are Locke's[6] (7.04%), Benrath and Thiemann's[13] (7.06 by interpolation), or the early figure of Tobler[7] (7.2%). Our figure for nickel sulfate heptahydrate, 28.97%, is in accord with the findings of Benrath and Thiemann[13] (28.98% by interpolation) and of Tobler[7] (29.85%), but higher than found by Steele and Johnson[14] (28.4% by interpolation), and very much higher than Caven and Gardner's[8] (27.82% by interpolation). The whole isotherm of Caven and Gardner seems to us to be too high in ammonium salt and too low in nickel salt. Our extrapolations of tie-lines for this isotherm fall upon the calculated composition of the double salt with an average deviation of only 0.34%. Benrath and Thiemann[13] give the isothermally invariant points for this system.

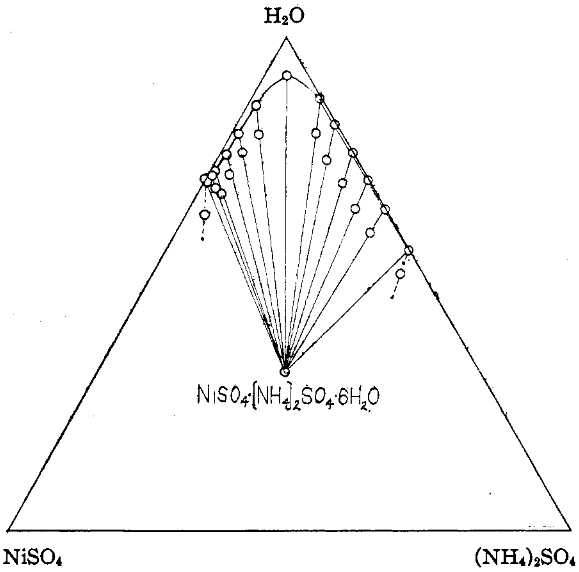

Fig. 2.—The system $NiSO_4$–$(NH_4)_2SO_4$–H_2O at 25°.

The isotherm for the copper ammonium salt, which has been investigated at 25° by Caven and Mitchell,[15] we did not repeat.

Zinc Ammonium Sulfate and Copper Ammonium Sulfate.—The two double salts used were prepared by mixing hot concentrated solutions of the simple salts, the precipitated solid then being recrystallized from hot water. It was found that if either double salt was filtered off immediately after recrystallization, dried and analyzed, a water content was found considerably in excess of that required by the formula, pointing to rather excessive occlusion of mother liquor as the probable cause of the variation. This was obviated by allowing the solutions to cool slowly with continuous mechanical stirring, which was continued for twenty-four to forty-eight hours; material thus obtained, after washing and air-drying, was found to have the calculated composition within a few hundredths of one per cent. The crystals were ground to pass a forty-mesh sieve before being weighed out for the solubility experiments, which were carried out in duplicate as described earlier in this paper so as to approach equilibrium from two directions.

In order to determine whether diffusion occurred within the solid phase in this system, as

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[12] Treadwell and Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1930, p. 134.

[13] Benrath and Thiemann, *Z. anorg. allgem. Chem.*, **208**, 177 (1932).

[14] Steele and Johnson, *J. Chem. Soc.*, **85**, 113 (1904).

[15] Caven and Mitchell, *ibid.*, **109**, 325 (1924).

has been shown to be the case with the solid solution of potassium and ammonium alums,[4] a large well-formed crystal of the zinc double salt was suspended in a solution of the copper salt and rotated for several weeks. The experiment failed somewhat of the clear-cut results obtained with the alum, because of small overgrowth of the crystal which could not be avoided; however, upon removing the crystal and breaking it up, it could be seen that the blue color of the copper salt had penetrated some distance toward the center. The outer parts of the crystal showed upon analysis a content of 8.9% of copper salt, the inner part 4.9%, and the liquid solution, originally zinc free, contained 0.13% zinc salt. It is therefore clear that extensive diffusion in the solid phase occurs in this series of salts as well as in the alums, though at a slower rate.

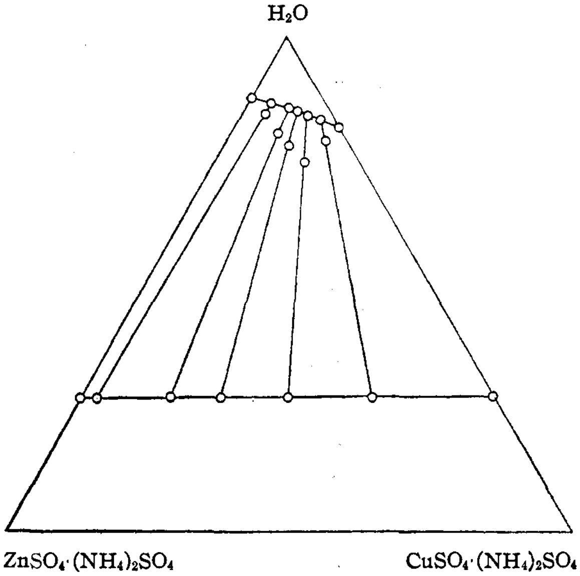

Fig. 3.—The system $CuSO_4 \cdot (NH_4)_2SO_4$–$ZnSO_4 \cdot (NH_4)_2SO_4$–$H_2O$ at 25°.

Experiment showed that while equilibrium in the solid phase was reached occasionally after three weeks of rotation, in the majority of cases the rate of approach showed a tendency to slow down greatly after a week's time, so that equilibrium was still unattained after three months. This slowing appeared to be due to an increase in size of the crystals, giving presumably a surface layer of material still considerably removed from the final composition and of course covering up material still further removed from the end condition, so that as the crystals grew larger the rate of change would become less and less. It was found possible however to remedy this condition by opening the tubes after a week's time and grinding the solid within the tube with a rounded glass rod. This brought about no error except that due to the removal of a few drops of liquid adhering to the rod, and they of course of a composition approaching equilibrium. It was found that in no case were more than two grindings necessary, with intervals of one week between.

The solutions were analyzed by precipitating the copper electrolytically from sulfuric acid solution; the filtrates were evaporated to small volume and titrated for zinc with ferrocyanide as previously described. Solid phases were filtered on Gooch crucibles carrying a disk of filter paper and centrifuged for a half hour at 1800 to 2000 r. p. m. before being analyzed. The results are given in Table III and Fig. 3. Complexes marked A were made with the copper salt as original solid phase, B with the zinc salt. The analysis of the solid phases indicates that the equilibrium composition is known to within less than 1%. Extrapolation of the tie-lines confirms this estimate; the average deviation from the analysis is 0.83%. Line 4 gives the solid composition by extrapolation alone. Our figure of 18.58% for the solubility of the copper salt is close to that found by Caven and Mitchell[15] (18.53%).

TABLE III

SYSTEM $CuSO_4$–$(NH_4)_2SO_4$–H_2O AND $ZnSO_4$–$(NH_4)_2SO_4$–H_2O AT 25°

	Original complex		Saturated solution		Solid phase	
	Wt., % $CuSO_4 \cdot (NH_4)_2SO_4$	Wt., % $ZnSO_4 \cdot (NH_4)_2SO_4$	Wt., % $CuSO_4 \cdot (NH_4)_2SO_4$	Wt., % $ZnSO_4 \cdot (NH_4)_2SO_4$	Wt., % $CuSO_4 \cdot (NH_4)_2SO_4$	Wt., % $ZnSO_4 \cdot (NH_4)_2SO_4$
1	...	0.00	18.58	0.00	72.97	0.00
2 A	17.51	3.80	14.75	2.39	51.75	21.08
B	17.51	3.80	14.83	2.31	50.05	21.98
3 A	16.07	9.55	11.99	4.13	36.69	36.33
B	16.07	9.55	11.99	4.13	36.48	36.56
4 A	11.51	10.39	9.84	5.75	(25.05)	(48.00)
B	11.51	10.39	9.85	5.75		
5 A	8.53	10.81	7.82	6.78	16.47	57.08
B	8.53	10.81	7.83	6.76	16.42	56.57
6 A	4.23	11.53	4.28	9.22	3.53	69.53
B	4.23	11.53	4.30	9.24	2.57	70.51
7	0.00	...	0.00	12.24	0.00	73.09

Zinc Ammonium Sulfate and Nickel Ammonium Sulfate.—The double salts were prepared as previously described and the solubility experiments carried out in the same manner. For the analysis, water was determined by direct evaporation of samples at 115–120° to constant weight, which took long periods because of the very slow loss of water from the zinc sulfate monohydrate. Nickel was determined by precipitation with dimethylglyoxime, in the presence of excess ammonium salt to prevent precipitation of zinc by the ammonium hydroxide. The results are given in Table IV and Fig. 4.

TABLE IV

SYSTEM $ZnSO_4$–$(NH_4)_2SO_4$–H_2O AND $NiSO_4$–$(NH_4)_2SO_4$–H_2O AT 25°

	Original complex		Saturated solution		Solid phase	
	Wt., % $ZnSO_4 \cdot (NH_4)_2SO_4$	Wt., % $NiSO_4 \cdot (NH_4)_2SO_4$	Wt., % $ZnSO_4 \cdot (NH_4)_2SO_4$	Wt., % $NiSO_4 \cdot (NH_4)_2SO_4$	Wt., % $ZnSO_4 \cdot (NH_4)_2SO_4$	Wt., % $NiSO_4 \cdot (NH_4)_2SO_4$
1	...	0.00	12.24	0.00	73.09	0.00
2 A	11.67	3.32	9.29	1.54	45.80	27.19
B	11.67	3.32	9.34	1.51	44.78	28.24
3 A	11.19	6.01	8.27	2.16	37.08	35.86
B	11.19	6.01	8.30	2.15	36.12	36.78
4 A	8.76	6.24	6.93	2.75	28.75	44.06
B	8.76	6.24	7.19	2.70	27.65	45.17
5 A	5.44	6.56	5.11	3.94	13.87	58.99
B	5.44	6.56	5.23	3.86	13.69	59.06
6 A	2.12	6.89	1.97	5.70	5.72	66.89
7	0.00	...	0.00	7.09	0.00	72.63

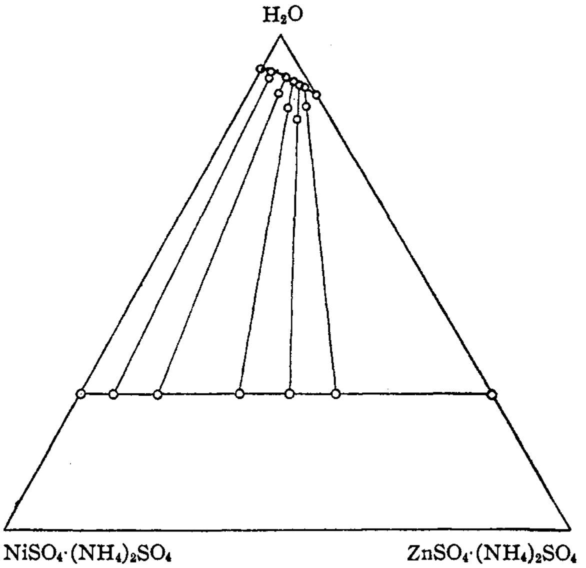

Fig. 4.—The system $ZnSO_4 \cdot (NH_4)_2SO_4$–$NiSO_4 \cdot (NH_4)_2SO_4$–$H_2O$ at 25°.

The A complexes were made with solid zinc salt, the B with nickel salt. Despite the less trustworthy analytical method, the results appear to be in nearly as good accord as in Table III; the extrapolated tie-lines show that the results are somewhat less dependable, the average deviation from the analytical result being 1.35%.

Copper Ammonium Sulfate and Nickel Ammonium Sulfate.—The salts were prepared and the complexes made up as in the cases previously discussed. Analysis of liquid solutions and of solid phases after two grindings of the solid and a total of four weeks' time, consisted of an electrolytic determination of the copper and subsequent precipitation of the nickel with dimethylglyoxime. The results follow in Table V and Fig. 5. In the table the A complexes were made up with the copper salt as initial solid phase.

TABLE V

SYSTEM $CuSO_4$–$(NH_4)_2SO_4$–H_2O AND $NiSO_4$–$(NH_4)_2SO_4$–H_2O AT 25°

	Original complex		Saturated solution		Solid phase	
	Wt., % $CuSO_4 \cdot (NH_4)_2SO_4$	Wt., % $NiSO_4 \cdot (NH_4)_2SO_4$	Wt., % $CuSO_4 \cdot (NH_4)_2SO_4$	Wt., % $NiSO_4 \cdot (NH_4)_2SO_4$	Wt., % $CuSO_4 \cdot (NH_4)_2SO_4$	Wt., % $NiSO_4 \cdot (NH_4)_2SO_4$
1	...	0.00	18.58	0.00	72.97	0.00
2 A	17.89	2.29	15.81	0.64	48.90	23.87
B	17.89	2.29	15.81	0.64	47.67	24.97
3 A	17.08	5.43	14.60	0.90	35.87	36.79
B	17.08	5.43	14.71	0.88	34.76	34.97
4 A	13.78	5.74	12.60	1.44	26.06	46.80
B	13.78	5.74	12.71	1.41	25.51	47.25
5 A	9.00	6.21	8.87	2.50	12.14	60.68
B	9.00	6.21	8.97	2.45	11.35	61.50
6 A	4.29	6.67	4.28	4.58	4.93	67.67
B	4.29	6.67	4.37	4.62	4.75	67.90
7	0.00	...	0.00	7.09	0.00	72.63

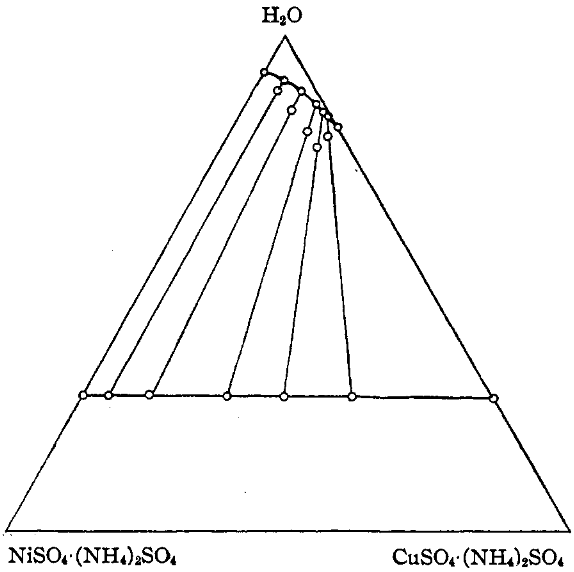

Fig. 5.—The system $CuSO_4 \cdot (NH_4)_2SO_4$–$NiSO_4 \cdot (NH_4)_2SO_4$–$H_2O$ at 25°.

The analyses of the solid phases again show displacement from the equilibrium point of less than 1%; extrapolation of the tie-lines was in somewhat less close agreement, the average deviation being 1.38%.

TABLE VI

DISTRIBUTION OF SALTS BETWEEN LIQUID PHASE AND SOLID PHASE

$Cu(NH_4)_2(SO_4)_2$ with $Zn(NH_4)_2(SO_4)_2$			$Zn(NH_4)_2(SO_4)_2$ with $Ni(NH_4)_2(SO_4)_2$			$Cu(NH_4)_2(SO_4)_2$ with $Ni(NH_4)_2(SO_4)_2$		
y	x	y calcd. = $x^{0.42}$	y	x	y calcd. = $x^{0.34}$	y	x	y calcd. = $x^{0.13}$
0.864	0.704	0.863	0.857	0.616	0.848	0.962	0.660	0.947
.745	.503	.749	.790	.498	.789	.940	.491	.911
.633	.344	.635	.719	.384	.722	.897	.351	.873
.538	.225	.534	.566	.187	.565	.781	.159	.787
.319	.042	.264				.480	.066	.702

Distribution between Liquid Solution and Solid Solution.—In order to study the distribution of components between the liquid and the solid solutions, the results of Tables III, IV and V have been recalculated to the basis suggested by Roozeboom[16] in his work on the classification of solid solutions. In Table VI, the y values represent the molar fraction of the more soluble salt in the liquid phase, x its molar fraction in the solid phase.

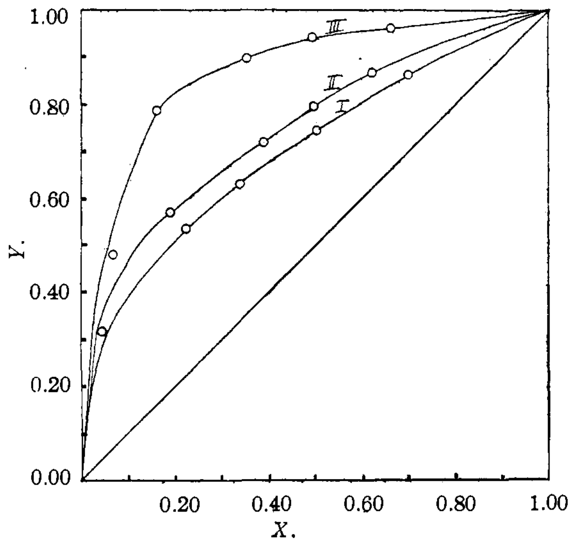

Fig. 6.—Distribution between aqueous solution and solid solution at 25°: Curve I, the copper and zinc ammonium sulfates; II, the zinc and nickel ammonium sulfates; III, the copper and nickel ammonium sulfates.

These results are shown graphically in Fig. 6. All three systems belong to Class 1 of Roozeboom's classification, that is, one component remains in higher concentration in the liquid phase than in the solid throughout the continuous series of solid solutions. It is to be noted that here, as with the alums previously reported upon, the curve for the x-y relationship varies furthest from the diagonal when the difference in aqueous solubility is greatest, approaching the diagonal when the solubilities are equal, as was found for the exceptional case of the potassium alum and ammonium alum.[4] It has been found that the x-y relationship of these curves can be expressed with considerable accuracy by the equation $y = x^{m}$; values of y calculated by such equations are included in Table VI. The agreement between the experiments and the exponential equation is satisfactory except where the values of x are small. Further data will be assembled before an attempt is made to go more fully into the meaning of Roozeboom's curves. Experiments are being continued with various alums and with other members of the picromerite series.

Summary

The 25° isotherms for the systems $ZnSO_4$–$(NH_4)_2SO_4$–H_2O and $NiSO_4$–$(NH_4)_2SO_4$–H_2O have been described. The formation of solid solutions has been studied for three pairs of salts of the picromerite series, $CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, and the distribution of salts ascertained between liquid solution and solid solution under conditions ensuring equilibrium. The relation between molar concentrations in liquid phase and in solid phase can be expressed approximately by an exponential equation, in which the exponent approaches 1.0 when the aqueous solubilities of the salts are equal, and has diminishing values as the ratio of the solubilities becomes greater.

NEW YORK, N. Y.

RECEIVED FEBRUARY 1, 1938

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(16) Roozeboom, *Z. physik. Chem.*, **8**, 504 (1891).